

A STUDY OF POLYMERIC PLATINUM(II) COMPOUNDS AND
NANOSCALE MATERIALS

by

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ABSTRACT

The photophysical and structural properties of the tetra- μ -pyrophosphitodiplatinate(2-) anion have been well studied in the past. One such analogue of this compound is a phosphorescent red compound of unknown structure. A new synthesis route has been found for both the tetra- μ -pyrophosphitodiplatinate(2-) and the red anionic compounds. By synthesizing the pyrophosphorus ligand outright and reacting that with tetrachloroplatinate(2-) either the tetra- μ -pyrophosphitodiplatinate(2-) or the red anionic compounds can be synthesized depending on the amount of the phosphorus acid that is present. It was found from light scattering measurements and with the usage of ^{31}P NMR spectroscopy that the red platinum(II) compound is structurally different than that of tetra- μ -pyrophosphitodiplatinate(2-). A revised synthetic route was made for the synthesis of pyrophosphorus acid which was found to be an insoluble, highly reactive ligand. Reactions of pyrophosphorus acid with normal alcohols led to the formation of phosphorus acid and the corresponding monoalkylated phosphorus acid. With the use of the monoalkylated phosphorus acids, an extensive series of dialkylated pyrophosphorus acids could be prepared thus creating a whole new series of novel platinum(II) compounds.

The structural properties of two types of oligomeric platinum compounds were investigated. When saturated solutions of the bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) salts were exposed to a direct current at a potential of 1.5V, partial oxidation of the platinum center occurred and polymerization of the platinum complexes was observed. It was found, using optical microscopy, atomic force microscopy, scanning electron microscopy and transmission electron microscopy that bundles of these polymers were formed having sizes on the macroscopic or nanoscopic scales. The polymeric one-dimensional, linear-chain compounds were found to be "template guidable" on both the macro and nano scales in order to form polymers with virtually any diameter. The smallest of these partially oxidized polymers were measured as having diameters as little as three to four nanometers wide.

CHAPTER 1

INTRODUCTION

Early History of Platinum Metal

Platinum chemistry has a wide and varied history. Platinum metal, which was commonly mistaken for silver metal, has been found in ancient Egyptian artifacts and has been commented on in classical Greek and Roman literature¹. Platinum chemistry has been widely studied over the past 150 years and various mononuclear platinum compounds were first synthesized over 100 years ago.

Platinum metal appears silver in color and is highly reflective when found in large quantities. When found in smaller quantities, platinum metal appears black in color. Platinum can be found having a number of oxidation states, the most common being II and IV. When found in the IV state, platinum forms complexes having octahedral geometry where the orbitals on the platinum are filled and the d_z^2 and $d_{x^2-y^2}$ orbitals are vacant. In the II state, platinum forms complexes having square planar geometry where the $d_{x^2-y^2}$ orbital is vacant, the d_{xy} , d_{yz} , d_{xz} are filled and a filled d_z^2 orbital extends above and below the plane of the square planar molecule.

Binuclear Platinum Complexes

Although monomeric platinum complexes have been known for over 100 years, the first reported multinuclear platinum compound was proposed by Blondel² in 1905. He proposed a platinum(III) compound containing coordinated sulfate ligands. A revised

synthesis³ and a detailed crystal structure⁴ for Blondel's platinum/sulfate compound were reported by Cotton in the mid 1970's and mid 1980's respectively. The crystal structure of Blondel's $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})^{2-}$ compound is illustrated in Figure 1.

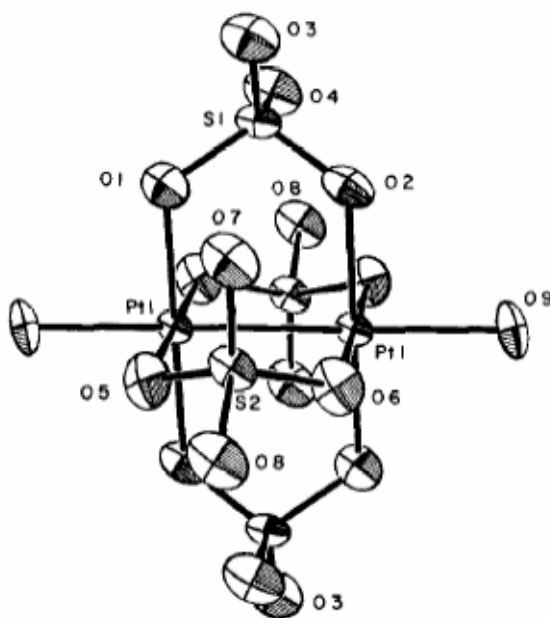


Figure 1. ORTEP of Blondel's $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})^{2-}$ binuclear platinum compound.

Cotton's work supported Blondel's determination of the III oxidation state on the platinum nuclei in the $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})^{2-}$ compound. The four sulfate ligands bridge the binuclear platinum center forming a structure having, what is known as the 'lantern (or paddle wheel) configuration'.

Another, more optically interesting compound which had been studied prior to Blondel's compound was the anionic pyrophosphite bridged binuclear platinum(II) compound, tetra- μ -pyrophosphitodiplatinate(2-). In 1977, Roundhill found that the heating of the potassium salt of tetrachloroplatinate(2-) with pure phosphorus acid at 100°C yielded a compound which, when exposed to UV radiation, would brightly

phosphoresce green in color^{5,6}. This compound was initially thought to be the monomeric compound $\text{Pt}(\text{OP}(\text{OH})_2)_2(\text{P}(\text{OH})_3)_2$ which had been discovered in the early 1960's by Troitskaya⁷ but was later found to be the tetra- μ -pyrophosphitodiplatinate(2-) $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ anion. The structure of this compound is shown in Figure 2.

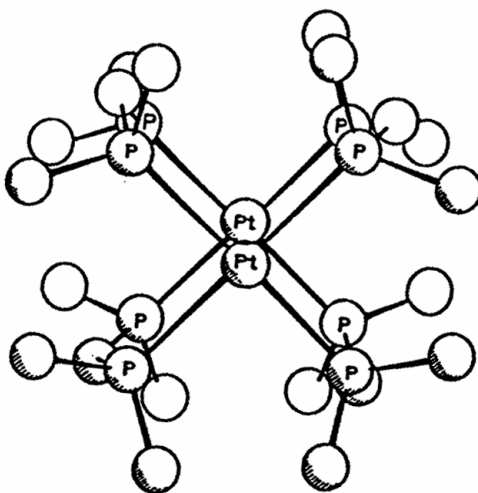


Figure 2. “Ball and Stick” model of the highly florescent $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ anion. (Waters of hydration are omitted.)

Each platinum atom is surrounded by four phosphorus(III) atoms which connect the two platinum atoms by four phosphorus-oxygen-phosphorus bridges. It should be noted that the configuration of the $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ anion has the same ‘lantern’ configuration as that of Blondel’s $\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})^{2-}$ anion. However, in the case of the $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ anion, the platinum atoms are in the II oxidation state rather than the III state, which means there is no bond between the two adjacent platinum atoms. However, when the compound is exposed to light, the electrons within the d_z^2 orbitals are excited and are promoted to a higher energy orbital which leads to the temporary bond formation

between the two platinum atoms⁸. This excitation occurs from the major absorption of 370nm light which, upon relaxation, is then released as green light as a 515nm emission. The phosphorescence is relatively long lived having a lifetime of 10.3 μ s⁹ and the quantum yield (the ratio of photons absorbed to photons emitted through phosphorescence) for that phosphorescence is a stunning $52\% \pm 0.3\%$ ¹⁰. The ³¹P nuclear magnetic resonance spectrum for the Pt₂(P₂O₅H₂)₄⁴⁻ anion is a simple pseudo-triplet centered at 69.4nm⁶. The ¹⁹⁵Pt NMR spectrum shows a quintet of quintets caused by each of the platinum atoms being coupled to the four phosphorus atoms to which it is directly bound as well as being coupled to the phosphorus atoms on the adjacent platinum atom⁶.

Much work has been done on the Pt₂(P₂O₅H₂)₄⁴⁻ anion in order to break the symmetrical nature of the compound. It has been found that the addition of various chemical oxidants led to the oxidation of the platinum(II) atoms to the III oxidation state and the subsequent axial addition of the oxidant involved^{11,12,13}. The oxidation of the platinum atoms led to a loss of luminescence and the permanent formation of a chemical bond between the platinum atoms.

The most interesting discovery concerning the Pt₂(P₂O₅H₂)₄⁴⁻ anion was found by Roundhill in the early 1980's. He found that heating a mixture of the potassium salt of tetrachloroplatinate(2-) along with phosphorus acid at 170°C rather than 100°C, led to the formation of a very dark green compound with a bright red luminescence¹⁴. He believed that the compound was a trimeric compound consisting of three platinum atoms connected by four phosphorus-oxygen-phosphorus-oxygen-phosphorus (POPOP) bridges.

Roundhill found that this new compound had a rather broad resonance pattern centered at 62.1ppm. Unfortunately, Roundhill gave very little support for the possibility of his trimeric platinum species or the existence of the POPOP ligand. Along with this green compound was also a ‘vermillion red’ compound that was insoluble in water or organic solvents. In the late 1980’s and early 1990’s, Bedgood revisited Roundhill’s work and found that the only compound that could be formed from Roundhill’s synthetic method was the compound that appeared ‘vermillion red’. Bedgood also found that that red compound was very soluble in water and yielded an NMR spectrum consisting of a pseudo-triplet centered at 62.9nm which was almost exactly what Roundhill had found for his uncharacterized dark green compound. Elemental analysis performed on the red compound yielded a possible structure consisting of 5 platinum atoms bridged by alternating phosphorus-oxygen-phosphorus bridges.

Roundhill and Bedgood were unable to obtain an X-Ray quality crystal of the red compound and no definitive data were obtained about its structure. The actual structure of this compound would be of great interest and its luminescent properties and could yield an answer as to why the $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ anion is so highly absorbing. This dissertation will expand on Roundhill and Bedgood’s work where a new conclusion of the structure(s) of this unknown red compound will be made.

Polymeric Platinum Complexes

Within the past 25 years, a great deal of interest has arisen in nanoscale to molecular scale, conductive materials. Many papers about organic and inorganic nano

and molecular conductive materials have been written, yet very little exploratory chemistry has been done on the actual compounds themselves.

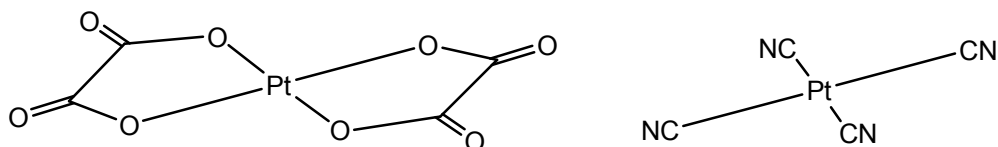
The field of nanomaterials has expanded and many new nanoscale compounds have been made. With materials such as nanoscopic gold coated cylinders¹⁵ being used as microscale inorganic electrodes and the discovery of conductive carbon nanotubes¹⁶, the industrial applications of nanoscale electrical conductors have been realized. One such set of potential nanomaterials that have been overlooked are one-dimensional (or 1D), partially oxidized (PO) conductive platinum polymers.

1D conductors are interesting compounds in themselves and have very unique properties. In theory, when trying to pass an electrical current through a 1D conductor, the electrons are more apt to travel along only one dimension than the other two. 1D compounds are normally conductors along one axis and an insulator (or a very poor conductor) along the other two.

Recently, people have realized the potential use of these compounds in the fabrication of nanoscale electrical components. With the use of 1D conductors, one could reduce the size of already ‘miniaturized’ electronic components by at least 1 to 2 orders of magnitude. If 1D conductors were used in place of common electrical wire, they would need no insulating coating on their outer surface due to their conductivity along only one axis.

PO platinum complexes can come in a variety of forms. There are cation deficient salts such as $K_{1.81}Pt(C_2O_4)_2$ and anion deficient salts such as $K_2Pt(CN)_4Br_{0.3}$. Specifically, the most promising of these compounds are the various PO salts synthesized

from the square planar, anionic platinum(II) complexes of bisoxalatoplatinate(2-) $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$ and tetracyanoplatinate(2-) $[\text{Pt}(\text{CN})_4]^{2-}$ which are displayed in Figures 3 and 4 respectively.



Figures 3 and 4. The square planar bisoxalatoplatinate(2-) [left] and the tetracyanoplatinate(2-) [right] anions.

The bisoxalatoplatinate(2-) anion was thoroughly studied by Krogmann and Dodel in the mid-1960's^{17,18} where they found that the potassium salt of bisoxalatoplatinate(2-) would polymerize to form bronze colored, needle-shaped crystals when exposed to a chemical oxidizing agent. Common chemical oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7$, PtCl_6^{2-} , Cl_2 , Br_2 were used by Krogmann but others have been used such as H_2O_2 ¹⁹ and O_2 as well. The oxidation led to the stacking of the platinum complexes along the z-axis of the molecule (which would be the d_z^2 axis of the platinum atoms). These polymerized bisoxalatoplatinate salts were found to be only partially oxidized, meaning that there were an overall non-integral number of electrons per platinum atom within the polymeric chain.

Numerous unoxidized salts containing both monovalent and divalent cations are known for the bisoxalatoplatinate(2-) anion, many of which were found to form PO polymers²⁰. Conversely, from the large collection of tetracyanoplatinate(2-) salts, only three of the monovalent cations salts are known to form PO polymers²¹.

Crystals of unoxidized salts containing tetracyanoplatinate(2-) are known to vary in color depending on the platinum-platinum distance within their crystal structure²². The color of these crystals was found to change on exposure to various solvents. These compounds are known as vaporchromic and its occurrence in tetracyanoplatinate(2-) salts has been studied extensively by Mann²³ and his co-workers. Ultimately, as the platinum-platinum distances decrease, a bond between the platinum atoms is formed. The formation of a chemical bond between the platinum atoms gives these PO compounds a bronze color and metallic sheen.

Bisbipyridylplatinum(I) is the only example of a 1D polymeric platinum(I) system and was reported by Pierpont²⁴ in 1996. What is usually observed for platinum(I) complexes is dimerization rather than polymerization. Polymers consisting of reduced bisbipyridylplatinum(I) form hollow cylindrical tubes that are about 10 μ m in diameter instead of forming a completely solid structure as what is seen for the PO polymers formed from the bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) anions. Pierpont reported a platinum-platinum distance of 3.56Å for the bisbipyridylplatinum polymers and a room temperature conductivity of 10⁻¹ cm⁻¹.

In 1976, Joel Miller found that when solutions of potassium tetracyanoplatinate(2-) were exposed to a voltage of 1.5V, they would form PO polymers similar to those formed by chemical oxidation²⁵. Miller's method of electrochemical oxidation was also successful in forming PO polymers from various bisoxalatoplatinate(2-) salts as well.

Miller found that the electrochemical formation of these polymers was much quicker than polymerization caused by chemical oxidants. Using electrochemical

oxidation, polymers having lengths of five or more centimeters could be formed in a couple of hours rather than weeks or months as with chemical oxidants.

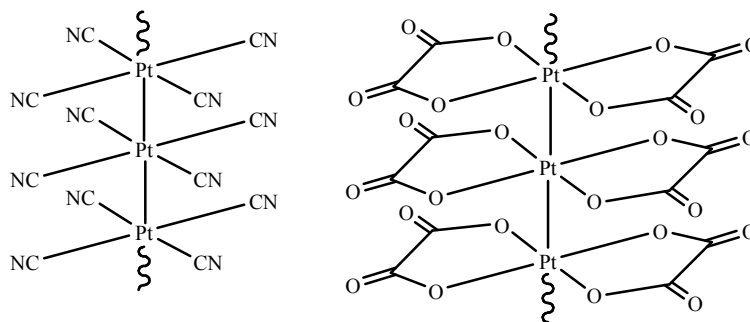
Although the bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) anions form similar cation deficient PO polymeric structures, their properties can vary to a large extent depending on the counter cation involved. The degree of partial oxidation [DPO] or how much of a total electron is removed from the platinum center, the platinum-platinum distances ($d_{\text{Pt-Pt}}$) within the PO polymers and the conductivity of the polymers are all variable depending of the cation and platinum(II) complex involved. Table 1 contains a brief summary of these variables.

	BOP Salts	TCP Salts
Cation-deficient	Yes	Yes
Monovalent	Yes	Yes
Divalent	Yes	No
Anion-deficient	No	Yes
Hydrated	Yes	Yes
Anhydrous	No	Yes
$d_{\text{Pt-Pt}}$ (Angstroms)	2.81-2.876	2.798-2.963
Range of DPO	0.19-0.36	0.19-0.4
Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	$10^2 - 10^{-2}$	$(2 \times 10^3) - 1$

Table 1. A summary of the properties of PO polymers formed from the various bisoxalatoplatinate(2-) (BOP) and the tetracyanoplatinate(2-) (TCP) salts.

As stated previously, platinum(II) complexes form square planar molecules. The electron configuration of a platinum(II) atom has a lone pair of electrons occupying the d_z^2 orbital. The oxidation occurs by partially removing a electron from the d_z^2 orbital of the platinum atom which allows the platinum(II) complexes to stack along the z, or

platinum d_z^2 axis. The resulting stacked polymer exhibits metal-like conduction along the z-axis and semiconductive, or insulative behavior along the x and y axes. A graphical representation of the PO tetracyanoplatinate and bisoxalatoplatinate polymers is shown in Figures 5 and 6.



Figures 5 and 6. The stacking of the PO polymers seen in the salts containing the tetracyanoplatinate (left) and bisoxalatoplatinate (right) anions.

The differences in conductivities between the two PO platinum polymers can vary to a large degree based on which anion is involved and which counter cation is used. For polymers containing the PO tetracyanoplatinate anion, it has been found that the conductivity along the platinum bonding axis is approximately 5 orders of magnitude larger than the other two axes. The conductivity along the platinum bonding axis of those PO polymers containing the bisoxalatoplatinate anion have been found to be 2 to 3 orders of magnitude when compared to the conductivity along the other two.

The distance between the adjacent platinum atoms ($<3.0\text{\AA}$) indicates that there is a true chemical bond formed between the platinum complexes. The reason for the bond formation was explained by Krogmann using valence bond and molecular orbital theories²⁶.

The valence bond representation of a platinum(II) atom within a square planar complex is shown in Figure 7. Four ligands donate a pair of electrons which occupy the $5d_{x^2-y^2}$, $6s$, $6p_x$ and $6p_y$ orbitals on the platinum atom which are combined to form the four dsp^2 hybrid orbitals used for bonding in a square planar complex. In a d^8 square planar complex, the $6p_z$ orbital on the platinum atom is unoccupied at this stage.

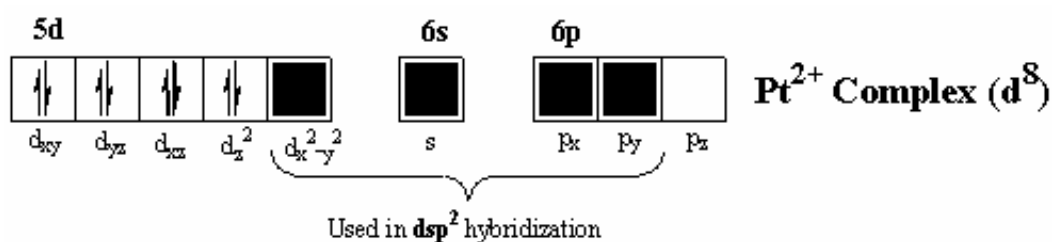


Figure 7. The valence bond representation of a platinum(II) atom within a square planar complex.

By forming a set of dp hybridized orbitals using the occupied $5d_{z^2}$ orbital and the unoccupied $6p_z$ orbital, a platinum(II) complex would be able to form two additional bonds along its z -axis (Figure 8).

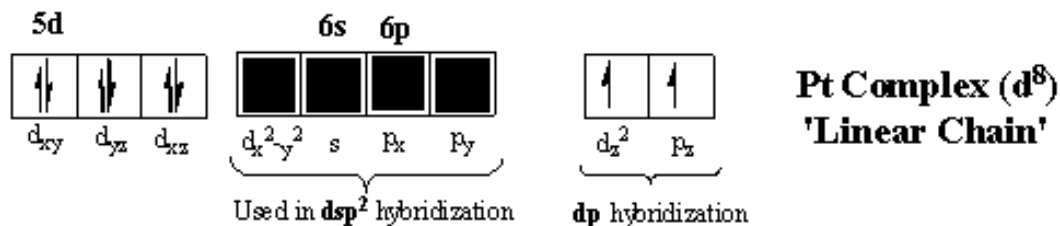
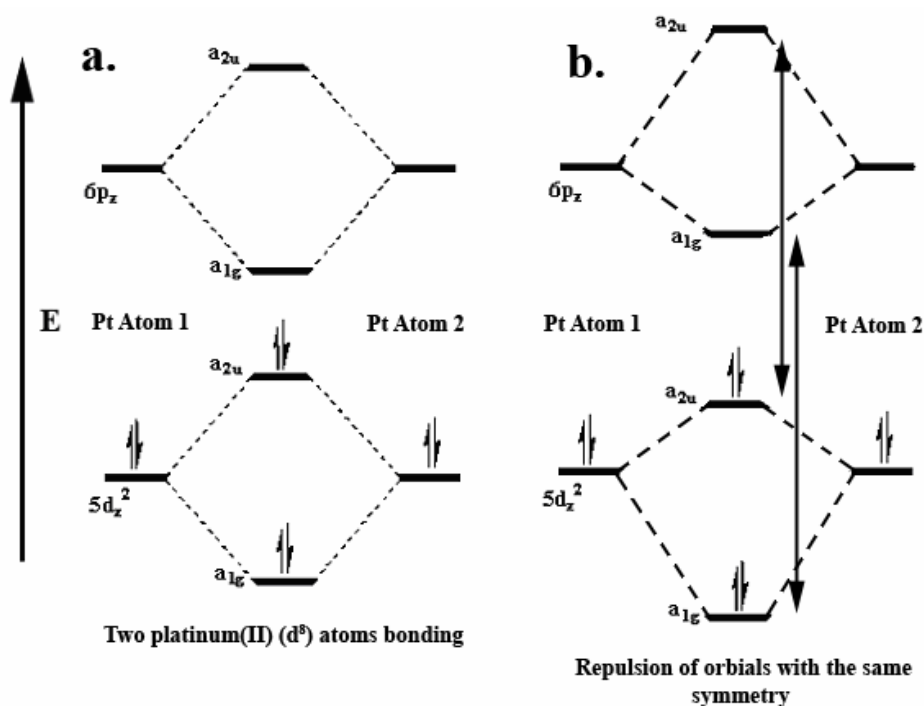


Figure 8. The valence bond representation of a platinum(II) atom hybridizing in order to form a linear chain of platinum complexes.

Although the valence bond representation explains how the polymers could possibly form from multiple platinum(II) complexes, it fails to explain how the bond

distances between the adjacent platinum atoms vary. For that explanation, the theory proposed by Rundle²⁷ and again by Miller²⁸ involving molecular orbitals in conjunction with band theory can be used. Figure 9a shows the $5d_z^2$ and $6p_z$ atomic orbitals of two platinum(II), d^8 atoms which have split to give antibonding and bonding molecular orbitals. The antibonding and bonding orbitals have a_{2u} and a_{1g} symmetries respectively.



Figures 9a and 9b. (a) The molecular orbital representation of two platinum(II) atoms bonding. (b) The repulsion of the molecular orbitals due to configuration interactions.

In Figure 9a, the a_{1g} and a_{2u} molecular orbitals formed from the $5d_z^2$ atomic orbitals are the only molecular orbitals occupied as platinum has no electrons in the $6p_z$ subshell. This arrangement of electrons would yield no net bond between the two platinum(II) atoms. However, non-degenerate orbitals that are close in energy and that

have the same symmetry repel each other. This repulsion is known as a ‘configuration interaction’.

As seen in Figure 9b, this configuration interaction would result in the lowering in energy of the a_{2u} antibonding orbital associated with the $5d_z^2$ atomic orbitals and a rising in energy of the a_{2u} antibonding orbital associated with the $6p_z$ atomic orbitals. A lowering in energy would occur for a_{1g} bonding orbital associated with the $5d_z^2$ atomic orbitals and a rising in energy would occur for the a_{1g} bonding orbital associated with the $6p_z$ atomic orbitals.

With the decrease in energy of both the occupied bonding and antibonding orbitals, an overall net bonding effect would occur. Also, through the configuration interaction, those molecular orbitals formed from the ‘d’ atomic orbitals would gain some ‘p’ character and the molecular orbitals formed from the ‘p’ atomic orbitals would gain some ‘d’ character which would support the dp hybridization of the ‘d’ and ‘p’ orbitals explained in the valence bond representation.

The molecular orbital representation explains how two platinum(II) atoms could possibly form a bond but, since the PO polymers consist of a multitude of platinum complexes, band theory must be used to explain the overall bonding between the partially oxidized platinum atoms and the conductivity observed for the PO polymers.

The expansion of the molecular orbital representation for the interaction of two platinum(II) atoms to include an almost infinite number of platinum(II) complexes, would yield a set of orbitals similar to what is seen in Figure 10. As the number of platinum atoms within a polymeric chain increases, the number of molecular orbitals

derived from the $5d_z^2$ atomic orbitals would increase as well. These molecular orbitals would become closer in energy as the number of bonding platinum atoms increase. After reaching an almost infinite number of platinum(II) atoms, the molecular orbitals would form a nearly continuous band of orbitals.

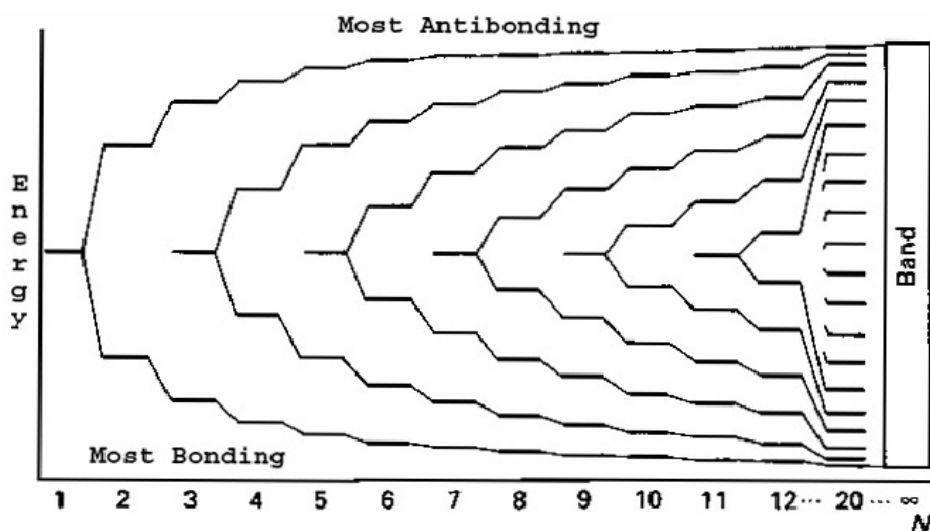


Figure 10. The continuous band of electrons formed from the molecular orbitals from an almost infinite number of platinum atoms ($N = \#$ of Atoms)

At this stage there still would be no net bonding effect between the platinum atoms due to the lower half of this continuous band of orbitals consisting of bonding molecular orbitals which are negative in energy and the upper half consisting of antibonding orbitals which are positive in energy relative to the initial d_z^2 atomic orbital. Another band which was higher in energy consisting of the unoccupied molecular orbitals from the $6p_z$ atomic orbitals would be formed above the band formed from the $5d_z^2$ orbitals.

Taking into account the configuration interaction between the antibonding and bonding molecular orbitals derived from the $5d_z^2$ and $6p_z$ atomic orbitals, a shifting of the

band would cause the overall lowering in energy of the band thus causing a net bonding effect. Since the platinum atoms within the polymers are partially oxidized, electrons would be removed from the top section (the antibonding section) of the band thus strengthening any bonding that occurred (Figure 11). Since the molecular orbitals are emptied, the removal of these electrons allow for a possible 'opening' within the band for electrons to pass if an external current was applied to the polymers.

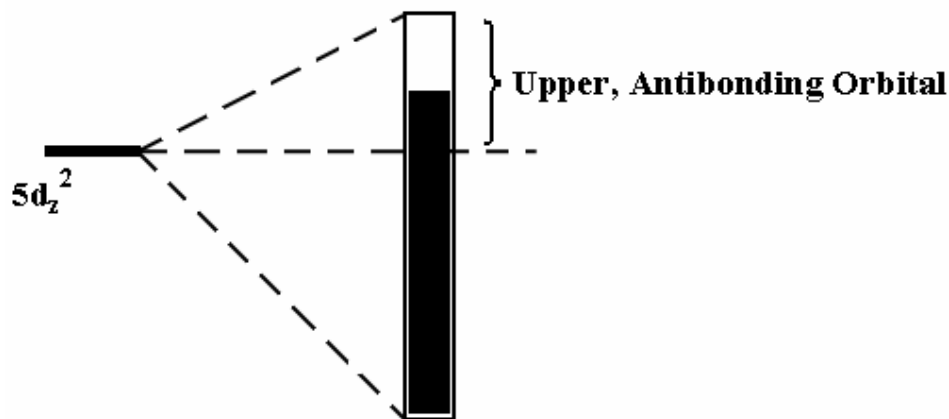


Figure 11. The band of molecular orbitals formed when the configuration interaction between the molecular orbitals and the partial oxidation of the platinum atoms is taken into account.

The polymers that are formed from the platinum complexes are, in actuality, crystals. Each crystal consists of numerous PO platinum chains surrounded by counter cations and waters of hydration both of which are shared amongst the anionic platinum chains. The unit cell and crystal structures for the various PO polymers are dependent on the counter cation(s) involved.

The scope of past research projects concerning the PO polymers formed from the bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) anions had been limited to the

possibility of their formation and their subsequent conductivity measurement. No work had been done on the physical properties of the PO polymers. How long and thick were these polymers able to form? Was it possible to form the PO polymers which had exclusively been formed via chemical oxidation using the electrochemical methods discovered by Miller? How rigid were these linear chain polymeric crystals? These questions and other physical data about the PO polymers consisting of the bisoxalatoplatinate and tetracyanoplatinate anions were studied and will be answered in the latter half of this dissertation.

The polymeric nature of both the unknown red compound and the PO platinum polymers seemed to compliment each other. The formation of the platinum-platinum bond seen in the excited state of the tetra- μ -pyrophosphitodiplatinate(2-) anion alluded to the possibility that the unknown red compound could possibly be forming a platinum-platinum bond or bonds during its excitation as well. With the formation of a platinum-platinum bond, the red compound could possibly become a conductor similar to that of the PO polymers.

Attempts to react tetra- μ -pyrophosphitodiplatinate(2-) with the PO platinum polymers yielded no results. With the similarity in properties between the tetra- μ -pyrophosphitodiplatinate(2-) and the unknown platinum red anion, it was theorized that a reaction between the red compound and PO polymers might yield photo-switchable, conductive nanowires. In order to achieve this goal, the structure of the red compound needed to be determined along with the physical properties of the PO platinum polymers.

CHAPTER 2

EXPERIMENTAL

Synthesis of Platinum CompoundsStarting Materials

Potassium Tetrachloroplatinate(2-) [K_2PtCl_4] was purchased from both Pressure Chemical Company and Alfa Aesar. Oxalic Acid [$H_2C_2O_4$] and Potassium Cyanide [KCN] were purchased from Sigma-Aldrich. Phosphorus Acid [H_3PO_3] and Phosphorus Trichloride [PCl_3] was purchased from Fisher Scientific. All purchased reactants were used without further purification. All organic solvents were purchased from Fisher Scientific and used with out any further purification. All water was deionized and subsequently distilled.

Synthesis of Pyrophosphorus Acid [$H_4P_2O_5$] (1)

A variation of Auger's method²⁹ was used. 5g of phosphorus acid was added to a 100ml round bottom flask. The flask was then heated at 4mm Hg to 30 °C for 10 minutes. Using adequate protection and with the usage of a fume-hood, an excess of PCl_3 was added (7mL.) The reaction was stirred under flowing argon at 30 °C for 5 hours. The evolution of HCl was evident. After the reaction reached completion, the flask was cooled with liquid nitrogen to solidify the $H_4P_2O_5$. The reaction was allowed to warm to room temp. Once the PCl_3 liquefied, it was poured off and the remaining PCl_3 was

pumped off and discarded. The thick, mobile liquid was allowed to sit for 12 hours and solidify. (1) was had with a 89-95% yield.

Potassium Tetracyanoplatinate(2-) [K₂Pt(CN)₄] (2)

Martellaro's method for the synthesis of **2** was used²². 15mL of distilled water was heated to 50 C. To this was added approximately 1g of potassium tetrachloroplatinate(2-). To the stirring solution was added a slightly greater than four fold molar excess of potassium cyanide. The solution was allowed to reflux for an hour upon which the red colored solution became clear. The majority of the solvent was removed via rotary evaporation. Upon removal of the solvent, pale blue-green crystals formed which, when exposed to UV light, fluoresced blue. The resulting crystals were redissolved in a small quantity of near freezing water. The solution was then placed in an ice water bath to accelerate the recrystallization of **2**. The crystals were removed from the solution via vacuum filtration. Multiple recrystallization and filtration cycles were repeated in order to collect the entire quantity of synthesized product. A yield of 90% to 95% was obtained.

Potassium Bisoxalatoplatinate(2-) [K₂Pt(C₂O₄)₂] (3a)

The method of Krogmann and Dodel was used^{2,3} for the synthesis of **3a**. To 30mL of distilled water was added approximately 1g of potassium tetrachloroplatinate(2-). A three fold excess of oxalic acid was added to the solution. The mixing solution was sealed, wrapped in aluminum foil and allowed to stir for three days. After three days, a white precipitate was visibly present in the solution. The precipitate was removed from

the solution via vacuum filtration. The collected solid was washed with a small amount of cold water. The product was allowed to dry in an evacuated desiccator overnight. A yield of 80% to 85% was obtained.

Dihydrogen Bisoxalatoplatinate(2-) [$\text{H}_2\text{Pt}(\text{C}_2\text{O}_4)_2$] (**3b**)

For the synthesis of **3b**, a slight variation on Krogmann's method¹⁸ was employed. To a stirring solution of 3.5mL of deionized water in a 50mL round bottom flask was added 0.085g of AgNO_3 (5×10^{-4} mole). To this solution was added a 0.5 molar equivalent of **3a** (0.100g, 2.22×10^{-4} mole) and precipitation of $\text{Ag}_2\text{Pt}(\text{C}_2\text{O}_4)_2$ commenced immediately. The solution was allowed to stir for ten minutes to assure the complete reaction of **3a** and AgNO_3 after which the solution was passed through a medium porosity glass fritted filter (10-15 porosity rating). The filtrate was discarded and the filter cake was placed in a desiccator and allowed to dry for 24 hours. The $\text{Ag}_2\text{Pt}(\text{C}_2\text{O}_4)_2$ was then weighed and a yield of 90-95% was had on average.

To 5mL of degassed, deionized water was added 0.100g (1.7×10^{-4} mole) of $\text{Ag}_2\text{Pt}(\text{C}_2\text{O}_4)_2$. To the stirring solution was added a 0.37mL (or 2 mole equivalent) of 1M HCl. The immediate precipitation of AgCl occurred. The solution was allowed to stir for 10 minutes to assure the complete reaction of the HCl and $\text{Ag}_2\text{Pt}(\text{C}_2\text{O}_4)_2$. The solution was filtered after which the solution was passed through a medium porosity glass fritted filter (10-15 porosity rating). This filtrate was collected, degassed with argon, covered with aluminum foil and stored in a dark place.

Monovalent Cation Bisoxalatoplatinate(2-) [M₂Pt(C₂O₄)₂] [M=Li, Na, NH₄, Guanidinium] (**3c-3f**)

A variation on Watkins' and Underhill's method³⁰ for the synthesis of the divalent salts of Pt(C₂O₄)₂²⁻ was used. A freshly prepared sample of **3b** was taken and placed in a small round bottom flask that had been purged with argon. If lithium was the cation used then a 2 molar equivalent of LiOH was added to the solution. When the Na, NH₄ or guanidinium cations were employed, the nitrate salt of those cations was added. An immediate color change occurred whereupon the displacement of the proton from **3b** for the 'M' cation was apparent. The solution was purged with argon and used immediately in the partially oxidized linear chain polymer experiments.

Divalent Cation Bisoxalatoplatinate(2-) [MPt(C₂O₄)₂] [M=Ni, Co, Fe, Cu, Sr, Pb, UO₂, Ba, Cd] (**3g-3o**)

A variation on Watkins' and Underhill's method³⁰ for the synthesis of the divalent salts of Pt(C₂O₄)₂²⁻ was used. A freshly prepared sample of **3b** was placed in a small round bottom flask purged with argon. To this solution was added the nitrate salt of the appropriate cation. An immediate color change occurred whereupon the displacement of the proton from **3b** for the 'M' cation was apparent. The solution was purged with argon and used immediately in the partially oxidized linear chain polymer experiments.

Divalent Cation Bisoxalatoplatinate(2-) [MPt(C₂O₄)₂] [M=Zn, Mg, Mn] (**3p-3r**)

A variation of Watkins' and Underhill's method³⁰ for the synthesis of the divalent salts of Pt(C₂O₄)₂²⁻ was used. A freshly prepared sample of **3b** was placed in a small round bottom flask purged with argon. To this solution was added the sulfate salt of the

cation of choice. An immediate color change occurred whereupon the displacement of the proton from **3b** for the 'M' cation was apparent. The solution was purged with argon and used immediately in the partially oxidized linear chain polymer experiments.

X Tetra-μ-pyrophosphitodiplatinate(2-) [$X_4Pt_2(H_2P_2O_5)_4$]
 $\{X=K^+, \text{tetra-}n\text{-butylammonium}^+, \text{tetra-}n\text{-heptylammonium}^+, \text{tetra-}n\text{-octylammonium}^+\}$
(4a-d)

4a was synthesized as follows. To 15mL of refluxing distilled water was added 0.360g of potassium tetrachloroplatinate(2-). To the stirring solution was added a 12 times molar excess of phosphorus acid. This solution was allowed to reflux approximately one to two hours until the reddish solution became colorless. The colorless solution was then transferred to a Petri dish and placed in an oven at a temperature of 110 C. The complete evaporation of the solvent was allowed to progress for twelve hours (overnight). The resulting brilliantly green solid was vacuum filtered and washed with methanol to remove any excess phosphorus acid and dried with diethyl ether. The green solid was placed into an evacuated desiccator and allowed to dry overnight. A yield of 80% to 85% was obtained.

$((C_4H_9)N)_4Pt_2(H_2P_2O_5)_4$ (**4b**) was synthesized by following Gray's method³¹. 0.500g of (**4a**) were added to a mixture consisting of 20mL of water and 20mL of methylene chloride. To the stirring mixture was added slightly less than a four molar equivalence of tetrabutylammonium bromide. The mixture was allowed to stir for one hour. The organic phase was extracted and the solvent was removed via rotary evaporation. A yield of 95% was obtained.

$((\text{C}_7\text{H}_{15})\text{N})_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4$ (**4c**) was synthesized by following a variation of Gray's method. 0.500g of (**4a**) was taken and added to a mixture consisting of 20mL of water and 20mL of diethylether. To the stirring mixture was added slightly less than a four molar equivalence of tetraheptylammonium chloride. The mixture was allowed to stir for one hour. The organic phase was extracted and the solvent was removed via rotary evaporation. A yield of 95% was obtained.

$((\text{C}_8\text{H}_{17})\text{N})_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4$ (**4d**) was synthesized by following Grey's method³². 0.500g of (**4a**) were taken and added to a mixture consisting of 20mL of water and 20mL of diethylether (or 20mL of pentane). To the stirring mixture was added slightly less than a four molar equivalent of tetraoctylammonium chloride. The mixture was allowed to stir for one hour. The organic phase was extracted and the solvent was removed via rotary evaporation. A yield of 35% to 95% was obtained for this reaction.

Potassium Red (**5a**)

The synthesis method for the potassium red compound was similar to that of (**4a**). To 10mL of distilled water refluxing at 100 °C was added 0.360g of potassium tetrachloroplatinate. To the stirring solution was added a 12 times molar excess of phosphorus acid. The solution was allowed to reflux approximately one to two hours until the reddish solution became colorless. The colorless solution was then transferred to a petri dish and placed in an oven at 175 °C. The evaporation of the solvent was allowed to progress for one hour. As the solvent evaporated, the clear solution became yellowish-red in color. Once the solution became a thick viscous liquid, the petri dish was removed and allowed to cool on a bench top. As the dish cooled, the viscous

material solidified and became vermillion red in color. The resulting red solid was vacuum filtered and washed with methanol to remove any excess phosphorus acid and was dried with diethyl ether. The red solid was placed in an evacuated desiccator and allowed to dry overnight.

Tetraheptylammonium Red (**5b**)

A small quantity of impure (**5a**) was added to 10mL of distilled water and 10mL of diethylether. A small amount of tetraheptylammonium chloride was then added to the stirring mixture. The organic layer was extracted and the solvent was removed via rotary evaporation. The solid was then redissolved in a small quantity of diethylether. The solution was placed in a vial and stored in a refrigerator at 5 °C.

Tetraoctylammonium Red (**5c**)

A small quantity of impure (**5a**) was added to 10mL of distilled water and 10mL of diethylether. A small amount of Tetraoctylammonium chloride was then added to the stirring mixture. The organic layer was extracted and the solvent was removed via rotary evaporation. The solid was then redissolved in a small quantity of diethylether. The solution was placed in a vial and stored in a refrigerator at 5 °C.

Methyltriphenylphosphonium Red (**5d**)

A variation on Bedgood's method³⁵ was used for the synthesis of **5d**. To 5mL of deionized water was added 0.100g of **5a**. The reaction was allowed to stir for 4 minutes where upon an excess of methyltriphenylphosphonium nitrate $[(CH_3)(C_6H_5)_3P-NO_3]$ was added to the solution until all **5a** was precipitated. The precipitation of **5d** occurred

immediately. The resulting flocculent dark red solid was filtered using a glass fritted filter, washed three times with 10mL of deionized water and washed once more with 20mL of acetone. The yellow-colored filtrate was discarded and the filter cake was placed in a desiccator overnight or until dry.

Tetraphenylarsonium Red (**5e**)

A small impure quantity of **5a** was added to 10mL of distilled water. A small amount of tetraphenylarsonium chloride $[(C_6H_5)_4AsCl \cdot HCl]$ was added dropwise to the stirring mixture until the precipitation of **5a** ceased. The resulting flocculent dark red solid was filtered using a glass fritted filter, washed three times with 10mL of deionized water and washed once more with 20mL of acetone. The yellow-colored filtrate was discarded and the filter cake was placed in a desiccator overnight or until dry.

Monoalkylated Phosphorus Acids $[CH_3(CH_2)_xH_2PO_3, X=0 \text{ through } 11]$ (**6a-k**)

$CH_3(CH_2)_xH_2PO_3, [X=0 \text{ through } 11]$ (**6b-k**) were prepared by adding 1g of (**1**) to a stirring solution of the appropriate normal alcohol. **6a-k** were obtained with a yield of 95-98%.

Dialkylated Pyrophosphorus Acids $[\{CH_3(CH_2)_x\}_2H_2P_2O_5, X=0-11]$ (**7a-k**)

A variation of Zwierzak's method³³ was followed. To 10mL of dry Benzene was added 1g of **1**. To the mixture was added the appropriate normal alcohol. The mixture was allowed to stir at room temperature until **1** completely reacted (1-2 hours.) To this solution was added 2.68mL of 1.28M dicyclohexylcarbodiimide (DCC) in Benzene. The precipitation of dicyclohexylurea (DCU) was evident. The solution was filtered and the

filtrate was collected. The amount of dialkylated pyrophosphorus acids formed was not calculatable.

Synthesis of potassium bissquaratoplatinate(2-) [$K_2Pt(C_4O_4)_2$] (8)

Toftlund's method for the synthesis of potassium bissquaratoplatinate(2-) was used³⁴. To 10mL of 0.2M $Pt(H_2O)_4$ (in 1M $HClO_4$) was added 0.1g of Squaric Acid. The solution was heated at 55°C for 1 hour. During that time the solution turned blue/black in color 0.5mL of $NaClO_4$ was added to the solution. The solution was placed in a refrigerator to minimize any decomposition that could occur.

Instrumentation and Techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy

All ^{31}P NMR spectra were performed on Bruker WM250, AC300, AM500 or AM600 spectrometers using no lock solvent. The WM250 was equipped with an Inverse Broadband probe tuned to phosphorus. The AC300 was equipped with a $^1H/^{13}C/^{31}P/^{19}F$ nucleus capable probe. Both the AM500 and AM600 were equipped with broadband probes tuned to phosphorus.

Light Scattering Experiments

All light scattering experiments were performed on a Wyatt Technologies, Inc. Dawn DSP Multi-angle Light Scattering instrument in single sample mode. The samples of **5a** were prepared by taking a weighed amount of solid **5a**, dissolving it in water and

making five more dilutions each half as concentrated as the previous one. These dilutions were then placed in a glass vial and measured.

Ultra Violet/Visible (UV/Vis) Spectroscopy

All UV/Vis spectra were obtained from a Shimadzu UV-2401PC UV/Vis spectrophotometer using quartz sample cuvettes. All work-ups of these data were performed using Shimadzu's UVPC Personal Spectroscopy Software v3.9 on an IBM compatible PC running Windows 95.

Scanning Electron Microscopy (SEM)

All SEM work was done on a JEOL Model 6100/NORAN/Röntec/Oxford scanning electron microscope. All samples were prepared by attaching the samples to 20cm iron disks using conductive carbon sticky tape. The samples were then sputter coated with a platinum/iridium alloy to a thickness of 1.33nm. After sputter-coating, the samples were connected together and grounded to the iron base plate by placing another piece of carbon sticky tape along the tops of the samples and attaching the tape to the iron plate.

Atomic Force/Scanning Tunneling Microscopy (AFM/STM)

All AFM and STM work was done on a Digital Instruments Multimode scanning force microscope. All samples were prepared in a similar manner as that of the SEM samples minus the platinum/iridium sputter coating. All AFM work was done in "tapping mode."

Transmission Electron Microscopy (TEM)

All TEM work was done on a Zeiss 912 Transmission Electron Microscope. All samples were prepared by placing an already polymerized sample in water and then placing a droplet of that solution on a FormvarTM coated copper wire screen.

X-Ray Crystallography and Mass Spectroscopy

All x-ray crystallography work was done by the X-ray Crystallography Facility at Montana State University where a Nicolet R3m/E diffractometer was employed to determine the crystal structures of samples for this dissertation. All mass spectroscopy work was done on a VG 70E-HF double focusing magnetic mass spectrometer. The sample introduction was by direct probe and chemical ionization was done by using NH₃ as the reagent gas.

CHAPTER 3

RESULTS AND DISCUSSION

The Red Compound and Its VariantsEarly Work on the Red Compound (variant **5a**)

In previous attempts by others to synthesize the unknown red compound, a hotplate was used. Attempts to synthesize the red compound using a hot plate made it apparent that that was a poor choice of a heat source because it was difficult to accurately clock the amount of time need for the reaction to complete due to the rapid heating of the samples. Inconsistencies in hot plate temperatures and the overall lack of the temperature's fine control were major downfalls to this method. Temperature variations on the plate's surface made it even more difficult to replicate experimental conditions when repeating the experiment. It was found that if all of the solvent was removed, in this case H₂O, then the green, **4a** would be formed. If a small amount of water was left before the solution completely evaporated then the red, **5a** compound would be formed. If the reaction was heated too long and the majority of the water was boiled off to form **4a**, the reaction could be salvaged by adding 5mL of water and reheating the solution at 170 C to yield the **5a** product. If the reaction failed and water had to be added too many times, the synthesis of **5a** would cease.

It was found that rapid heating of the solution of H₃PO₃, K₂PtCl₄ and water was unnecessary. Rather than heating the solution on a hot-plate, one could just heat the solution in an oven at 170 C. This is not too dissimilar to the synthetic method for the

formation of **4a** (and its derivatives) except that the temperature was approximately 70 C higher. It was found that as the temperature was increased from 100 C, the formation of **4a** decreased and the formation of **5a** increased. 170 C was found to be the optimal temperature for the synthesis of **5a**. The usage of temperatures higher than 170 C led to the break down of H_3PO_3 and the subsequent formation of products such as phosphine and other phosphorus oxide derivatives. The conversion of the reactants to the **5a** product was not 100%. The formation of **4a** still occurred but to a much lesser extent than what occurred when the reaction was done at 110 C.

Varying parameters such as increasing or decreasing the initial amount of H_3PO_3 , changing the size of reaction vessel used or varying the amount of time for the initial reflux had little chemical effect on the formation of the **4a** side product. Decreasing the starting amount of H_3PO_3 too much caused the reaction to cease completely. What did have an effect was varying the amount of water used in the initial reflux. If the amount of water used was 10mL or higher, **5a** was more apt to form which contained only a small amount of **4a**. Conversely, if the initial amount of water was decreased below 10mL, crystals of **4a** would form along with a small amount of **5a**. It was also found that as the reaction neared completion, the reaction vessel needed to be cooled rapidly. It was found that placing the Petri dish on a bench top at a slight angle as to pool the solution to one side, led to the maximization of the formation of **5a**.

Initial Inspection of **5a** versus **4a**

5a was found to be a hard, red colored solid. The shelf life of **5a** was found to be dependant on how well the compound was filtered and dried during the initial preparation

stage. If the compound was washed with methanol and well dried, then the solid was found to be stable for two months to many years. If **5a** was exposed to any moisture or solvents during its storage, decomposition would occur rapidly and small green blotches of **4a** would become visible after a few days.

5a was found to be soluble in water, DMF and ethylene glycol. Any attempts to dissolve **5a** in other polar solvents such as THF, CH₃CN, acetone or various alcohols failed. Unfortunately, **5a** is also very water sensitive and will decompose over a short period of time (usually about one week depending on the temperature and whether the sample container was exposed to light). It was thought that if **5a** were dissolved in water and frozen, solutions of **5a** could be made and stored for a short time until needed. Freezing aqueous solutions of **5a** only expedited its decomposition. Freezing aqueous solutions of **5a** overnight yielded yellow/orange solutions which, by morning, were found to contain **4a** along with a very small amount of **5a**.

The ideal method for quantitative analysis of these two compounds would have been NMR spectroscopy. Unfortunately, due to the fact that **5a** has a very low sensitivity to NMR another instrumental method had to be used. Since these are both visibly colored compounds, UV/Vis spectroscopy was used as the preferred method of analysis. The spectroscopy of **4a** has been well studied⁶ and UV/Vis spectrum of **4a** has been explored as well (Figure 12).

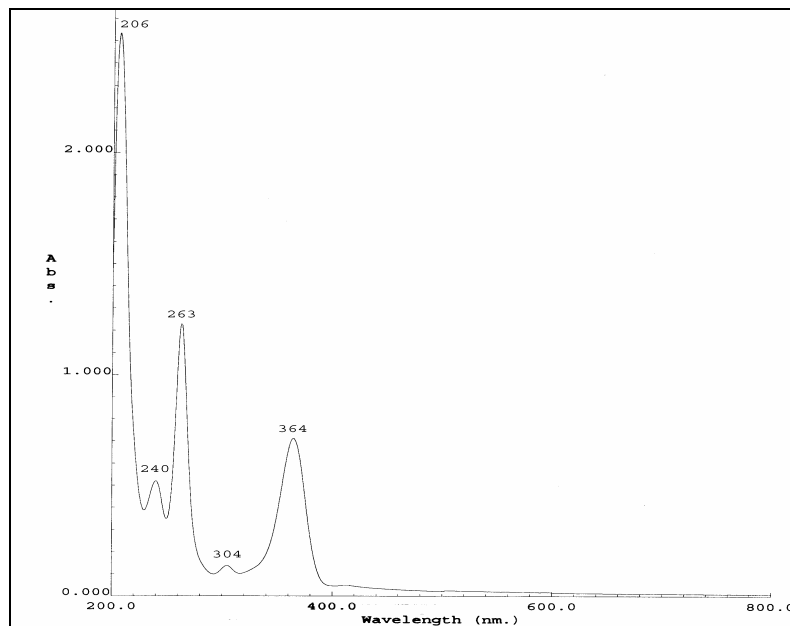


Figure 12. UV/Vis spectrum of **4a** in water.

The intensely green **4a**, as reported in the literature, has a major absorbance peak at 368nm and two smaller peaks at 345nm and 285nm. The two peaks at 345nm and 285nm are known to be solvent and/or cation dependant as those two peaks were never seen to match the reported values when using salts of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ other than potassium. The peak at 368nm was ever present and is reported to have an extinction coefficient of $33,500\text{M}^{-1}\text{cm}^{-1}$.⁶

5a has a similar UV/Vis spectrum (Figure 13) to that of **4a**. **5a** has only one prominent peak which the Abbott group found to appear on average at 570nm. In the spectrum in Figure 13, the absorption peak for **5a** appears at 532nm.

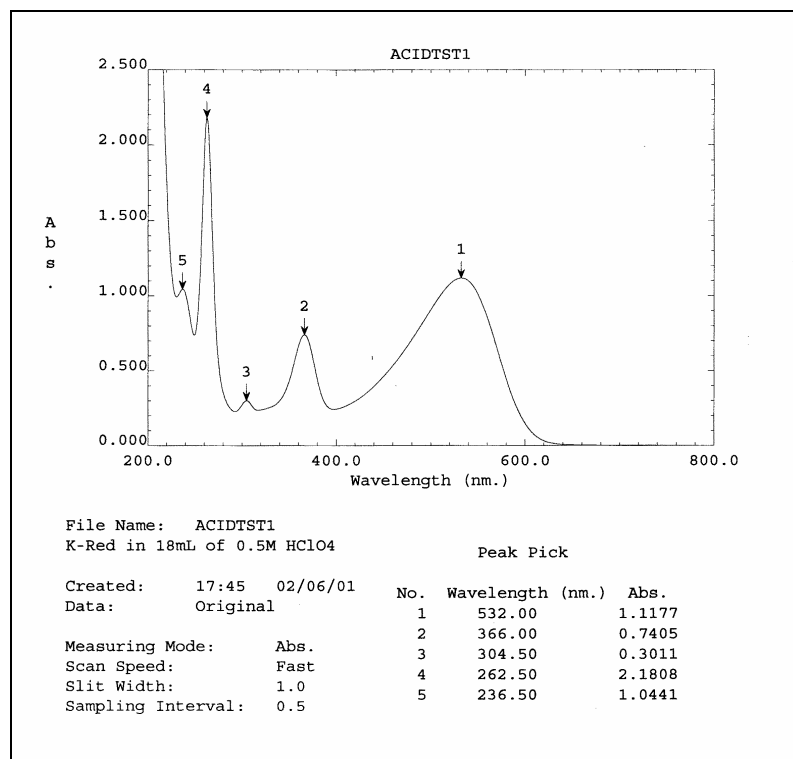


Figure 13. UV/Vis spectrum of **5a** in a 0.5M HClO₄ solution.

Roundhill, in his initial work on **5a**, found the single absorption peak to reside at 580nm¹⁴. As noted before, when using the oven method for the synthesis of **5a**, a small amount of **4a** was almost always formed as well. Peak #2 at 366nm in Figure 13 corresponds to the **4a** impurity. Roundhill found this peak to be present in his samples of **5a** as well. Conversely, Bedgood found the peak associated with his red compound to have a maximum at 500nm.

When performing experiments on **5a**, even a small amount of the **4a** impurity would cause major problems during crystallization attempts and lead to inaccurate elemental analyses. Numerous attempts at crystallizing **5a** were made by Bedgood³⁵ yet no crystals were obtained. By using the oven method for the synthesis of **5a**, it was

hoped whatever impurities that had hindered Bedgood's crystallization attempts would be eliminated.

4a Impurity Percentage Experiment

A quick experiment was run on a number of **5a** samples in order to find the amount of the **4a** synthesized during **5a**'s initial synthesis. Since **4a** had been heavily studied in the past its molar absorptivity was known. Using Beer's Law, the molar absorptivity for **4a** and the UV/Vis absorbance values for **4a**'s 369nm absorbance peak, the amount of **4a** could be calculated. The different samples of impure **5a** were weighed prior to addition to water. After the UV/Vis spectrum was obtained, the molar concentration of **4a** was converted to weight and the w/w percentage of **4a** was found. Table 2 displays the data calculated for this experiment.

Sample #	Percent 4a (Weight 4a/Total Weight)*100
1	15.7%
2	11.6%
3	17.9%
4	13.4%

Table 2: Percent of **4a** present in any given sample of **5a** (w/w)

It appeared that the amount of **4a** present in any given sample of **5a** was fairly constant and only varied from 11.6% to 17.9%. This was a surprising find since the intensities of the absorbance peak for **5a** seemed to fluctuate by a greater amount than what the calculated percentages of **4a** warranted. In some instances, it seemed that there was not enough red compound to make up the difference between the total mass and the

mass of **4a** calculated from the UV/Vis spectra. Other impurities were most likely what made up the remaining mass after the subtraction of **4a** and **5a** which meant the red compound needed to be purified.

Attempts at Crystallizing the Red Compound

Three common techniques for growing crystals were employed. One such method was layered differential solubility. In layered differential solubility, a concentrated solution of the compound to be crystallized is placed in a container such as a flame-sealed Pasteur pipette. A solvent to which the compound to be crystallized is insoluble is carefully layered on top of the solution whereupon the container is covered. Most often the two solvents are not completely insoluble and a very small amount of the solution will dissolve in the other solvent. During the mixing, which is diffusion controlled, a small amount of compound will be transferred over to the insoluble solvent side whereupon it is deposited on the side of the container. As more and more compound is transferred to the insoluble solvent, the compound will begin to combine with the compound already deposited on the side of the container. The mixture is usually allowed to sit undisturbed for many weeks until crystals form.

An aqueous solution of **5a** was used in conjunction with a variety of other solvents in an attempt to form crystals of **5a** via layered differential solubility. Although, it was already known that **5a** was water sensitive, it was hoped that any **5a** remaining in an aqueous solution would crystallize out before it could completely decompose. Bedgood had previously performed a large number of layered differential solubility

combinations during the research for his dissertation, so only a few incomplete experiments needed to be reexamined.

Solvent Combination	Result
H ₂ O / Acetone	Decomposition before any crystal formation could occur
H ₂ O / Methanol	Decomposition before any crystal formation could occur
DMF (H ₃ PO ₃) / Acetone	Solution remained red for some time No crystal formation occurred. Eventually decomposed.
Ethylene Glycol / Acetone	Solution remained red for some time No crystal formation occurred. Eventually decomposed.

Table 3. The four solvent combinations used in conjunction with the layered differential solubility technique to form crystals of **5a**

Table 3 summarizes the results for the layered differential solubility experiments. It was found that **5a** decomposed much too quickly in water to form any crystals. In the case of the acidified DMF/acetone combination, it was found that **5a** was soluble and stable for a longer period of time in DMF when compared to water. Regrettably, the DMF appeared to decompose **5a**. Water is soluble in DMF so it was assumed that it was dissolved water within the DMF that caused the decomposition of **5a**. On further thought, using DMF as a solvent may have been a poor choice. DMF contains a nitrogen with an available lone pair. The available lone pair on the nitrogen could easily attack the platinum atoms within the **5a** compound. Although platinum makes fairly strong bonds with phosphorus, platinum makes even stronger bonds with nitrogen. Also the DMF needed to be acidified in order to get **5a** to dissolve; this was done by adding a small amount of H₃PO₃. **5a** is readily soluble and stable in ethylene glycol yet crystal formation did not occur. It was apparent that **5a**, with its high sensitivity toward water,

was not going to be a suitable salt to use in the slow crystallization experiments. One or more salts with varying solubilities would have to be synthesized.

Tetraphenylphosphonium red, **5e**, is a salt of the red compound that had not been thoroughly studied prior to this work. **5e** has a number of benefits to that of **5a** namely that it is water insoluble. The solubility of **5e** was tested and found to be insoluble in H₂O, CHCl₃, dichloromethane, methanol, ethanol and ethyl ether. However, it was found to be soluble in acetonitrile (CH₃CN) and acetone and only slightly soluble in DMF.

The stability of **5e** in solution was found to be much greater than that of **5a**. Although decomposition still occurred when in solution, samples of **5e** were found to last from two to three weeks in acetonitrile versus **5a**'s three to four days in H₂O. In DMF or acetone, **5e** was found to be more stable than **5a** in water by only a couple of days. The UV/Vis spectrum of **5e** in CH₃CN (Figure 14) was found to be very similar to that of **5a**.

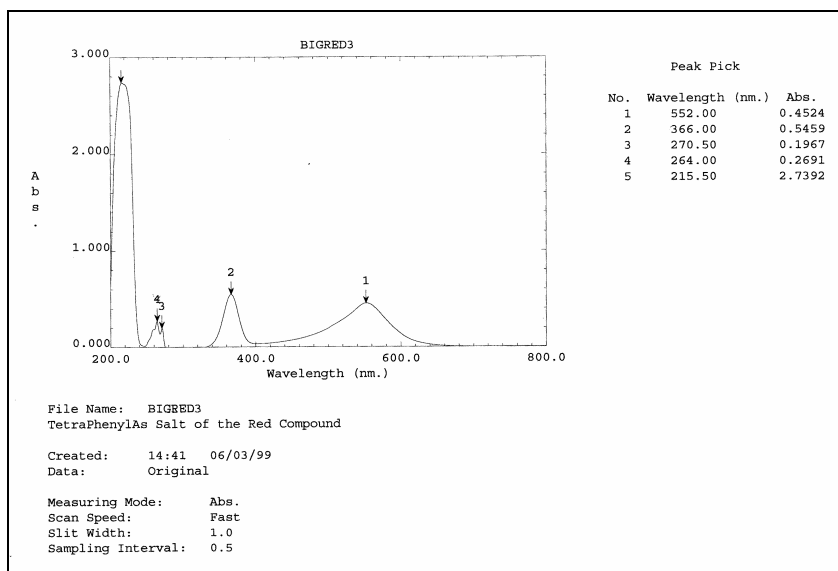


Figure 14. **5e** UV/Vis spectrum in CH₃CN

The peak associated with the red compound at 552nm was shifted to a higher energy compared to that of **5a**. This was most likely caused by the change of solvent. Also, it was apparent that the green impurity was still present in the solution and that the potassium counter cation in **4a** was replaced by tetraphenylarsonium cation to form $[(C_6H_5)_4As]_4Pt_2(P_2O_5H_2)_4$.

Using **5e**'s newly found stability in CH_3CN , another attempt at the crystallization of the red compound was made by slow evaporation. Slow evaporation crystallization entails making a concentrated solution of the compound to be crystallized and solvent to which the compound has high solubility. The solution is then placed in a desiccator in the open air if the compound is air/moisture stable or a Dewar if the solvent is highly volatile upon which solvent is allowed to evaporate. As the solvent evaporates off, the solution will become increasingly concentrated. The compound to be crystallized will slowly drop out of solution and, if the evaporation is slow enough, crystals will form.

A concentrated solution of **5e** and CH_3CN was placed in a Petri dish, locked in a drawer and allowed to evaporate in air until all the solvent was removed. At the end of one week, a larger amount of red colored solid was visible on the bottom of the Petri dish. **5e** appeared to have coagulated and formed large, red colored translucent crystals during the evaporation process. Upon closer inspection under an optical microscope, it was found that these structures were not crystals but were amorphous globules of **5e** that had coagulated. These globules were checked under a polarizing microscope to verify

that no crystals were present. Along with the formation of small globules of **5e**, a large sheet of **5e** covering the bottom of the dish was visible as well. This method was repeated a number of times and yielded the same results after each trial. It was thought that the evaporation occurred too quickly and that the amorphousness of the solids formed was caused by the rapid condensation of **5e** so a slower method was employed.

Another sample of **5e** in CH₃CN was made, placed in a graduated cylinder, and placed in a freezer at -10 °C. The solution was cooled to slow the solvent evaporation rate thus allowing the **5e** material to condense at a much slower rate. The solution was allowed to remain in the freezer for two months after which all the solvent had been removed. A red translucent solid was present on the bottom of the flask that was inspected via an optical polarizing microscope. It was found that the solid was the same amorphous material that was precipitated during the slow evaporation experiments in air. Numerous other attempts were made following the above method all of which had similar results.

Another, more controlled method of crystallization was employed: distillation crystallization which is just another name for slow evaporation. Figure 15 illustrates the apparatus used in distillation crystallization.

First, the entire system is flame dried and purged with an inert, dry gas prior to the introduction of any solvent. After the pre-preparation is completed, the compound to be crystallized is placed in flask 'A'. Next, a solvent trap is made by placing flask 'B' in ice water. The entire system (minus flask B) is left at room temperature and the solvent from flask 'A' is allowed to evaporate. Similarly to slow evaporation, as the solvent from

flask 'A' evaporates, it will be condensed and collected in flask 'B' and the concentration of the compound to be crystallized in flask 'A' will increase. As the concentration of the compound to be crystallized nears the saturation point, small amounts of materials will begin to crystallize. If the evaporation of the solvent from flask 'A' is slow enough, the compound to be crystallized will form crystals.

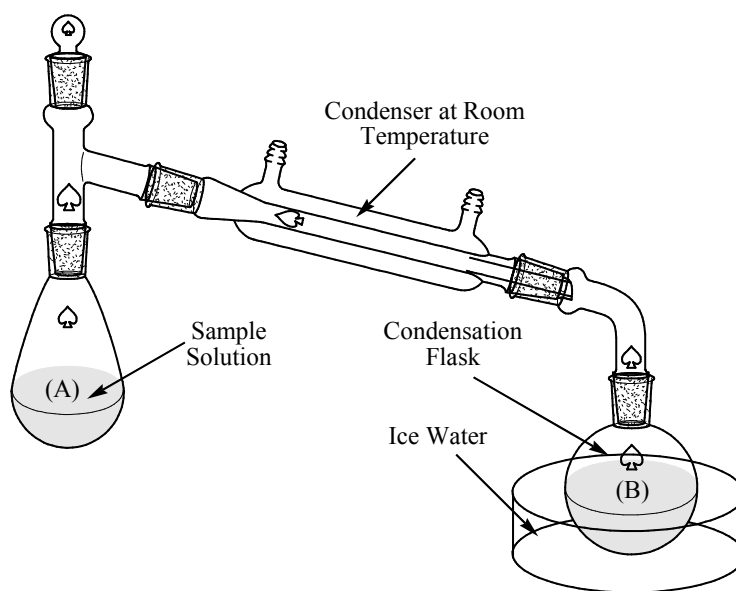


Figure 15. Distillation crystallization apparatus for the crystallization of **5e** from CH_3CN

This method was found to have definite benefits to that of the standard slow evaporation. First, the environment was better controlled as the surrounding atmosphere was kept dry and free of oxygen. Secondly, if the solvent in flask 'A' was boiling off too slowly or quickly, the temperature of flask 'A' could be controlled.

Referring to Figure 15, about 0.0291g of **5e** was placed in 20mL of CH_3CN and of that solution 8mL was placed in flask 'A'. Prior to the solution's introduction, the entire glassware system was dried and purged with dry argon. The CH_3CN was allowed

to evaporate off over a period of two weeks. The dark red solution became paler as the weeks progressed. At the end of the three weeks, the solution was very pale red. A limited number of small crystals of the tetraphenylarsonium salt of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ had formed but no crystals of **5e** were evident. It appeared that the CH_3CN was decomposing **5e** to form the tetraphenylarsonium salt of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$. The distillation crystallization method was performed a number of times on **5e** but yielded no interesting crystals. It appeared that the same crystallization problems that had plagued previous workers continued to be a problem.

Another salt, Methyltriphenylphosphonium red (**5d**), was synthesized and was found to have properties different from that of **5a** and **5e**. Like **5e**, **5d** is insoluble in water. Secondly, it is very soluble in DMF and CH_3CN and quite stable in those solvents for up to three weeks compared to **5a**'s three days in water. Bedgood worked quite extensively on **5d** and numerous crystallization attempts were made to no success. Bedgood's dissertation covered almost every crystallization technique that could possibly be done on **5d** so no further crystallization attempts were made using that salt.

After more thought about why crystallization of **5a**, **5d** and **5e** was unobtainable, it was concluded that the ever-present impurities were the major culprit. More impurities than just **4a** seemed likely, due to the crude method of preparation for **5a** and based on the UV/Vis spectrum for **5a** and its salts. Upon revisiting the UV/Vis spectrum for **5a** (Figure 16) it was apparent that more unknown compounds were present in solutions of **5a** (and **5d** and **5e** as well.)

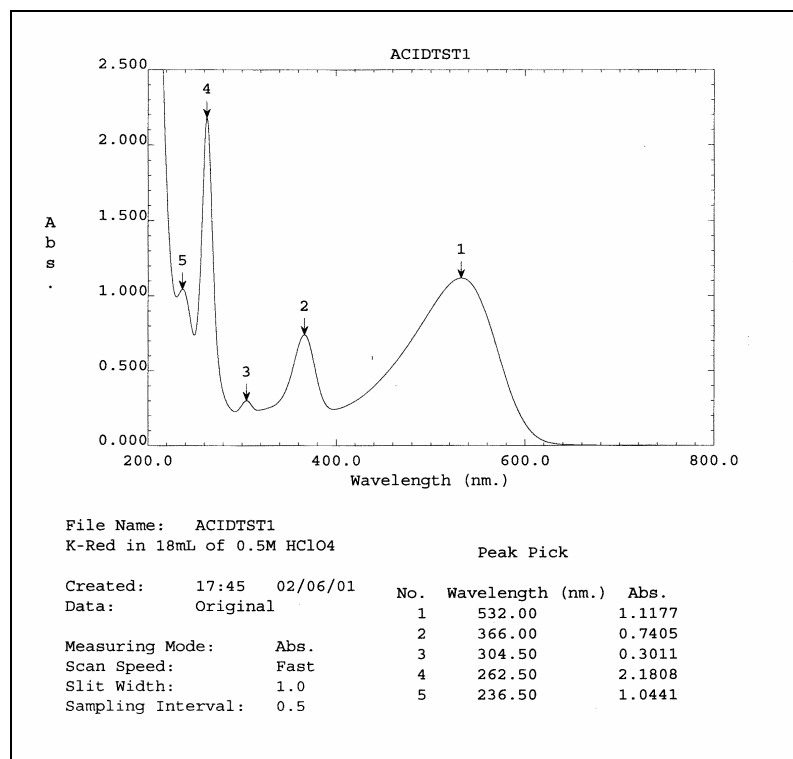


Figure 16. UV/Vis spectrum of **5a** in a 0.5M HClO₄ solution.

In Figure 16, it was notice that the peak at 532nm corresponding to the red compound was not completely symmetrical. The right side of the peak decreased following a nice gaussian curve whereas the left side of the peak trailed off. In UV/Vis spectroscopy when two UV/Vis peaks are close in wavelength they can overlap. When this happens, the two peaks will become additive and a new peak is made. This peak will no longer have a nice bell shape but rather a large, broad peak will be seen³⁶. The original, multiple peaks that make up this newly combined peak can be determined mathematically and the original, non-added spectrum can be plotted.

Using the graphing and mathematical program *Origin*, the UV/Vis spectrum of **5a** was manipulated and a mathematical deconvolution routine was applied to the spectral

data. A spectrum that showed all the possible peaks that made up the original **5a** peak was calculated. It was apparent that three peaks, one at 565nm, the other at 531nm and the final peak at 500nm were adding together to form the complete peak seen in all of **5a**'s UV/Vis spectra.

The need for the complete purification of the red compound was now apparent. After searching the literature, it was a surprise to find that no one had tried to purify any salts of the red compounds using methods other than recrystallization. Chromatographic methods such as thin layer chromatography (TLC) and column chromatography seemed ideal for separating the red compound from its impurities. Differential solubility, which will be covered later in this chapter, was also another viable option.

Thin Layer Chromatography (TLC) on **5a**, **5d** and **5e**

Initially, TLC was used to see what optimal conditions were needed for the separation of **5a**. A **5a** and water solution was made, spotted on Baker-Flex Aluminum Oxide IB-F TLC plates and eluted with acetone. It was noted that the moment **5a** came in contact with the TLC plate; the red color associated with the red compound disappeared. After completion of the elution, no spots or streaks were visible. **5a** had reacted with separation material on the TLC plate. Baker-Flex Silica Gel IB-F TLC plates were also used on **5a** but the same reaction/decomposition results were seen. Attempts to separate the red compound from its impurities using both the Aluminum Oxide and Silica Gel TLC plates were made on the **5d** and **5e** salts as well. It was believed that, by using solvents other than water, the stability of the red compound would be increased. Unfortunately, similar decompositions were observed for **5d** and **5e** as

what had been previously observed for **5a**. It appeared that both of the TLC plate separation coatings were too harsh for the red compound. Attempts were made at separating the various salts of the red compound from its impurities using Silica Gel and Alumina packed columns. These packing materials (the same ones used in the TLC plates) decomposed **5a**, **5d** and **5e** upon contact with the column bed. It was found that a gentler separation material was needed if the red compound was to be purified via column chromatography.

Differential Solubility Experiments

When a small amount of $\text{MePh}_3\text{PNO}_3$ was added to a solution of **5a**, a dark red compound was precipitated. This compound, on average, had an absorbance maximum of 560-580nm. The solution was then treated with Ph_4AsBr to yield a light red precipitate with an absorbance between 450nm and 500nm.

It was noted that upon adding Ph_4AsBr to a solution of **5a**, the color of the precipitated product changed. Depending on the amount of cation added the color would vary between light red and dark red. This didn't appear to be something of importance until the UV/Vis spectra of each of the compounds were recorded. Figure 17 is the spectrum of the 'light red' compound made by adding a small amount (much less than an equivalent) of Ph_4AsBr to a stirring solution of **5a**.

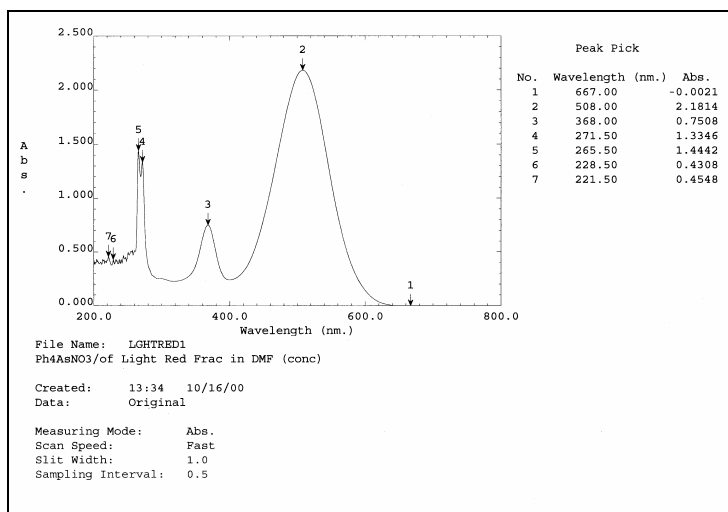


Figure 17. Light Red compound precipitated from **5a** and Ph_4AsBr .

The major absorbance peak for this red compound was 508nm. Figure 18 is the spectrum for the ‘dark red’ compound that was precipitated by adding a large amount of Ph_4AsBr to the remaining **5a** in solution.

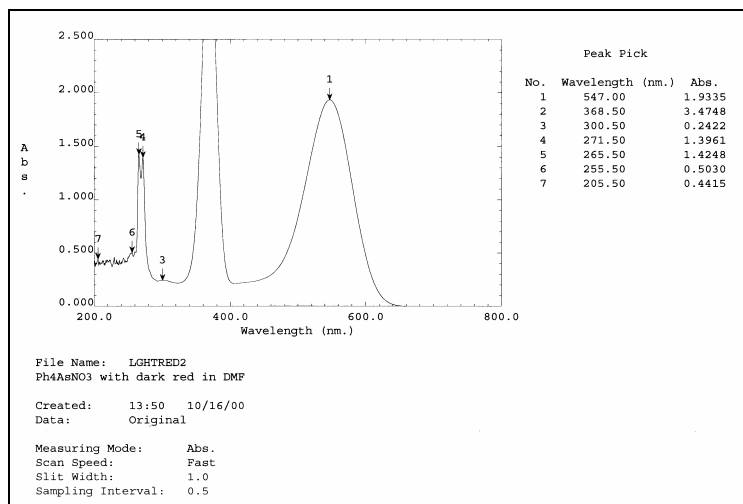


Figure 18. Dark Red compound precipitated from **5a** and Ph_4AsBr

The major absorbance peak for this compound was found to be 547nm. It was apparent that some compounds were being precipitated during the cation exchange.

The idea that two different compounds could be separated via cation exchange was not illogical. Two different compounds in solution could have very different affinities toward the Ph_4As^+ cation. If only a small amount of cation were added, say an amount less than what was needed to completely exchange with the anionic compound present, it would be expected that the anion with the most affinity toward Ph_4As^+ would be the first to exchange. In the case of Ph_4AsBr and **5a**, the ‘light red’ compound most likely favored the Ph_4As^+ cation versus K^+ whereas the ‘dark red’ compound had a slightly greater affinity toward the K^+ cation than the ‘light red’ compound.

In another trial, a slightly larger amount of Ph_4AsBr was initially added to a solution of **5a**. The ‘light red’ compound that formed was not quite as light as seen in previous trials. Rest of the solution was precipitated with Ph_4AsBr which produced the ‘dark red’ compound. The UV/Vis spectrum revealed the absorbance maximum for the ‘light red’ compound to be 495.5nm that was quite similar to what was seen in other trials. The UV/Vis spectrum for the ‘dark red’ compound gave an absorbance maximum of 519.5nm, much less than what was previously seen. The most likely explanation for this lower energy-shifted peak is that not enough of the Ph_4AsBr was added to the solution and the precipitation of both the ‘light red’ compound the ‘dark red’ compound occurred after the second addition of Ph_4AsBr . The spectra of the two peaks were added together to form the peak at 520nm.

To test whether varying the amount of the ‘dark red’ or ‘light red’ compounds in solution would affect the overall UV/Vis spectrum for the red compound, a sample of the ‘light red’ and ‘dark red’ salts of Ph_4As^+ were scanned separately and then mixed in varying quantities and rescanned to observe the difference in the red peak position. Figure 19 shows the results of this experiment.

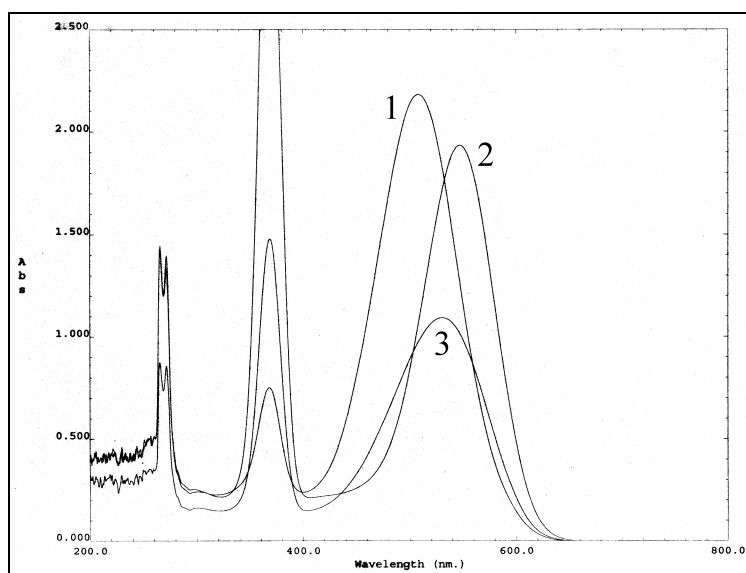


Figure 19. Light Red (1) and dark red (2) salts of Ph_4As^+ mixed together to yield peak (3)

Although the concentration of the samples was reduced, it is clear that by mixing a small amount of ‘light red’ Ph_4As^+ salt (Figure 19, Peak 1) with ‘dark red’ Ph_4As^+ salt (Figure 19, Peak 2) led to the addition of the two peaks yielded a new peak (Figure 19, Peak 3). This experiment showed that the ‘light red’ and ‘dark red’ compounds were two separate compounds. The complete red compound was a combination of at least two compounds which control the position of the absorbance peak for the red compound.

DEAE Cellulose Chromatography on Salts of the Red Compound

Historically, chromatographic work on sensitive metal compounds had been done using diethylaminoethyl (DEAE) cellulose and an appropriate polar solvent. Our initial test proved that the less harsh DEAE chains did not destroy the salts of the red compound. For samples containing **5a**, the DEAE cellulose was prepared by soaking it in 0.5M HCl for one hour, filtering and washing with deionized water, soaking the cellulose in 0.5M KOH for 30 minutes and filtering and washing until a pH neutral filtrate was obtained. The columns were prepared by placing a small amount of glass wool in the base of the column followed by sand and then packed with the DEAE cellulose in water. Layering the top of the cellulose with another layer of sand completed the column. Through the column was passed three column volumes of the chosen eluent.

Two different solvents were used as eluents for the separation of **5a**, 1M H₃PO₃ and 1M HClO₄. When eluting **5a** with 1M H₃PO₃, very little separation was observed and much of the loaded material remained on top of the column. Eluting **5a** with 1M HClO₄ gave much better results.

Numerous separations with 1M HClO₄ yielded what appeared to be four differently colored compounds. A yellow compound was the first to be separated followed by an orange compound. Both of these compounds were highly fluorescent. Lastly, a pink/purple band was the last to exit the column. This purple compound had no fluorescence and took quite a while to be removed from the column. A colorless band, which was highly fluorescent, remained on the top of the column. This band was most likely a small amount of residual **4a**. Since **4a** has such a high quantum yield and large

extinction coefficient, a small amount of compound would be very visible to the naked eye.

The same instabilities of **5a** in water were seen during and after the separations of **5a** in the 1M HClO₄. Once the compounds were taken off the column, they appeared to decompose rather rapidly. This limited the possibility of obtaining accurate UV/Vis data and in some cases data were completely unobtainable.

Switching to **5e** helped control the decomposition somewhat although decomposition was still seen. Unfortunately, instead of the four colored bands which were visible while running the separation of **5a** in 1M HClO₄, four new bands were seen. In order of elution from the column were an orange band and a faint light red band. Stuck on the top of the column were a green band and a red band both of which were highly fluorescent. Useful UV/Vis data were not obtained for these trials.

The salt that had the greatest promise was **5d**. Using the DEAE cellulose and DMF as an eluent, **5d** yielded five bands versus the four bands seen in the other two separations. The bands, in order of elution from the column were a yellow/orange band, small red band and a purple/pink band. Both a red and green band remained on the column. The separations did not proceed as hoped. It became apparent after a number of trials that the separated and collected compounds were decomposing to form other colorless compounds.

Light Scattering Study of **5a**

Roundhill and others believed **5a** to be a higher polymer similar in structure to that of **5a**. The cellulose separations and UV/Vis study of **5a** and **5d** alluded to the

existence of other compounds (or a series of compounds) contained in solution. If, as Roundhill stated, **5a** were actually a trimeric platinum compound, why then would it stop at only being a trimer? Based on elemental analyses, Bedgood concluded that the **5a** was in actuality a heptameric platinum species. It seems that both may have been correct in the length of the platinum chain (just not the absolute configuration.) Light scattering experiments suggested that the red compound was a series of compounds ranging from trimeric platinum chains up to very large oligomers. In an effort to better understand the size of the particles in a solution of **5a**, an 18-point light scattering study was done. Light scattering is used most often for determining the molecular weight and size of molecules. If the atoms composing the molecule are known, a fairly accurate estimation of size of the molecules can be obtained.

Brief Explanation of Light Scattering and its Theory

When light is impinged upon a sample solution, the light hitting the molecules within the solution will be scattered. There are two predominate ways that light can be scattered by the molecules in solution. The first method is Rayleigh scattering. Rayleigh scattering is the same phenomenon that causes the Earth's sky to appear blue. Molecules on the order of or smaller than the wavelength of visible light (up to about 1/10 the wavelength of light) will cause the light to be elastically scattered in all directions. The scattering of light by molecules smaller than the wavelength of visible light is possible due to scattering via an induced dipole moment with the molecule caused by the electromagnetic nature of the light wave.

Molecules that are larger than the wavelength of a light wave will cause scattering known as Mie scattering. The math corresponding to these two methods is beyond the scope of this research and will not be discussed. The degree of light scattering is dependant on the size of the molecules or particles in solution and the degree of polarizability of those molecules.

Normally, a sample of known concentration is taken and a series of dilutions of that sample are made. The samples are scanned at a single wavelength and the scattered light is measured. Using a series of equations, the data for each of the samples is plotted. From these plots, the root-mean-radius of gyration (RMG), which is a value of how large the average particles are, and the molecular weight can be determined.

Experimental Execution and Analysis of Light Scattering Data of **5a**

A dry sample of **5a** was used in five solutions of varying concentration for the light scattering experiments. **5a** in an aqueous solution was used instead of the more stable tetraalkylammonium/organic solvent combination due to diffraction issues caused by using solvents other than water. The initial samples appeared to have large particles such as dust and other foreign matter suspended in the solution. This problem was remedied by filtering the samples through 1.0 μ m cellulose filters. The filtering process seemed to have no effect on the aqueous sample other than to remove the macroscopic particulate matter. After the samples stabilized and were scanned, two different mathematical plots were used on the data. Of the five solutions made, one data point had to be discarded due to rapid degradation of the sample. The Berry plot and Zimm plot for the data are shown in Figures 20 and 21 below.

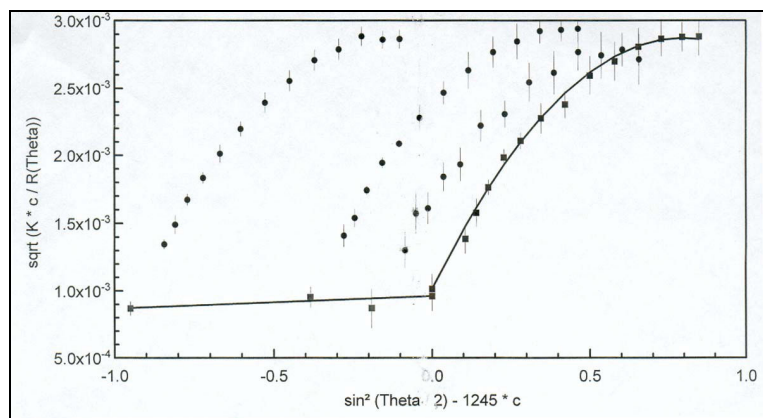


Figure 20. Berry Plot for aqueous samples of **5a**

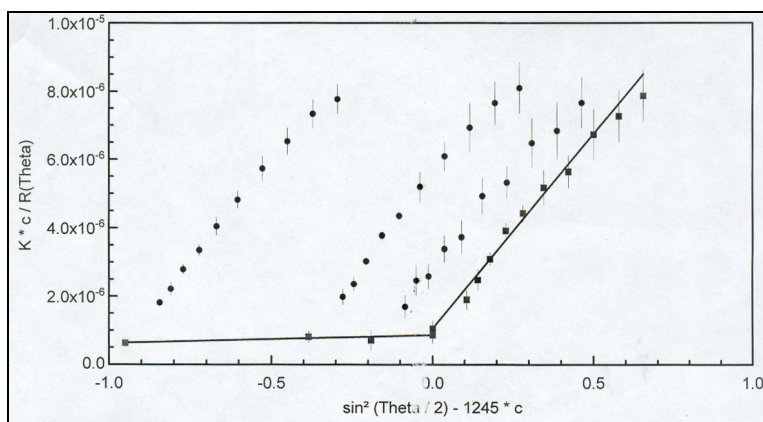


Figure 21. Zimm plot of aqueous samples of **5a**

There are three major plots that can be made using data obtained from a light scattering experiment: Zimm, Berry or Debye. A Debye plot was attempted but gave very poor fits for the data. A Berry plot was used and proved to be better than the Debye but still was not a “good” fit. Upon inspection of the Berry plot in Figure 20 it is noticeable that as the series of points are fairly linear until they surpass 2.5×10^{-3}

$\sqrt{K * \frac{c}{R * \theta}}$. Any of the three-dimensional plots should be fairly flat in order to get a

respectable fit. It was found that the Zimm plot, with its near linear points, was a much better fit. The value for the RMG for the Zimm plot was 234.9 $\pm$ 27.7nm. This value is surprising for two reasons. It shows that the red compound is much larger than what was previously hypothesized. Also it is very close to the RMG value of 217.4 $\pm$ 18.8nm obtained from the poorly fitted Berry plot.

The RMG value of 234.9nm means that the platinum material that was in solution was 234.9nm in diameter. This could mean that the platinum material were ovoid in shape or were long polymeric formations that were tumbling rapidly. Assuming that the platinum atoms are POP bridged, the average distance between two platinum atoms bridged by a POP ligand is 2.925Å⁶. Assuming that the platinum ‘red’ compound was a long polymer, there would be approximately 750 to 800 individual platinum atoms contained in a single “red-compound” molecule.

As always, there was a small amount of the dimeric **5a** present and some was formed during the experiment. Keeping in mind that the RMG value is in fact an average value of all the various sizes of molecules present in a solution, more than likely there are much larger and smaller species present as well. The RMG value obtained from the light scattering study is most likely due to a wide range of compounds present in a solution of **5a** varying from small to large in size.

Shifting Peaks for the Red Compound Maximum

After investigating a number of UV/Vis spectra associated with the **5a**, **5d** and **5e** salts, it was noticed that the absorbance maximum associated with the red compound, which usually occurred at 530nm to 540nm, never appeared at the same location.

Shifting caused by a solvent change is quite common in all spectroscopic measurements but it was apparent that something else was affecting the absorbance maximum peak position. A study was done where the three salts, **5a**, **5d** and **5e** were diluted in various solvents. Assuming that the highly colored red salts followed Beer's Law, the absorbance maximum should be easily calculated for each dilution and no difference in the peak positions should occur.

A small portion of the 'dark red' compound precipitated from **5a** and Ph_4AsBr was placed in a small amount of DMF. The solution was diluted by two-thirds and two-fifths its original concentration. The UV/Vis spectra for these three concentrations were overlaid and are displayed in Figure 22.

In Figure 22 peak 1, the peak associated with the original sample of Ph_4As - 'dark red' had an absorbance maximum of 527nm, peak 2, which is associated with the diluted to 66% of the standard had an absorbance maximum of 514nm and an absorbance maximum of 503nm was found for the sample diluted to 40% of the standard (peak 3). A total blue-shift of 24nm was seen for the complete series. The green impurity visible at 371nm decreased in intensity as expected while being diluted.

When diluting samples of the 'light red' salt of Ph_4As^+ , the maximum absorbance wavelength shifted as well. In one particular instance, a sample of Ph_4As - 'light red' diluted to 16% and 10% of its original concentration shifted a total of 19.5nm. Since the molecular weight of the red compound is unknown and the purity was found to vary between subsequent samples, the UV/Vis spectra obtained prior to this discovery were thought to be inaccurate.

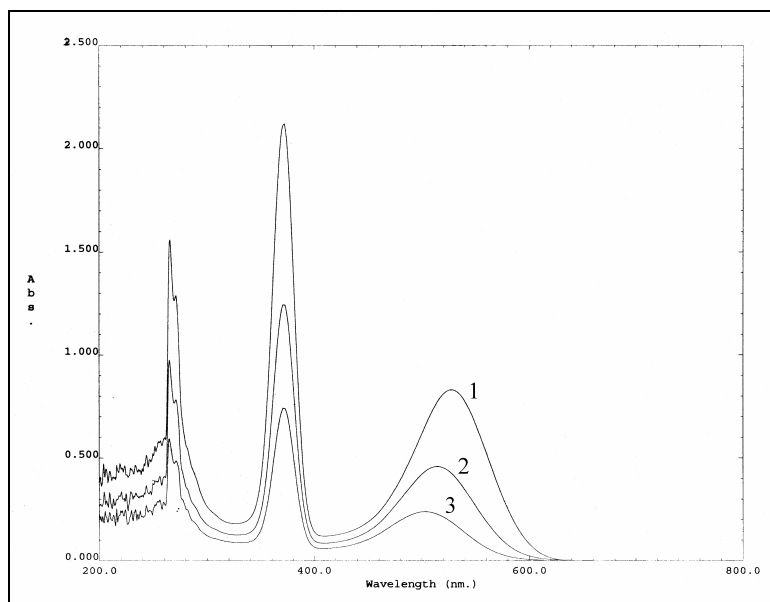


Figure 22. Three varying concentrations of Ph_4As -‘dark red’ in DMF. Standard sample (Peak 1), 66% of the standard (Peak 2) and a sample diluted to 40% of the standard (Peak 3)

A number of studies were done on the three salts to verify the concentration-based shifting. A slight shift for **5a** in a 1M HClO_4 solution was visible upon dilution of the samples (Table 4). The solution of **5a** was quartered in concentration yet the absorbance maximum wavelength only shifted 4.5nm.

Fraction of Initial Concentration	Absorbance Wavelength	Absorbance Maximum
1	532.00	1.1177
2/3	532.00	0.7050
1/2	530.00	0.4936
1/3	529.50	0.3700
1/4	527.50	0.2152

Table 4. UV/Vis Data for the dilution experiment of **5a** in a 1M HClO_4 solution.

Samples of **5d** diluted with DMF or CH₃CN yielded only a slight absorbance peak shift. The absorbance maximum wavelength for a solution of **5d**, dissolved in DMF and diluted to one-tenth its original concentration only shifted 5nm (Table 5).

Concentration (g/mL)	Absorbance Wavelength	Absorbance Maximum
2.9×10^{-4}	510.50	2.2742
2.42×10^{-4}	511.50	1.9635
1.933×10^{-4}	513.00	1.4458
9.67×10^{-4}	514.50	0.7154
4.83×10^{-5}	513.00	0.3589
2.42×10^{-5}	505.50 (very broad)	0.1787

Table 5. UV/Vis Data for the dilution experiment of **5d** in a DMF solution.

It seemed the DMF wasn't playing a part in the shifting peaks seen in the **5e**, Ph₄As- 'light red' or Ph₄As- 'dark red' UV/Vis spectra.

Based on the collected data, it appeared that the red compound(s) containing the Ph₄As⁺ cation yielded puzzling UV/Vis spectral results when in solution. To a solution of **5e** was added more of the colorless Ph₄AsCl. The absorbance peak associated with the red compound initially had a wavelength of 500nm. After the addition of Ph₄AsCl, the **5e** peak red-shifted 25nm to reside at 525nm. This experiment was repeated a number of times on different samples of **5e** and each time the peaks red-shifted anywhere from 15nm to 25nm. If more Ph₄AsCl was added to a solution already containing an excess of Ph₄AsCl, no shifting was seen. When working with **5a** or **5d**, no shifting was visible upon addition of excess cation. It was found that Ph₄AsCl affects the red compound in some way, either by reacting with it or by interacting with it in solution. Data dealing with **5a** and **5d** were deemed accurate where data that dealt with **5e** was considered

suspect. A better set of salts of the red compound and a good way of purifying the red compound was needed.

Synthesis and Investigation of the Tetraalkyl ammonium Salts of the red compound

While working with the potassium, Ph_4As^+ and MePh_3P^+ salts of the red compound it was found that those salts would not be ideal for experimental purposes. The potassium salt, **5a**, was found to be very unstable in water. The Ph_4As^+ salt, **5e**, was only soluble in a few solvents and would eventually decompose in those solvents. The Ph_4As^+ cation itself was found to cause anomalies in the UV/Vis spectra obtained from the samples of the red compound containing this salt. The MePh_3P^+ salt of the red compound, **5d**, was considered most ideal in that it was found to only be stable up to three weeks in one of the few solvents in which it was soluble: CH_3CN . A search of the literature found that the tetrabutylammonium salt of $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)^{4+}$ had been synthesized³¹. The tetra-alkylammonium cations usually have solubility characteristics similar to that of the normal alcohols containing the alkyl chains. Therefore, the usage of tetraalkylammonium cations allowed any red salts formed containing these cations to be soluble in virtually any organic solvent.

Initially, the tetrabutylammonium-red salt was made by adding an equivalent of tetrabutylammonium iodide to a stirring mixture of **5a** and CH_2Cl_2 . This salt was found to be soluble in water as well as other polar solvents. It was also found that the majority of the red compound remained in the aqueous phase as well. Since the purpose of this task was to completely remove the red compound from the presence of water other, higher alkyl chain ammonium cations were investigated. Salts of the red compound were

made using tetrapentylammonium iodide and tetrahexylammonium iodide. The tetrapentylammonium-red and tetrahexylammonium-red salts were soluble in solvents such as CH_3CN and ethyl ether. Both of these two salts were very promising except that the two compounds were still slightly soluble in water and a complete extraction into the organic solvents was not possible. These two salts, when explored via UV/Vis spectroscopy were found to be very stable in organic solvents such as ethyl ether and CH_2Cl_2 . The tetrapentylammonium-red and tetrahexylammonium-red salts were allowed to remain in solution for a number of months where, upon reinvestigation via UV/Vis spectroscopy, no decrease in absorbance peak intensity was visible. The next step was to see whether a decrease in concentration would cause a shift in the absorbance maximum wavelength similar to what was seen for the **5e** salt. No change in peak position was seen. The absorbance maximum wavelength was much higher for the tetra-alkylammonium salts of the red compound as well compared to that of **5a**, **5d** and **5e**. On average the peak wavelength was between the range of 560nm to 580nm, a much greater difference than the 480nm to 580nm range that was seen for the non-alkyl red salts.

When working with the tetrapentylammonium-red salt, a new peak began appearing in the UV/Vis spectra. A large peak at 442nm was seen increasing in intensity as the solution of tetrapentylammonium-red salt in CH_2Cl_2 was allowed to sit. At first, it was thought that the some sort of slow rate decomposition reaction was occurring. It was later realized that the new peak corresponded to an axially substituted $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ compound. The $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ anion was still in solution and could be formed from the

decomposition of the red compound and any residual water contained in the CH_2Cl_2 . An oxidizing agent (oxygen) was present but it was unclear as to what was axially substituting the $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ anion. It was found that the compound, $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{I}_2^{4-}$ was forming from the $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ impurity, oxygen in the air and I^- anion from the initial tetrapentylammonium iodide cation exchange. In later experiments, after purging CH_2Cl_2 with argon prior to performing any cation exchange, the formation of the axially substituted dimeric platinum(II) compound was halted.

In the hopes of completely eliminating the possibility of water interacting with the red compound, salts were made using the chloride salts of the tetraheptylammonium and tetraoctylammonium cations. Both of these chloride salts were known to be soluble in slightly polar solvents such as ethyl ether to non-polar solvents like hexane. The transition to non-polar organic solvents decreased the possibility of water being present in solution.

The tetraheptylammonium salt of the red compound, **5b** was synthesized according to the experimental procedure contained in this dissertation. **5b** was found to be soluble in ethyl ether, CH_3CN , benzene and CHCl_3 . Similarly, the tetraheptylammonium salt of the red compound, **5c** was found to be soluble in ethyl ether, CH_3CN , n-pentane and slightly soluble in CHCl_3 . Both of these compounds were found to be almost infinitely soluble in ethyl ether and infinitely stable as well. Samples kept for over four have been found to have the same absorbance spectrum as what they had when initially synthesized.

The UV/Vis spectra of both of these compounds gave an absorbance maximum near 580nm, very similar to what was found by Roundhill during his initial studies. The absorbance maximum wavelength for all the tetraalkylammonium salts were relatively similar when compared to the wildly variable absorbance wavelength seen with **5a**, **5d** and **5e**. Table 6 shows the peak positions observed for the tetraalkylammonium salts of the red compound.

Compound	Solvent	Common Absorbance Peak Wavelength (nm)
Tetrabutylammonium-red	CH ₂ Cl ₂	565.00
Tetrapentylammonium-red	CH ₂ Cl ₂	581.50
Tetrahexylammonium-red	CH ₂ Cl ₂	573.00
5b	Ethyl Ether	577.00
5c	Ethyl Ether	575.50

Table 6. UV/Vis Data for solutions of the tetraalkylammonium salts of the red compound

It appeared that the other impurities (i.e. the light red compound) that were present in the **5a**, **5d** and **5e** were left behind in the aqueous phase during the solvent extraction. Although the unknown impurities were removed, the green, $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ impurity still remained.

Tetraalkylammonium-Red Separations

In order to further separate any impurities from the red salts, Sephadex LH-20 chromatographic medium was used. Sephadex is a size exclusion chromatographic medium that is also known to be very gentle toward sensitive compounds. CH₂Cl₂ was used to swell the LH-20 medium. **5c** was added to the column and ether was used as the

eluent. It was found that the amount of **4a** initially seen in the **5c**/ether solution was drastically reduced. What didn't appear to happen was the removal of any other impurities. The other tetraalkylammonium salts of the red compound were passed through Sephadex columns yielding similar results.

As previously stated, when working with solutions of the tetrabutylammonium salt of the red compound, it was noticed that a large amount of **4b** was removed from solution. It was also stated that the majority of the impurities remained in the aqueous phase when **5a** was treated with either tetraheptylammonium or tetraoctylammonium chloride. Using two subsequent cation extractions, a relatively pure sample of the red compound was obtained. The absorbance wavelength was found to be 571nm, again this was very similar to what Roundhill found in his studies.

The major problem limiting any salts of the red compound being investigated via NMR spectroscopy was the fact that the samples would decompose over a short period of time. In past investigations, this did not allow for very good NMR spectra to be obtained. With the purification of a sample of **5b**, its stability and excellent solubility in organic solvents allowed for its investigation via NMR spectroscopy to commence.

Higher Order NMR Spectra of **5b**

Early NMR Work on the Red Compound

Early ^{31}P NMR studies by both Roundhill and others found that **5a** was what appeared to be a broad triplet centered at 62ppm. This triplet was found to have a single platinum-phosphorus coupling (J_{ax}) value of 3200Hz. A coupling constant of this size is

characteristic for couplings in other phosphorus containing platinum(II) compounds. NMR spectra of **4a** and its salts have a similar splitting pattern (a pseudo-triplet) along with the phosphorus-platinum coupling constant of 3200Hz. It was asserted by these other investigators that the red compound, since its spectrum only differed by its chemical shift and the fact that the peaks were slightly broader than that of the peak seen for **4a**, was not very different in structure compared to that of the $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ dimer.

The recent work contained in this dissertation shows that the red compound is a bit more complex than just being a minor derivative of the $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ dimer. Samples of the newly purified **5b** red compound salt in ethyl ether were initially investigated via ^{31}P NMR spectroscopy on a 101.2MHz instrument. The data from this spectrum is displayed in Table 7.

	Roundhill's Data ¹⁴	Bedgood's Data ³⁵	Initial Data
^{31}P Chem Shift	N/A	62.1ppm	62.5ppm
$J_{\text{Pt-P}}$ Coupling	3300Hz	3300Hz	3300Hz

Table 7. NMR data from past NMR experiments and current experiments.

The ^{31}P chemical shift and splitting pattern obtained from the NMR spectral data of **5b** was exactly what Roundhill reported for **5a** and what Bedgood reported for **5d**. In an attempt to better resolve the NMR spectral peaks for **5b**, a temperature study at 202.4MHz was performed on a pure sample of **5b** in ethyl ether. The peaks sharpened slightly as the temperature was increased and broadened slightly as the temperature was decreased (which is what you would expect for this type of experiment.) What was puzzling was the shifting of the peaks as the NMR field was increased. The chemical

shift of peaks seen in a spectrum obtained in a low field NMR will shift when measured at a higher magnetic field. This shift will be uniform if the peaks are associated with nuclei in a single molecule. Upon moving to a higher magnetic field, the peaks were observed to shift randomly. This led to the belief that there was more than one compound present. After careful study of the data and general NMR theory, a better conclusion was made.

Analysis of NMR Data for **5b**

Multiple ^{31}P NMR spectra of one pure sample of **5b** were recorded at four different magnetic fields at 101.2, 121.4, 202.4 and 242.9MHz. An attempt to explain the splitting pattern as if they were simple first-order spectra yielded puzzling results. Since coupling constants are independent of the external magnetic field, any coupling seen in a 101.2MHz spectrum should be visible in a 242.9MHz spectrum as well. Initially, there appeared to be no coupling between any of the phosphorus or platinum nuclei. After closer analysis, it was apparent that the spectra were non-first order. It was determined that not only were the spectra higher-order but contained both an AB and an ABX splitting pattern.

Simple AX Spectra

When dealing with a simple first order spectrum, it is quite easy to explain why the recorded splitting pattern is as it appears. The two factors that dictate the splitting pattern of a nucleus are the chemical shift (how the nucleus interacts with the external applied magnetic field) and the spin coupling between the nucleus and the other nucleus

or nuclei with which it interacts, if any. The coupling constant, J , between two unequivalent nuclei is only dependent on how the two nuclei interact with each other and is completely independent of the applied magnetic field. When dealing with two nuclei (designated by the letters 'A' and 'X') that have a simple first order spectrum, it can be said that the ratio of the difference between the unsplit chemical shift of nucleus A and X (ν_{AX}) in Hertz versus the coupling constant between nucleus A and X (J_{AX}) in Hertz is equal to or greater than 25. That is to say that ν_{AX} is usually much larger than J_{AX} . Once this ratio falls below 25, a deviation from first order behavior is had and perturbation (distortion) of the resonance peaks is observed.

Higher-Order AB Spectra

A first-order, AX splitting pattern becomes an AB splitting pattern as the difference between the A and B chemical shifts (ν_{AB}) over the AB coupling constant (J_{AB}) approaches 1. The classical model used to explain simple first order spectra cannot be used for complex AB spectra although the peak positions as well as peak intensities can be calculated using a series of simple equations^{37, 38}. Figures 23a and 23b are used to illustrate the change from a first order AX pattern to a higher order AB pattern.

The observed pattern is dependent on the initial unsplit chemical shift of both the A and B nucleus (ν_A and ν_B respectively) and J_{AB} . As ν_{AB}/J_{AB} approaches 1, the doublets in Figure 23a will close in and the inner '2' and '3' peaks in will grow in intensity and move inward toward each other (but not cross) whereas the outer peaks will not shift but decrease in intensity as shown in Figure 23b. This is true for all higher-order AB splitting patterns.

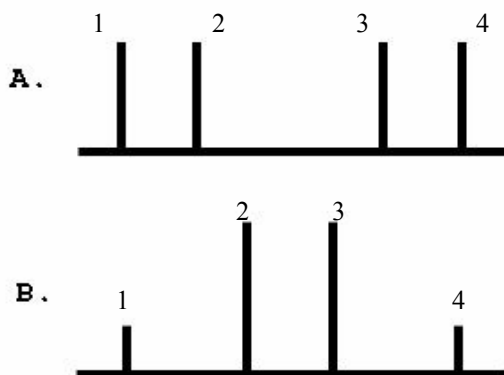


Figure 23a and b. (a) A simple first-order spectrum where δ_{AB} is much larger than J_{AB} .
 (b) A non-first-order spectrum where the value of δ_{AB} is approaching J_{AB} .

If the energies of the nuclear transitions are to be calculated for an AB pattern, all that is needed are the equations in Table 8.

Transition	Energy	Relative Intensity
3 $\rightarrow$ 1	$0.5 \cdot J_{AB} + C$	$1 - \sin 2\theta$
4 $\rightarrow$ 2	$-0.5 \cdot J_{AB} + C$	$1 + \sin 2\theta$
2 $\rightarrow$ 1	$0.5 \cdot J_{AB} - C$	$1 + \sin 2\theta$
4 $\rightarrow$ 3	$-0.5 \cdot J_{AB} - C$	$1 - \sin 2\theta$

Table 8. Transition Energy and Intensity Equations for an AB splitting.

The coupling constant J_{AB} is obtained by measuring the distance in Hertz between peaks 1 and 4 or 2 and 3. δ_{AB} can be calculated using Equation 1.

$$\delta_{AB} = \sqrt{(\delta_1 - \delta_4) \cdot (\delta_2 - \delta_3)}$$

Equation 1. Calculation of distance between unsplit chemical shift

Lastly, all that is needed are the positive quantity C and the angle θ (in radians.)

These two unitless variables can be calculated using Equations 2 and 3a or 3b.

$$C = [(\delta_{AB})^2 + J_{AB}^2]^{1/2}$$

Equation 2. The calculation of C

$$C \cos 2\theta = 0.5 \delta_{AB}$$

$$C \sin 2\theta = 0.5 J_{AB}$$

Equations 3a and 3b. Two ways of calculating θ .

If the initial unsplit A and B resonances are of interest, δ_A and δ_B can be calculated using Equations 4 and 5. The position of these peaks becomes important when dealing with more complex non-first order spectra.

$$\delta_A = \delta_1 - \frac{[(\delta_1 - \delta_4) - \delta_{AB}]}{2} \quad \delta_B = \frac{(\delta_1 - \delta_4) - \delta_{AB}}{2} + \delta_4$$

Equations 4 (left) and 5(right). The calculation of δ_A and δ_B

Higher-Order ABX Spectra

An ABX spectrum is similar to that of an AB spectrum except there is now another nucleus, X, which can be the same element as A or B or a completely different element. X interacts with the A and B nuclei in a first order fashion. The splitting of an ABX pattern can also be calculated and is dependent on the initial unsplit chemical shift of the A, B and X nucleus (δ_A , δ_B and δ_X) as well as J_{AB} and the coupling constants between nucleus A and X and B and X (J_{AX} and J_{BX} .) Four more variables D_+ , D_- , D_+ and D_- are needed to calculate the transition energies for the AB part of an ABX system. D_+ and D_- can be calculated with Equation 6.

$$D_{\pm} = 0.5 * \{ [\delta_A - \delta_B \pm 0.5 * (J_{AX} - J_{BX})]^2 + J_{AB}^2 \}^{1/2}$$

Equation 6. Equation used for the calculation of D_+ and D_- .

Once D_+ is found, either Equation 7a or Equation 7b can be used to calculate ϕ_+ .

$$\begin{aligned} D_+ \cos 2\phi_+ &= 0.5 * (\delta_A - \delta_B) \pm 0.25 * (J_{AX} - J_{AB}) \\ D_+ \sin 2\phi_+ &= 0.5 * J_{AB} \end{aligned}$$

Equations 7a and 7b. Equations used for the calculation of ϕ_+

ϕ_- can be calculated with D_- and either Equations 8a or 8b.

$$\begin{aligned} D_- \cos 2\phi_- &= 0.5 * (\delta_A - \delta_B) \pm 0.25 * (J_{AX} - J_{AB}) \\ D_- \sin 2\phi_- &= 0.5 * J_{AB} \end{aligned}$$

Equations 8a and 8b. Equations used for the calculation of ϕ_- .

There are 8 possible peaks visible in the AB portion of an ABX pattern: 4 peaks associated with the A nucleus and 4 peaks for the B nucleus. Table 9 illustrates the eight equations corresponding to the eight possible transitions as well their relative intensities. The X portion of the spectrum can be calculated using the equations in Table 10.

The $7 \rightarrow 2$ transition for the X spectrum is forbidden so it will have zero intensity. Transitions $5' \rightarrow 4'$ and $6' \rightarrow 3'$ may become strong, visible lines if J_{AB} becomes small. Conversely, as J_{AB} increases then the relative intensities will decrease toward zero.

Transition	Origin	Energy	Relative Intensity
8 --> 6'	B	$v_{AB} + 0.25*(-2*J_{AB} - J_{AX} - J_{BX}) - D_-$	$1 - \sin 2\phi_-$
7 --> 4'	B	$v_{AB} + 0.25*(-2*J_{AB} + J_{AX} + J_{BX}) - D_+$	$1 - \sin 2\phi_+$
5' --> 2	B	$v_{AB} + 0.25*(2*J_{AB} + J_{AX} + J_{BX}) - D_-$	$1 + \sin 2\phi_-$
3' --> 1	B	$v_{AB} + 0.25*(2*J_{AB} + J_{AX} + J_{BX}) - D_+$	$1 + \sin 2\phi_+$
8 --> 5'	A	$v_{AB} + 0.25*(-2*J_{AB} - J_{AX} - J_{BX}) + D_-$	$1 + \sin 2\phi_-$
7 --> 3'	A	$v_{AB} + 0.25*(-2*J_{AB} + J_{AX} + J_{BX}) + D_+$	$1 + \sin 2\phi_+$
6' --> 2	A	$v_{AB} + 0.25*(2*J_{AB} - J_{AX} - J_{BX}) + D_-$	$1 - \sin 2\phi_-$
4' --> 1	A	$v_{AB} + 0.25*(2*J_{AB} + J_{AX} + J_{BX}) + D_+$	$1 - \sin 2\phi_+$

Table 9. AB Transition Energies and Intensity Equations for an ABX pattern. $V_{AB} = \delta_{AB}$ in this table.

Transition	Origin	Energy	Relative Intensity
8 --> 7	X	$v_X - 0.5*(J_{AX} + J_{BX})$	1
5' --> 3'	X	$v_X + D_+ - D_-$	$\cos^2(\phi_+ - \phi_-)$
6' --> 4'	X	$v_X - D_+ - D_-$	$\cos^2(\phi_+ - \phi_-)$
2 --> 1	X	$v_X + 0.5*(J_{AX} + J_{BX})$	1
7 --> 2	Comb.	$2*v_{AB} - v_X$	0
5' --> 4'	Comb. (X)	$v_X - D_+ - D_-$	$\sin^2(\phi_+ - \phi_-)$
6' --> 3'	Comb. (X)	$v_X + D_+ + D_-$	$\sin^2(\phi_+ - \phi_-)$

Table 10. X Transition Energies and Intensity Equations for an ABX pattern. $V_X = \delta_X$ and $V_{AB} = \delta_{AB}$ in this table.

How Platinum Affects the NMR Spectra of 5d

Platinum has six stable isotopes of which only one has a non-zero spin that is 'visible' to the NMR. Platinum-195, which is a spin $\frac{1}{2}$ nucleus, has a natural abundance of 33.832% whereas the other 5 spin-zero isotopes make up the remaining 65.372%. This means that two thirds of the phosphorus is bound to a spin zero platinum nucleus yielding an AB splitting pattern and one third of the phosphorus is bound to a spin $\frac{1}{2}$ nucleus, yielding an ABX splitting pattern. The 101.2MHz ^{31}P spectrum for **5d** is shown in Figure 24.

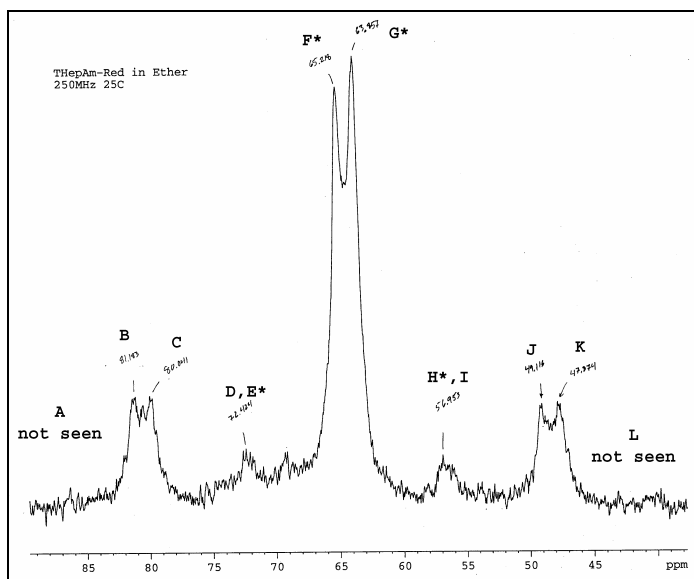


Figure 24. 101.2MHz ^{31}P spectrum of the Tetraheptylammonium salt of **5a**.

Roundhill originally obtained a spectrum similar to that of Figure 24. From this spectrum he determined the structure of **5b** to be the trimeric diplatinum compound $\text{Pt}_3(\text{H}_2\text{P}_3\text{O}_7)_4^{6-}$.¹⁴ Bedgood was able to repeat Roundhill's work in 1990 from which he determined the structure to be $(\text{CH}_3(\text{C}_6\text{H}_5)_3\text{P})_6[\text{Pt}_5(\text{P}_2\text{O}_5\text{H}_2)_8(\text{P}(\text{OH})_3)_4] \cdot \text{H}_2\text{O}$ (a pentameric platinum compound containing both bidentate phosphorus-oxygen-phosphorus ligands as well as phosphorus acid monodentate ligands). In both situations, the investigators were assuming that the spectrum was first-order and based their structures on that assumption. Investigation of the same sample at different frequencies would have made it apparent that the spectra were higher order. Figure 25 shows the ^{31}P spectrum of compound **5b** at 121.4MHz. Both sets of satellite "doublets", labeled B, C, J and K, seemed to be better resolved in this spectrum. Based on the equations in Table 10, increased intensity occurs when increasing the NMR field strength.

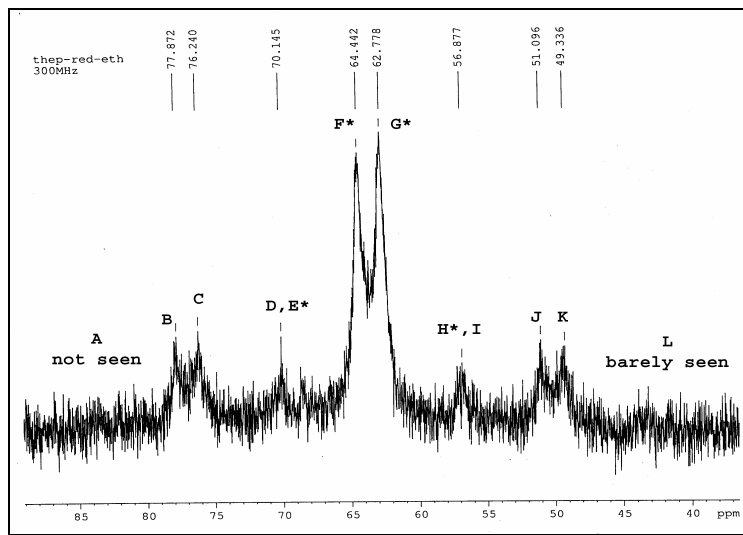


Figure 25. 121.4MHz spectrum of the tetraheptylammonium salt of **7b**.

The distance between to the two center peaks appeared to be increasing as well. Upon investigation of the two final spectra at 202.4 and 242.9 MHz, Figures 35 and 36 respectively, it is clear that the peaks were not behaving in a first-order fashion. All the peaks visible in Figures 24 and 25 were much more resolved in Figures 26 and 27 as well as much higher in intensity and new peaks were also visible.

The 12 peaks visible in the ^{31}P NMR spectra were designated by the letters A through L. At low frequencies such as 101.2 and 121.4MHz, some peaks were not observed due to low intensity, low signal to noise and baseline imperfections. The AB-peaks part of the spectrum were designated with the letters E* through H* and the ABX peaks were labeled A-D and I-L. All peaks from Figures 24, 25, 26 and 27 are listed in Tables 11 and 12.

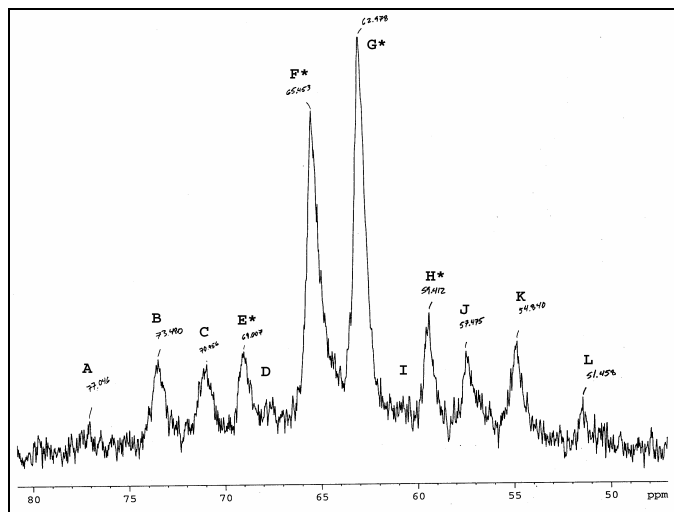


Figure 26. 202.4MHz ^{31}P spectrum of the tetraheptylammonium salt of **7b**

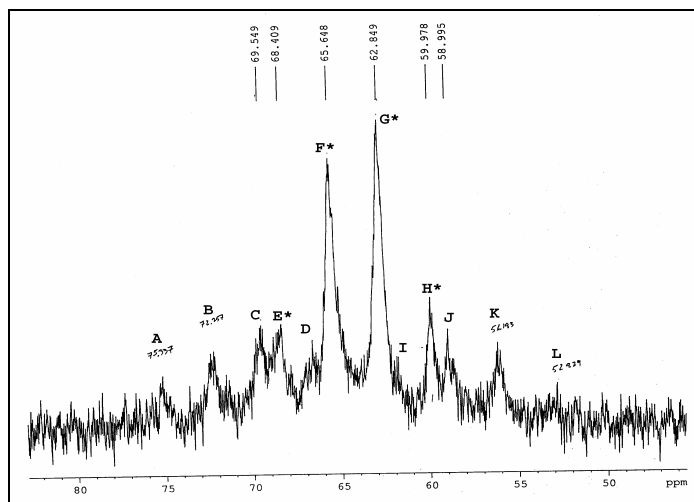


Figure 27. 242.9MHz ^{31}P spectrum of the tetraheptylammonium salt of **7b**.

Normally, in a simple first-order spectrum, a change in field strength leads to a uniform shifting of all visible resonances associated with a single molecule. This holds true to non-first order spectra as well. Due to the fact that there are two spectra for the same compound, the shifting caused by a change in field caused the peaks 'D' and 'E*' and 'H*' and 'I' to overlap at lower fields. At higher fields, the peaks 'E*' and 'H*' and 'I' to overlap at lower fields. At higher fields, the peaks 'E*' and 'H*' and 'I' to overlap at lower fields.

associated with the AB pattern surpass peaks ‘D’ and ‘I’. A comparison of Figures 25 and 26 illustrate this issue. Peaks ‘D’ and ‘I’ in Figure 26 (associated with the ABX part of the spectrum) shift more upfield and more downfield respectively when going to higher fields versus these same peaks in Figure 25. As stated before, this caused much confusion during the initial analysis of these spectra.

Peak	101.2MHz Spec		121.4MHz Spec	
	ppm	Hz	ppm	Hz
A	N/A	N/A	N/A	N/A
B	81.18	8215.72	77.87	9453.66
C	80.04	8100.15	76.24	9255.54
D	N/A	N/A	N/A	N/A
E*	72.42	7329.31	70.15	8515.60
F*	65.22	6600.06	64.44	7823.26
G*	63.86	6462.33	62.78	7621.25
H*	56.95	5763.64	56.88	6904.87
I	N/A	N/A	N/A	N/A
J	49.12	4970.54	51.10	6203.05
K	47.87	4844.85	49.34	5989.39
L	N/A	N/A	N/A	N/A

Table 11. All peaks and their parent splitting pattern in ppm and Hz. N/A denotes an inability to determine the precise peak position.

Peak	202.4MHz Spec		242.9MHz Spec	
	ppm	Hz	ppm	Hz
A	77.05	15594.11	75.34	18299.36
B	73.48	14872.35	72.26	17551.23
C	70.96	14361.49	69.55	16893.45
E*	69.01	13967.02	68.41	16616.55
D	N/A	N/A	N/A	N/A
F*	65.45	13247.69	65.65	15945.90
G*	62.98	12746.75	62.85	15266.02
I	N/A	N/A	N/A	N/A
H*	59.41	12024.99	59.98	14568.66
J	57.48	11632.94	59.00	14329.89
K	54.84	11099.62	56.18	13646.85
L	51.46	10415.10	52.83	12832.16

Table 12: All peaks and their parent splitting pattern in ppm and Hz. N/A denotes an inability to determine the precise peak position.

There are two resonances that would be visible if there was no coupling involved; one resonance for the 'A' nucleus (ν_A) which in this case is a phosphorus atom and another for the 'B' nucleus (ν_B) which is another phosphorus atom. This holds true for both the AB and ABX part of the spectrum. Now focusing on the AB part of the AB/ABX spectrum one sees a distorted quartet similar to what is seen in Figure 23b. Figure 28 is an edited AB-only spectrum of **5b** at 202.4MHz.

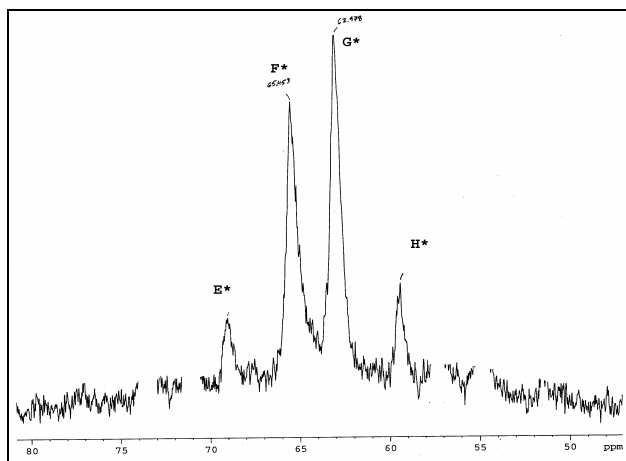


Figure 28. The AB only peaks of **7b** at 202.4MHz

After calculating J_{AB} and implementing Equations 1, 4 and 5 on the spectrum displayed in Figure 28, the values of 684.10Hz for J_{AB} , 1179.96Hz for ν_{AB} , 16182.58Hz for ν_A and 15002.62Hz for ν_B were had. With these numbers along with the Equations 2, 3a or 3b and those equations contained in Table 8, the values of all the peaks and their relative intensities were calculated. The calculated values from Table 8 versus the empirical values are summarized in Table 13.

Peaks	Calc'd (Hz)	Actual (Hz)
E*	16629.91	16616.55
F*	15945.90	15945.90
G*	15266.02	15266.02
H*	14582.02	14568.66

Table 13. Calculated and empirical peak positions and intensities for the AB pattern of the 202.4MHz spectrum.

The ability to calculate J_{AB} and J_{AB} from the AB spectrum simplifies the calculation the ABX spectrum. The edited ABX part of the 202.4MHz ^{31}P spectrum is visible in Figure 29.

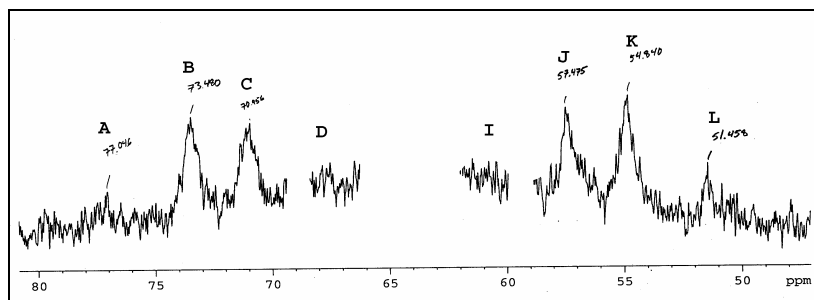


Figure 29. The edited ABX only peaks of **7b** at 202.4MHz.

J_{AX} and J_{BX} can be simply calculated by taking the difference between the two highest intensity peaks corresponding to a single nucleus (mainly the difference between peaks B and J for J_{AX} and the difference between peaks C and K for J_{BX} . It was found that both J_{AX} and J_{BX} were very close and had the values of 3239.42Hz and 3261.88Hz respectively at 202.4MHz. A slight variation in chemical environment could be the cause for this small deviation. Using the numbers for J_{AX} and J_{BX} , the numbers for J_{AB} , A , B obtained from the AB pattern along with Equations 6, 7a or 7b, 8a or 8b and Table 9

gives the values of all the peaks and their relative intensities. The calculated values from Table 9 versus the empirical values are summarized in Table 14.

Peaks	Calc'd (Hz)	Actual (Hz)	Calc'd ppm
A	15589.03	15594.11	77.02
B	14868.48	14872.35	73.46
C	14376.60	14361.49	71.03
D	13656.05	N/A	67.47
I	12347.45	N/A	61.01
J	11626.91	11632.94	57.45
K	11116.88	11099.62	54.93
L	10396.34	10415.10	51.37

Table 14. Calculated and empirical peak positions and intensities for the ABX pattern of the 202.4MHz spectrum.

Figure 30 graphically shows the addition of the data from Tables 13 and 14.

Figure 31 compares the collated AB and ABX pattern in Figure 30 to the actual 202.4MHz spectrum. The agreement of peaks strongly supports the notion that this is in actuality an AB/ABX spectrum.

Finally, it is very noticeable that the ^{31}P resonances are quite broad. This is most likely caused by the size of the platinum polymers being studied. NMR theory suggests that if a molecule has a slow tumbling rate, the resonances will be broad due to the rapid relaxation of the nuclei being studied. It has been shown, via light scattering measurements, that any solution of the red compound contains a wide variety of compounds that vary in molecular size. Larger polymers will have a slower tumbling rate thus yield broader peaks.

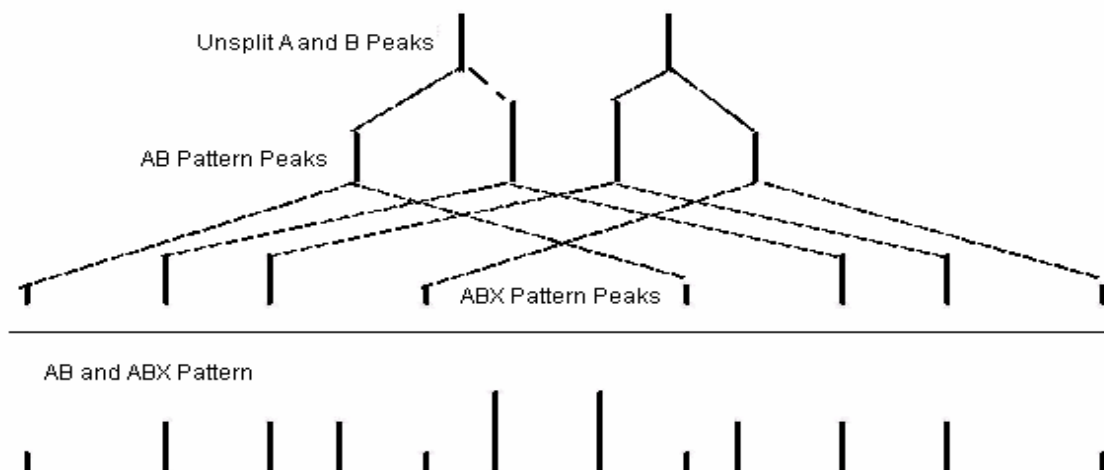


Figure 30. Graphical representation of data from Tables 13 and 14.

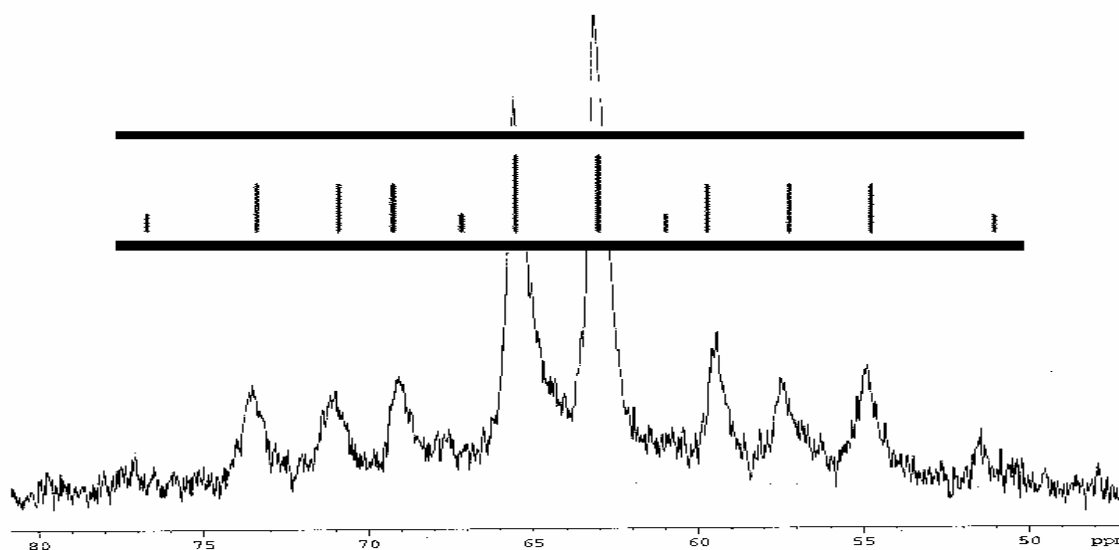


Figure 31. AB/ABX pattern overlaid over the ^{31}P 202.4MHz spectrum.

Discussion of the Total Data for **5b** and Conclusion

As previously stated, **5b** has a higher-order ABX splitting pattern which means there are two different phosphorus atoms bound to a single platinum atom in the red

compounds structure. Bedgood's structure shown in Figure 32 cannot explain the NMR spectrum observed for **5b**.

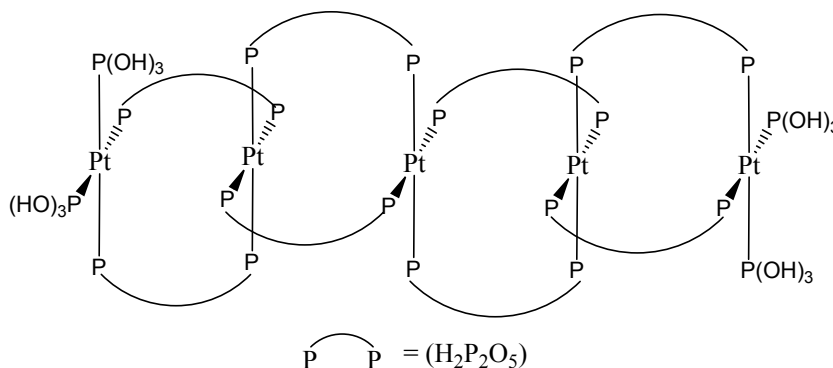


Figure 32. Bedgood's structure for the red compound.

The structure in Figure 32 does have two separate phosphorus atoms bound to platinum but the $\text{P}(\text{OH})_3$ monodentate ligands are too dissimilar to the phosphorus atoms contained in the $\text{H}_2\text{P}_2\text{O}_5$ bidentate ligands and very different chemical shift and coupling constant would be observed for those phosphorus atoms. The monomeric platinum compound, $\text{Pt}(\text{OP}(\text{OH})_2)_2(\text{P}(\text{OH})_3)_2$, which is essentially the end-caps of Bedgood's structure, is a symmetrical molecule, has a ^{31}P chemical shift of 86.7 and a $J_{\text{Pt-P}}$ of 3248³⁹. The monomeric phosphorus' in Bedgood's compound are nearly the same and should have resonances at or around 86ppm as well.

Roundhill proposed that at higher temperatures, **1** would polymerize further to form extended phosphorus/oxygen chains. Combining this higher phosphorus-oxygen-phosphorus chain would lead to the structure illustrated in Figure 33, a platinum polymer bridged by phosphorus-oxygen-phosphorus-oxygen-phosphorus (POPOP) bridges. Unfortunately, at higher temperatures, oxo-phosphorus compounds are known to

decompose to form phosphine⁴⁰ and the formation of the POPOP polymer from the chemical or thermal dehydration of H_3PO_3 (or $\text{H}_2\text{P}_2\text{O}_5$) has never been reported.

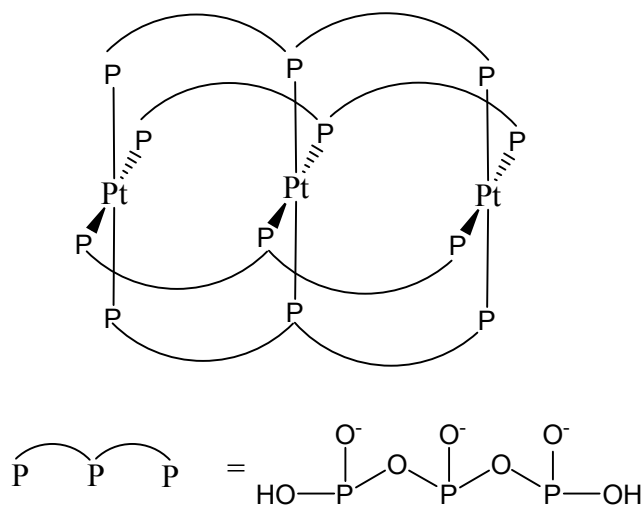


Figure 33. Roundhill's structure for the red compound.

Past structures were based upon NMR data using incorrect assumptions and on elemental analysis values that were obtained from impure samples of red compound salts. With the knowledge that has been acquired from the differential solubility and chromatography experiments, it is now known that there are a large number of impurities formed along with the red compound when using the oven or hotplate synthetic methods.

No conclusive information about the structure or structures of the red compound was obtained therefore no absolute structures can be written. What can be concluded is that the synthetic method for the red compound creates a number of other impurities along with the desired product. These impurities ranging from the very small dimeric platinum, **4a** compound, can be removed by using a series of cation extractions or by the more difficult chromatographical method.

The red compound is a series of platinum atoms bridged by phosphorus-oxygen-phosphorus chains to form long polymers. This is known from the coupling data that was obtained from the NMR spectra. The J_{AX} and J_{BX} coupling constants of $\approx 3250\text{Hz}$ correspond to the coupling between a phosphorus and platinum atom. The coupling constant of 684.10Hz for J_{AB} corresponds to the through-metal coupling of phosphorus atoms. The J_{AB} is much too large for a coupling constant between two phosphorus atoms bound directly together, which would be between $330\text{-}500\text{Hz}$ or the $15\text{-}20\text{Hz}$ coupling constant between two phosphorus' separated by an oxygen (which is the case of the $\text{H}_2\text{P}_2\text{O}_5^{2-}$ ligand)⁴¹. The platinum polymers are nearly symmetrical yet minutely different in structure due to the slight difference in the two platinum-phosphorus coupling constants that were calculated.

From the light scattering data, these polymers are highly varied in length and molecular size, containing at least four platinum atoms, up to very large chains containing well over 800 platinum atoms. As discussed previously, the large size of the polymers is also supported by the correlation between the tumbling rates for a molecule versus the broadness of the observed NMR peaks. For the red compound the broad peaks caused by the long polymers conceal the sharper peaks of the smaller polymer chains.

Synthesis and Characterization of Alkylated Phosphites

The History and Synthesis of **1**

In the project concerning Roundhill's red compound, **5a**, it was proposed by Bedgood as well as Roundhill that **5a** was, in actuality, a higher oligomer than that of the

florescent green, dimeric Pt(II) compound, **4a**. Roundhill proposed that **5a** was a trimeric Pt(II) compound bridged by a chain consisting of alternating phosphorus and oxygen atoms (Roundhill dubbed this chain the POPOP ligand.) Bedgood concluded that the Pt(II) oligomer was more pentameric in nature and consisted of Pt(II) atoms bridged by multiple, bidentate, dianionic pyrophosphorus acids (**1**) and terminated with monodentate phosphorus acid ligands.

Roundhill's POPOP ligand has never been synthesized or observed. Due to the high moisture sensitivity of the pyrophosphorus ligand in general (which will be discussed later), it is assumed that Roundhill's POPOP ligand would be even higher in energy, more moisture sensitive and less likely to occur. Bedgood's theory of a single pentameric, platinum(II) oligomer also seems unlikely do to the light-scattering work and UV/Vis data that has been obtained for **5a**.

In an effort to explore the possibility of Roundhill's POPOP ligand and in an attempt to modify the POP ligand in a way which would allow **4a** to be functionalized and attached to surfaces, **4a** was exposed to various oxidizing agents. It was hoped that the phosphorus' on either of the four bridging POP ligands would react and a new dimeric platinum(II) compound with broken symmetry would formed. With the addition of a single atom or group to the POP ligand on a **4a** molecule, the NMR spectrum would break from that of a simple singlet and doublet to something much more complex.

Unfortunately, it was found that any oxidizing agents added to aqueous solutions of **4a** or non-aqueous solutions of **4b-d** only led to the axial addition of the oxidizing reagent to the platinum(II) atoms and their subsequent oxidation to platinum(III). This

was dire since the removal of an electron from platinum(II) atoms occur from the d_z^2 orbital thus allowing bonding between the two adjacent platinum atoms which yielded a loss in the photophysical properties of the **4a** molecule.

As one can read in the experimental section of this dissertation, **4a** is synthesized from the base reagents of phosphorus acid, potassium tetrachloroplatinate and water. This “witches brew” of reactants is then heated in an oven to near-dryness and yields a surprisingly quite high percent yield of **4a**. This method of synthesis has worked beautifully for both chemists and physicists interested in studying **4a**’s properties. It was found that this archaic method of synthesis would no longer be suitable for our needs and that another; more systematic approach had to be taken.

Instead of reacting the completed **4a** with the oxidizing reagent of choice, it was postulated that the POP ligand, **1**, could be modified prior to its reaction with platinum. It was previously unknown if reacting **1** with any platinum complex would form **4a**. The most likely reason for this was **1**’s high instability in the moist atmosphere and its reactivity in water.

The Synthesis and Characterization of **1**

As seen in this dissertation’s experimental section, the synthesis of **1** is quite simple. The only precaution that should be noted is in the usage of PCl_3 which is quite hazardous. The entire reaction was done under argon. Reactions done under normal atmosphere resulted in reactions containing very little of the desired product, **1**, as well as a high amount of unreacted phosphorus acid.

1, upon its formation, is a white amorphous solid. If, during the synthesis of **1**, the excess PCl_3 is not completely removed, the product will remain as a thick mobile liquid that may produce small white chunks of pure **1** over time. If the reaction is not allowed to stir long enough and the PCl_3 is removed prematurely, phosphorus acid will remain and cause the solution to remain as a thick liquid. On rare occasions, where the PCl_3 was removed prematurely, **1** still solidified but the unreacted phosphorus acid co-crystallized within the white amorphous solid.

1 could never be obtained with a 100% yield. As ^{31}P NMR spectroscopy was the analysis tool of choice for determining the purity of **1**, a neat sample of an incomplete reaction of **1** gave a doublet corresponding to **1** at 0.8ppm and -6.9ppm as well as another doublet corresponding to phosphorus acid at 14ppm and 6.6ppm.

Numerous literature articles discussed of the simplicity of **1**'s synthesis yet they failed to mention its extremely high moisture sensitivity. Some even claim to have synthesized **1** under normal atmospheric conditions⁴² based solely on elemental analyses. This was found to be completely untrue. It was found that **1** must be kept completely dry and under argon in order to reduce the decomposition of **1** back to phosphorus acid (Figure 34).

1 in its white solid form is difficult to work with due to its high moisture sensitivity and its rather hard nature. The solid may be heated in order to liquefy the sample (since **1** does have a melting point around 34 °C) but this resulted in an increased rate of decomposition. When **1** was needed for an experiment, the desired amount was usually just chiseled from the reaction vessel under argon.

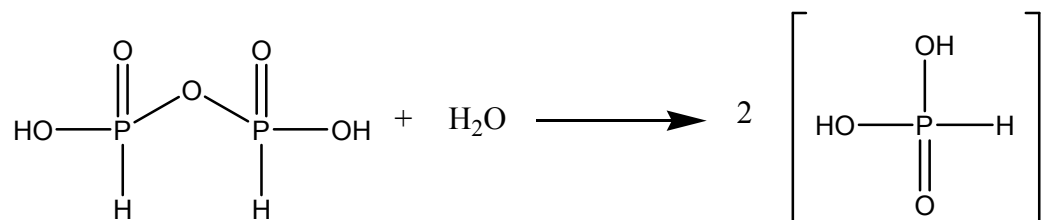


Figure 34. Reaction equation for decomposition of **1** by water.

If **1** was not kept completely moisture or oxygen-free, a water insoluble and flaky yellow compound was formed. This yellow compound had been previously observed by Zwierzak *et al*³³ and was proposed to be a higher oxidation state phosphorus oxide due to the high availability of oxygen from the atmosphere. After a successful synthesis was completed, the entire reaction vessel was placed into a +5 C refrigerator in an attempt to reduce or eliminate the decomposition of **1**. After a few days, the sample was examined whereupon the refrigeration seemed to have reduced the amount of decomposition slightly but a significant amount of the yellow material was still visible. The complete reaction equation for **1** is displayed below in Figure 35.

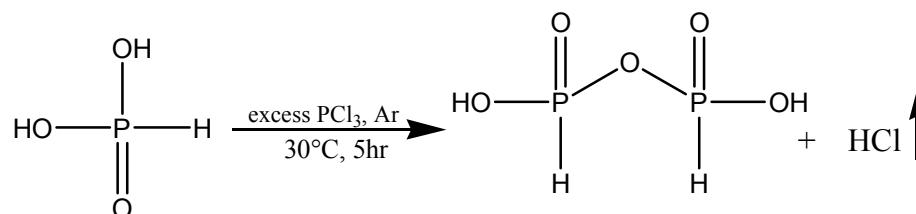


Figure 35. Complete reaction equation for the synthesis of **1**.

Derivations on the Synthesis of **1** and Characterization

Another, simpler method for the synthesis of **1** has been known for some time. By heating a sample a phosphorus acid at +140 C, one can dehydrate the H₃PO₃ and

form **1**. By using this method, one does not obtain a very high yield of **1** due to the fact that this is a solid state reaction. An attempt was made to synthesize the disodium salt of **1** by heating a Petri dish containing the monosodium salt of phosphorus acid (NaH_2PO_3) to 150 C. This yielded a large amount of the disodium pyrophosphorus acid.

The ^{31}P NMR spectrum of the disodium pyrophosphorus acid in water which is shown in Figure 36, was quite different from the NMR spectrum of **1**. The main difference between the two was that disodium pyrophosphorus acid was soluble and moderately stable in water. Referring to the spectrum in Figure 36, the doublet at 6.2ppm and 1.1ppm corresponded to the unreacted monosodium salt of phosphorus acid. The doublet of triplets at -1.4ppm and -6.9ppm corresponded to the disodium pyrophosphorus acid.

The splitting pattern for the monosodium salt of phosphorus acid was very easily explained. Monosodium phosphorus acid has a proton bound directly to the central phosphorus atom and another proton bound to an oxygen two bonds away. The hydrogen bound directly to the phosphorus is the only coupling seen for the phosphorus atom. The proton that is two bonds away is 'shielded' from the phosphorus atom by the oxygen. Since this is an aqueous solution, this proton is rapidly exchanging on and off of the oxygen which also reduces its coupling to the phosphorus atom. Therefore the only nucleus that will affect the phosphorus is the proton that is directly bound to it. This hydrogen-phosphorus coupling is quite large and has a J value of 620Hz, which is typical for a hydrogen directly bound to a phosphorus atom. The splitting pattern for the disodium salt of **1** is a bit more complicated.

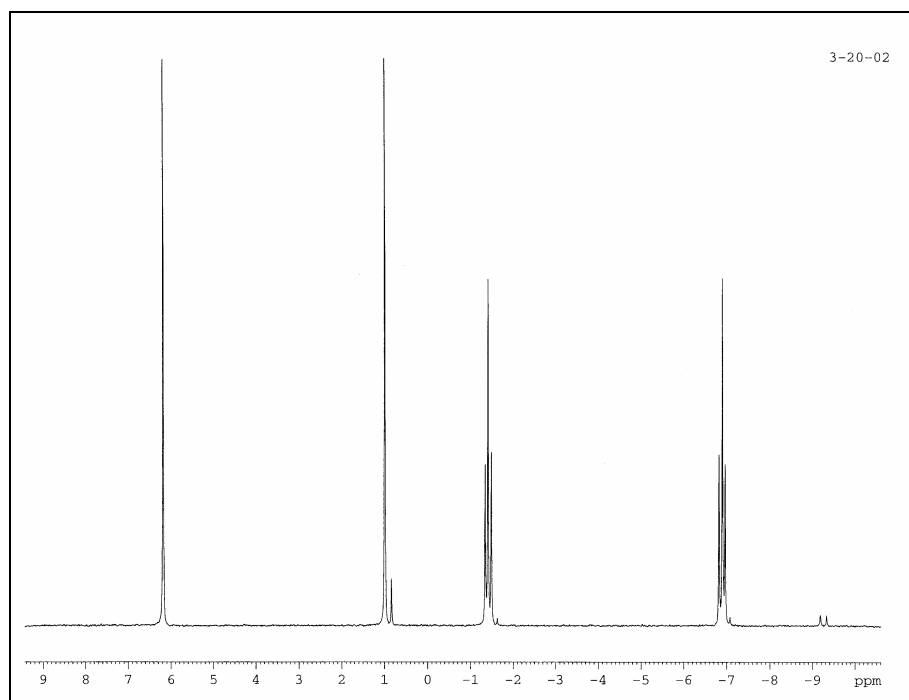


Figure 36. ^{31}P NMR spectrum of disodium pyrophosphorus acid and the monosodium salt of phosphorus acid.

The NMR important atoms have been labeled in Figure 37 in order to explain the splitting pattern of the disodium salt of **1** more easily. The phosphorus labeled (A) can be influenced by three other nuclei, two hydrogens (B and D) and one other phosphorus (C).

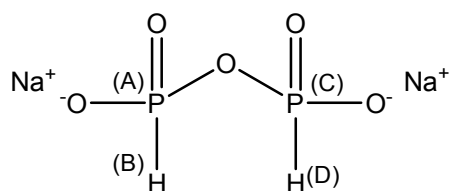


Figure 37. The structure of the disodium salt of **1**.

When (A) is split by hydrogen (B), a large splitting pattern is seen that is similar to what is seen for phosphorus acid. A coupling/splitting of 650Hz is seen. When (A) is split by hydrogen (D) or phosphorus (C) a much weaker coupling would be observed. The coupling between a phosphorus and a hydrogen that is three bonds away is around 11Hz whereas a coupling between a phosphorus and another phosphorus separated by an oxygen is also around 11Hz⁴¹. Since the two coupling constants between (A) and (C) and (A) and (D) are almost identical a triplet would be observed. The splitting pattern for the disodium salt of **1** cannot be compared to the splitting pattern of **1** due to the fact that **1** is insoluble in almost every solvent (which will be covered later) and the fact that the neat ³¹P NMR spectrum of **1** is too broad and yields very little information. The reduction of sample material (i.e. lowering the concentration) and the solvation of the disodium salt of **1** seemed to have allowed a more highly resolved ³¹P NMR spectrum to be obtained. Figure 38 shows the decomposition reaction that occurs between water and the disodium salt of **1**.

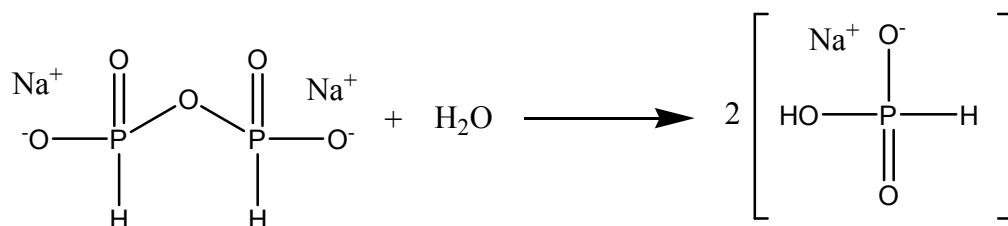


Figure 38. Decomposition reaction between water and the disodium salt of **1**.

A sample of the disodium salt of **1** was allowed to remain in solution for a number of days whereupon the sample was evaluated using ³¹P NMR spectroscopy in order to qualitatively determine how much if any of the disodium salt of **1** remained. After one

day, the concentration of the disodium salt was more than half of what was initially added (Figure 39). After two days, the amount remaining decreased even more yet the amount remaining was still enough to be detected by NMR (Figure 40). After 3 days, the sample appeared to be completely decomposed. During this time no new peaks were observed whereas the area under the peaks corresponding to the monosodium phosphorus acid increased relative to the areas under those peaks corresponding to the disodium salt of **1**.

1 was found to be insoluble in almost every non-polar solvent but was discovered to be very slightly soluble in dry ethyl ether and soluble in anhydrous THF and dioxane. In highly polar solvents, **1** was found to be reactive. In the majority of polar solvents, **1** reacted in such a way that the products were unidentifiable.

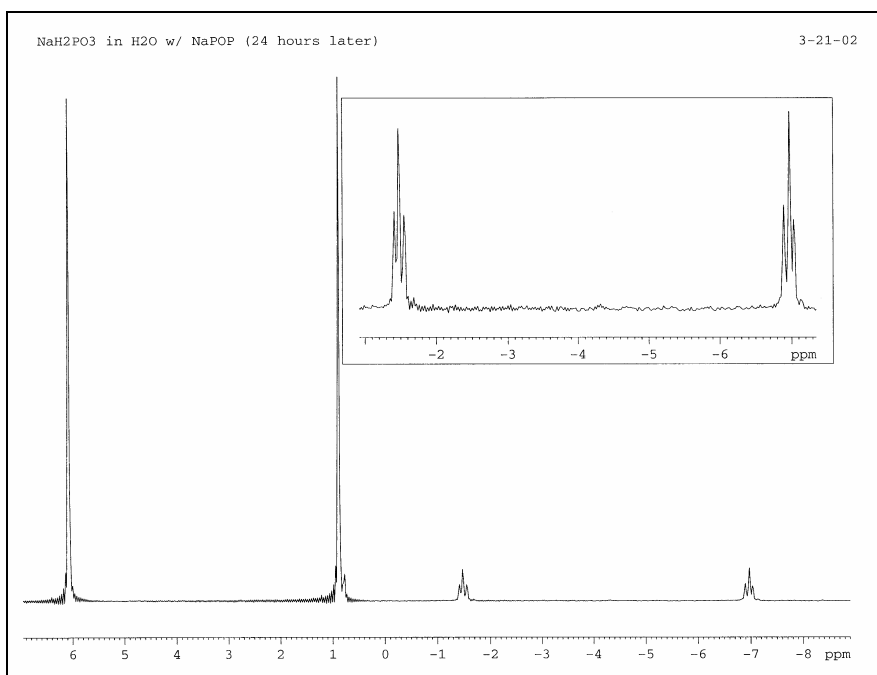


Figure 39. ^{31}P NMR spectrum of **1** after 1 day in H_2O .

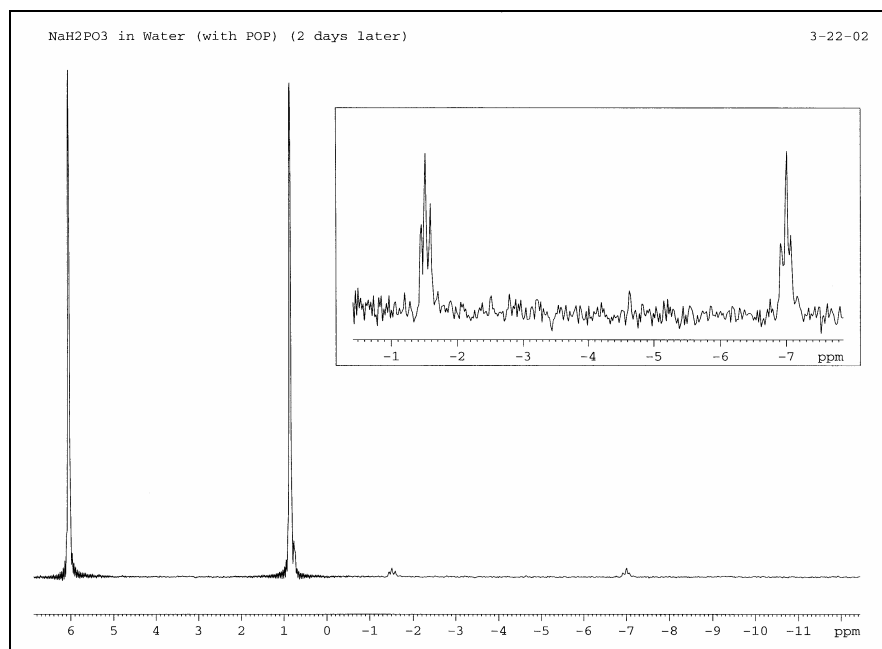


Figure 40. ^{31}P NMR spectrum of **1** after 2 days in H_2O .

Concerning the reaction with dioxane, it was found by using ^{31}P NMR spectroscopy, that the addition of **1** to a minimally wet sample of dioxane yielded both phosphorus acid and **1**. If a large amount of **1** was then added to the dioxane/**1** solution the area under the peaks corresponding to **1** increased.

In anhydrous THF, **1** was found to be quite stable for a number of days. The problem with using THF as a solvent is its high polarity and its ability to absorb large amounts of water. Getting completely anhydrous THF was a problem so any time THF was used as a solvent, **1** would have completely decomposed back to phosphorus acid after a couple of days. In an attempt to synthesize **4a** using more controlled methods, a small amount of tetraheptylammonium- PtCl_4 ($\text{THpA}_2\text{PtCl}_4$) was added to a stirring solution of THF and **1**. The reddish-brown solution (colored by the $\text{THpA}_2\text{PtCl}_4$) turned

pale red over a week. This red colored solution was immediately thought to contain **5a** so further investigation was warranted.

Very dry THF was obtained and to that solution was added 0.1g of dried $\text{THpA}_2\text{PtCl}_4$ along with an excess of what was thought to be a pure sample of **1**. ^{31}P NMR data were collected at one-hour intervals for two hours and then continued every 24 hours. The initial spectra illustrated the stability of **1** in the THF and allowed us to determine if any moisture was present or entering the reaction vessel that might cause **1**'s decomposition. It was found that there was a considerable amount of phosphorus acid present, much more than what would have been present in the initial sample of **1**. This was attributed to the THF still containing moisture. The reaction was allowed to continue and only checked every 24 hours thereafter even though the solution was contaminated with water.

After the reaction was allowed to stir for two days a more pronounced, deep red color appeared. A ^{31}P NMR spectrum (Figure 41) was taken which showed a small broad peak at 60ppm, almost exactly where **5a**'s resonance occurs (64ppm). **5a**'s resonance is usually very broad even when the sample is highly concentrated.

A UV/Vis spectrum was also obtained for this sample (Figure 42) which showed the characteristic UV/Vis spectrum of **4a/5a** (that is a major peak at 370nm for **4a** and a major peak 570nm for **5a**.) It was concluded that **5a** was formed from an impure sample of **1** and tetraheptylammonium tetrachloroplatinate(2-).

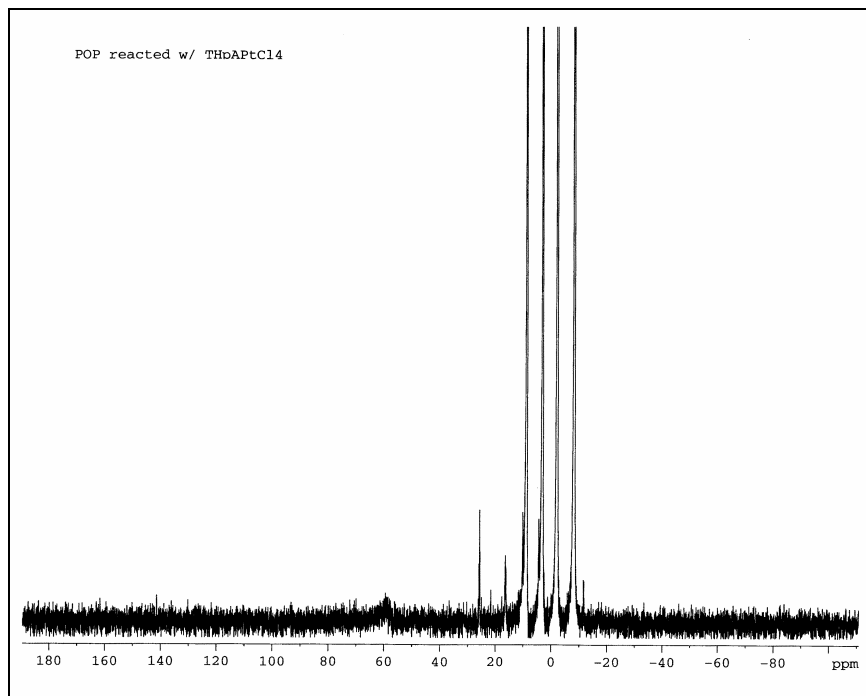


Figure 41. NMR spectrum of **1** after having been reacted with THpA₂PtCl₄ in THF.

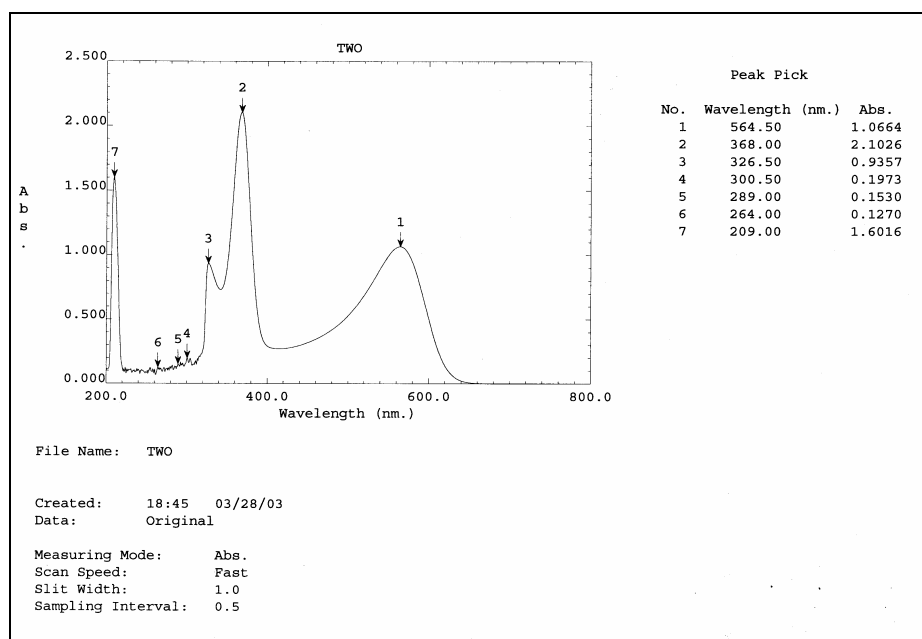


Figure 42. UV/Vis spectrum of **1** after having been reacted with THpA₂PtCl₄ in Ether.

Conversely, this same reaction was performed multiple times in anhydrous ethyl ether and, due to **1**'s poor solubility in ethyl ether, a two-phase system formed. One phase consisted of ethyl ether and the other, an etherate solution consisting of **5a**, unreacted phosphorus acid and unreacted **1**. This phase had a deep red color and the same UV/Vis spectrum as that of a **4a** and **5a** mixture. Unfortunately, no NMR spectra from those experiments were obtained in spite of many attempts. Next, a relatively pure sample of **1** (tested via NMR) was added to a solution of anhydrous ethyl ether and K_2PtCl_4 . After allowing this solution to stir for a week, a green colored etherate phase consisting of what appeared to be **4a** and unreacted **1** (which contained a very small amount of phosphorus acid) formed. This mixture was also evaluated using UV/Vis spectroscopy and it was found to have a spectrum exactly like that of **4a**. Unfortunately, no NMR spectra could be obtained for those samples.

It was concluded that the purity of the starting amount of pyrophosphorus acid, **1**, dictated which of the two compounds, **4a** or **5a**, were formed. As the samples of **1** decreased in purity, that is to say more phosphorus acid was present, the red colored compound, **5a**, seemed to be formed. As the purity of **1** increased, the dimeric platinum(II), green compound, **4a** was formed. Attempts to conduct a Job's Plot experiment on this visible phenomenon were not possible due to **1**'s poor solubility in ethyl ether and the decomposition caused by the moisture contained in the THF.

When **1** was reacted with various normal alcohols such as methanol, ethanol, propanol and butanol, it was thought for a short time that the reaction was occurring

between **1** and residual water that was dissolved in the alcohols. Table 15 shows the complete list of solvents investigated.

Upon moving to water insoluble alcohols and very dry samples of methanol, ethanol, propanol and butanol, it was realized that **1** was in fact reacting with the alcohols in a systematic manner.

Initially, the alcohol/**1** reactions were carried out using the alcohol as both the reactant and solvent. This allowed for a quick investigation as to whether a reaction occurred. After the reaction was verified using ^{31}P NMR spectroscopy, ethyl ether was used as the solvent. Ethyl ether was an ideal solvent since the majority of the alcohols were either completely soluble or slightly soluble in ethyl ether and **1** was slightly soluble and completely unreactive towards it. The amount of **1** and the alcohol could be accurately measured out and the stoichiometry of the reaction could be carefully calculated. It was found that upon completion of the reaction, the stoichiometry was 1 mole of alcohol for every 1 mole of **1**.

Solvent Used	Outcome
Ethyl Ether	Reacted (Ethyl Ether was found to have H ₂ O present)
Anhydrous Ethyl Ether	No Reaction – Slightly Soluble
Dioxane	Reacted (H ₂ O present)
Acetone	Reacted (H ₂ O present)
MET	Reacted
DMF	Reacted
DMSO	Reacted
Ethyl Acetate	Reacted (H ₂ O present)
Acetic Anhydride	Reacted
2-Methoxy Ether	Reacted
Pyridine	Reacted

Methanol	Reacted
Ethanol	Reacted
Butanol	Reacted
H ₂ O	Reacted
THF	Reacted (H ₂ O present)
Anhydrous THF	Soluble (H ₂ O was also found to be present)
Isopropanol	Reacted

Table 15. List of solvents used to determine the solubility of **1**.

The characterization of the products was performed using ³¹P NMR spectroscopy as well as mass spectroscopy. ¹³C's natural abundance as well as its small coupling constant when bound to ³¹P ruled out any usage of ¹³C NMR. ¹H NMR gave very little usable information as well. The ³¹P NMR spectra showed two doublets one of which was a doublet of singlets and the other a doublet of triplets (unless methanol was used then it was a doublet of quartets.) Table 16 lists the alcohols used and ³¹P NMR peaks seen.

Alcohol Used	Multiplicity of Observed Doublets	
Methanol	Quartet	Singlet
Ethanol	Triplet	Singlet
Propanol	Triplet	Singlet
Isopropanol	Doublet	Singlet
n-Butanol	Triplet	Singlet
n-Pentanol	Triplet	Singlet
n-Hexanol	Triplet	Singlet
n-Heptanol	Triplet	Singlet
n-Octanol	Triplet	Singlet
n-Nonanol	Triplet	Singlet
n-Decanol	Triplet	Singlet
n-Undecanol	Triplet	Singlet

Table 16. List of alcohols reacted with **1** and the multiplicity of the ³¹P peaks observed (these spectra are available in Appendix B of this dissertation).

Figure 43 shows a typical ^{31}P NMR spectrum for the reaction of any normal alcohol (other than methanol) with **1**.

The large coupling that is seen in both of the doublets is caused by the proton directly bound to a phosphorus atom since the calculated coupling constants matched almost perfectly with the literature value of 700Hz. The coupling seen for the higher splitting patterns are caused by protons that are two or more bonds away from phosphorus.

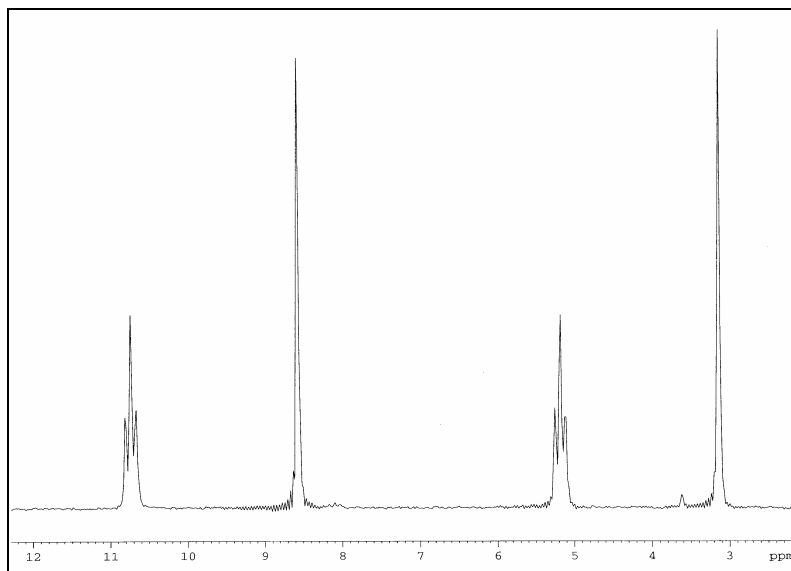


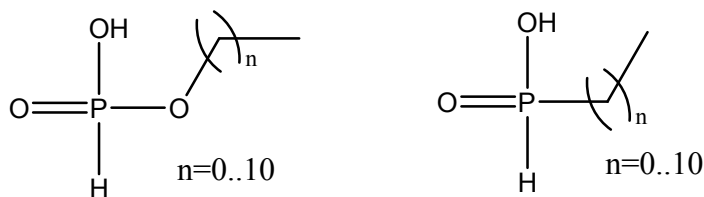
Figure 43. Typical ^{31}P NMR spectrum for the reaction of n-alcohols with **1**.

There were only two products formed no matter which alcohol was used, one of which appeared to be phosphorus acid. If the alcohols involved had a chain length of five carbon atoms or higher, the proposed phosphorus acid product was easily removed from the ethyl ether solution by washing it three times with a small amount of water. After

washing the organic phase with water, it was reexamined to determine whether the other product was still present. The ^{31}P NMR spectrum was identical to that of the spectrum prior to the washing minus the peaks associated with phosphorus acid. This showed that the newly formed product was much less water sensitive than **1** and that they could be handled without the usage of a dry box or airless glassware. If the alcohols used had a chain length of 4 carbon atoms or lower, both products were removed from the organic phase and both appeared in the ^{31}P NMR spectrum of the aqueous phase.

The ^{31}P NMR spectrum of the washing showed a doublet of singlets. Upon addition of phosphorus acid to the washings and its subsequent investigation via ^{31}P NMR spectroscopy, it was found that the peak intensity would increase as more phosphorus acid was added. The doublet of singlets was found to be phosphorus acid.

Based on the ^{31}P NMR data prior to the washing of the ethyl ether solution it was found that the other of the two resulting products formed from an alcohol and **1** could have been either of the two compounds shown in Figures 44 and 45.



Figures 44 (left) and 45 (right). The two possible structures for the product of an alcohol reacted with **1**.

^{31}P NMR spectroscopy should have been sufficient to determine the actual structure of the newly formed products but there was found to be a small quirk concerning ^{31}P spectroscopy. When looking at proton-phosphorus couplings, the J values

for the coupling of a proton to a phosphorus in a phosphorus bound methoxy group ($\text{CH}_3\text{-O-P}$) versus that of a proton to a phosphorus in a phosphorus bound methyl group ($\text{CH}_3\text{-P}$) are almost identical. For the product to be the compound pictured in Figure 45, the other product would have to have been a monoperoxide phosphorus acid instead of phosphorus acid, which seemed highly unlikely. Yet there was still the possibility that the compound in Figure 45 was the product, so to answer the question as to which of the two compounds was formed, mass spectroscopy was employed.

Of the 12 alcohols reacted with **1**, two of the completed reactions were investigated using GC/MS. The organic phase of washed samples of **1**'s reaction with n-hexanol and n-heptanol were both tested in order to get an accurate representation of the reaction. The organic layer was concentrated via rotary evaporation; the samples were redissolved in methylene chloride and their spectra taken. For the product from the n-hexanol and **1** reaction to have been the compounds pictured in Figures 44 or 45, the mass observed would have to have been 166amu or 150amu respectively. In the mass spectrum shown in Figure 46, it was found that the M+1 peak of 167amu matched up perfectly with the compound pictured in Figure 44.

The mass spectrum for the product of n-Heptanol reacted with **1** yielded an M+1 peak of 181amu which also matches perfectly with the compound shown in Figure 44. It was shown that the reaction of an n-alcohol with **1** yielded two products, one of which was phosphorus acid and the other was the alkyl phosphite where the alkyl corresponds to the chain length of the n-alcohol. Figure 47 shows this reaction.

The monoalkylated phosphites, **6a-k** all have very similar properties. As stated above, the set of 11 compounds all are moisture insensitive. The products have solubilities similar to that of the parent n-alcohol. **6a**, **6b** and **6c** are all water soluble and **6d** is slightly water soluble. **6e** through **6k** are all water insoluble. As the length of the alkyl chain increases, the less water soluble the phosphite becomes. All are viscous liquids at room temperature as well.

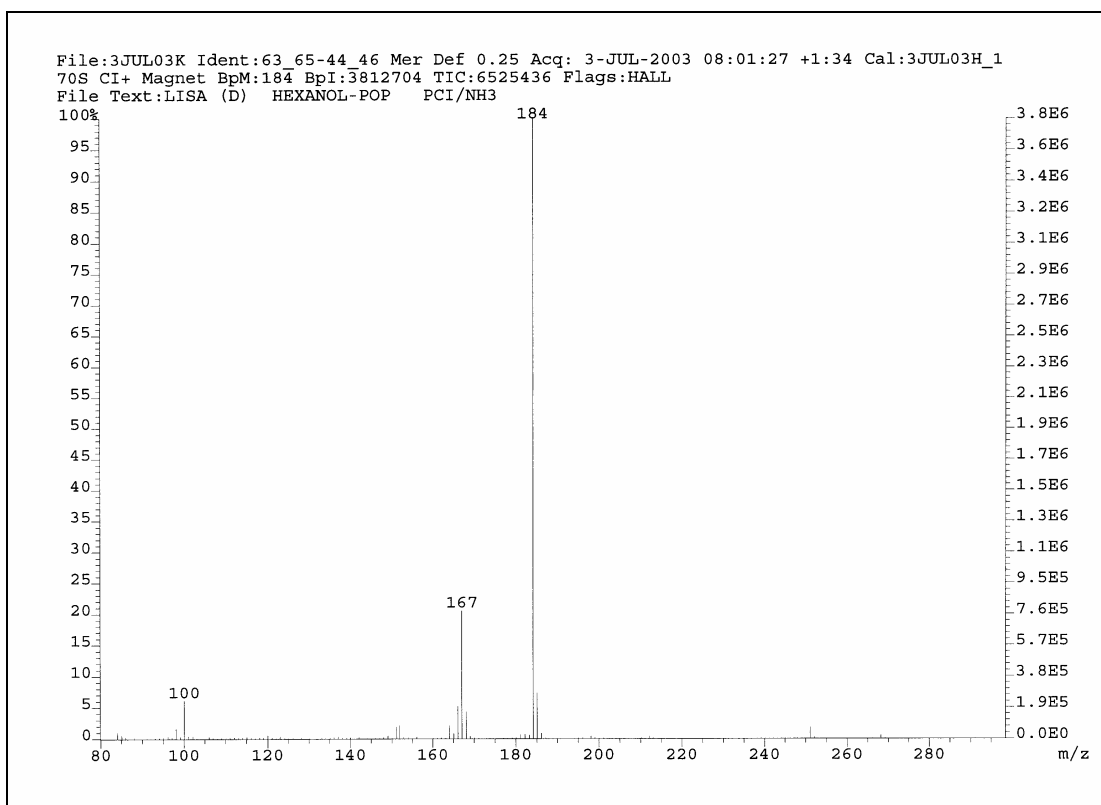
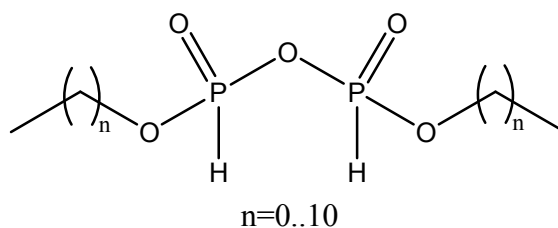


Figure 46. The mass spectrum of the product remaining in the organic phase from the reaction of n-Hexane with **1** (after washing with H₂O).

Even though all of the monoalkylated phosphites are known and have been synthesized before⁴³, our method of synthesis was much less labor intensive and required much less purification than what has been done previously.

It was realized that the newly formed monoalkylated phosphites (**6a-k**) might be used in the synthesis of a new dialkylated pyrophosphite illustrated in Figure 48.



Pyrophosphorus acid (**1**) has already been stated as being highly insoluble in almost all solvents (except ethyl ether, THF and Dioxane) and extremely moisture

sensitive. Dialkylated pyrophosphites, on the other hand, would benefit from the alkyl chains and could possibly be soluble in non-polar (water free) solvents. It was hoped that platinum could be reacted with the dialkylated pyrophosphites in non-aqueous media to produce a tetradialkylated phosphite platinate(2-) dimer similar in photophysical properties to that of **4a**.

Initial attempts to synthesize any one of the possible 11 dialkylated pyrophosphites yielded no results. The same method for synthesizing **1** was used except monoalkylated phosphites were used instead of phosphorus acid. The reaction mixture was allowed to stir for at least 2 hours up to 3 days. After that time, the reaction mixture was scanned using ^{31}P NMR spectroscopy. Both starting materials were visible and no new peaks were seen.

After a short literature search, it was found that the dimethyl and diethyl pyrophosphites had already been made³³. The synthesis described by Zwierzak entailed using an impure sample of the monoethylated phosphorus acid (which was made in a much more laborious fashion) in order to synthesize diethylated pyrophosphite. Using our method for the synthesis of **6a-k** and Zwierzak's method of the synthesis for diethyl pyrophosphite, nine new dialkylated pyrophosphites could be formed. An attractive feature of Zwierzak's method was the usage of the organic solvent: benzene. Water is only slightly soluble in benzene. Since little was known about the dialkyl pyrophosphites, by limiting the amount of water present one could reduce the chance of decomposing any newly formed dialkyl pyrophosphites. Another step to Zwierzak's method was the use of the benzene soluble dicyclohexylcarbodiimide (DCC.) DCC is a

well known dehydrating agent which, when exposed to water, forms the benzene insoluble, dicyclohexylurea (DCU.) For every two alkylated phosphites exposed to DCC, a water was removed according to the reaction equation in Figure 49.

Another benefit of DCC is that it is water scavenger as well and could be used to remove any remaining water from the benzene before any of the alkylated phosphites were added.

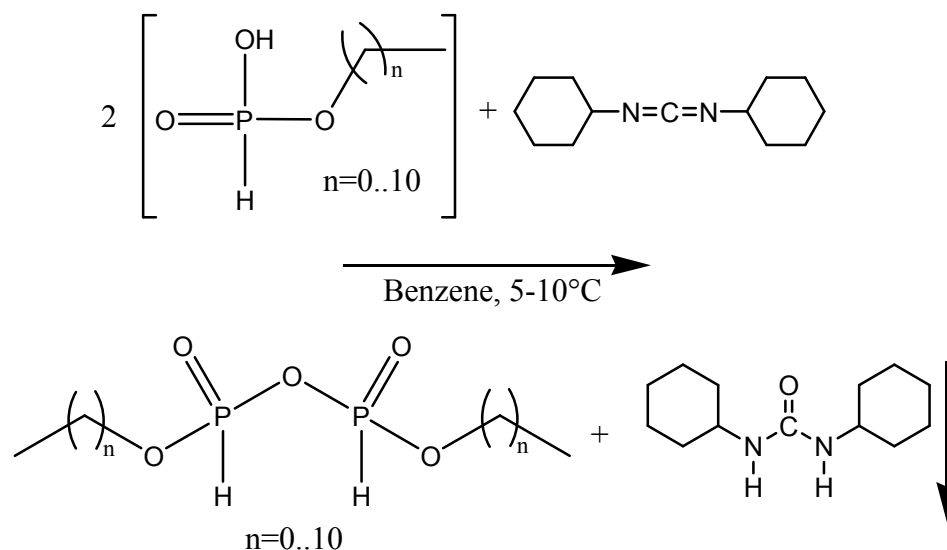


Figure 49. Complete reaction equation for the formation of dialkylated pyrophosphates.

A number of attempts were made to form the dialkylated pyrophosphites using our method for the synthesis of the monoalkylated phosphorus acids and Zwierzak's method for the formation of the dialkylated pyrophosphites but unfortunately no conclusive data was obtained. NMR spectra were taken of many of the reaction solutions for the dialkylated pyrophosphites. These spectra most often contained two sets of doublets, each of which were both doublets of singlets. At other times the same samples,

when scanned, yielded doublets of what appeared to be higher multiplets. One doublet corresponded nicely to the spectrum of phosphorus acid whereas the other doublet was initially thought to be that of unreacted monoalkylated phosphorus acids. Although the peaks were in the same general vicinity of those peaks associated with monoalkylated phosphorus acids, the majority of the time the peaks were not multiplets. When a solution of a completed attempt to synthesize diethyl pyrophosphite was investigated via ^{31}P NMR the spectrum in Figure 50 was obtained.

It was noticed that the doublet at 9.27ppm and 3.68ppm was only a doublet of singlets. If this were to be associated to the monoethyl phosphorus acid starting material the doublet should appear as a doublet of triplets. The NMR spectra of all other attempts to make dialkylated pyrophosphites had the same two sets of doublets of singlets. Mass spectrum analysis was also attempted and those spectra showed no signs of the dialkylated pyrophosphites.

The main problem that was suspected in the synthesis of the dialkylated pyrophosphites was moisture. As stated before, the characteristics of the dialkylated pyrophosphites are unknown. The sensitivity of the dialkyl pyrophosphites to water may have been the same as that of **1**. Other effects may have been a problem as well such as temperature and light. It is realized that more work needs to be performed on these pyrophosphites.

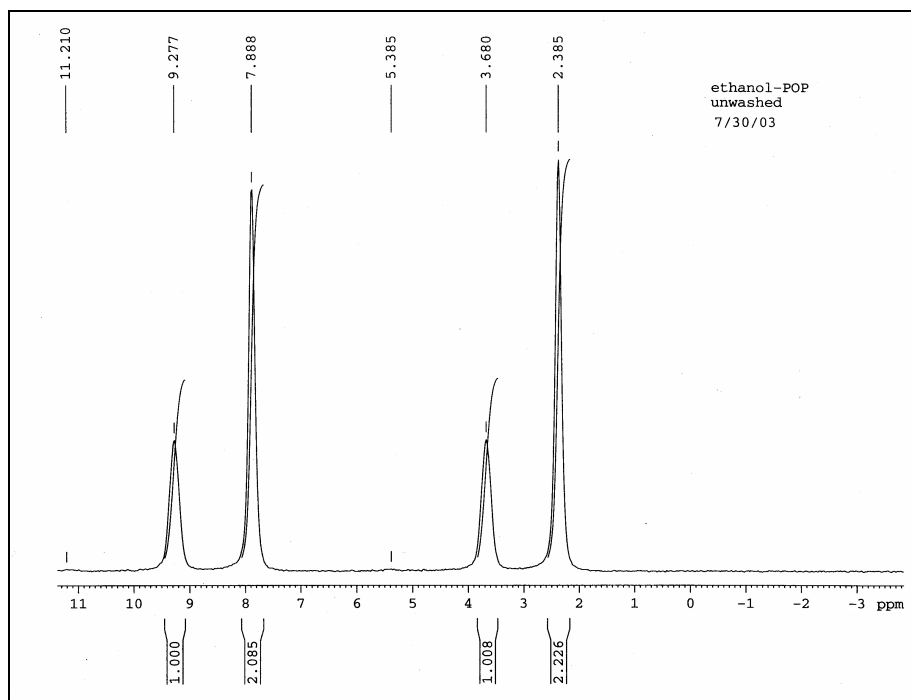


Figure 50. ^{31}P NMR spectrum of an attempt to synthesize **7b** (in Benzene).

In conclusion, it was found that **1** could be synthesized in a reliable manner using completely airless conditions. It was found that **1** could be used to simply and rapidly synthesize a number of monoalkylated phosphorus acids (**6a-k**) to an almost 100% yield. Preliminary data showed that Zwierzak's method for the synthesis of dialkylated pyrophosphites could be possibly be used in conjunction with **6a-k** to synthesize a number of dialkylated pyrophosphites which could then be used to make a new series of dimeric dialkylated-POP Pt(II) compounds.

Synthesis and Structural Studies of $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ and $\text{Pt}(\text{CN})_4^{2-}$ Linear Chain Polymers

Synthesis of the $\text{K}_2\text{Pt}(\text{CN})_4$ (**2**) and $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2$ (**3a**) Starting Materials

The complete synthetic method for a wide range of salts of the $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ anion can be found in the experimental section of this dissertation. One particular problem of note discovered during the initial syntheses of **3a**, was the reduction of the Pt(II) compounds in solution.

On rare occasions and for unknown reasons, reduced platinum Pt(0) (or platinum black) formed during some of the synthesis attempts of **3a**. This was quite noticeable as the usually orange and green solution would visibly turn dark grey or black in color. Even less frequently, the formation of reduced platinum would collect and plate out on the side of the reaction vessel yielding what is known as a platinum mirror. Due to Pt(0)'s autocatalytic nature, the formation of Pt(0) in any solution containing Pt(II), Pt(III) or Pt(IV) compounds is extremely problematic and usually results in the complete reduction of all higher valent platinum atoms. When and if that occurred, the black solution was removed from the contaminated vessel and diluted with water to dissolve any **3a** that had already been formed. Next, the solution was passed through a very fine, 10-15 porosity filter. This filtration method was usually sufficient to remove any reduced platinum. The filtrate solution was reduced via rotary evaporation to its initial volume whereupon the synthesis of **3a** was allowed to continue. The variable formation of reduced platinum limited the amount of starting material prepared during any single synthesis in order to limit the amount of platinum that could be affected by any reduced

platinum that could be formed. The synthesis of **3a** was concluded after its verification via elemental analysis.

The synthesis of **2** was much simpler than that of **3a**. No synthetic anomalies were found. The synthesis of **2** was also concluded following the compound's verification via elemental analysis.

Both of these compounds, once synthesized, were found to be stable over long periods of time if kept dry and stored in the dark. Much like during its initial synthesis, **3a**, if kept in solution will decompose and form platinum black. Solutions of **2** and **3a** were kept for a number of months where no degradation of the compound was seen.

The Partial Oxidation of **2** and **3a**: Electrolysis Cell Preparation and Procedure

The synthesis of the partially oxidized (PO) polymers via electrolytic methods was a relatively new process for the Abbott lab. The benefit of the electrolytic polymerization process was that polymerization experiments that sometimes took 2 to 3 months to complete via chemical methods now only took a matter of hours. The process that was developed in the Abbott Lab was not much different than what was proposed by Miller²⁵ in the late 1970's. The electrolysis cell was built in a similar fashion to the one depicted in Figure 51.

Two, 2cm long by 0.2mm wide pieces of platinum wire were used as electrodes in the early electrolysis experiments. These electrodes were folded over the side of a 2.5cm wide mini-petri dish as to allow about 1.5cm of the wire to hang into the dish. The electrodes were connected to copper electrical wires containing alligator clips on each

end. The alligator clips on the opposite end of the copper wires were connected to the positive and negative ends of a standard 1.5V dry-cell, alkaline battery.

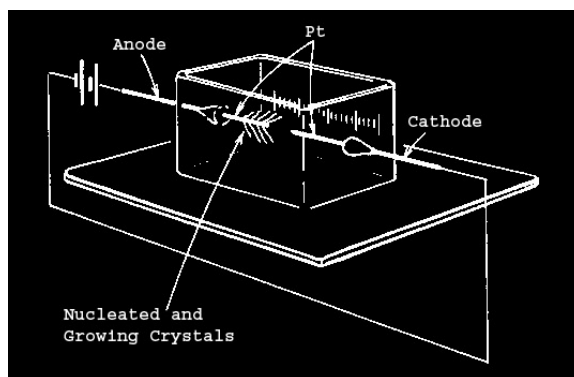


Figure 51. Basic electrolysis cell setup for the polymerization of **2** and **3a**.

In the early phases of the polymerization, the platinum wires were only held in place by the alligator clips. After a short time, it was realized that the platinum electrodes needed extra support and needed to be completely immobilized. The wires were then secured to the side of the Petri dish by a small amount of quick setting epoxy. This not only tightly secured the platinum electrodes but also insulated the exposed portion of the electrodes so that the only the part of the electrodes capable of conduction were inside the Petri dish.

The alligator clips would sometimes slip off the electrodes and contact would be lost. This was remedied by soldering Fe electrical wire to the electrodes. The alligator clips were then attached to the iron wire.

Since K_2PtCl_4 , the starting material for both the synthesis of **2** and **3a**, is rather expensive, a small Petri dish, one with a volume of 5mL was used as an electrolysis cell.

The only reason for using a dish this size was to keep materials costs down. The size of the dish was only limited by the amount of solution that was available.

0.060g of **3a** was added to 10mL of distilled water, which was then placed in the electrolysis cell. Once the solution touched the two electrodes, the electrolysis was initiated and polymer formation was immediately evident.

In early experiments, attempts to electrolyze solutions containing variable amounts of **3a** yielded mixed results. Solutions with a small amount of **3a** present were difficult to electrolyze. It was found that a solution of **3a** had to be nearly saturated in order to get polymer formation to occur. It was found that the optimal concentration of **3a** required was $1.56 \times 10^{-2} \text{M}$ (or 7g/L).

For **2**, solutions needed to be concentrated in order for polymerization to commence. The optimal concentration needed for **2** was a bit more difficult to determine. Unlike **3a**, which is only partially soluble in water and reaches its saturation point at around $1.56 \times 10^{-2} \text{M}$, **2** is almost infinitely soluble in water. Initially, the common practice for the preparation of solutions of **2** was to put a small amount of **2** into 10mL of water, place the solution in the electrolysis vessel and begin the polymerization. Then as the water was allowed to evaporate, the solution would become more concentrated and polymerization would commence. Unfortunately, depending on the temperature of the surrounding air, the initial amount of water or initial amount of **2** added, the time before the polymerization would occur was found to be anywhere from 30 minutes to 2 days. It was found that the ideal preparation method for polymerization **2** was to place 0.5g of **2**

in 5mL of water. A solution that was approximately 0.27M of **2** would begin polymerization on contact with the active electrodes.

The Partial Oxidation of **2** and **3a**: Bulk Polymerization Study

All past studies on the electrolytically or chemically prepared PO polymers of **2** and **3a** (and other various salts of these two compounds) focused on conductivity of those polymers. Prior work usually consisted of forming the polymers, measuring their conductivity and then moving on to the next set of polymers. It was overlooked that these compounds had interesting physical and structural properties to go along with the heavily studied electrical properties. It was hoped that information could be collected that would give a greater insight to the macroscale, microscale and nanoscale polymerization of these compounds and from that information, general rules for their formation could be made.

As stated previously, the work done on the linear chain PO polymers formed from the salts of $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ and $\text{Pt}(\text{CN})_4^{2-}$ was most often done via chemical oxidation. This slow process was excellent for forming X-ray quality polymer crystals but it was a poor choice for anyone wanting to characterize the polymers growth patterns.

The initial step in characterizing the growth patterns of **2** and **3a** was to bulk polymerize the two compounds and observe any differences in how the polymers formed. Separate solutions of both **2** and **3a** were allowed to polymerize following the procedure described above. After applying a direct current at a potential of 1.5V to both solutions for 3 hours, the voltage was removed and the polymers were inspected.

For electrolyzed solutions of **3a**, the small petri dish was found to be nearly completely filled with what appeared to be a large amount of brown gelatinous material. This material was in fact the PO polymer that was formed previously via chemical oxidation by others^{44,45} and designated the gamma form of the partially oxidize polymer of **3a** ($\text{K}_{1.81}\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ or $\gamma\text{-KOP}$).

The individual polymer crystals were indiscernible by visual inspection. The polymers, while still hydrated, were found to be quite flexible and could be pulled from the solution and drawn out on various surfaces. Upon drying, the polymers would become more copper colored and would exhibit a metallic-like luster. The polymers were found to be very brittle. As the solvent was removed, the polymers formed from **3a** would become attached to any material that they were in contact with. Attempts to remove the dried polymers from these surfaces would result in the polymers chipping and flaking away in large flat sheets.

The electrolyses of concentrated solutions of **2** were found to take a bit longer to polymerize. After an hour, instead of the reaction vessel being completely filled as what was seen with solutions of **3a**, the polymers were measured to have grown only one centimeter. The PO polymers of **3a** appeared to have more structural uniformity and definition than the **3a** PO polymers. The PO polymers of **2** were more ordered and were visibly thicker than those of **3a**. Individual polymer strands 1mm thick were visible and the color varied slightly as well. Instead of the dark brown color seen for the PO polymers of **3a**, the polymers of **2** were light brown and copper colored. A metallic luster was present even while the polymers were still in solution. The polymers were much

easier to handle than the PO polymers of **3a** and could be removed from solution and manipulated even after they were allowed to dry. The increased durability of the polymers formed from solutions of **2** was attributed to their larger size and the uniformity in their structure. The polymers formed from **2** were found by elemental analysis to have the formula, $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$.

Electrode Polymerization Observations of **2** and **3a**

As previously stated, platinum wire electrodes were placed flush along the sides of the petri dish-electrolysis chamber. Immediately after solutions of **2** or **3a** were added to the active electrolysis cell, a color change was visible around the anode. Normally for unoxidized solutions of **3a**, the color of the solution is pale green. When solutions of **3a** were added to the active electrolysis cell, the color around the anode became pale yellow. This color change was most likely caused by the formation of short, pentameric or less PO bisoxalatoplatinum chains prior to the extended polymer formation⁴⁶. The same color change around the anode was visible for solutions of **2**.

After the color change was observed in the electrolyzed solutions of **2** or **3a**, the polymerization of either of the two compounds was visually evident after 30 seconds or less. For solutions of **2**, a small amount of PO polymer was noticeable on the surface of the anode which turned a lustrous, bright copper color similar to what was seen of the PO **2** polymers. After the deposition of the PO polymer on the surface of the anode, micro-fine PO **2** polymers would be visible after 1 hour.

The polymerization of **3a** was more rapid than that of **2**. After the initial 30-second color change, a light brown ‘fuzzy’ material was visible on the surface of the

electrode. After a number of minutes, the ‘fuzzy’ material became more defined and appeared whisker-like in appearance. After watching the polymerization for 30 minutes, the distance traveled by the polymer strands was nearly quadruple that of the PO polymers of **2** (around 4cm).

The oxidation and polymerization of the **2** and **3a** occurred off the anode in a radial fashion. The anode, which was situated flush with the interior wall of the Petri dish, had polymers form in all directions possible. Growth off the sides and bottom of the platinum wire anode occurred similarly to what is illustrated in Figures 52 and 53.

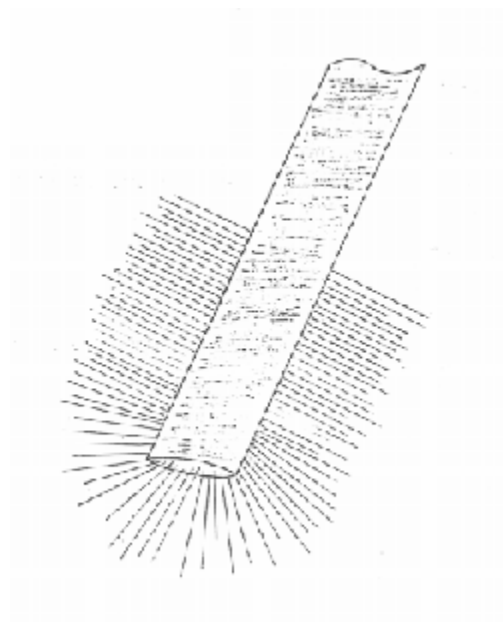


Figure 52. Polymerization pattern of **2** and **3a** off of a platinum anode wire.

The electrolysis cell was modified in order to get a better view of the polymerization pattern of the polymers bundles off of the platinum anode. The anode was removed from the side of the Petri dish and placed 0.5cm from side of the dish. This allowed for the viewing of the anode from all angles and directions. A solution of **3a** was

electrolyzed and observed for 30 minutes. The polymer bundles were seen extending radially from all exposed sections of the anode. A top view of the polymerization of **3a** off of a platinum wire anode is shown in Figure 53.

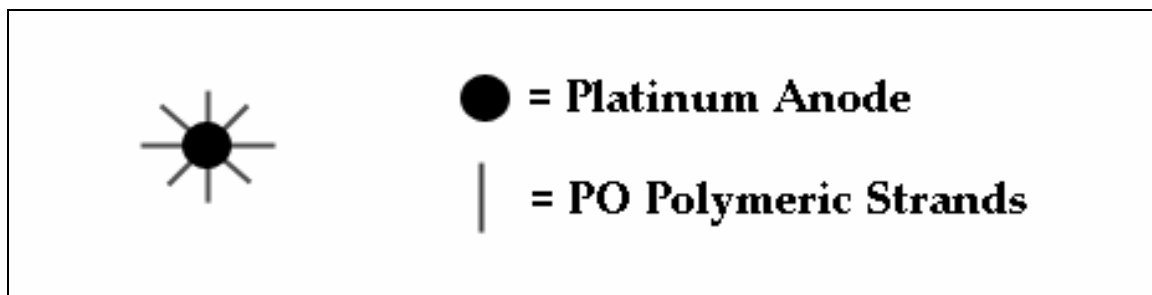


Figure 53. Radial **3a** polymer growth off of a platinum wire anode.

As the polymers neared the cathode, the polymerization ceased completely. It was hoped that the polymers would approach and attach to the cathode thus creating a completed circuit. This appeared to be very unfavorable for the PO polymers. After careful thought it was realized that there were a number of reasons why it would be impossible to have polymers form a connection to the cathode.

First, chemistry is occurring at both the anode and cathode. Since, the polymers are formed on the anode and not the cathode it would be safe to assume that the reduction potential of the platinum complexes is highly negative and therefore readily oxidizable in the electrolytic polymerization cell which means that there is a high potential for the polymers to be oxidized rather than reduced. If the polymers did touch the cathode, an unfavorable reduction of the entire polymer chain would have to occur.

For the oxidation of the platinum(II) complexes to occur, another reduction would have to occur as well. During the oxidation of the platinum compounds, a large amount

of gas is formed at the cathode. The only other compound in solution (other than the counter cations) is water. This gas was found to be H₂ and the half reaction occurring at the cathode is displayed in Equation 9.



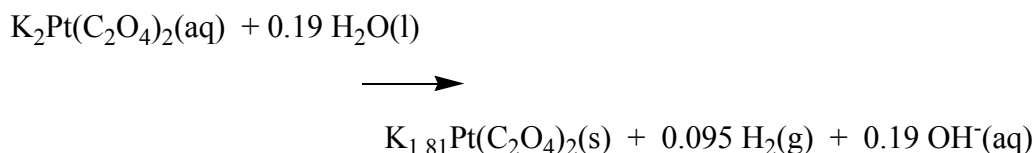
Equation 9: Half-Cell reaction for the reduction of water

Notice that not only is hydrogen gas formed at the cathode but hydroxide as well. Hydroxide anions are known to attack platinum complexes to form monomeric and dimeric hydroxide bridged platinum compounds.⁴⁷ It was proposed that as the PO polymers formed from solutions of **2** or **3a** neared the cathode, the free hydroxide in solution attacked the platinum nuclei and halted the polymer formation. To test this theory, a small amount of HCl was added to a solution of **3a** prior to its exposure to the electrolysis cell whereupon the polymerization was commenced. As the PO polymers neared the cathode, the polymerization continued until they reached the cathode. After a number of minutes, the light brown polymers around cathode turned black (which was a result of the platinum being reduced from Pt^{2.19-} to Pt⁰). The battery was removed and a voltmeter was connected between the two platinum electrodes. If the polymers had connected to both the anode and cathode then the voltmeter would have read 0.00V. The voltage display on the voltmeter fluctuated wildly which indicated that no electrical connection was formed between the two electrodes. HCl was not added to any solutions of **2** in order to minimize the risk of forming lethal hydrogen cyanide (HCN) gas.

The complete electrochemical reactions observed for the PO polymerization of **2** and **3a** in the electrolysis cell are shown in Equations 10 and 11.



Equation 10: The complete electrochemical reaction for the polymerization of **2**



Equation 11: The complete electrochemical reaction for the polymerization of **3a**

Synthetic Attempts on Other Viable Pt(II) Complexes

It has long been known that both the $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ and $\text{Pt}(\text{CN})_2^{2-}$ anions can be polymerized via chemical or electrolytical oxidative methods and these were the only two platinum compounds that were found to form PO linear chain polymers. The polymerization of these polymers seemed fairly straight forward and it was thought that just about any square planer platinum compound should be able to be partially oxidized and polymerized. **3a** seemed to be a special case in that the driving force for its polymerization was caused by the lowering of energy due to the overlap of the d_z^2 orbitals on the adjacent platinum atoms and by the overlap of the antibonding orbitals on the C_2O_4 ligands⁴⁸. No special bonding has been proposed in the case of the formation of the PO polymers from solutions **2** and polymerization has only been attributed to the overlap of the d_z^2 orbitals of the adjacent platinum atoms. Unfortunately, polymerization attempts on other square planer platinum complexes have only yielded negative results.

It was questioned as to whether PtCl_4^{2-} could possibly be partially oxidized in order to form a new series of polymers. PtCl_4^{2-} is a good stable ion in water and is square planar as well. A number of attempts were made to polymerize solutions of K_2PtCl_4 yet only negative results were obtained. It was believed that the ligands involved, in this case chloride atoms, hindered the formation of the PO polymers. A rough calculation was made on a fictitious polymeric chain consisting of a series of PtCl_4^{2-} molecules stacked on top one another where the platinum-platinum distance within the polymer was $2.85\text{\AA}$. It was found that the stacking of the PtCl_4^{2-} complexes in an eclipsed fashion would be very sterically hindered and the electron clouds of the chloride anions would be in too close of proximity. If the complexes were to stack in a staggered formation, the polymerization could possibly occur even though the electron clouds of the chlorides would be almost in contact with one another. It was realized that elements higher than row two would most likely be too large to accommodate polymerization.

Polymerization was briefly attempted on solutions of $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ and $\text{Pt}(\text{CH}_3\text{CN})\text{Cl}_3$ in order to compare them to PtCl_4^{2-} . Both compounds were planar and the number of row two elements (chlorides) was reduced which would allow for a less sterically hindered PO polymer. It was found that neither of the two compounds was soluble in water and had to be dissolved in acetone. Past attempts to electrolyze any platinum(II) complex, including the various salts of $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{C}_2\text{O}_4)^{2-}$, in a solvent other than water yielded no PO polymers. Electrolyzing solutions of $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ or $\text{Pt}(\text{CH}_3\text{CN})\text{Cl}_3$ in acetone yielded no PO polymer formation.

The polymerization of $\text{K}_2\text{Pt}(\text{C}_3\text{H}_2\text{O}_4)_2$ (Pt-Mal) [where the bismalonic acid is abbreviated as Mal] was studied by Keller in the mid-1990's. It was found that Pt-Mal would form a series of polymers upon chemical oxidation ranging from a dimeric to a pentameric species⁴⁶. However, the lifetime of these species was found to be considerably short where upon after 15 minutes the polymeric compounds decomposed to their original monomeric form.

Based on the observations made on the PO polymers of $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ and the failed attempts to polymerize solutions of K_2PtCl_4 and Pt-Mal, a new set of rules were devised which dictated what types of elements needed to be present in any platinum(II) square planer complexes in order for PO polymerization to occur.

The rules are as follows:

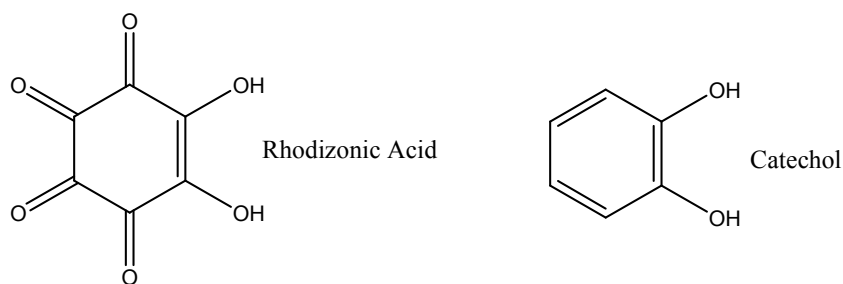
1. When a platinum(II) square planer compound is formed, the ligands must be oriented in such a way as form a nearly flat compound. The space between two bonding platinum atoms in a PO polymers can range anywhere from 2.8 to 2.97Å. For the platinum(II) complexes to polymerize, there must be no steric issues caused by parts of a molecule hanging above or below the plane of the molecule
2. The platinum(II) complexes must be water soluble. No PO polymers had been formed from any solvent other than water.
3. The atoms within the ligands bound to the platinum(II) atom must be second row elements. This is also a steric requirement. Large atoms, as stated previously, would cause too much repulsion between adjacent platinum(II) complexes.

4. The complexes used in polymerization must be negatively charged. Specifically
 2. The charge on the overall complex dictates the size of the d_z^2 orbital on the platinum(II) atom. The greater the size of the d_z^2 orbital, the greater the d_z^2 - d_z^2 overlap would be between two adjacent platinum complexes and the better the chance of a platinum-platinum interaction occurring.

Attempts to Synthesize other Potential Partially Oxidizable Platinum(II) Complexes

Using the above rules for PO polymerization as a guideline, a couple of new ligands and two previous known platinum compounds were found which agreed with the above requirements for polymerization to occur.

The two newly proposed ligands that agreed with the PO polymerization rules were Rhodizonic Acid and Catechol (Figures 54a and 54b respectively).



Figures 54a (left) and 54b (right). Rhodizonic Acid and Catechol.

Both Rhodizonic acid and Catechol were excellent ligands in the sense that they both were flat and rigid, contained only second row elements and had similar bite angles as that of oxalic acid. These two potential ligands had all the characteristics that were desired for the formation of new PO platinum polymers, unfortunately the synthesis of the platinum(II) complexes containing either of the two compounds was never achieved.

Solutions of K_2PtCl_4 mixed with various amounts of either of the two potential ligands ended up yielding brown/black tar-like solutions. The brown mixtures were diluted with water and any attempts to electrolyze those solutions yielded no polymer formation.

In reactions with catechol, the protons were neutralized with two equivalents of KOH to yield the dipotassium salt of catechol. Reactions using K_2PtCl_4 as the platinum(II) source were attempted using the dipotassium salt of catechol instead of the acid salt. These reactions yielded the same brown sludge that was found in prior experiments. Attempts to electrolyze the brown mixtures of K_2PtCl_4 and the dipotassium catechol salts yielded no polymer formation.

Revisiting the Pt-Mal work done by Keller in mid-1990's revealed that her attempts at polymerization involved chemical means with the use of compounds such as $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, K_2PtCl_6 and $\text{Pt}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2$. It was thought that rather than using the slower method of chemical oxidation to form polymers of Pt-Mal, employment of the faster electrochemical method, which was used to polymerize compounds **2** and **3a**, would also form visible polymers of Pt-Mal in a short amount of time. Since the polymerization of **2** and **3a** only seemed to occur if the solutions containing these two compounds were saturated it was assumed that the solutions of Pt-Mal would need to be saturated as well.

Saturated solutions of Pt-Mal were made by adding a small amount of water to a large amount of Pt-Mal. The liquid was centrifuged, decanted and placed in an electrolysis cell at an applied potential of 1.5V. The solution stayed a light orange color throughout the entire oxidation process and no polymers were formed during that time.

After closer inspection of the Pt-Mal compound it was found that both of the $C_3H_2O_4$ ligands extend above and below the plane of the complex. This would lead to steric problems and thus inhibit any extended polymer formation.

With the work on Pt-Mal complex complete, 75mL of a concentrated solution of Pt-Mal was placed in a refrigerator for long-term storage. After one year, the solution had become cloudy, brown in color and appeared to contain PO platinum polymer. The mixture was filtered and the filter cake was washed three times with water. The collected brown material had the metallic luster characteristic to the PO polymers of **2** and **3a**. The sample was characterized via elemental analysis and the PO polymers were found to have a molecular weight of 486.2843g/mol which, within a 3.5% error, gave the formula of $K_{1.61}Pt(C_2O_4)_2 \cdot 2H_2O$. It appeared that the potassium salt of the Pt-Mal decomposed to form **3a** and then was oxidized either by O_2 from the atmosphere to form the PO polymers of **3a**. It was found that malonic acid ($C_3H_4O_4$), the Mal ligand prior to deprotonation, could be oxidized upon exposure to IO_4^- and H_2O to form oxalic acid and carbon dioxide. This multistage oxidation pathway is illustrated in Figure 55⁴⁹.

With the usage of a strong oxidizing agent such as IO_4^- , the oxidation of malonic acid to oxalic acid proceeded in a matter of hours. Malonic acid has also been shown to form oxalic acid when exposed to other oxidizing agents as well^{50,51}. Exposure to a weaker oxidizing agent over a longer period of time could also lead to the formation of oxalic acid from malonic acid. Based on the elemental analysis data obtained from the PO polymers formed for the solution of Pt-Mal and the reaction equation in Figure 53, it is

clear to see that Pt-Mal's exposure to atmospheric oxygen for such a long period of time led to its decomposition to **3a** and CO₂.

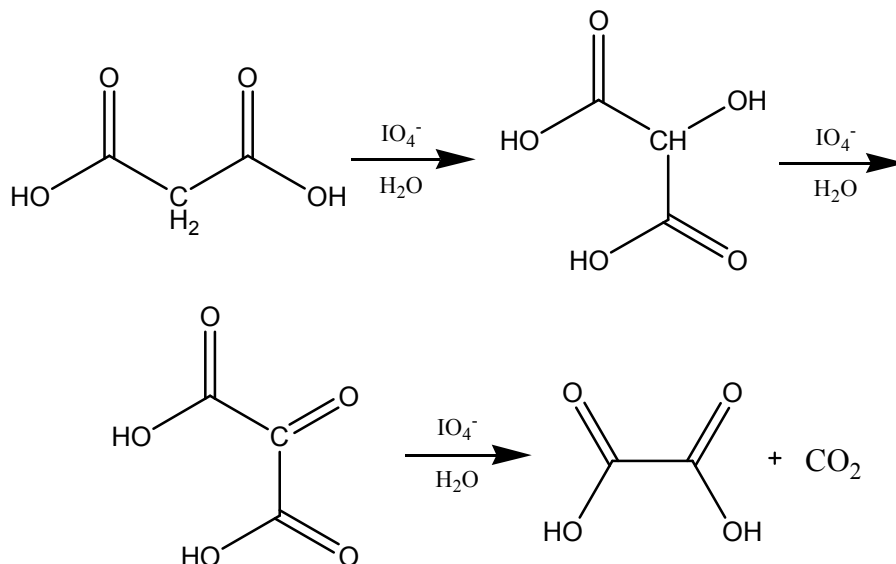


Figure 55. Complete Oxidation process for the conversion of Malonic Acid to Oxalic Acid.

The final, potentially polymerizable compound to be studied was the potassium salt of bis(squarato)platinum(II). The interest in the squarate ligand was the fact that with its reaction with platinum(II), Toftlund had briefly reported it as a new PO oxidizable platinum(II) polymer⁵² only to comment a few years later as it being a new dimeric platinum(II) bridging ligand³⁴. The evidence for calling bis(squarato)platinum(II) a new PO polymer was lacking but it seemed plausible that this compound was partially oxidizable thus polymerizable.

The synthetic route for the formation of the potassium salt of bis(squarato)platinum(II) **8**, is covered in detail in the experimental section of this dissertation. Due to the unfavorability of squarate anions replacing the chlorides on

PtCl_4^{2-} , $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ had to be used. Solutions of squaric acid and $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ yielded solutions blue/black in color. The blue/black color of the solution was most likely caused by mixtures of small polymeric platinum compounds known collectively as the platinum blues^{53,54,55}. Toftlund stated that solutions of squaric acid and $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ yielded dark solutions containing black crystals of the PO polymer. No crystals were evident in the squaric acid and $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ solutions.

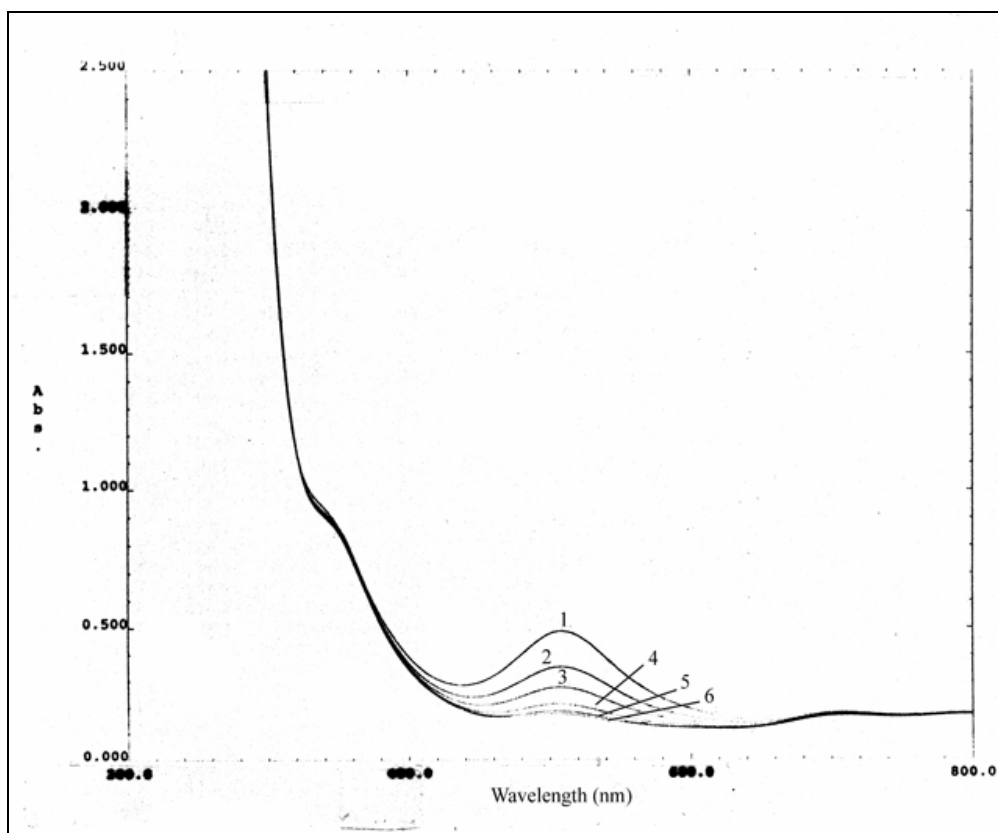


Figure 56. UV/Vis experiment on potassium salt of bis(squarato)platinum(II). Five scans 3 minutes apart were taken. Peaks 1, 2, 3, 4, 5 and 6 were taken at 0, 3, 6, 9, 12 and 15 minutes respectively.

A 5mL sample of the blue solution was removed from the reaction vessel and placed in an active electrolysis cell. After one day of electrolysis, no PO polymers were

visible. Another 1mL sample of the blue/black solution was taken, placed in the electrolysis cell and diluted to 5mL. After 15 minutes the color of the solution had completely disappeared. It was initially believed that the electrolysis was causing the color change. To test this hypothesis a 1mL sample of the blue solution was placed in a quartz cuvette, diluted to 5mL, placed in a UV/Vis spectrometer and scanned every 3 minutes (Figure 56). It was apparent that the various short polymers contained within the blue/black solution were decomposing upon dilution and after 15 minutes were almost completely destroyed.

After the attempts to polymerize other square planar platinum(II) compounds, the unknown reason as to why $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ were able to form the PO polymers while other square planar platinum(II) compounds were not, still remained.

Macroscale Polymerization of the PO Polymers of **2** and **3a** Off of Various Conductive Surfaces for STM Imaging

The electrolytic method of PO polymer formation employs the usage of platinum wire as electrodes. Platinum metal is ideal due to it being fairly inert and not easily oxidized. All electrolytic polymerizations of **2** and **3a** took place with the usage of platinum wire. It was questioned as to whether the PO polymers of **2** (K-PtCN) and the PO polymers of **3a** (K-PtOx) could be formed using other conductive surfaces.

Wood performed some preliminary electrolyses of both **2** and **3a** using highly ordered pyrolytic graphite (HOPG) as the anode⁵⁶. The focus of Wood's research was to obtain high quality scanning tunneling microscopy (STM) images of the surfaces of the K-PtCN and K-PtOx polymers. It was hoped that, based on the STM data, it could be

determine if the crystal structures of the electrolytically polymerized compounds matched the structures of the polymers formed via chemical methods.

Early attempts to obtain good STM images yielded very little results. This was in part due to the sensitivity of the scanning tunneling microscope and well as the non-uniformity and random polymerization pattern of the PO polymers. The K-PtOx polymers formed within the electrolysis cell were very disordered and quality images of the K-PtOx polymers were a rare occurrence. Although the formation of long, visibly well-defined polymers of K-PtCN was easily obtainable, STM images of these polymers were also a rare occurrence. For an image to be obtained via scanning tunneling microscopy, the sample being investigated needs to be conductive as well as grounded, that is to say the sample needs to be physically connected to the STM sample plate in order for the slight current passed by the scanning probe of the microscope to be measured. The PO polymers not only needed to be well-defined crystals but they needed to remain connected to the conductive surface from which they were polymerized.

The main problem in using the platinum wire as an anode was that the polymers formed on the surface of the platinum wire were broken off quite easily. Any slight agitation of the anode would result in the destruction the PO polymers. The purpose of using the HOPG as the anode was to form polymers of a more order fashion. The very thin and conductive HOPG could be attached to various solid surfaces where the PO polymers could then be formed. When the polymerization was complete, the anode could be removed, dried and placed directly in scanning tunneling microscope for analysis without disturbing the PO polymers.

The process for building the HOPG anode and polymerizing a solution of **2** or **3a** was quite simple. The HOPG crystalline material was placed on a flat surface. A piece of double-sided Scotch™ tape was placed on top of the crystal and slowly peeled away, bringing with it a single layer of HOPG. The tape was then attached to a 12mm iron disk. A small amount of colloidal silver paste was painted on the iron disk and the HOPG in order to assure a connection between the two materials. A small piece of aluminum foil was placed between the iron disk and a small magnet. The positive end of a 1.5V dry-cell battery was connected to the aluminum foil. To the negative end of the 1.5V battery was attached a small piece of platinum wire. The end of the wire was brought to within 3mm of the HPOG surface. Then, a small droplet of a saturated solution of **2** or **3a** was placed on the surface of HPOG so that it was in contact with the platinum wire. The electrolysis was initiated and PO polymer formation occurred within 5 minutes. The iron disk containing the PO polymers was removed and lightly washed with deionized to remove any unreacted platinum(II) complex. The disk was allowed to dry and subsequently scanned via STM a day later.

The conductivity problems that plagued the polymer samples grown off the platinum wire anode were repeated for those samples grown off of the HOPG. Nicely formed PO polymers extending vertically off the surface of the HOPG were visible but having the scanning tunnel microscope probe engage the PO sample (i.e. detect conductivity) was virtually impossible.

Closer inspection of polymers attached to the HOPG surface showed that the polymers were not as vertical as what was initially believed. The actual polymerization

pattern of the polymers seemed to be more crater-like, that is to say very little polymerization occurred in the center of where the droplet had been. It was found that polymer formation occurred along the edge of where the droplet had been. Also, the polymers were angled and not completely vertical in what appeared to be an attempt to polymerize more toward the cathode.

After careful consideration, it was determined that two major problems might be affecting the collection of good STM data. One problem was that the removal of any unreacted platinum(II) complex may not have been complete. If any unreacted platinum(II) complex remained, it could potentially coat the surface of the PO polymers and inhibit their conduction. The other problem might have been that some of the polymer strands were not connected to the HOPG surface. It was found that, when polymerized in bulk, K-PtCN and K-PtOx became very brittle after drying. The polymers, even though they appeared to be secured to the surface of the HOPG, may have become dislodged during the washing phase or during transportation. Even though few STM images were obtained, the polymerization of the PO polymers off of the surface of the HOPG proved that the PO polymers could be formed off of a conductive material other than platinum wire.

Other conductive materials were used as both the anode and cathode for various electrolyses of **2** and **3a**. Gold wire was used as electrodes for the polymerization experiments of **2** and **3a** which yielded light brown polymers formed during the electrolyses involving **3a** and light copper colored PO polymers were formed for

electrolyses involving **2**. The usage of gold wire seemed to have no effect on the polymerization of **2** or **3a**.

Nickel wire was successfully used as electrodes as well. Polymerization of both **2** and **3a** was had using nickel wire as the anode. On rare occasions, a blue/black solid would be formed on the surface of the nickel cathode opposite the PO polymers. This other compound appeared to be reduced platinum. This blue/black solid was not characterized.

K-PtCN and K-PtOx were formed off of a number of conductive foils as well. The wire electrodes were replaced with platinum foil in an attempt to form polymers off of an anode with a larger surface area. It was found that the polymers took much longer to form and the polymerization only seemed to occur off of the edges of the foil. The polymers were ill-defined and of poor quality when compared to the polymers formed from the platinum wire.

Silver foil was used in a similar fashion as the HOPG. A small piece of silver foil was placed horizontally under a piece of platinum wire. A small droplet of concentrated **2** or **3a** was placed so that it was in contact with both the silver foil and platinum wire. A voltage of 1.5V was applied and polymerization occurred. The polymers that formed were as good of quality as the polymers formed via the platinum wire and the HOPG. STM images of the polymers formed from the silver foil were attempted but no images were obtained.

Zinc foil and copper foil were also explored as possible electrodes. K-PtCN and K-PtOx were formed from these metals but the high electrochemical reactivity of copper and zinc discouraged their usage as electrodes in long term experiments.

The vertical growth of the polymers was still of high priority and the focus on obtaining good STM images was of importance as well. Small sheets of glass coated with Indium Tin Oxide (ITO, $\text{In}_2\text{O}_3\cdot\text{SnO}_2$) were acquired and used as electrodes for the growth of the PO polymers. To use the ITO sheets as electrodes they had to be modified in order to attach the alligator leads from the electrolysis source. To two sheets of ITO glass were attached small pieces of aluminum foil which enabled connection between the ITO and the 1.5V battery. A prepared ITO sheet was placed horizontally and secured to an immobile surface. Instead of using a single ITO sheet as an anode and a piece of platinum wire as the cathode, another prepared sheet of the ITO glass was used as the cathode. It was hoped that by using a flat cathode and flat anode, the E-field lines emanating from the anode surface would be more linear and less curved causing any PO polymer formed to be vertical in orientation. The ITO cathode was attached to an adjustable arm so that it could be maneuvered as to be parallel with the ITO anode. A small amount of concentrated **2** or **3a** solution was placed between the two plates. A 1.5V potential was applied whereupon the ITO cathode was placed just above the ITO anode so the droplet was on contact with both ITO electrodes.

Polymerization occurred and the PO polymers that were formed appeared to be higher quality and much more ordered than what was previously seen using the HOPG as an anode. The polymers formed almost perpendicular to the surface of the ITO glass.

Unfortunately, the polymerization did not occur uniformly across the surface of the ITO anode. A small patch, in the middle of where the droplet was placed contained a large bundle of polymers 1mm in diameter and 1mm tall. This bundle appeared to form in the manner depicted in Figure 57.

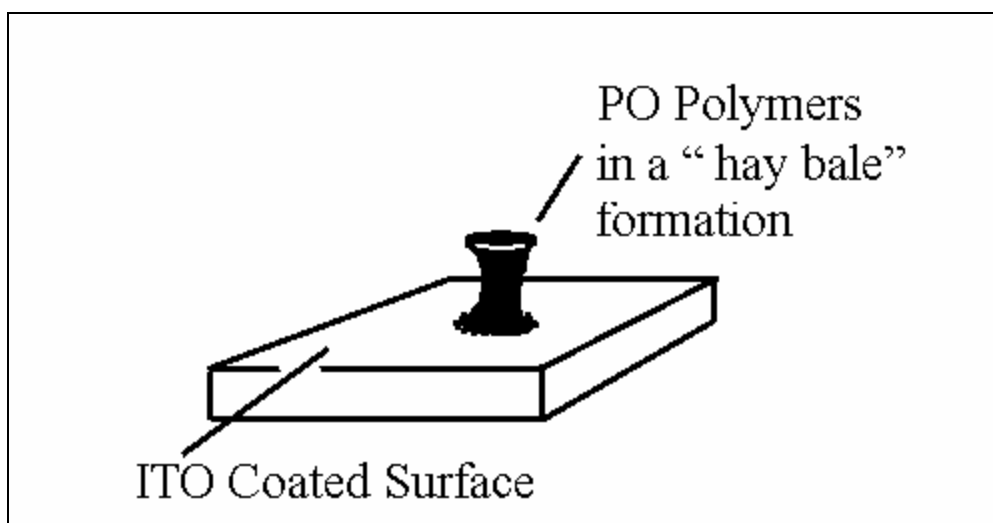


Figure 57. K-PtOx formed off the surface of ITO. Polymers were grouped in a “hay bale” formation.

The structure seen in Figure 57 looked much like a “hay bale.” The polymers were not completely vertical off the surface of the ITO but tapered inward, off of the surface of the ITO, perpendicular to the surface in the middle of the structure and tapered outward as it neared the ITO cathode. The structure was not a single polymer but a large collection of polymers that had bundled together to form the much larger superstructure. It was noticed that the polymers on the out edge of the surface seemed to bow inward as to combine with the other polymers around them.

These ‘linear-chain’ PO polymers were supposedly strictly linear in nature and very rigid and inflexible. The polymerization off the ITO showed that the polymers did have a small amount of flexibility and that the polymers could be made to form vertically off of a surface. Attempts to image the top of this structure via STM yielded no usable images. The polymers still appeared to be unattached from the surface of the ITO anode. It was realized that if any STM images of the polymers were to be obtained, they would need to be formed in a more confined area and secured to a conductive surface.

The final conductive material to be tested as a possible electrode was aluminum foil. Aluminum foil (Al-F) was chosen because of its relatively inexpensiveness, its good conductivity and its low chance of possible side reactions. Initial experiments involved polymerizing solutions of **3a** in a Petri dish to see whether PO polymers could be formed. After it was shown that formation of K-PtOx from an Al-F anode was possible, a new experiment was undertaken.

A piece of Al-F was covered with a thin layer of paraffin wax which was then allowed to cool and harden. A series of 1mm holes were made through the wax by using a small piece of heated metal. A solution of **3a** was forced into the holes by the means of a syringe. After the holes had been filled, a thin layer of solution was placed on the top of the wax. A piece of platinum wire was placed in the solution and connected to the negative end of a 1.5V battery. The aluminum foil was attached to the positive end of a 1.5V battery whereupon the electrolysis of the solution commenced.

The lithography of materials and the subsequent growth of materials off their surface have been used in many situations. Being able to form a macrostructure and then

polymerizing a solution of either **2** or **3a** would be novel in itself. Past bulk-polymerization experiments of **2** and **3a** were uncontrolled and the polymers formed with random orientations off of the anode. Being able to control where the polymers formed on a surface and where they polymerized to would make the STM (and other electron or optical imaging) of the polymers much easier.

The purpose of layering the Al-F with wax was for one single purpose: control. Wax is a cheap, unreactive and moldable substance. By using wax, one could etch out any type of pattern or mold in order to form PO polymers of a specific orientation. The wax insulated the Al-F from the electrolyte solution except for those parts where the wax had been removed. By boring holes through the wax, individually segregated channels were made where the Al-F was exposed and polymers could occur.

Two Al-F/wax samples were made and to both were added solutions of **3a**. The samples were agitated slightly to assure that the solutions had penetrated the wax holes. After 5 minutes of gentle rocking, the electrolysis of those solutions was begun. After 2 minutes, thin light brown ‘fur’ was seen protruding from the waxless holes. This brown ‘fur’ was the K-PtOx polymer. The polymerization was allowed to continue for a total of 30 minutes after which the 1.5V potential was disconnected.

Before any samples were scanned via the STM, one of the two PO samples was lightly rinsed with water and the other was left alone. Both were allowed to dry before any measurements were done. It was noticed that the PO polymer chains had extended up through the waxless holes, folded over and were lying on the top of the wax surface similar to what is seen in the graphical representation of a single wax hole (Figure 58.)

This was the second time that the K-PtOx polymers were seen deviating from their linear nature. It was apparent that the PO polymers were actually more flexible than what was previously believed.

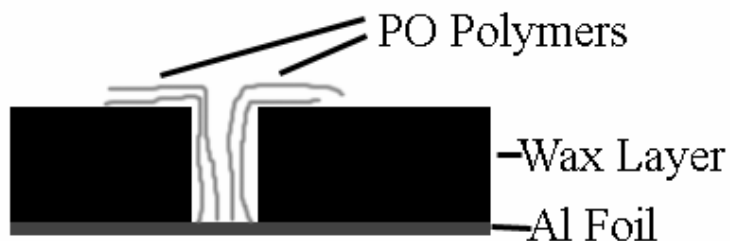


Figure 58. PO polymers of **3a** polymerized off of Al Foil, passing through a wax channel and laying on the surface of the wax after the solvent was removed.

After drying, the Al-F sheets were trimmed (in order to decrease their size) and their investigation via STM was initiated. After many attempts to image these samples, neither sample gave any usable images.

After the numerous attempts to image the PO polymers via scanning tunneling microscopy it was apparent that the conductivity of the polymers was too unpredictable and that the different methods of characterization would have to be employed.

Bulk Templated Growth of the K-PtCN and K-PtOx through Capillary Tubes

The next step of this project was to observe how thin K-PtOx and K-PtCN could be polymerized. The polymers seemed to form fairly thick when polymerized in bulk and the amount of disorder within the bulk polymers seemed quite high. After observing the disorder of the polymer formations of **2** and **3a** when polymerized in bulk and the polymers ability to form off of aluminum foil and through wax channels, it was theorized

that, with the usage of other prefabricated materials, the polymers could be forced to form in a more controlled and ordered fashion. It was already known that the polymers could be forced to polymerize within narrow channels templated in wax. These wax channels, which had a cross section of 1mm, were relatively large. Although the polymers formed within these channels were more ordered, the visual inspection of the polymers was difficult due to the inability to visually ‘see’ the initial nucleation point on the anode within the wax channel. The next step was to decrease the size of the polymer structures but do it in a way that would still allow inspection of the final product. The simplest, cheapest and transparent prefabricated templates commercially available were simple microcapillary tubes.

Work with capillary tubes and K-PtCN and K-PtOx was initially done by Wood in 1998⁵⁶. Wood found that filling a capillary tube with a solution of **2** or **3a**, placing two small pieces of platinum wire in opposite ends of the capillary tube and attaching the wires to a 1.5V battery yielded PO polymers. The end result of Wood’s work was that it was found that K-PtCN and K-PtOx were able to form within the capillary chamber.

In order to observe the formation of the PO polymers in-situ, work was resumed with the polymerization of solutions of **2** and **3a** within various sized capillary tubes. First, it was found that working with the capillary tubes was quite difficult. Wood’s experimental set-up for the polymerization of the PO polymers within the capillary tubes was quite cumbersome. The addition of the solutions of **2** or **3a** had to be done with the aid of a syringe. Handling the capillary tubes after the solution of **2** or **3a** was added was very difficult and the subsequent attachment the battery leads to the exposed electrodes

was nearly impossible. Each end of the capillary tubes were wrapped in Parafilm™ to limit the loss of solution and the tubes were held horizontally as the electrolyses took place. In Equation 9 it was shown that H_2 gas was formed at the cathode as the electrolyses occurred. By capping the ends of the capillary tubes, H_2 gas was unable to be released which forced the solution away from the cathode and halted the polymerization. Although this method did produce well formed polymers of relatively short length, a better, cleaner method was developed.

A small apparatus was made to aid in the polymerization of solutions of **2** or **3a** in which pressure was used to fill and maintain the solution within the capillary tube. The apparatus pictured in Figure 59 was made in order to allow the continuous polymerization of **2** and **3a** without the need to handle the capillary tube and to eliminate the buildup of H_2 gas at the cathode. The construction of the apparatus is as follows.

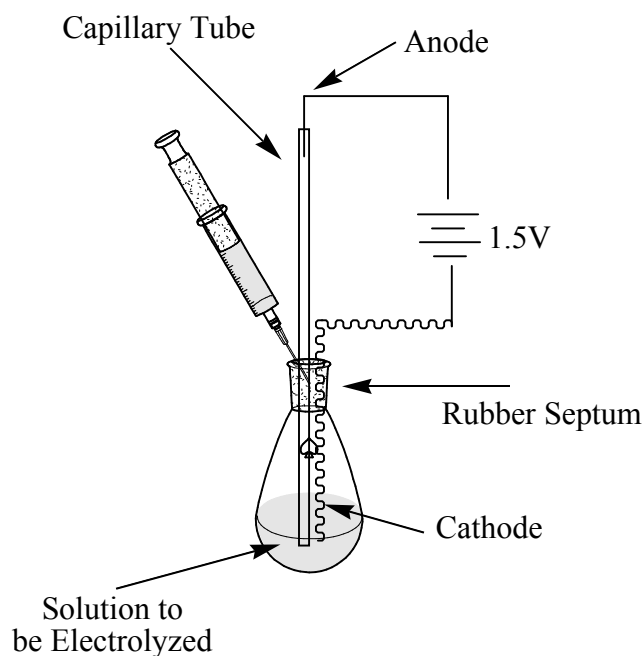


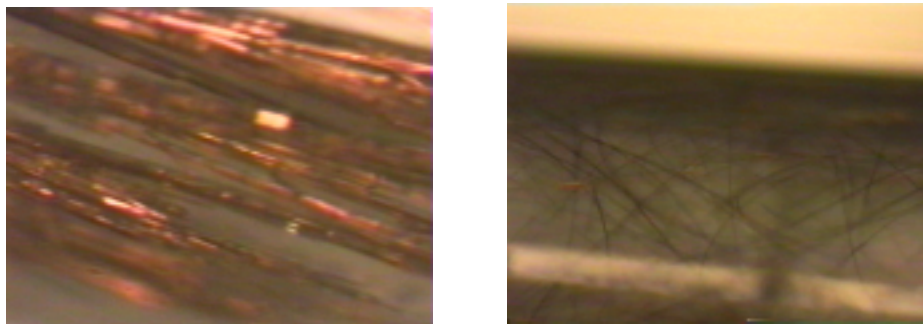
Figure 59. Pressurized polymerization apparatus used to form PO polymers of **2** and **3a**.

A small 15mm piece of Pt wire was soldered to a 20cm piece of electrical wire; which was to be used as the cathode during the electrolyses. A small 10mL single-necked flask was fitted with a rubber septum that had been previously perforated with two holes. Into one hole in the septum was placed the makeshift platinum/electrical wire cathode. Into the last of the two holes was gently fitted a 20cm long capillary tube. A syringe was filled with a saturated solution of either **2** or **3a** which was then injected into the bottom of the flask through the rubber septum. The capillary tube was situated so that it was submerged 2-3mm within the solution. The syringe's plunger was fully extended and the syringe was reinserted into rubber septum. The plunger was gradually forced down as to pump the solution up the column of the capillary tube. Once the tube was completely filled, a 5mm piece of platinum wire was wrapped in Parafilm™ and inserted in the top of the tube. The 5mm piece of wire was attached to the positive end of a 1.5V battery and the makeshift cathode was attached to the negative end.

The main benefit in using this apparatus was that the cathode was isolated from the capillary tube. There was still an electrical connection between the two electrodes but now, as H₂ gas was evolved, it filled the flask instead of the capillary tube. The evolution of this gas also pressurized the chamber so that the capillary tube always remained at positive pressure and filled with solution.

The polymerization of solutions of **2** and **3a** occurred from the top of the capillary tube. Magnified optical investigation of the polymers contained within capillary tubes having a 1500μm inner diameter yielded some interesting results. It was found that K-

PtCN appeared to be much thicker than the K-PtOx polymers. Figures 60a and 60b show the K-PtCN and K-PtOx polymers formed within the 25 μ L capillary tubes.



Figures 60a (left) and 60b (right): K-PtCN (left) and K-PtOx (right) [x10 Mag.]

Upon inspection of the two polymer samples at 10x magnification, the difference in color between the two polymers was very apparent. Also the polymer diameter and rigidity was found to be very dissimilar as well. The color difference between the two polymers is believed to be caused by the difference in the bond length between adjacent platinum atoms within the polymer chain. The more metallic-like a compound is (in electrical conductivity and thermal conductivity terms) the more metallic-like a compound will look. The thickness of the polymers could also be playing a part in their color. The thinner a metal polymer is the more dark it will become⁵⁷. Since the Pt-Pt bond length found for the K-PtCN polymer is 2.965Å and 2.837Å for K-PtOx, it is believed that the color is due to the latter.

The K-PtCN polymers appeared to form ten times thicker than that of the K-PtOx polymers. The average diameter of the K-PtCN polymer strands seen in Figure 60a were about 41 μ m whereas the average diameter of the polymers of K-PtOx in Figure 60b was

$\approx 4\mu\text{m}$. The measurements made in Figures 60a and 60b were verified by measurements made in subsequent capillary based polymerization experiments.

The other striking observation was the amount of flexibility seen in the K-PtOx polymers. When referring back to Figure 60a, one can see the near linearity of the K-PtCN polymers versus the slight to massive bending seen the K-PtOx polymers in Figure 60b. The flexibility of the K-PtOx polymers seemed to be much greater. This was thought to be caused by the thinner diameter of the K-PtOx polymer strands.

In another capillary polymerization experiment, massive bundling of the K-PtCN polymers was seen. Figure 61 shows a section of the capillary tube magnified by ten times.

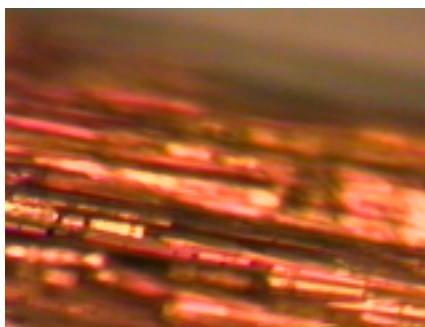


Figure 61. K-PtCN polymerizing in bundles [x10 Mag]

When observing the polymers without the aid of a microscope, it was noticed that the polymers seemed much thicker than normal. Under the microscope, it was quite clear that the individual polymer strands were stacking laterally or bundling. After contemplating this observation, this bundling of polymers seemed very understandable.

As stated in the introduction, the K-PtOx and K-PtCN polymers are in fact large crystals where counter cations are shared amongst the anionic PO platinum polymers.

This sharing of cations between the platinum polymers is, in very simple terms, the glue that holds these polymers together. If the potential used in an electrolysis is done slowly enough or if the general conditions for the crystal/polymer formation is optimal, then polymers of very large diameter can be formed. In this experiment, it seemed that the conditions for the formation of thick polymers were optimal. It was unknown what variable(s) had been changed and any attempts to change variables in order to form thicker or thinner polymers yielded inconclusive results.

A capillary tube containing a large amount of K-PtCN polymer was reexamined four days after it had initially synthesized. The capillary tube had been shaken slightly during attempts to observe the polymers within. Figure 62 displays a section of the same capillary tube containing the K-PtCN polymers seen in Figure 61.

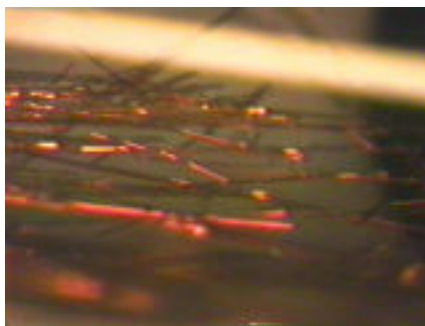


Figure 62. K-PtCN polymers unbundling after agitation [x10 Mag]

The shaking and disruption of the solution still contained within the capillary tube caused the polymer bundles to unravel which led to splintering of the K-PtCN polymers. The bundling of the K-PtCN polymers seemed to be possible if the solution was left undisturbed. Conversely, if the solution was agitated in any way, the polymer bundles were easily fragmented.

Micro-Growth of the K-PtCN and K-PtOx through Capillary Tubes

As previously stated, it was observed that the polymers of K-PtCN were much thicker than those of K-PtOx. It was thought that since the K-PtOx polymers were so thin in diameter that, maybe they would be able to form in a more constricted environment. Conversely, in the case of the K-PtCN polymers, it was thought that their large size would limit the size of polymerization vessel used. In the case of both K-PtCN and K-PtOx, the length of the polymers formed seemed only limited by the length of the polymerization vessel. When polymerized within a Petri dish, the K-PtOx polymers completely filled the dish and the K-PtCN polymers would nearly polymerize along the entire length of the dish if allowed to polymerize long enough. With those observations in mind, it was hoped that the polymers could be forced to grow through thin channels as well as long lengths.

Capillary tubes with an inner diameter of 25 μ m were heated over a flame and ‘pulled’ in order to decrease the inner diameter of the tubes as well as increase their length. An approximation of thickness was made for inner diameter of the pulled capillary tubes which were found to be 5 μ m to 10 μ m wide. Numerous ‘pulled’ capillary tubes with varying lengths were made in order to understand how long the polymers could form. The ‘pulled’ capillary tubes were used in conjunction with the apparatus illustrated previously in Figure 59. The same general electrolysis method as with all polymerization experiments involving capillary tubes was followed.

Upon initiation of the electrolyses, the once instantaneous polymerizations appeared to have been completely stopped by the now ultra-thin capillary tubes. Numerous attempts to polymerize solutions of **2** or **3a** yielded no results. Initially, the electrolyses were only allowed to continue for a few hours. One attempt to polymerize a solution of **2** was allowed continue for one complete day. Upon inspection of the active anode after a 24 hour period, a small amount of bronze colored, K-PtCN polymer was visible. The amount and density of formed K-PtCN polymer was much greater than what had been observed in previous experiments. The polymers, which usually formed off of the platinum anode in random locations, were only forming from under the section of platinum anode that was wrapped in Parafilm™.

The length of these K-PtCN polymers was only about 2mm. K-PtCN polymers formed within a normal, unmodified capillary tube would have been many centimeters if allowed to polymerize overnight. It seemed that the reduction of the capillary diameter increased the amount of time needed for the PO polymers to form lengthwise.

The polymerization was allowed to continue for 10 more hours and the capillary tube was reexamined. It was found that the polymers of K-PtCN were able to form the entire length of the capillary tube. This observation was very surprising since the diameter of the K-PtCN polymers, when formed in bulk, was always much thicker than that of the inner diameter of the ‘pulled’ capillary tubes. It appeared that the K-PtCN polymers were able to vary their diameter in order to continue polymerizing toward the cathode.

Numerous repetitions of this experiment were performed on a number of pulled capillary tubes, all of varying length. The polymer formation off of the anode always took about twelve hours to extend 2mm. In another 12 hours, the polymers were able to extend through however long of a channel that was formed within the ‘pulled’ capillary tube. Closer examination of the polymers within the narrow portion of the capillary tube showed that the polymers were able to completely pass through the narrow section in 2 to 5 hours.

The characteristics for the formation of the K-PtOx polymers through ‘pulled’ capillary tubes were very similar to the formation of the K-PtCN polymers. One major difference between the two polymers was that the K-PtOx polymers were always very small in diameter and never formed very thick structures. The distance traveled by the PO polymers was still very slow during the initial phase but became very rapid when the polymers entered the narrow portion of the capillary.

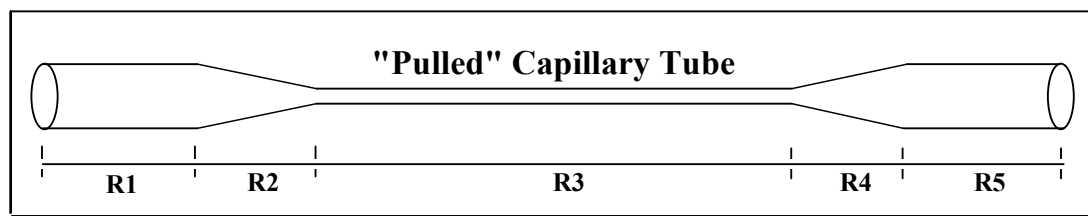


Figure 63. Polymerization of K-PtCN and K-PtOx through micro capillaries. R1 and R5 is where the anode and cathode were housed respectively.

For both the K-PtCN and K-PtOx polymers, their formation through the pulled capillary tubes was nearly identical. When referring to the graphical representation of a pulled capillary tube (Figure 63), in the region labeled ‘R1’ the amount of time needed to

travel that distance by either of the two samples would take anywhere from 1 to 2 days. In the region labeled 'R2', the polymers, specifically the K-PtCN polymers, were able to reduce in diameter in order to penetrate the 5 to 10 micron region of 'R3'. Once the polymers decreased in diameter, the complete formation of polymers through the 'R3' region only took 2 to 5 hours depending on the length of the pulled capillary. As the polymers exited the 'R3' region, they maintained the diameter of the polymers seen in the 'R3' region and no polymer rebundling was seen. The distance traveled by the polymers slowed in the 'R4' region and completely stopped once the 'R5' region was reached. The slowing of the distance traveled by the polymers in 'R5' region was not surprising as that region was most likely quite concentrated with OH⁻.

The experiments with the pulled capillary tubes seemed quite successful but in order to get a better representation as to whether the PO polymers could form within small confined areas, a more accurately measured set capillary tubes would have to be used. A number of capillary tubes varying in volume were purchased and polymerization of **2** and **3a** within these tubes was explored. Five tubes ranging with volumes of 100μL, 50μL, 25μL, 10μL and 5μL were found to have inner diameters of 1196μm, 846μm, 647μm, 380μm, and 269μm respectively.

The polymerization of samples of **2** and **3a** was successful when 100μL to 25μL capillary tubes were used. The PO polymers formed within the 100μL were of similar diameter as those polymers formed during the bulk polymerization experiments. As the diameter of the capillary decreased, the thickness of polymers decreased as well.

Polymerization of through the 10μL and 5μL capillaries proved to be a rather

problematic. The main issue with the 10 μ L and 5 μ L capillaries was the inability to form a good electrical connection. The diameter of the capillary column was too small to insert the standard platinum wire electrodes that had been used in past experiments so a 0.5 μ m wide platinum wire had to be used instead. Even after a connection had been made, no polymers would form. Numerous attempts to polymerize samples of **2** and **3a** in the 10 μ L and 5 μ L capillaries yielded only minimal results. In one attempt, a sample of **3a** formed a small amount of polymer around the anode during the first five minutes of its electrolysis. That reaction was allowed to continue for three more days where no further polymerization was seen. The length traveled by the PO polymers of **3a** within 100 μ L capillary tubes was recorded at set time intervals and was found to be fairly consistent. Three polymerization experiments of **3a** within a 100 μ L capillary were performed. The polymerization distance was measured at 15 minute intervals where the data from those three experiments (Table 17) was plotted and are displayed in Figure 64.

100 μ L Capillary ($K_2Pt(Ox)_2$ [0.0103M])

Time(s)	Time2(s)	Time3(s)	Distance(mm)
0	0	0	0
955	630	676	5
1794	1589	1488	10
2562	2425	2327	15
3327	3161	3091	20
4195	3941	4034	25
5000	4724	4756	30
5864	5523	Died	35
8880	Stopped Early		40
Died			45
			50

Table 17. Polymerization experiment data of K-PtOx though 100 μ L

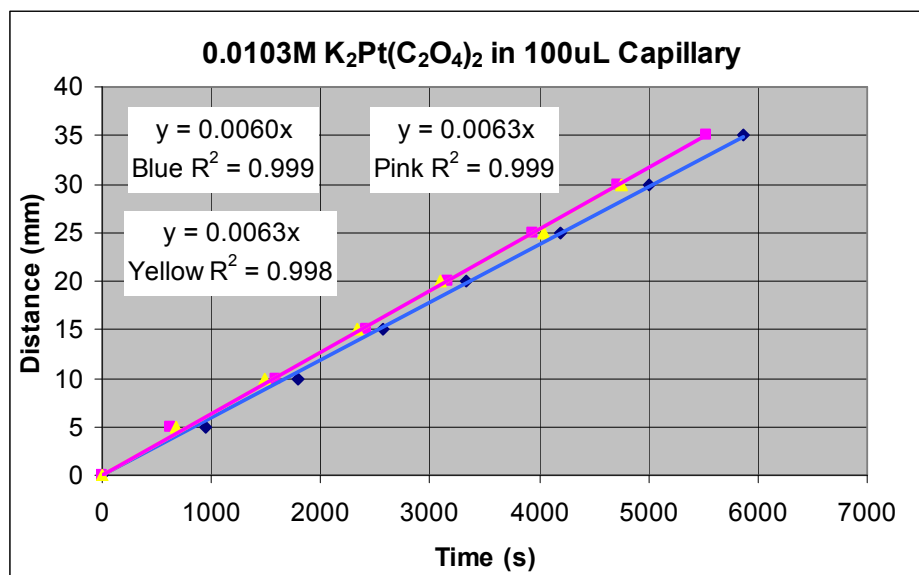


Figure 64. Polymerization experiment of K-PtOx through 100μL capillaries.

The data in Figure 64 shows that the formation of the polymers is linear and that the length of formation over time for K-PtOx polymers within the 100μL capillaries was equal to the slopes of the lines for each of the experiments. The speed or the amount of time needed for the polymers to travel through the capillary tubes (trials 2 and 3, the yellow and pink lines within Figure 64 respectively) were 6.3μm/second and the rate for trial 1 (the blue line) was 6.0μm/second.

The time needed to travel down the capillary tubes for the K-PtOx polymers within the 100μL capillary tubes were very similar to those found for K-PtOx polymers in 50μL capillaries. Table 18 displays the data and Figure 65 displays the graphical data for the polymerization of a 0.0103M solution of **3a** within a 50μL capillary tube. The amount of time needed for the polymers to travel through the capillary tubes calculated for polymerization experiment 1 (the blue line) was found to be 7.0μm/second whereas

the distance traveled over time calculated for experiment two was found to be 6.1µm/second. The difference between the formations of the polymers within a 100µL capillary versus 50µL capillary was almost nonexistent.

The final growth experiment for the polymerization of a solution of **3a** was performed in a 25µL capillary tube. The data is displayed in Table 19 and plotted data in Figure 66.

The formation of K-PtOx polymers within a 25µL capillary tube was found to be 5.9µm/second. It was surprising to see that all polymerizations were roughly between 5.9µm/second and 7.0µm/second no matter if a 100µL, 50µL or 25µL capillary was used.

50µL Capillary (K₂Pt(Ox)₂ [0.0103M]

Time(s)	Time2(s)	Distance(mm)
0	0	0
804	1064	5
1524	2024	10
2263	2794	15
2908	3509	20
3642	4345	25
4421	5108	30
5095	5873	35
5850	6585	40
6530	7264	45
7836	8786	55
8535	9473	60
9120		65
9777		70

Table 18. Polymerization experiment data of K-PtOx though 50µL capillaries.

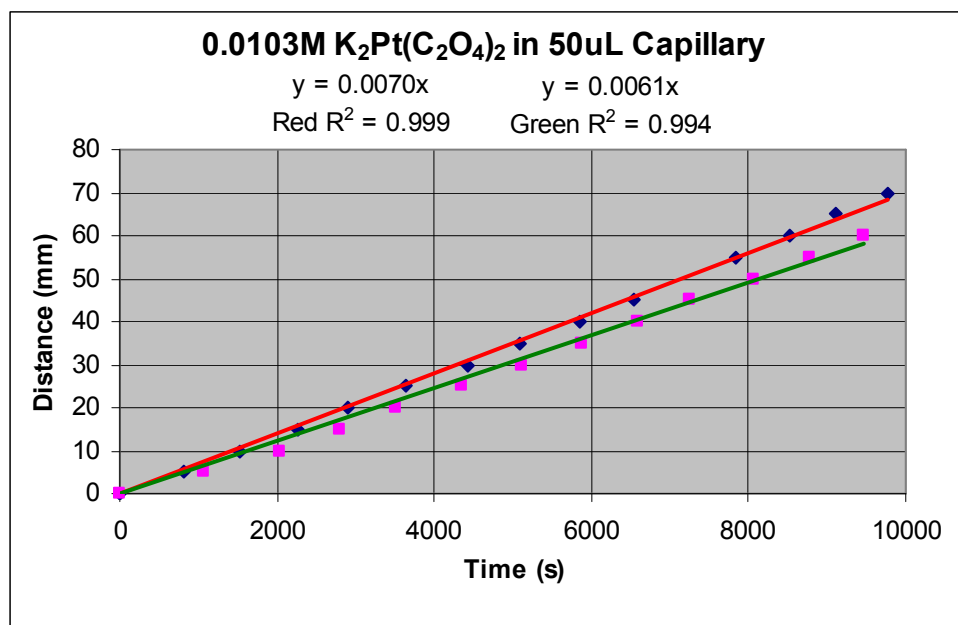


Figure 65. Polymerization experiment of K-PtOx though 50 μ m capillaries.

25 μ L Capillary ($K_2Pt(Ox)_2$ [0.0103M])

Time(s)	Distance(mm)
0	0
920	5
1619	10
2311	15
3080	20
4175	25
5037	30
5949	35
6710	40
7625	45
8474	50
9320	55

Table 19. Polymerization experiment data of K-PtOx though 25 μ L capillaries.

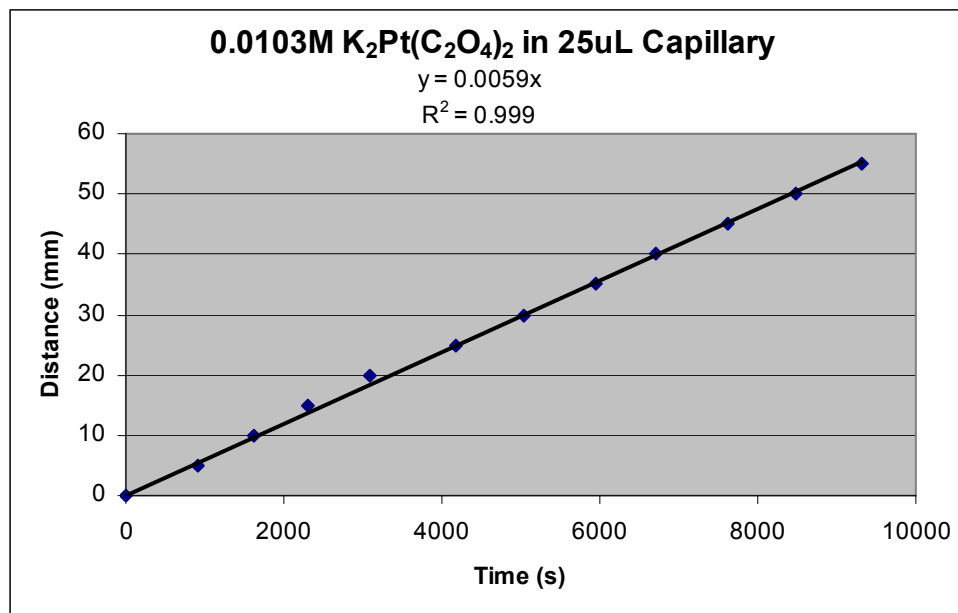


Figure 66. Polymerization experiment of K-PtOx through 25 μ L capillaries.

As stated before, no polymer formation occurred in 10 μ L or 5 μ L capillary tubes. It appeared that no polymerization occurred due to a lack of electrical connection between the anode and cathode. The thin platinum anode was difficult to handle and due to the capillary's small size, there were issues keeping it pressurized and filled with solution. Most often the capillary would empty before any PO polymers would form.

Removal of K-PtCN and K-PtOx from the Capillaries and Simple Conductivity Study

One of the most impressive attributes of the polymers was the fact that they were able to polymerize over very long distances. The polymers were able to form through pulled capillary tubes ranging in length from 25mm to 533mm which is five times greater in length than what had been previously observed and it was found that as long as the PO

polymers stayed connected to the anode, they could easily be removed from the capillary tubes.

The PO polymers, in all actuality, are just very fine, conductive wires. The polymers were unable to form a physical connection to the cathode during their polymerization. In the past, electrodes were physically placed on the bulk polymers in order to get conductivity measurements. Since electrodes could be temporarily placed on the polymers, it was thought that one could permanently attach electrodes to the polymers as well.

A sample of the K-PtOx polymer was formed within a 25 μ m diameter, 10cm long capillary and carefully removed after the electrolysis was complete. The polymer was carefully placed on a plastic Petri dish and allowed to dry. Two very small droplets of fluxless, electronics solder were used to physically secure the polymer to the surface of the dish. The dish with the immobilized polymer is displayed in Figure 67.



Figure 67. K-PtOx pulled from a capillary tube and secured to a plastic Petri dish with solder.

This sample was connected to a 1.5V battery and the voltage was measured with a volt meter. The measured voltage was 1.5V. This proved evidence that a physical connection to the polymers was formed.

Another K-PtOx polymer strand was polymerized within a 25 μ m diameter, 10cm long capillary tube, carefully removed and placed in a plastic Petri dish. The polymer strand was gently washed with deionized water and allowed to dry. This time pieces of iron wire were soldered to the opposite ends of the polymer strand in order to create permanent attachment points for a battery (Figure 68). Some attempts to solder the iron wire to the polymer strand failed and no electrical connection was made. Finally, after four attempts to form a K-PtOx/solder/iron wire connection, a 1.5V battery was attached to the iron wires and a potential of 1.5V was measured across the surface of the polymer strand. This sample was allowed to sit for two weeks where a potential of 1.5V was applied to the polymer strand and the measured voltage again was 1.5V. After sitting for one year, a potential of 1.5V was again applied to this sample where the potential measured across the polymer strand was found to be 1.5V.

It was surprising that these so-called brittle and air-sensitive polymers could be heated to the high temperatures need to adhere the solder and still remain connected and conductive over such a long period of time. The immobilized sample in Figure 67 has not decomposed or broken apart in any way. Even though clear physical damage to the K-PtOx polymer strand was visible, after three years, the sample in Figure 68 still remained conductive.

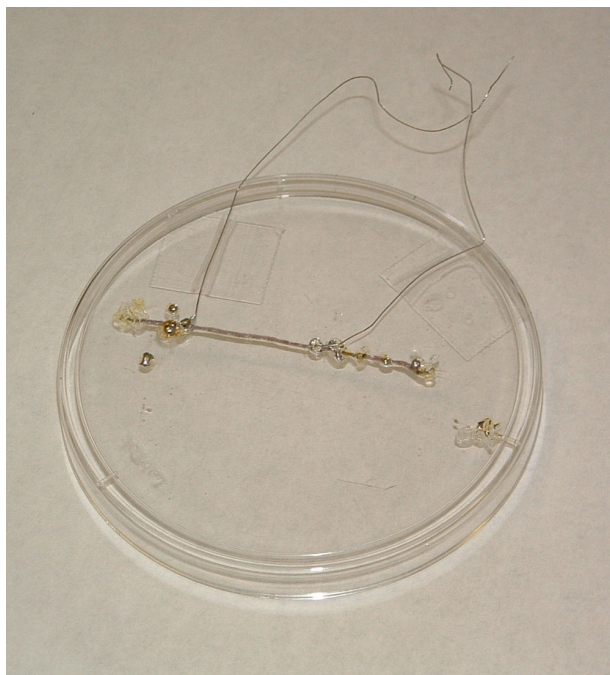


Figure 68. A K-PtOx polymer strand with iron wire soldered on opposite ends.

Polymerization of **2** and **3a**: Multi-electrode Study

It was observed that the polymerization of the PO polymers, K-PtOx and K-PtCN through various capillary tubes was driven by the placement of the electrodes within in the polymerization vessel. The formation of the polymers was only done by using two electrodes, an anode and a cathode. It was speculated that the formation of the polymers could be controlled by where the cathode was placed. If more than one cathode was present would the polymers divide and continue their formation toward the nearest cathode? To test this theory, a growth vessel was made out of a plastic pasteur pipette according to the diagram in Figure 69.

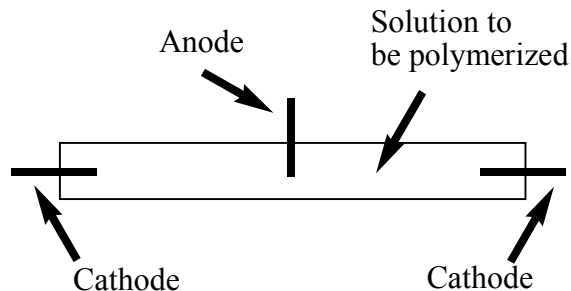


Figure 69. Electrolysis vessel with multiple cathodes.

Two platinum electrodes were placed 6cm apart and connected to the same negative terminal of a 1.5V battery. Another piece of platinum wire was placed between the two cathodes and connected to the positive end of a 1.5V battery. This setup would form two cathodes each with the same potential relative to the single anode (the cathodes are connected parallel to each other). A solution of **3a** was placed into the pipette and electrolysis commenced.

After one hour, a spherically shaped ball of K-PtOx was visible at the anode and no K-PtOx polymers were visible within any other part of the pipette. It was believed that the placement of the cathodes ‘confused’ the polymers as to which direction to form. Since it has been shown that the K-PtOx polymers can very easily bend in order to accommodate changes within a polymerization vessel, the polymers could have continually bent during their formation in an attempt to polymerize toward each of the active cathodes and ultimately becoming entangled.

The multi-cathode experiment definitely had an effect on the polymerization of the PO polymers so another effort was made to direct the formation of the polymers using two cathodes. A new, dual cathode electrolysis apparatus was made that better separated

the cathodes and allowed better viewing of any PO polymers that formed. This time, instead of placing the cathodes directly across from each other, the cathodes were each placed in separate capillary tubes situated 45° off center from a central capillary which housed the anode (Figure 70). The apparatus was filled with a concentrated solution of **3a** and a potential of 1.5V was applied.

After 3 hours the central capillary contained a large amount of PO polymers. In each of the cathode arms of the apparatus, PO polymers of K-PtOx were visible as well. The reason for the formation of the K-PtOx in both cathode arms in the apparatus in Figure 70 is fairly straight forward and can be easily explained.

In the initial stages of the polymerization, all the formed polymers are essentially equidistant from the cathodes. As the polymer strands near the separation point between the two cathodes, the electrical resistance (which is dependent on the length of the resistor, in this case the solution within the electrolysis cell) is decreased for those polymers nearer to one of the two cathodes. Those polymers on the left side of the central capillary will have a higher conductivity with the left cathode and form along that channel whereas those polymers on the right side will have a higher conductivity with the right cathode and form within the right channel. This experiment showed that the formation of PO polymers was not only possible when using multiple electrodes but where the polymerization occurred could be controlled as well.

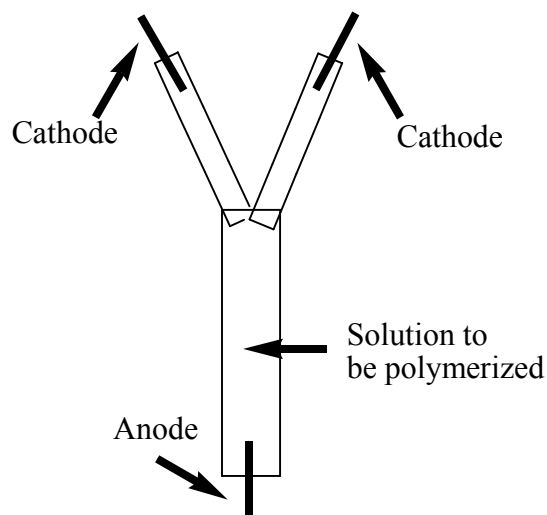


Figure 70. Electrolysis vessel with multiple cathodes. (45° from each other)

K-PtCN and K-PtOx Polymerization Around Various Materials

In an attempt to form micro-sized polymers from solutions of **2** and **3a**, two separate 3cm columns were made: one was filled with glass beads and another was filled with alumina and, in both cases, platinum wire electrodes were attached to opposite ends. It was hoped that the packed materials within the columns would form small “template” channels for the polymers to form through. Neither solutions of **2** or **3a** formed polymers in the column filled with alumina. Allowing solutions of **3a** to electrolyze for one day yielded a blue colored compound near the anode. This compound appeared to be coating the surface of the alumina and the compound could not be removed. Electrolyses of **2** within the alumina column yielded no visible formations of PO polymers.

Within the glass bead column, solutions of **3a** formed a network or web of polymers that covered the surface of the glass beads. It was hypothesized that the network of polymers was caused by the binding of the polymers to the cations contained on the surface of the glass beads. If the glass beads did contain cations, a lowering in the

overall energy of the polymer chains would be attained if they were allowed to share those cations. Another probable cause for the polymer network/web was that the polymers now had multiple paths to travel along during its polymerization toward the cathode. Since the polymers generally form from different places on the anode, the polymers would most likely follow different paths during their formation. It was unknown which theory was correct but a glass beaded column treated with NaOH and rinsed with water in order to reduce the number of cationic sites, still formed a polymer web during an electrolysis of a solution of **3a**. Solutions of **2** formed a polymer web as well but not to the large extent as seen with the **3a** solutions.

Bending and Distortion Experiments of the K-PtCN and K-PtOx Polymers

It was noticed in the experiments involving the polymerization of K-PtCN and K-PtOx though the capillary tubes and around other materials, that the PO polymers of these two salts appeared to bend. The flexibility of the K-PtOx PO polymer was noted in the early experiments involving their polymerization within capillary tubes and their removal from those tubes. A set of experiments were devised that would test whether the polymers would be able to be bent during their templated formation.

The first set of experiments dealt with the polymerization of solutions of **2** and **3a** through vessels that were non-linear in nature. Capillary tubes were once again employed as polymerization vessels due to their ease of modification under high temperatures. A 25 μ m capillary tube was heated and bent by 45° near the center of the tube. The tube was placed in the polymerization apparatus pictured in Figure 59 and a solution of **3a** was electrolyzed. It was found that the polymers were able to form

around the corner in order to polymerize toward the cathode. A solution of **2** was polymerized through a 45°-bent capillary tube as well. No problems were observed during either of these polymerization experiments and the formation of the polymers seemed to proceed unhindered by the bent capillaries.

A solution of **3a** and one of **2** was electrolyzed through capillary tubes which contained a 90° bend three fourths of the way down the capillary tube. After one hour, both platinum complexes had polymerized through the distorted tubes. A bend of 90° seemed to have little effect on the polymerization of either of these two solutions. It was surprising to see the 'linear-chain' polymers polymerizing past such large angles. After the K-PtOx and K-PtCN polymers were observed forming through the 90° angles, the polymerization of solutions of **2** and **3a** through even larger and more complicated distortions of the capillary tubes were attempted.

A 25µm capillary tube was modified in such a way that a curve of 225° was formed. The capillary tube was filled with a solution of **3a** and the solution was electrolyzed. The polymers of K-PtOx were evident after a short while and after one hour the polymers had nearly traveled the complete length of the capillary (Figure 71).

The path of the K-PtOx polymers through the 225° bend is shown in Figure 72. There was no noticeable rate of formation differences in the polymerization of the K-PtOx polymers through a capillary tube containing a 225° bend versus a completely linear capillary. The K-PtCN polymers formed from a solution of **2** also formed with no noticeable differences compared to their formation through a completely linear capillary.

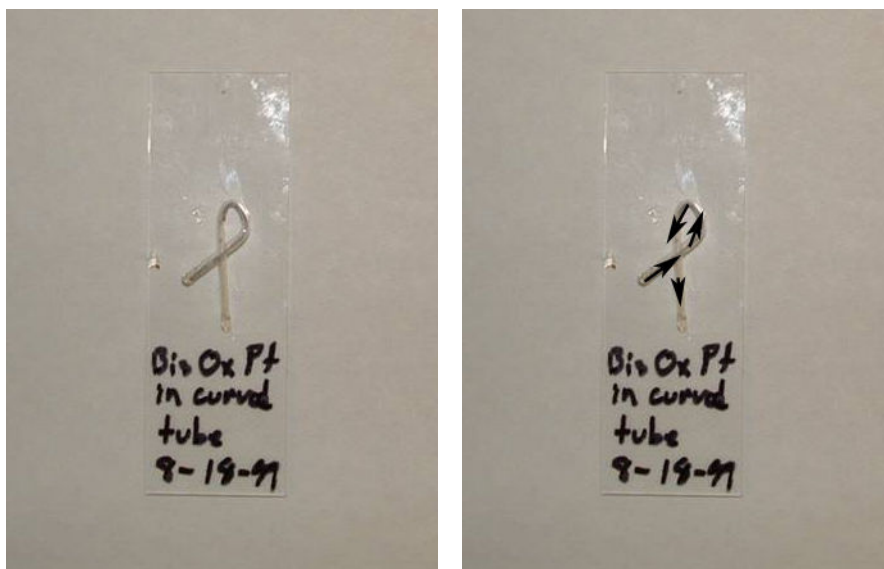


Figure 71 (left) and 72 (right). A 225° bent capillary tube containing K-PtOx polymer (left image). The polymerization path of the K-PtOx polymers. (right image)

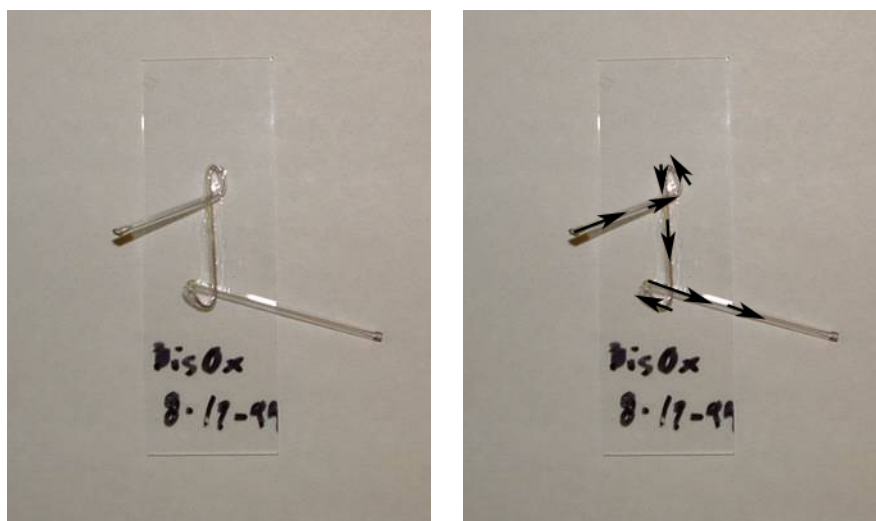


Figure 73 (left) and 74 (right): (left) A dually modified capillary tube containing K-PtOx polymer. (right) The polymerization path of the K-PtOx polymers.

A final distortion experiment was attempted on the K-PtOx and K-PtCN polymers this time using a capillary that had been modified twice. Figure 73 shows one of the dually modified capillary tubes. The bend angle again was around 225° but, in this case, the bends were much tighter than what had previously been used. It was thought that the small, tight angles as well as the multiple bends involved would hinder the polymer formation. After a solution of **3a** was added and the electrolysis commenced, the K-PtOx polymers formed without incident. The formation of the K-PtOx polymer proceeded in the direction illustrated in Figure 74. After numerous polymerization attempts through various modified capillary tubes, it was found that both the K-PtOx and K-PtCN polymers were unaffected by distortions along the polymerization pathway. At first it seemed very remarkable that the polymers were able to bend in order to accommodate the variations in the capillary pathway. After a few basic calculations were made, the observed bending of the PO polymers did not seem as improbable.

Two platinum complexes within a PO polymer are displayed in Figure 75. Distance W is the platinum-platinum bond distance where the bonding angle between the two platinum atoms is signified by the two distances XY and YZ or $\angle XYZ$. 'W' within either a bisoxalatoplatinate(2^-) or tetracyanoplatinate(2^-) PO polymer chain can range anywhere from $2.798\text{\AA}$ to $2.963\text{\AA}$. If a PO polymer chain consisting of 91 platinum(II) atoms had to bend 90° , $\angle XYZ$ were only allowed to be 1° and assuming that XY and YZ was half of distance W, the total distance needed for the PO polymer chain to bend 90° would be 26.667nm to 26.685nm .

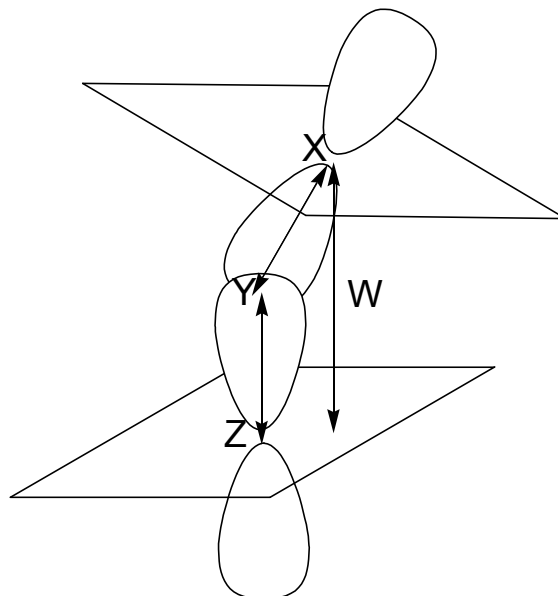


Figure 75. The bending of a single platinum complex within a PO platinum polymer chain. W is the distance between two platinum atoms and XYZ is the angle of bending.

Now if $\angle XYZ$ were only allowed to be 0.1° , it would take 91 platinum complexes a total length of 266.67nm to 266.85nm to be able to bend 90° . The 225° bends in the capillary tubes that were observed were more on the order of 7mm. It would take 2.5×10^6 to 2.37×10^6 individual platinum complexes bending only $9.0 \times 10^{-5}^\circ$ to $9.5 \times 10^{-5}^\circ$ to form 7mm and bend the complete 225° . The complexes would have no problem bending so little and this extremely small loss in orbital overlap would most likely have no effect on the stability of the overall polymer chain.

Another possibility for the ability of the PO polymers to bend is the fact that, due to the rapid polymerization/crystallization of the polymers, numerous flaws can occur in the polymer strands during polymerization. These flaws were occasionally visible via the naked-eye. In order to obtain a better view of these flaws, a solution of **3a** was

polymerized between two glass slide plates using carbon sticky tape as the electrodes.

Figure 16f displays the results of this experiment.

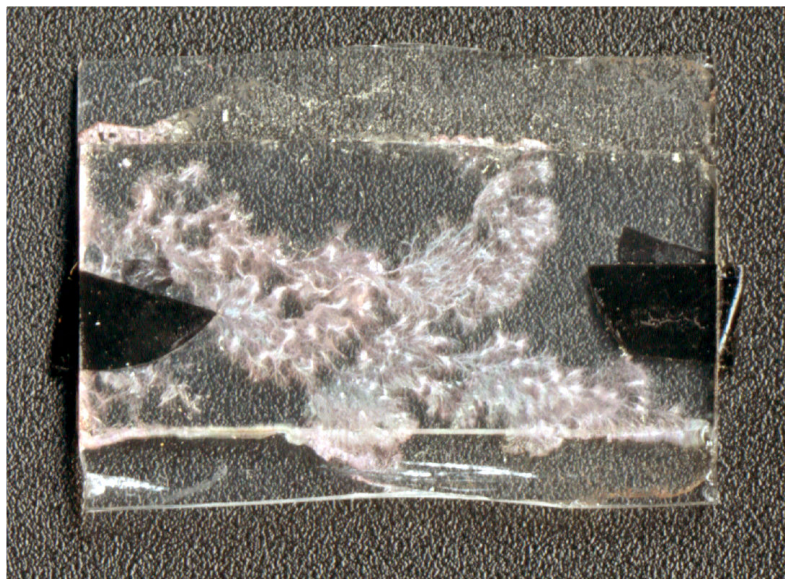


Figure 76. The PO polymers, K-PtOx formed between two glass slide plates. Branching was visible.

What is shown in Figure 16f was that the K-PtOx polymers formed off of the carbon anode on the right of the figure and formed branching polymers. Pockets of densely packed PO polymer are visible throughout the slide plate and from these pockets are numerous polymer strands. Although the polymers were seen branching, it will be shown in later experiments detailed in this dissertation that the PO K-PtOx polymers were in fact bending as they navigate changes within the electrolysis vessel and that they are able to bend unhindered at even greater angles over much smaller distances than what had been previously seen.

Usage of Crown Ethers for the Reduction of the PO Polymer Diameter

It has been stated before that both the K-PtCN and K-PtOx polymers are in fact a bundle of anion platinum chains held together by a cationic glue. The cations that allow the formation of PO polymers of bisoxalatoplatinate(2-) or tetracyanoplatinate(2-) seem to be limited by their size. Normally, only small cations can be used. In the case of the cation deficient PO polymers of tetracyanoplatinate(2-), only monovalent cations consisting of the alkali metals K, Rb and Cs are known. In the case of the cation deficient PO polymers of bisoxalatoplatinate(2-), both monovalent and divalent, single element cations are known and their structure elucidated²⁰. It was believed that cations too large in size disrupt the polymer formation and halt the stacking of the anionic platinum complexes. The size of the cations would play a part since they are shared amongst many different anionic chains. Increasing the size of just one cation within any given PO polymer would disrupt the overall stability of the crystal.

In an attempt to modify the size of the potassium cation used in the K-PtCN and K-PtOx polymers without replacing the potassium cation, crown ethers were employed. Crown ethers are essentially organic ring systems consisting of ethane segments separated by single oxygens. These ring systems can range anywhere from 14 atoms to 22 atoms total. The numerous crown ether rings were found to have very interesting and different binding properties to various alkali, alkaline earth and heavy metal picrates depending on which crown ether was used⁵⁸. The crown ether that was found to be most important to this work was (1,4,7,10,13,16)-hexaoxycyclooctadecane which is also known as 18-crown-6 (Figure 77).

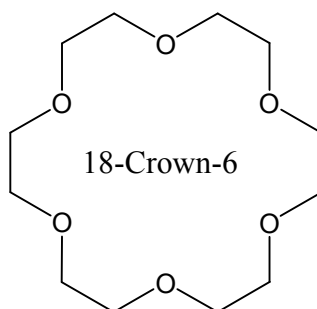


Figure 77. The structure of 18-crown-6.

The structure of 18-crown-6 was elucidated by Dunitz in the mid-1970's⁵⁹. What was interesting about 18-crown-6 was that the cavity in the middle of the molecule is almost large enough to encompass a single potassium atom. The oxygens within the ring would be able to bind to any atom small enough to fit inside the molecule. The work done by Ouchi showed that the 18-crown-6 molecule had the greatest binding affinity to potassium and that 18-crown-6 would essentially bind to 69% of all potassium in solution⁶⁰.

A solution of **2** was treated with two equivalents of 18-crown-6 in the hopes of binding to a majority of the potassium atoms in solution. The solution was then electrolyzed in a micro-petri dish in an attempt to form crystals of PO crown/potassium bisoxalatoplatinate(2-) polymers. After two days, no polymer formation was observed. The solution was set aside and the solvent was allowed to evaporate off. After three days an amorphous mass had solidified on the bottom of the micro-petri dish. Attempts to obtain quality crystals of this compound were unsuccessful. Focus returned to compound **3a**, where two equivalents of 18-crown-6 were added to a solution of **3a**. The sample was electrolyzed in a micro-petri dish and no polymers were obtained. The dish was

allowed to sit and the solvent was allowed to evaporate off. After three days green crystals were visible in the bottom of the micro-petri dish. These crystals were imaged and a structure and unit cell was obtained for the crystals.

It was found that the 18-crown-6 did in fact bind to the potassium in the **3a** solution. The increase in size when going from a relatively small diameter of 2.66Å for the potassium atom to a diameter of ≈ 7.0 Å for the crown ether/potassium cation was enough to halt the polymerization of the bisoxalatoplatinate(2-) but not enough to halt the crystallization of the unoxidized complex. The ORTEP of the compound is illustrated in Figure 78.

The molecular formula for the compound was determined to be $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$. Here the potassium is seen in the center of the crown ether, bound to all six of the oxygens on the ring. The potassium atom is also seen associating with two oxygens on both of the carbonyl's of the oxalate ligand. This binding of the potassium to the carbonyl oxygens is not surprising considering the potassium atoms are seen binding in a similar fashion in the unoxidized crystals of **3a**⁶¹.

The packing of the molecules within the unit cell is much more ordered than that of the unit cell for crystalline **3a**. The potassium/crown ether atoms seen in Figure 79 are coordinated with the carbonyl oxygens on both sides of the bisoxalatoplatinate(2-) complex.

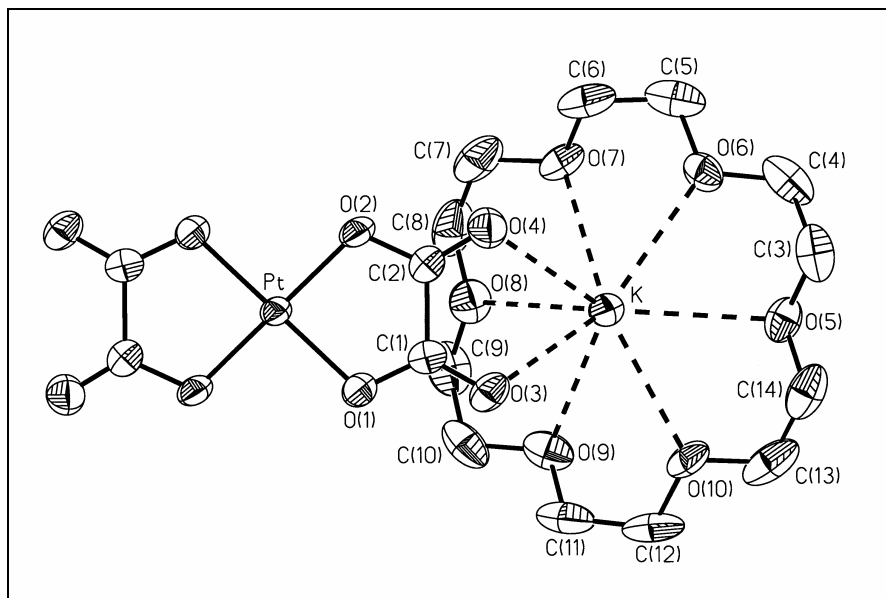


Figure 78. The ORTEP of the bisoxalatoplatinate(2-) and potassium/crown ether compound.

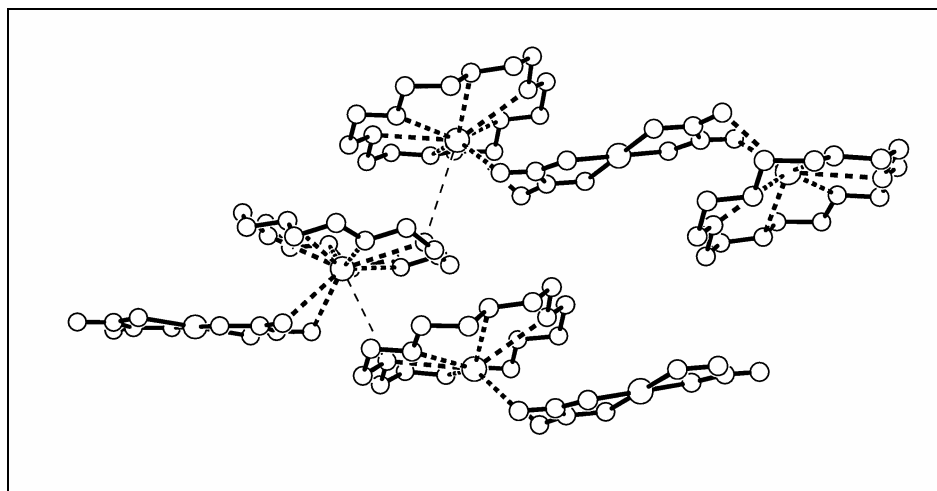


Figure 79. Unit Cell Positions within a crystal of $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$.

At this angle, the potassium atoms are seen sitting slightly out of the plane of the 18-crown-6 ligand. When observing the stacking pattern of a number of these molecules, it appeared that there is a slight amount of interaction between the potassium and oxygens

in adjacent crown ether complexes. Based on the molecular formula obtained for these crystals and the stacking pattern and unit cell data, it is clear that there are no platinum-platinum interactions as seen in the PO K-PtCN and K-PtOx polymers. The distances between the platinum atoms in a $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$ crystal were 7.811 Å. This distance is around 2.5 times larger than the platinum-platinum distances seen in any of the PO platinum polymers.

Since all other PO polymers of the bisoxalatoplatinate(2-) salts involve sharing a “non-integral” number of cations, the $\text{KC}_{12}\text{H}_{24}\text{O}_6$ cations could be too large to be shared between the multiple platinum anionic complexes. It seems that too large of a cation did not stop non-oxidized crystal growth but it did halt partial oxidation of the platinum complexes. The complete crystal data set for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$ can be found in Appendix A of this dissertation.

Syntheses of Other bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) Salts and Their Subsequent Electrolysis

Since an increase in the cation diameter was found to hurt the polymerization of the bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) salts, a reinvestigation of the cations that were already known to form the PO polymers was considered. In the early, exploratory work done by others studying the bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) salts, partial oxidation of those compounds were only attempted with the usage of chemical oxidants. Most often, it took a number of weeks for the PO polymers of the various salts to form. It was hoped that the electrolysis method that was used in the polymerization of solutions of **2** and **3** would work with the other salts, speed

up their partial oxidation and allow their templated polymerization through various materials.

For all remaining PO polymerization experiments, no cations other than potassium were used with the tetracyanoplatinate(2-) anion. It was felt that, since there were a limited number of cation deficient PO polymers of tetracyanoplatinate(2-) versus the large selection of PO polymers of bisoxalatoplatinate(2-), focus should be shifted to the bisoxalatoplatinate(2-) salts.

The synthesis of compounds **3b-3r** can be found in the Experimental section of this dissertation and will not be discussed further. Although a number of the syntheses for the **3c-3r** compounds are similar, many of the unoxidized bisoxalatoplatinate(2-) salt had very different properties. In the case of the strontium, cadmium, barium and guanidinium unoxidized bisoxalatoplatinate(2-) salts, all were found to be insoluble to very slightly soluble in water. Although one might think that insoluble bisoxalatoplatinate(2-) salts would be unable to form partially oxidized polymer but it was found that some of the insoluble salts, such as the guanidinium salt, was still able to form PO polymers.

The polymerization of the **3c-3r** salts were initially done in a similar fashion as the bulk polymerization of solutions of **3a** using a petri dish as the electrolysis cell and platinum wire as electrodes. Table 20 contains a list of the unoxidized salts that were synthesized, their properties and whether PO polymers were formed via the electrolytic oxidation method.

Bisoxalatoplatinate salt	Cation/Compound used in bisoxalatoplatinate salt	Observed Solubility of Unoxidized Salt	Electrolysis Potential	Were PO Polymers Formed?
3c	Li^+	Soluble	1.5V	Yes
3d	Na^+	Soluble	1.5V	Yes
3e	NH_4^+	Soluble	1.5V	Yes
3f	Guanidinium ⁺	White Precipitate	1.5V	Yes
3g	Ni^{2+}	Soluble	1.5V	Yes
3h	Co^{2+}	Soluble	1.5V	Yes
3i	Fe^{2+}	Soluble	1.5V	No
3j	Cu^{2+}	Soluble	1.5V	No
3k	Sr^{2+}	Yellow/Red Precipitate	1.5V	No
3l	Pb^{2+}	Yellow/Red Precipitate	1.5V	No
3m	UO_2^{2+}	White Precipitate	1.5V	No
3n	Ba^{2+}	Yellow/Orange Precipitate	1.5V	Yes
3o	Cd^{2+}	Orange Precipitate	1.5V	No
3p	Zn^{2+}	Soluble	1.5V	Yes
3q	Mg^{2+}	Soluble	1.5V	Yes
3r	Mn^{2+}	Soluble	1.5V(0.82V)	Yes

Table 20. Complete list of bisoxalatoplatinate(2-) salts and whether PO polymers were electrolytically formed.

Almost all water soluble salts, except for the copper and iron salts, **3i** and **3j**, formed PO polymers. When electrolyzing solution of **3i**, a copper sheen was visible on the cathode after 2 minutes. This was most likely the reduction of Cu^{2+} to copper metal. Solutions of **3j** yielded no discernable color change within the solution or on either of the electrodes.

The sodium, nickel, cobalt, zinc and magnesium salts (**3d**, **3g**, **3h**, **3p** and **3q**) all readily formed PO polymers. After solutions of any of these three compounds were

made, the electrolysis of those solutions led to the rapid formation of their PO, lustrous dark brown polymer analogues. Solutions of the lithium salt (**3c**) needed to be electrolyzed for extended periods of time. Solutions of **3c** most often needed to be electrolyzed for up to two days before any PO polymers were visible. The shiny, tan polymers were much lighter in color than any PO polymers previously seen.

From solutions containing the bisoxalatoplatinate(2-) insoluble salts of guanidinium, strontium, lead, uranium oxide, barium, cadmium and manganese (**3f**, **3k**, **3l**, **3m**, **3n**, **3o** and **3r**) only solutions of **3m** and **3r** formed PO polymers. An extensive literature search revealed no references for the electrolytical formation of the PO polymers from either of the **3m** or **3r** salts. The electrolysis of solutions of **3r** at a potential 1.5V usually resulted in the formation of a black material at the anode which was most likely a higher valent Mn species. It appeared that, in the case of the manganese salt, an electrolysis potential of 1.5V was too high.

The potential for the electrolysis of solutions of **3r** was adjusted with the usage of simple home-built variable potentiostat (Figure 80). The output voltage (V_o , electrolysis voltage) of the variable voltage device is dictated by Equation 12.

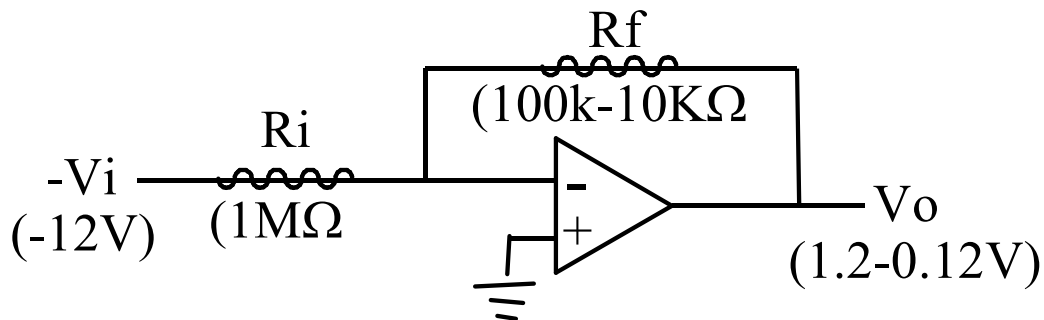


Figure 80. Variable voltage source for the electrolysis of voltage sensitive compounds.

$$V_o = V_i \frac{-R_f}{R_i}$$

Equation 12: Calculation of the output voltage from the variable voltage source pictured in Figure 80.

By using a variable voltage source, the electrolysis voltage could be changed to accommodate voltage sensitive compounds. With the aid of the variable voltage source, it was found that lowering the electrolysis voltage from 1.5V to 0.820V caused the formation of PO polymers from solutions of **3r**. Also, it was found that the electrolyzing solutions of **3f** at 0.800V or 1.5V led to the formation of PO polymers of bisoxalatoplatinate(2-) containing guanidinium as the counter cation.

In order to ensure that the electrochemical method used was giving the PO polymers that were known to be synthesized via chemical oxidation, elemental analyses were performed on the PO Pt-Ox salts of potassium, nickel, sodium, barium and the newly synthesized guanidinium (guan) salt. The molecular formulas for the five salts are as follows: $K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$, $Ni_{0.80}Pt(C_2O_4)_2 \cdot 6H_2O$, $Na_{1.62}Pt(C_2O_4)_2 \cdot 4H_2O$, $Ba_{0.83}Pt(C_2O_4)_2 \cdot 4H_2O$ and $(Guan)_{1.61}Pt(C_2O_4)_2 \cdot H_2O$. All five of these analyses indicated that the PO forms of these polymers were present. (Ba salt - experimental results: Ba 20.43%, Pt 34.98%, C 8.81% - calculated values: Ba 20.62%, Pt 34.94%, C 12.90%) (K salt - experimental results: K 12.90%, Pt 40.10%, C 9.72%, H 0.79%- calculated values: K 13.37%, Pt 41.50%, C 10.20%, H 0.80%) (Na salt - experimental results: Na 7.89%, Pt 41.35%, C 10.77% - calculated values: Na 7.98%, Pt 40.51%, C 9.97%) (Ni salt –

experimental results: Ni 8.68%, Pt 35.96%, C 9.06% - calculated values: Ni 9.37%, Pt 36.89%, C 9.08%) (Guan salt – experimental results: H 1.68%, Pt 40.20%, C 13.94%, N 14.07% - calculated values: H 2.40%, Pt 40.20%, C 13.87%, N 13.99%)

A sample of the PO manganese salt was analyzed but no manganese, carbon or platinum was found to be present. That analysis was found to be questionable.

Bulk Polymerization of bisoxalatoplatinate(2-) Salts and Their Investigation Via Atomic Force Microscopy

The main goal of this project was to observe the polymerization habits of the PO polymers and modify their structural formation if at all possible. Up until this point the majority of characterization of the PO polymers was done via optical investigation by either the naked-eye or an optical microscope. Both of these methods, although simple, had poor resolution which limited the viewing of the surface features of the PO polymers.

It was hoped that STM would yield more information about the atomic surface structure of the PO polymers. Unfortunately, as stated earlier, STM images of the PO polymers were unobtainable. An alternative to STM was atomic force microscopy (AFM). Similar in design to STM, AFM was more advantageous in that, since AFM images samples via physical contact and not by electrical contact, the samples to be imaged needed not be conductive. AFM analysis was performed on the bulk PO polymers of the zinc and potassium Pt-Ox salts. A small section of the K-PtOx polymers was imaged via AFM and is seen in Figure 81.

It was quite apparent in the initial AFM images that the optically visible K-PtOx polymer formations were in fact a collection of smaller K-PtOx polymer structures which

were bundled together. The K-PtOx salt has a similar bundled superstructure as that of the optically visible macroscale K-PtCN PO polymers. The individual polymer strands appear to be more physically attached to one another versus the loosely bound K-PtCN polymer bundles.

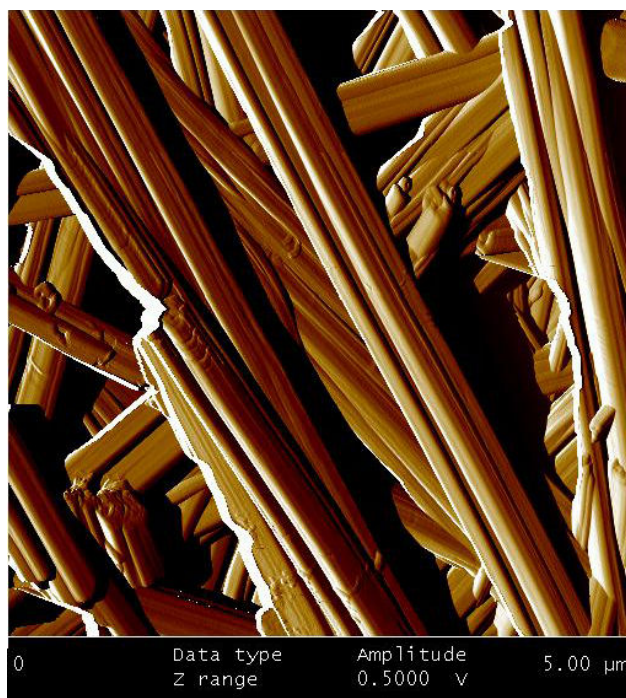


Figure 81. 5μm by 5μm AFM image of the bulk polymerized K-PtOx PO polymers.

Macroscopically, the K-PtOx polymers seemed to be fairly uniform in size. After their imaging via AFM, they appeared to be roughly uniform in size nanoscopically as well. The polymeric bundles contained uniform nanoscale polymer strands.

In an expanded image of the K-PtOx polymers (Figure 82), measurements A, B, C and D ranged in size from 154nm to 285nm. This was common for all K-PtOx polymer bundles imaged via AFM. As discussed earlier, massive branching was commonly observed when polymerization occurred at a fast rate. Closer inspection of Figure 82,

label E shows a flaw in a polymer bundle where the 'E' polymer formation had begun to branch off of and polymerize perpendicular to another polymer strand. The relatively flat top of this strand was clearly visible. Up and to the left of label E, another flaw was visible where a polymer had branched off of another, larger bundle. It was apparent that the K-PtOx polymer bundles preferred to form having diameters at and around 200nm even after branching.

Flaws in the polymer structure did not always lead to branching. To the left of label A in Figure 82, small divots are visible on the surface of a single polymer strand. These divots did not appear to affect that polymer's formation as it was visible that that strand polymerized another 400nm after the first flaw appeared.

For the PO zinc salt of bisoxalatoplatinate(2-) (Zn-PtOx), the substructure of the bulk polymer was less visible. Figure 83 shows a 2.5 m by 2.5 m area of bulk oxidized PO Zn-PtOx polymer.

The structures formed during the bulk polymerization for the PO Zn-PtOx polymers strands seemed to polymerize having a much wider diameter and more ordered than that of the K-PtOx polymers. The polymer formation measured under Figure 83 label A had a diameter of 702.4nm. This was about 2.5 times larger than those polymers seen for the K-PtOx polymers. The Zn-PtOx macroscopic polymer bundles seem to be much more tightly packed and less flawed as well. The center structure in Figure 83 had a much smaller repeating pattern on the outer surface of the polymer formation. These features alternated in size from 62nm to 113 nm. Measurement F appeared to be a

polymer strand that was almost completely incorporated within a much larger polymeric structure. This protrusion was found to have a thickness of 121.2nm.

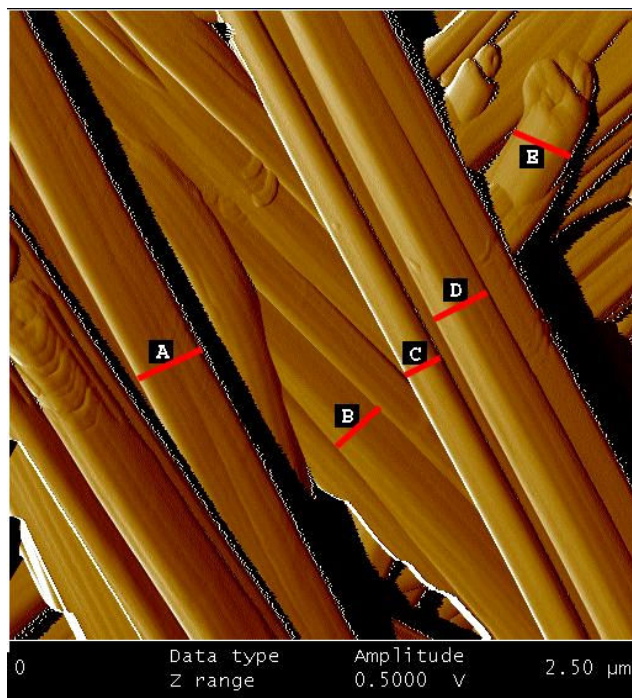


Figure 82. K-PtOx PO polymers imaged via AFM. Measurements: A-284.6nm, B-228.3nm, C-157.5nm, D-236.4nm, E-251.9nm.

Based on the AFM data obtained, it was now believed that all the macroscale PO polymer formations were made up of a large number of much smaller polymeric bundles. With this new information, the validity of all prior electrical measurements of the PO polymers was questionable. Instead of measuring the electrical conductivity of a single PO polymer strand, the conductivity data obtained was most likely for the complete polymeric system (the individual polymer strands, the array of nanoscopic polymer strands and the physical associations of the macroscale arrays).

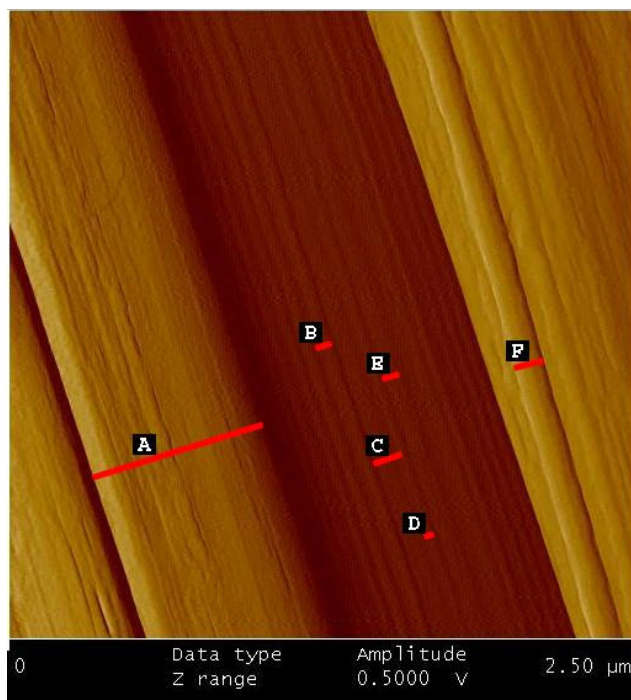


Figure 83. Zn-PtOx PO polymers imaged via AFM. Measurements: A-702.4nm, B-62.0nm, C-113.1nm, D-41.9nm, E-67.0nm, F-121.2nm.

Bulk Polymerization of bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) Salts and Their Investigation Via Scanning Electron Microscopy

After obtaining the wealth of information from the AFM images of the PO K-PtOx and Zn-PtOx polymers, it was determined that other micro/nanoscope images should be recorded for the other PO bisoxalatoplatinate(2-) salts as well as PO K-PtCN polymer formations. The most common and non-intrusive microscopic images could be had by imaging the PO polymer samples via scanning electron microscopy (SEM). Rather than give an in depth explanation about the inner workings of a scanning electron microscope a brief explanation will be given here.

SEM essentially obtains images by recording the number of electrons that do not pass through any given sample. In a scanning electron microscope, a sample is placed

below an electron gun. The electrons within this gun can be accelerated to any energy but the most common accelerating voltages range from 8,000KV to 15,000KV. Due to the high voltages involved, the sample chamber is held under vacuum. The electrons are focused into a beam and impinged on the sample surface.

There are a number of things that can happen when the electrons interact with the surface of the sample. The two most important types of electron interactions are ones that create the overall image of the sample: backscattered electrons and secondary electrons⁶².

Backscattered electrons are caused by the elastic scattering of the high energy electrons interacting with the nuclei of the atoms within the sample. Some of these deflected electrons can exit the sample, be recorded and an image of the sample can be obtained. Atoms with a higher atomic mass deflect more electrons and appear brighter than those that have low atomic mass. Backscattered electrons show qualitative elemental data about a sample.

Secondary electrons are caused by the high energy electron's interaction with the inner core electrons of an atom within the sample. The high energy electron can pass some of its energy on to a core electron which, in the end, leads to its ejection from the atom. These secondary electrons are collected and from them can be obtained topographical information about the sample. The coating of samples with a thin layer (usually 1nm to 15nm) of a platinum/iridium alloy is a common practice. The coating of the samples usually leads to the images having better topographical contrast and better charge dissipative properties.

Bulk polymerized samples of K-PtCN and K-PtOx were imaged under a scanning electron microscope. Figure 84 is an image of one sample of bulk polymerized K-PtCN.

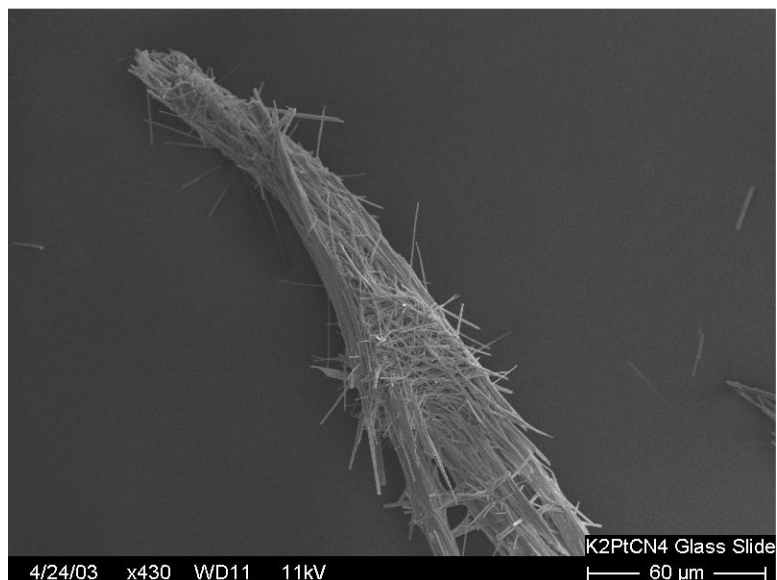


Figure 84. SEM image of a sample of K-PtCN polymer bulk polymerized (x430 Mag.)

The pile of PO K-PtCN polymers was found to contain numerous PO polymer strands with an average diameter of 750nm. The K-PtCN polymers seemed to polymerize much thicker than those PO polymers of K-PtOx when formed during the bulk electrolysis method. The disorder seen in the polymer pile was most likely caused by the sample preparation method which entailed removing some of the PO K-PtCN polymer from the bulk electrolysis cell with a spatula.

Closer inspection of the polymer bundles yielded two interesting observations. Figure 85 shows a highly magnified section of the polymer pile seen in Figure 84.

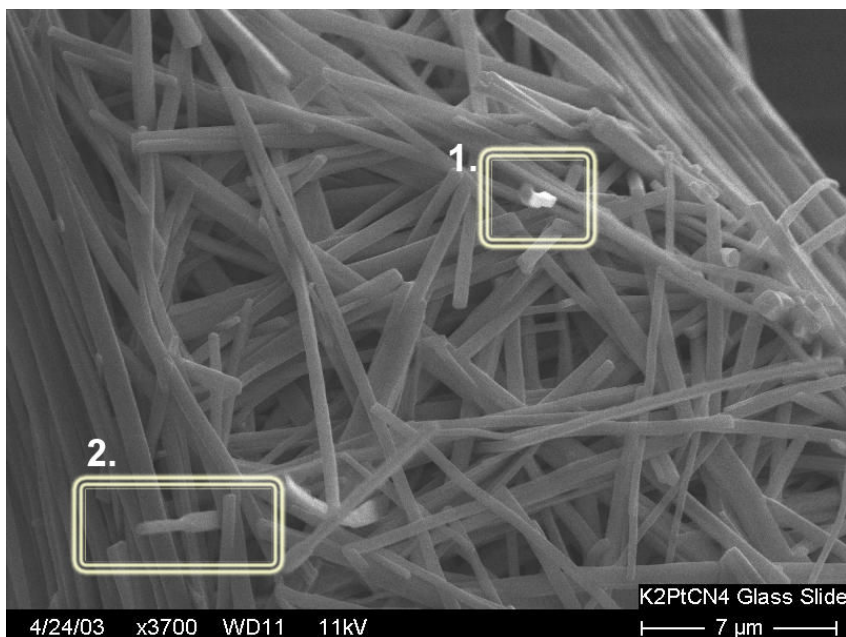


Figure 85. SEM image of a sample of K-PtCN polymer bulk polymerized (x3700 Mag.)

The first observation dealt with the polymer strand in the box labeled '1'. Closer inspection of the sides of the polymer strand clearly showed a distinct edge to the polymer. The PO polymer bundles of K-PtCN were not circular but a more rectangular in shape.

The end of the polymer strand in the box labeled '2' seemed to narrow down near the tip of the formation. This narrowing of the polymer strands may be an indication as to why these PO polymers are able to polymerize through the small channels formed from the 'pulled' capillary tubes. This narrowing could mean that the K-PtCN polymers initially form as small and thin polymer strands that eventually expand laterally as the polymerization continues.

This tapering of the K-PtCN PO polymers was visible once the microscope was focused near the bottom of the polymer pile. Figure 86 shows what appeared to be the

ends of the polymer strands. The magnification of the polymers in Figure 86 was only x950 but even the large polymer strands were visibly narrowing in diameter near the ends of the fibers.

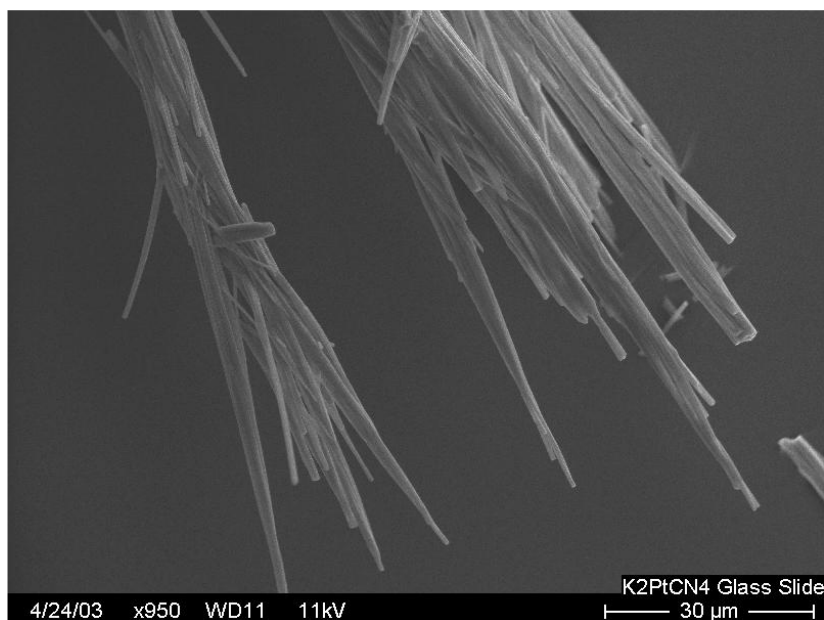


Figure 86. SEM image of a sample of K-PtCN polymer bulk polymerized. Tapered ends are visible (x950 Mag.)

The SEM images of the bulk polymerized PO K-PtOx yielded a completely different picture. Figure 87 shows a section of bulk polymerized K-PtOx. It was noticed that the PO polymer strands were much less ordered than those of the K-PtCN strands and that the polymers were massively intertwined with one another.

The average thickness of the K-PtOx PO polymers was found to be 200nm but polymeric strands as thick as 500nm were seen. The observed thickness was 3 to 4 times less than that of the K-PtCN polymers. The K-PtOx strands also seemed to be much more densely packed than those of the K-PtCN polymers. The flexibility of the K-PtOx

PO polymers also seemed much greater than the K-PtCN polymers. Some of the K-PtOx polymers are visibly bending 90° or more in the jumbled mass of polymers which could be due to the K-PtOx polymers increased flexibility as well as their decreased thickness.

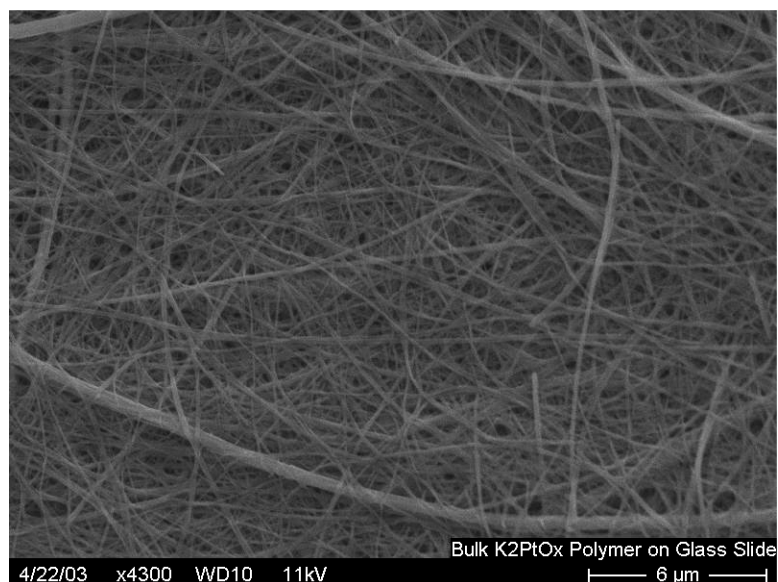


Figure 87. SEM image of a bulk polymerized sample of K-PtOx polymer. Average polymer thickness of 200nm. (x4300 Mag.)

The K-PtOx polymer bundles seemed more apt to remain adhered than those of the K-PtCN. When samples of the macroscale K-PtCN polymers bundles were agitated, the nanoscale K-PtCN polymers disassociated into single nanoscale polymers fibers (as seen previously in Figure 84). The K-PtOx polymers bundles would remain together but fracture instead of dissociating. Figure 88 shows a small section from a sample of bulk polymerized K-PtOx polymer that had been disturbed during its preparation for SEM imaging.

The splintering of the PO K-PtOx polymers was clearly visible versus the disassociation of the nanoscale polymers seen in the K-PtCN samples.

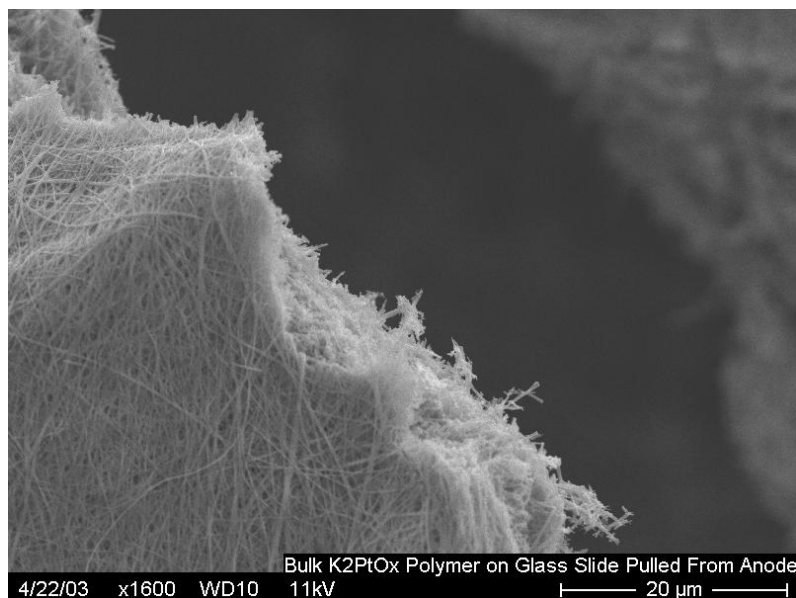


Figure 88. SEM image of a bulk polymerized sample of K-PtOx polymer that had been disturbed (x1600 Mag.)

It could be said that the inter-polymer associations of the macroscale K-PtOx polymers was much higher than those for the macroscale K-PtCN polymers.

The tips of the K-PtOx polymers also seem to narrow near the tips of the strands. Figure 89 shows the edge of a sample of K-PtOx that was bulk polymerized. The rather large polymer formation labeled as '1' was found to have a thickness of 750nm near the center of the strand. Measurements near the end of the strand gave a thickness of 350nm. The smaller polymer strand labeled as '2', was found to have a thinner central thickness of 500nm and an end thickness of 100nm. Large decreases in thicknesses (50% or more) of other polymeric strands were visible all along the edge of the sample. The tapering of the ends of the K-PtOx and K-PtCN polymers seemed common for both polymer sets which meant that the thickness of the PO polymers could most likely be controlled.

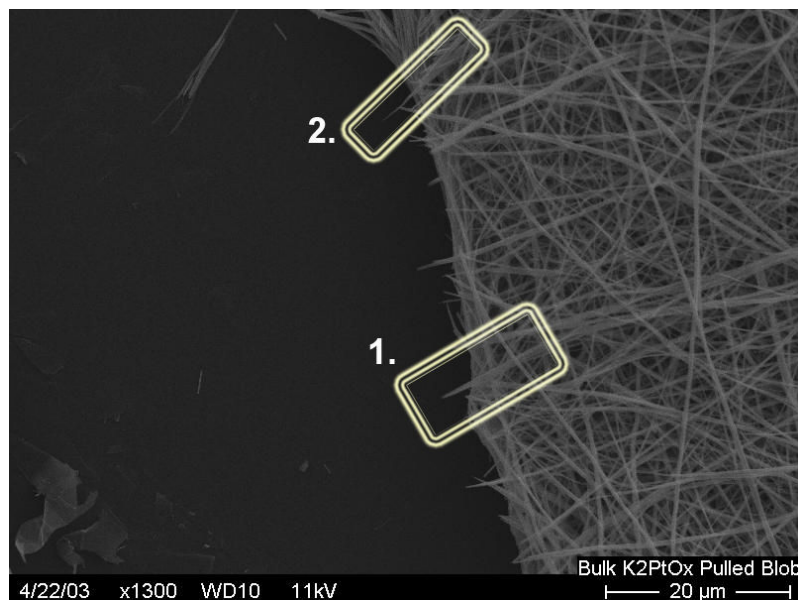


Figure 89. SEM image of an edge of a bulk polymerized sample of K-PtOx polymers with tapered edges. '1'-Central thickness of 750nm tapered thickness of 350nm. '2'- Central thickness of 500nm tapered thickness of 100nm. (x1300 Mag.)

SEM images of the PO polymers formed for their potential imaging via STM were obtained which explained why the STM experiments with the PO polymers were unsuccessful. Figure 90 shows one such image. The formation of these K-PtOx polymers was done using the vertical polymerization method consisting of an iron STM sample disk coated HOPG as an anode and a single platinum wire as a cathode. As stated previously in this dissertation, during the investigation of the PO polymers via STM, the imaging probe of the scanning tunneling microscope failed to engage any the of samples. In Figure 90, it was apparent why this occurred.

Most often the polymer strands were seen lying horizontally on the surface of the iron disk. The electrolysis method used for the formation of the STM samples did

nothing more than form the same PO polymer structures in the same formations as in the standard bulk polymerization process. The horizontal PO polymers are much less conductive than the PO polymers with a vertical orientation and, since the samples imaged via STM must be fairly conductive; obtaining images along that axis would be very difficult.

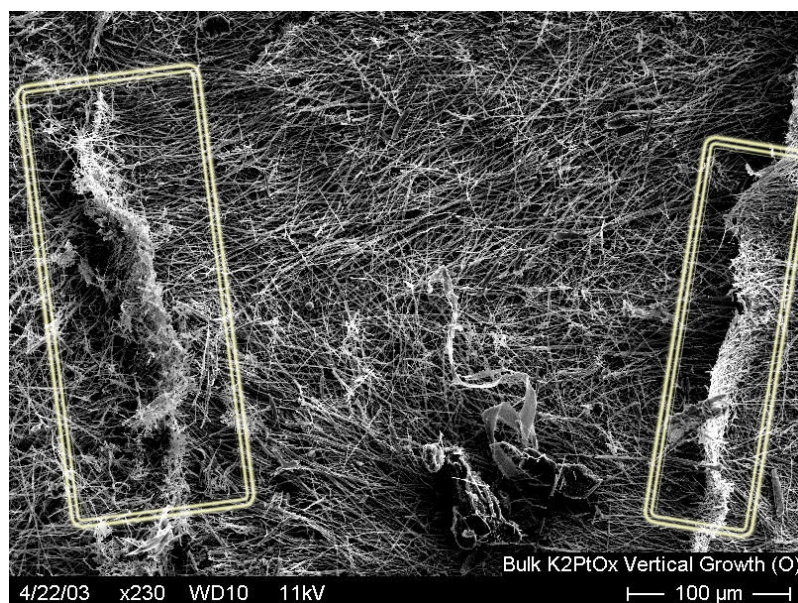


Figure 90. SEM image of K-PtOx PO polymers prepped for STM imaging. (x230 Mag.)

The polymer formations in the double yellow lined boxes in Figure 90 appear to be vertical, much like what was initially hoped for. Unfortunately, the sizes of these structures are very small. The row of vertical polymers in the left double yellow lined box was only about 18 μ m thick which would be very difficult to align with the STM probe. For STM images to be obtained, a new method for the vertical polymerization of the PO polymers was needed that provided a reliable way of orienting the STM probe with the ends of the PO polymers.

The Determination of an Adequate Template and the Construction of a New Electrolysis Device

A new experiment was devised after observing the polymers ability to change diameter in order to accommodate changes in the polymerization vessel as seen during the capillary experiments and the nanoscale PO polymer formations seen in the AFM investigation.

Using anodically grown aluminum oxide (AAO) substrates as scaffolds for self-assembling carbon nanotubes and other compounds has been used in the past⁶³ and are currently used as of late⁶⁴. In past experiments involving the AAO filters, the manufacturing of these AAO substrates was most often done in-house. After researching alternate sources of AAO substrates it was found that one such interesting potential scaffold were the Anodisc™ aluminum oxide nanoporous filters supplied by Whatman Inc. These filters, which can be used in filtrations, were commercially available from Fisher Scientific for a relatively inexpensive price and had interesting properties that would be beneficial in the templated formation of the PO polymers.

First off, the AAO filters are rigid and very durable much like the capillary tubes used in the macroscale polymerization experiments of the PO polymers. Unlike the single channel capillary tubes, the AAO filters contained a large array of nanoporous, nearly linear channels evenly distributed throughout its body. Figure 91 shows a SEM image of the top of one of the AAO filters magnified 16000x. The dark spots in Figure 91 represent the nanopores within the AAO filter which range in size from 150nm to 300nm. With this AAO filter sample, the average the pore diameter was found to be

200nm. A sample of a 200nm pore AAO filter was split in half and the side of the filter was imaged via SEM (Figure 92). The near linear and ridged channels passing through the filter were clearly visible. The pore size of 200nm was perfect for the bisoxalatoplatinate(2-) salts since that was how thick they formed when polymerized in bulk.

A number of different AAO filters varying in size and pore diameters were available which ranged from 20nm-1 μ m in diameter depending on the model purchased. The variation in pore and channel diameter allowed for the standardization of the polymerization channels which was something that was unobtainable when using the ‘pulled’ capillary tubes as electrolysis vessels. Also, the AAO filters were ideal in that they were inert toward the electrolysis solvent (water) as well as unreactive toward the platinum complexes used in the formation the PO polymers.

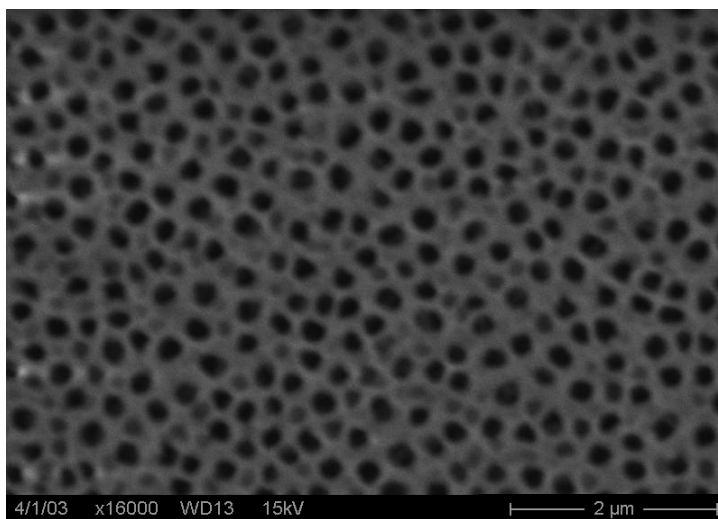


Figure 91. Surface SEM image of an AAO filter with an average 200nm pore diameter. (x16000 Mag.)

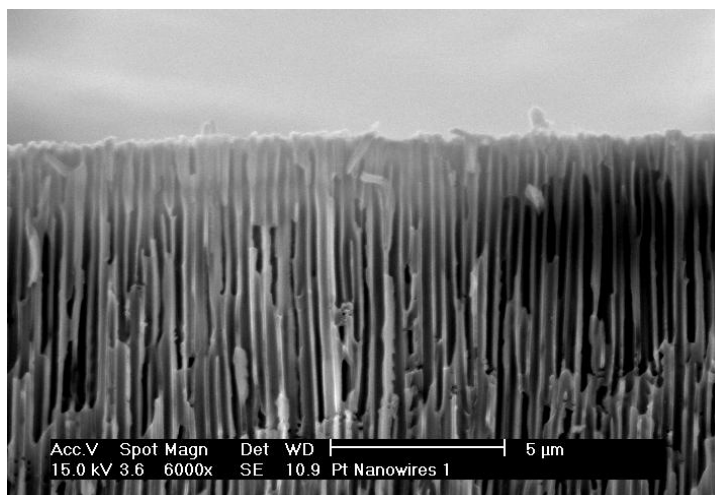


Figure 92. Side view of a 200nm pore of an AAO filter illustrating the channels therein. (x6000 Mag.)

Initially, these filters were placed in solutions of either **2** or **3a** and allowed to soak for a day. The filters are said to have capillary properties⁶⁵ so it was believed that the channels would fill themselves when placed in solution. The filters were removed from the solutions and two small conductive carbon sticky tabs were placed on both sides of the pretreated AAO filters and a potential of 1.5V was applied. The pretreatment of the nanoporous filters in this fashion yielded no PO polymer formation within the filters although formation of PO polymers outside of the filters were seen. It was unclear whether the solution had not penetrated the channels within the filter, whether the solvent had penetrated the filters but the solvent had evaporated before any PO polymers could form or whether the PO polymers were unable to form within the filters. It was thought that rather than soaking and removing the filter from a solution of **2** or **3a**, electrolyzing the filter while it was still in solution might increase the chances of forming PO polymers within.

The Whatman 200nm AAO filters were allowed to soak in a solution of either **2** or **3a** for two days. During that two days period, solution was passed through the filters with the aid of a plastic pipette. While the filter was still in solution, a platinum electrode was placed on each side of the filter and a potential of 1.5V was applied. It was hoped that the polymers, in an attempt to polymerize toward the cathode, would pass through the filter. Since the electrolysis took place while the filter was still wetted by the solution, it would not have a chance to completely dry out. When either solutions of **2** or **3a** were used, PO polymers were visible in the solution on the anode side of the filter after 2 hours. SEM images showed that no PO polymer formation occurred within the AAO filter. The polymers were more apt to polymerize around the filter rather than through. This was most likely due to the polymers following the path of least resistance. Since the solution outside of the pores has a greater cross sectional area, the resistance would be less than the resistance within the pores. Also, the ion migration and electron transportation would most likely be better outside of the filter as well. After numerous attempts of trying to polymerize the PO polymers through the AAO filter using indirect methods, it was realized that the polymers would have to be forced into forming through the AAO filter channels in order for the polymerization to occur.

It was realized that three things needed to be true in order for the PO polymers to form through the nanoporous AAO channels. First, the filters needed to be continually exposed to the platinum complex containing solution during its electrolysis. The filter needed to stay moist to ensure that there was enough platinum material available during its electrolysis as well as to complete the electrical connection between the anode and

cathode. Secondly, the polymers needed to have only one path available during its formation toward the cathode. If other, larger passages were an option during the polymerization then the polymers would form there and not within the AAO filter. Thirdly, the AAO filter needed to be held stationary in order to preserve the polymers that might possibly form within. Any movement of the filter during the polymers formation could possibly disrupt the polymers that had already formed within the filter.

In order for all of these “rules” to be followed during the electrolysis, a special device to house the AAO filters was made. The device in Figure 93 was specifically made for the purpose of forming the PO polymers through the AAO filters.

The design for the device was fairly simple but gave excellent results in the end. Two pieces of Plexiglas were milled so that one contained a small horizontal channel and the other contained a much larger horizontal and vertical channel. These blocks were attached to a pre-made aluminum vice and, to the fronts of both of the Plexiglas blocks, was attached a rubber O-ring. Into the Plexiglas block containing the small horizontal channel was placed a small piece of platinum wire and in the top of the vertical channel within the second Plexiglas block was placed another piece of platinum wire. An expanded image of the sample area of the device is displayed in Figure 94.

The side view of the sample area of the AAO polymerization device displays the inner working of the sample cell area. The AAO filter in Figure 94 was placed in between the two halves of the Plexiglas sample cell. The rubber O-rings provided two features. Since the O-rings were made of a flexible material, they were used to secure the moderately fragile AAO filter in place without it breaking, while the O-rings also were

able to form a tight seal between the surface of the filter and the surface of the Plexiglas sample cell. The right-half of the cell in Figure 94 was considered the anode section of the sample cell and the left half was the cathode.

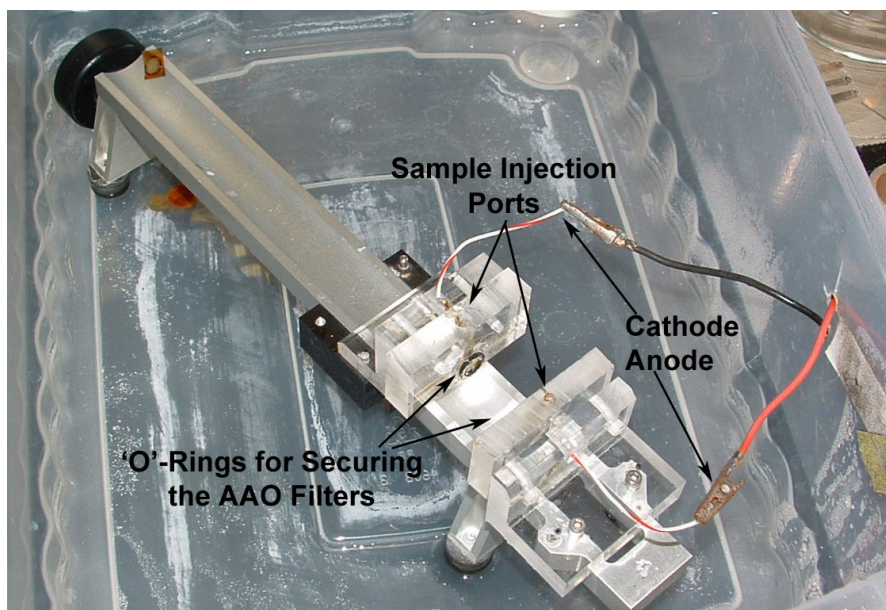


Figure 93. Device built for the polymerization of PO polymers through the AAO Filters.

Once the AAO filter was secured between the two O-rings, the sample solution to be electrolyzed was injected into the inlet in the top of the ‘anode’ Plexiglas block. A portion of the sample solution was also added to the ‘cathode’ half of the cell through channel in the top of the Plexiglas block.

There were a number of reasons for the design difference between the ‘anode’ and ‘cathode’ sides of the electrolysis cell. The anode side of the cell needed to hold as minimal a volume of solution as possible, the reason being that that half would contain the majority of the of PO polymers formed during the electrolysis. The quicker the PO polymers reached the AAO filter, the more material that would still be available to

polymerize through the filter and the less time would be needed for the experiment to complete. There was no need to worry about the PO polymers traveling back up the sample inlet in the anode block since the previously performed multi-electrode experiment showed that the polymers always traveled the path that led them towards the cathode.

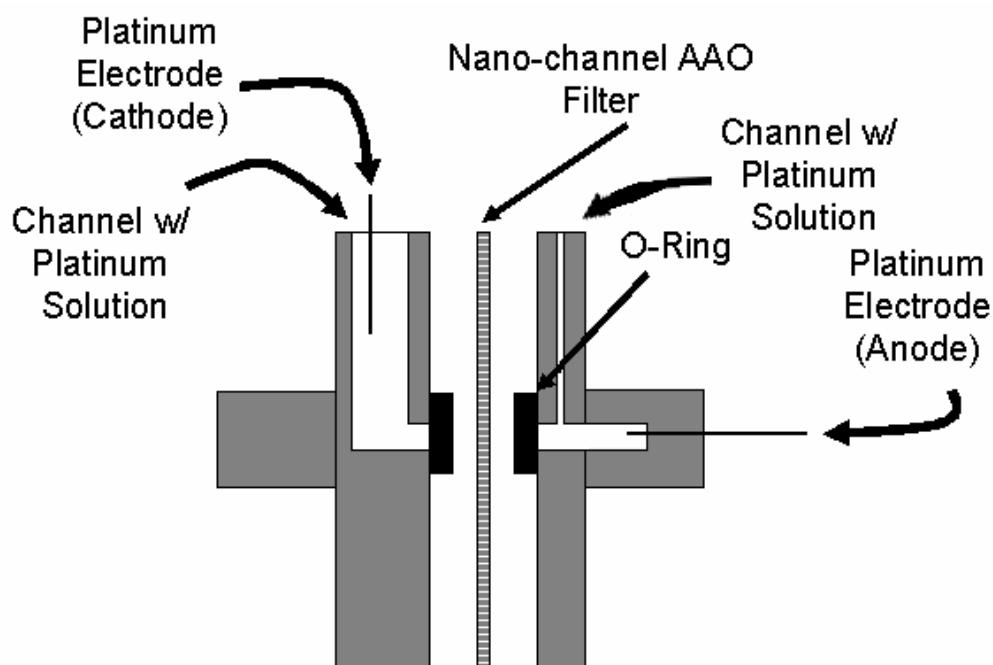


Figure 94. Expanded image (side view) of the sample area of the device used to form PO polymers within the AAO filters.

The cathode side needed to be much larger and open. The platinum wire used as the cathode was placed as far away from the AAO filter as possible in order for the PO polymers to be unhindered by any OH^- ions formed. Having the cathode sample section open allowed for the H_2 gas, which is also formed at the cathode, to escape easily.

Since the cathode side needed to be exposed to the atmosphere in order to remove

the H₂ gas from the system, the loss of the solution to the open air needed to be stopped. It was found that by placing the entire electrolysis device in a sealable 0.50m by 0.30m by 0.30m Rubbermaid™ container filled with water to a depth of 15mm the humidity would remain at a high enough level to halt the evaporation of the electrolysis solvent.

Once the solution was added to the sample cells, a small amount of pressure was applied to the sample inlet on the anode side in order to force some of the solution through the AAO filter. Doing this guaranteed the saturation of the AAO filter with the electrolysis solution. After the introduction of the sample solution, the electrodes were attached to a 1.5V potential and polymerization was commenced.

Templated Nanoscale Polymerization of potassium tetracyanoplatinate(2-) within 200nm channels and its Investigation Via Scanning Electron Microscopy (SEM)

Initially solutions of **2** were placed in the electrolysis device along with 200nm porous AAO filters and allowed to polymerize overnight. After 12 hours, the electrolysis was halted and the filters were imaged via SEM. A section of the filter was gently washed with deionized water to remove any remaining unoxidized material, allowed to dry and imaged. Figure 95 is a wide angle image of the small AAO filter section.

The ridges caused by the fragmenting along the nanoporous channels of the AAO filter are seen on the sides of the filter fragment. On the surface of the filter was visible a number structures as well as the protrusion of numerous sets of K-PtCN polymers. These polymer strands were quite long and thick.

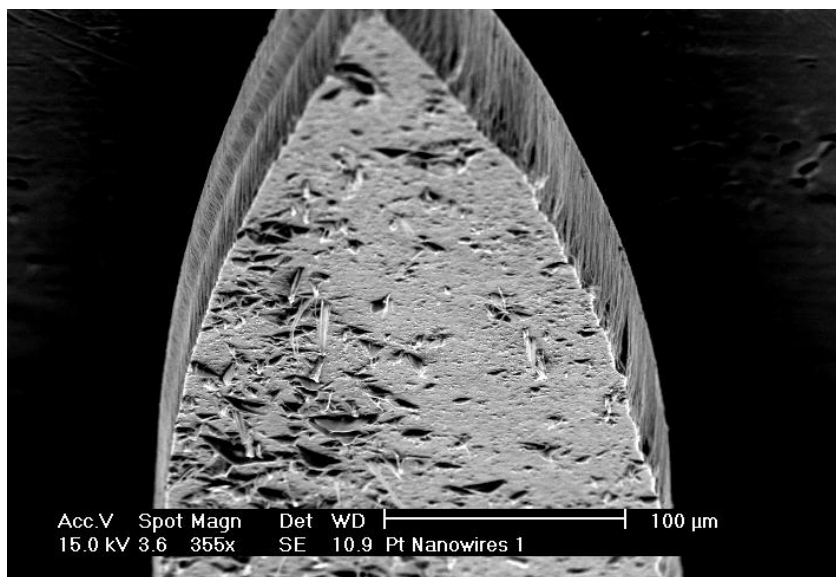


Figure 95. K-PtCN polymer bundles protruding from a section of an AAO filter (x355 Mag.)

Unfortunately, it was unclear which side of the filter (either the side exposed to the anode or the side exposed to the cathode) was being imaged but it is believed that it was the cathode side. A closer view of one of the polymeric structures is shown in Figure 96.

When measured, the PO polymer strands varied in thickness from 490nm to 700nm. The thicknesses of the polymers were all greater than the diameter of the AAO filter pores but less than the average thickness seen for the polymers formed during the bulk polymerization process. The red arrow in Figure 96 points to an interesting occurrence. At least six polymeric formations, once they exited the AAO filter, seemed to have recombined to form a larger and thicker polymer strands having a thickness of 1.8μm.

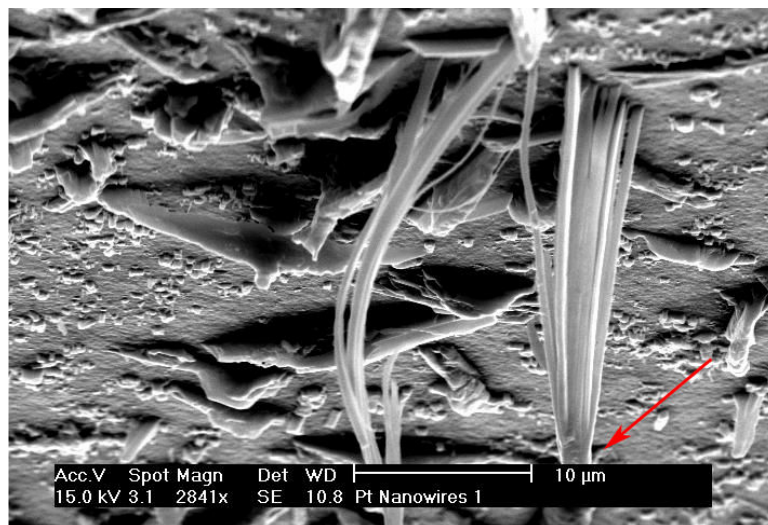


Figure 96. Close-up of K-PtCN polymer bundles protruding from a section of an AAO filter. Red arrow points to recombination (x2841 Mag.)

Other amorphous material was visible on the surface of the filter along with the PO polymers. It is unknown whether that material was unoxidized **2** or K-PtCN polymers that had bundled immediately after exiting the filter. The 200nm pores of the filter should have been visible in either Figure 95 or 96 but too much of the conductive Platinum-Iridium coating was applied which led to the concealment of the pores.

The filter was imaged along the horizontal axis in order to verify if any PO polymers were visible within its channels. Figure 97 clearly shows the PO polymers still contained within the AAO filters channels.

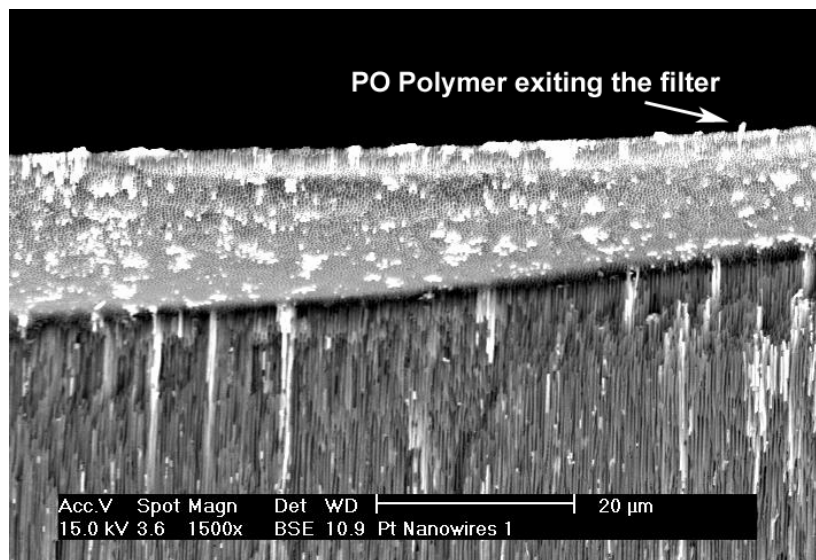


Figure 97. Side view of an AAO filter containing numerous channels of PO K-PtCN polymer (x1500 Mag.)

The image appeared quite confusing at first but it was realized that the side of the filter imaged was not completely flat. During the fragmentation process, it appears that the filter did not cleanly break. This led to the nearly flat section of the filter seen in the bottom half of Figure 97 and the gradually thickening section seen in the top one-fourth of the image. The bright white lines in the image are the K-PtCN PO polymer which have formed through a small minority of the channels. Some of the PO polymers appeared to stop polymerizing halfway through the filter. Closer inspection of the image showed that the wall of some of the channels did not completely break away during the fracture of the filter. This led to what appeared to be the disappearance and the reappearance of some of the polymers as it traveled through the filter.

The formation of the PO polymers within the honeycomb structure of the AAO filters was quite apparent in the greatly magnified image of Figure 98.

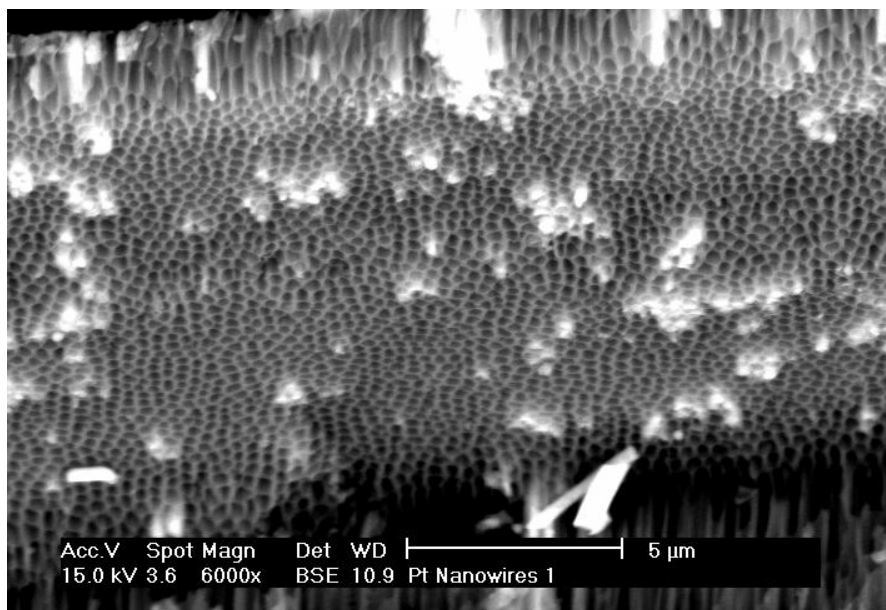


Figure 98. Closer view of an AAO filter containing numerous channels of PO K-PtCN polymer. Structure of the filter is evident. (x6000 Mag.)

The amount of polymer that actually penetrated the filter was quite low and, based on the number of channels filled with polymer, only 2% to 3% seemed to contain polymer. The reason for the small lengths of the PO polymers visible in Figure 98 was that these polymers were physically truncated during the fragmentation of the AAO filter prior to its SEM imaging.

Observing the surface of the filter horizontally showed that there was what appeared to be PO K-PtCN polymer on the surface of the filter in large clumps as well as polymer strands protruding from some of the filter's channels. Figure 99 shows a side view of the filter where some PO polymer has coagulated into a large globule and a 200nm strand of PO K-PtCN polymer exiting a nanoporous channel.

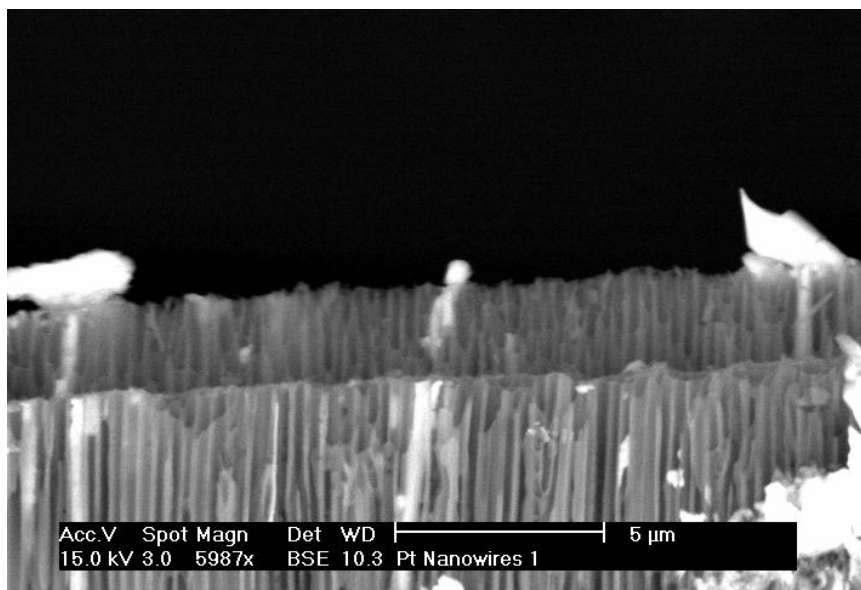


Figure 99. A PO K-PtCN polymer strand exiting the filter and larger masses of PO polymer.(x5987 Mag.)

The polymeric fiber visible in the middle of Figure 99 has a height of around 500nm outside of the filter. Its interesting to note that, due to the acceleration energy during these scans, some of the polymer strand was still visible even through it was encased in the AAO channel. On the surface of the filter, on either side of the polymer strand was seen two massive PO polymer blobs. Structures similar to these were most likely what caused the large amount of amorphous-like material that was seen on the surface of the filter in Figures 95 and 96.

Generally, the time needed for the K-PtCN polymers to penetrate the AAO filters was similar to what was needed for the polymer to form during bulk electrolysis. Not all polymerizations of solutions of **2** led to the formation of the PO polymers within the AAO filters and in some rare cases the filters, when imaged, yielded no PO polymers at all. Due to the lack of alternate cations and the amount of material need for the partial

oxidation of K-PtCN, the focus of the nanoscale polymerization to shift to the numerous bisoxalatoplatinate(2-) salts.

Templated Nanoscale Polymerization of K-PtOx within 200nm channels and Its Investigation Via Scanning Electron Microscopy

With the great success of the formation of the K-PtCN PO polymers within the 200nm porous AAO filters, attempts to polymerize the various salts of bisoxalatoplatinate(2-) were undertaken. Using the special electrolysis device designed for the polymerization of the PO polymer through the AAO filters, a solution of **3a** was added to the both the cathode and anode sides of the electrolysis cell and pressurized (flowed) through the filter. An electrolysis potential of 1.5V was applied and the polymerization was allowed to occur overnight (10 hours). The AAO filter was removed, gently washed with deionized water and allowed to dry for one day. The filter was then imaged via SEM. This process was repeated many times and yielded many different K-PtOx/filter samples.

It should be noted that the filters used in the polymerization of the PO K-PtOx polymer were coated with platinum/iridium to a thickness of 1.33nm. It was found that this amount gave the optimal image quality yet still allowed for the PO polymers to retain their physical qualities during SEM investigations.

The polymerization characteristics of the PO K-PtOx polymers were quite different than what was seen for the K-PtCN polymers. Wide-field SEM images of the filters yielded only images of the surface of the 200nm porous AAO filters. Looking at the barren surface of the filters, one striking difference between filters containing K-PtOx

and the ones used in the polymerization of samples of **2** was that there appeared to be no amorphous material on the surface. Upon higher magnification of the filters (x200 and up), a large number of K-PtOx structures were visible. The wide area image in Figure 100 shows the PO polymers of K-PtOx protruding off of the surface of a 200nm AAO filter.

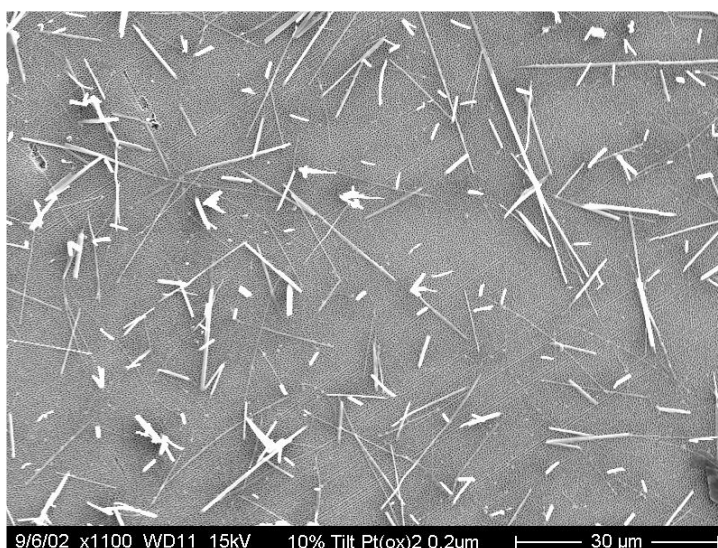


Figure 100. SEM image of PO K-PtOx polymer strands exiting a 200nm pore AAO filter. (x1100 Mag.)

The magnified filter surface in Figure 100 contained a large number of PO polymer strands that were still anchored within the pores of the filter. The bright white areas are the PO polymer still attached to the filter. Other darker crystals could either be fragmented PO polymer strands that had adhered to the filter's surface or unoxidized **3a** crystals that formed during the drying of the filter after it had been washed. The average size of the bright white polymer strands is 400nm to 550nm whereas the average length of the darker, nearly transparent polymers is 150nm to 300nm.

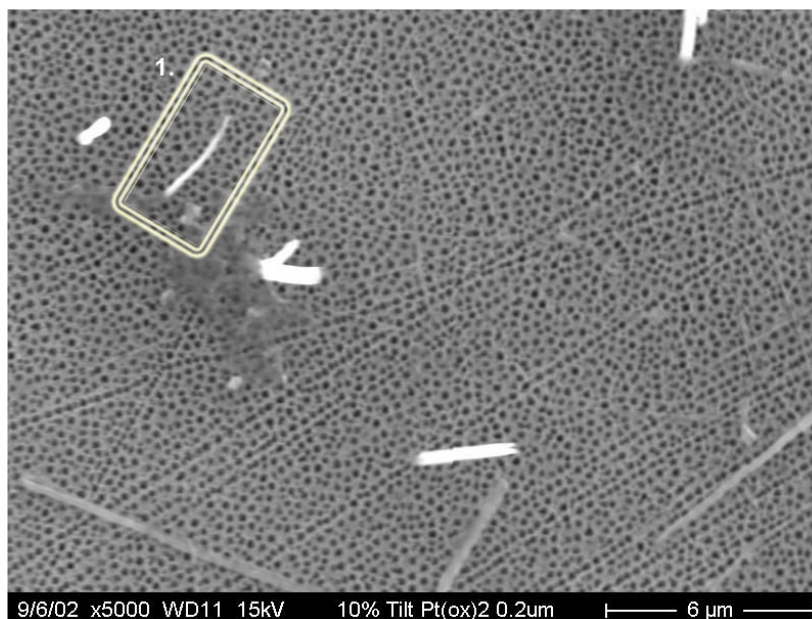


Figure 101. SEM image of PO K-PtOx polymer strands exiting a 200nm pore AAO filter. (x5000 Mag.)

In the highly magnified image in Figure 101, there were at least 7 different PO polymer strands visibility anchored to the filter. There was also a small amount of amorphous material visible on the middle-left portion of the filter. The average thickness of these polymers was found to be around 400nm although a few of the polymers were smaller. The polymer labeled as '1' in Figure 101 was found to have a diameter of 190nm, which is very close to that of the pore diameter of the filters.

It was surprising that the majority of the PO K-PtOx polymer strands that were still visibly attached to the surface of the filter were so much thicker than the filter pore size. After imaging another filter containing PO K-PtOx polymer, the reason for the large polymer strands was found.

After optimizing the SEM imaging parameters for a different set PO K-

PtOx/AAO filter samples, greater detail of the surface of the polymer strands became clear. What was apparent was that the thick PO polymers were not a single polymeric strand, but actually a number of smaller strands fused together similarly to what had been observed in the optical and AFM images of the K-PtOx polymers. Strands within adjacent pores seemed to bind together after exiting the filter. These strands all were found to be around 200nm to 300nm wide, the average size of the filter's pores. Figure 102 shows one of these conglomerations of PO polymers.

About three to four separate polymer strands appeared to make up the entire structure seen in Figure 102.



Figure 102. SEM image of a collection of K-PtOx polymers forming a larger polymer (x9000 Mag.)

Base on the measurements, the average polymer diameter was found to be 250nm to 300nm. It was noticed that a smaller polymer formation in a pore nonadjacent to the other three (signified by the arrow in Figure 102) was visibly orienting itself in order to

combine with the larger structure. This polymer strand was found to have a diameter of 90nm, which was about 110nm less than the average size of a single pore. The collection of polymers was not completely linear as a slight curvature was noticeable near the top of formation.

Many other multi-polymeric formations containing varying numbers of polymer strands were visible throughout the entirety of the data collection. Figure 103 shows another formation that contains about four different polymer bundles.

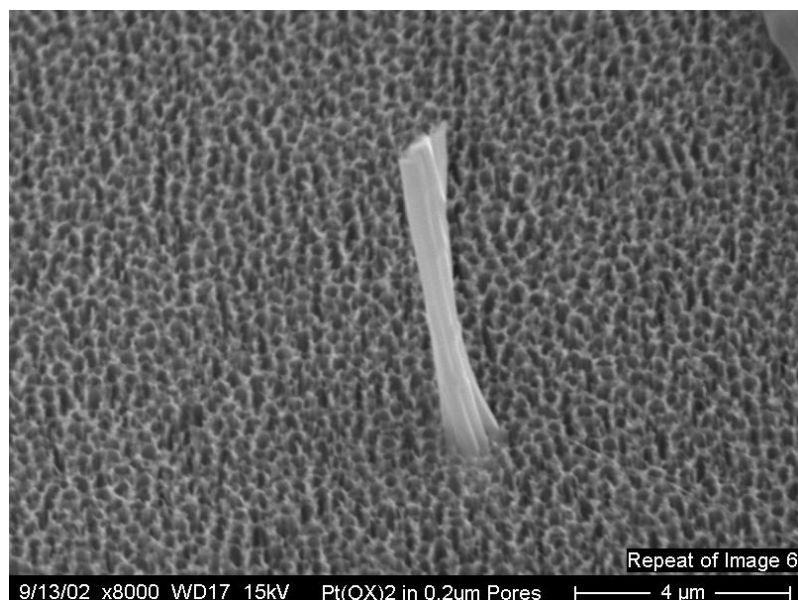


Figure 103. SEM image of a PO formation containing 4 different K-PtOx bundles.(x8000 Mag.)

These polymers seemed more rigid than the set of polymers seen in Figure 102. The single polymer strands were quite long as the height of the single polymer strands was found to be 6.5μm whereas the average diameter of the polymer bundles was 350nm. It was noticed that three of polymer strands were at a slight angle with respect to the

surface of the filter. The fourth polymer strand, behind the other three, was actually anchored in a pore a couple hundred nanometers behind the three and had polymerized normal to the filter's surface in order to combine with the other three.

The polymer formations were not limited to just three or four polymer strands as number of other multi-strand structures were seen. Figure 104 shows a seven strand rectangular array of PO K-PtOx polymers.

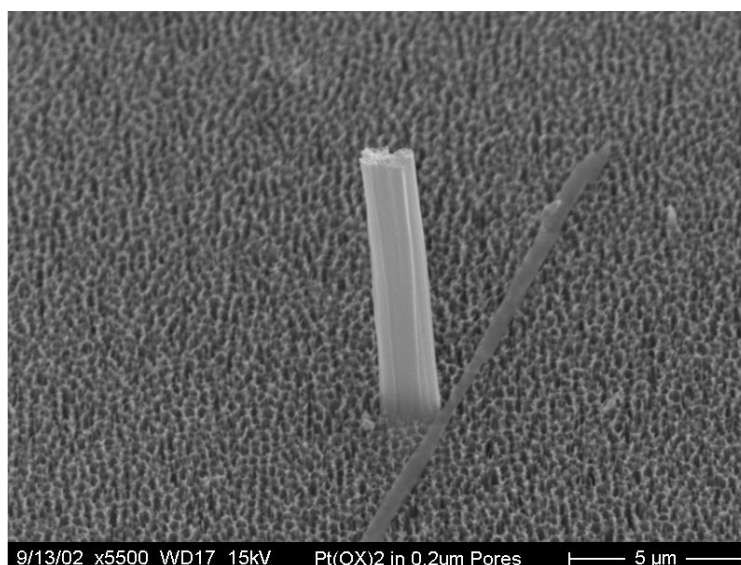


Figure 104. Array of 7 individual K-PtOx polymers (x5500 Mag.)

On the long edge, the polymer formation is around $1.2\mu\text{m}$ in length with each polymer strand having an average diameter of 350nm . The individual strands seemed to have fused together the instant the polymers had left the channels. The images shown thus far are the PO polymers that had traveled through the filter's channels on their way to toward the cathode. No matter how many individual polymer strands were visible, the top of the strands were all even with one another. The tops of the polymers in Figure 104

are perfectly aligned and appeared to have a slightly rough surface. This flatness of the top of the polymer formations suggests that the polymers are self-regulating even after binding with other PO strands. Instead of the polymer strands forming independently from one another, the platinum complexes stack uniformly across the entire array of polymer strands and polymerize at a uniform rate.

The array of PO K-PtOx polymers seen in Figure 105 had over fifteen different PO polymers strands contained within. Again, the uniformly flat top of the polymer formation is visible. This formation is especially quite interesting in that the strands contained within the total structure are seen twisting as a whole. Whether the numerous polymer strands began twisting prior to their combining or whether they twisted after combining with one another is unknown. Most likely the polymers twisted after they had recombined following departure from the AAO filter.

Finally, the largest polymer formation imaged via SEM is shown in Figure 106. This polymer formation consisted of what was believed to be 50 or more individual PO K-PtOx polymer bundles with a total cross sectional diameter of approximately $1.8\mu\text{m}$ and a height of well-over $3.9\mu\text{m}$.

The formation in Figure 106 did not appear any different from the rest except for three irregularities. The first irregularity indicated in Figure 106 arrow '1', is a polymer strand which seemed to have ceased polymerization prematurely compared to the rest of the strands within the massive structure. The polymer, which is 200nm shy of the top of the plateau, was the first and only strand ever imaged that didn't polymerize to the same length as the rest of polymers to which it was associated.

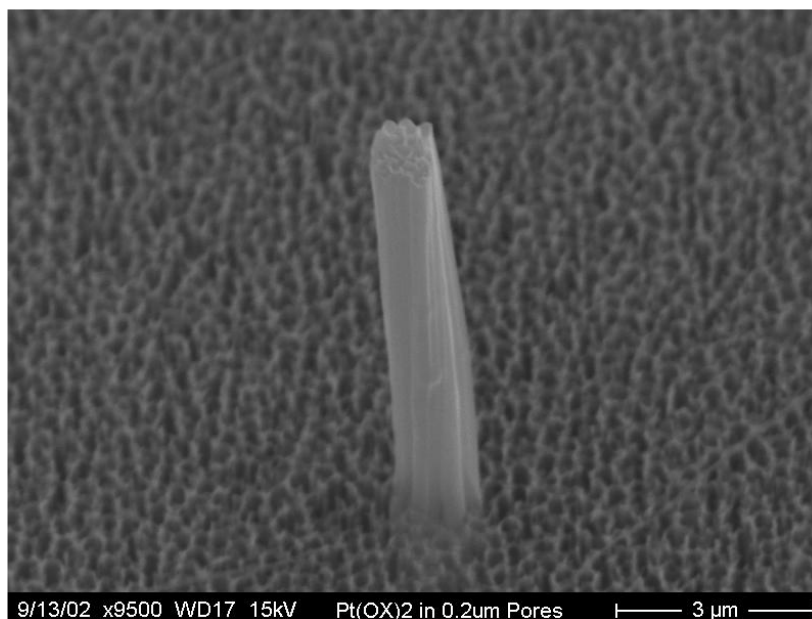


Figure 105. Larger array of individual K-PtOx polymers (x9500 Mag.)

The polymer bundles around the outer edge of the structure in Figure 106 were clearly distorting in order to bind with rest of the PO polymers contained in the large structure. When observing the polymer strands on the right-hand side of the structure, their bending was quite apparent. The polymers indicated in Figure 106 by arrow '3' were seen bending and bridging over a set of empty nanoporous channels in order to bind along with the rest of the polymers within the massive formation.

Unlike the other polymer bundles previously seen, it was noticed that one polymeric strand was much shorter when compared to the rest of the polymers within the array. The polymer shown in Figure 106 signified by arrow '2' was measured to be approximately 200nm tall. Why this polymer was so much shorter than the rest was unknown, although it probably is due to polymer fragmentation/sample handling prior to its SEM imaging. Unlike the rest of the polymer strands, the top of that polymer strand is

not flat which most likely indicates agitation of the polymer. After imaging numerous AAO filters, each of which contained numerous bundles of 200nm to 350nm K-PtOx polymeric strands, it was concluded that the polymers were apt to form large bundles of polymers rather than remain as a single strand.

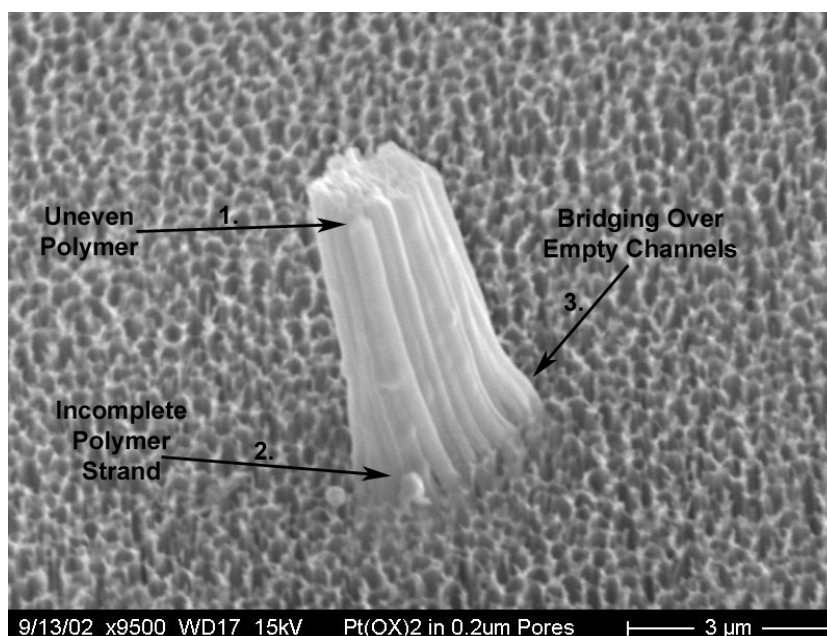


Figure 106. Massive array of individual K-PtOx polymers over 1.8μm across (x9500 Mag.)

Templated Nanoscale Polymerization of Other bisoxalatoplatinate(2-) salts within 200nm channels and Their Investigation Via Scanning Electron Microscopy

With the finding that both potassium salts of bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) could be forced to polymerize through 200nm channels, and that the other PO polymers from various salts of bisoxalatoplatinate(2-) could be formed very easily using electrochemical methods, attempts were made to form the other PO polymer bisoxalatoplatinate(2-) salts within the 200nm AAO templates.

The appropriate concentrations of bisoxalatoplatinate(2-) solutions containing cations other than potassium were prepared and placed in the sample cells of the prebuilt electrolysis device. An electrolysis potential of 1.5V was used during every polymerization except for those polymerizations where manganese was used as the counter cation; a potential of 0.825V was used in those cases.

The polymerization of the other bisoxalatoplatinate(2-) salts in the specialized electrolysis cell resulted in the formation of a number of the salts forming PO polymers within the 200nm AAO channels. The first salt imaged was the PO polymers of the cobalt salt, **3h**.

The surface of the AAO filters used in the experiments involving **3h** were mostly devoid of any PO polymeric formations, structures or strands. Figure 107, shows a single polymeric strand of a PO polymer of **3h** (Co-PtOx).

This polymeric strand was found to have a thickness of 164nm, which was half of what the K-PtOx polymers were typically measured. The single strand seen in Figure 107 was one of the few strands visible while imaging AAO filters used in experiments involving **3h** and of those visible, very few were actually still attached to the surface.

After the polymerization had ceased, macroscopic PO Co-PtOx polymers were definitely seen on both sides of the filter while it was still within the electrolysis device yet very few were visible during SEM imaging. Sample handling and preparation undoubtedly caused some of these observed changes.

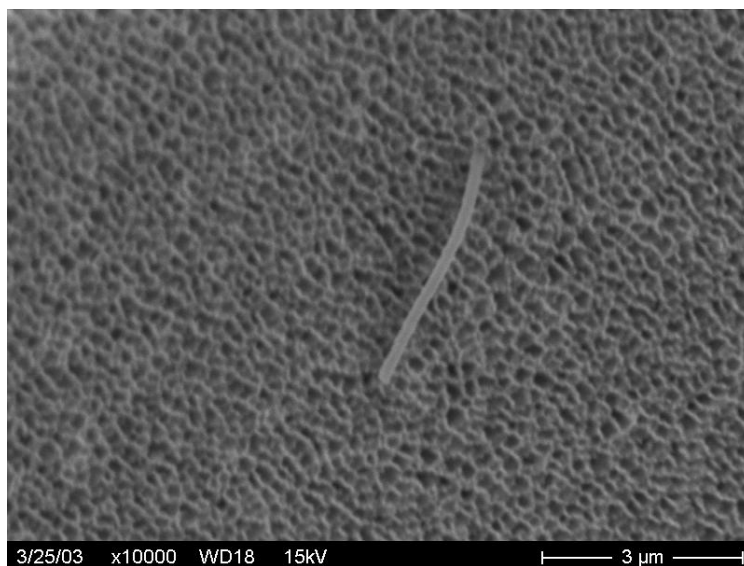


Figure 107. Single Co-PtOx strand measuring 164nm across attached to the surface of an AAO template. (x10000 Mag.)

Another Co-PtOx polymeric structure is shown in Figure 108. Prior to this image in a wide field, low magnification scan, the polymer strand extended off of the surface of the AAO filter. As the magnification of the image was increased, the polymer bundle appeared to be “pushed around” by the electron beam of the scanning electron microscope. It was clear that the polymer bundle had snapped off and was no longer attached to the AAO surface. This particular polymer bundle was measured as having a cross-sectional diameter of 953nm.

The ‘U’-shape of the PO polymeric formation in Figure 108 was much different than what had previous been seen. Instead of readily identifiable, 200 to 300nm polymeric strands bound together to form a larger super structure, this one seemed to be one continuous formation. The polymer formations seemed to have bound together and had become one single crystal.

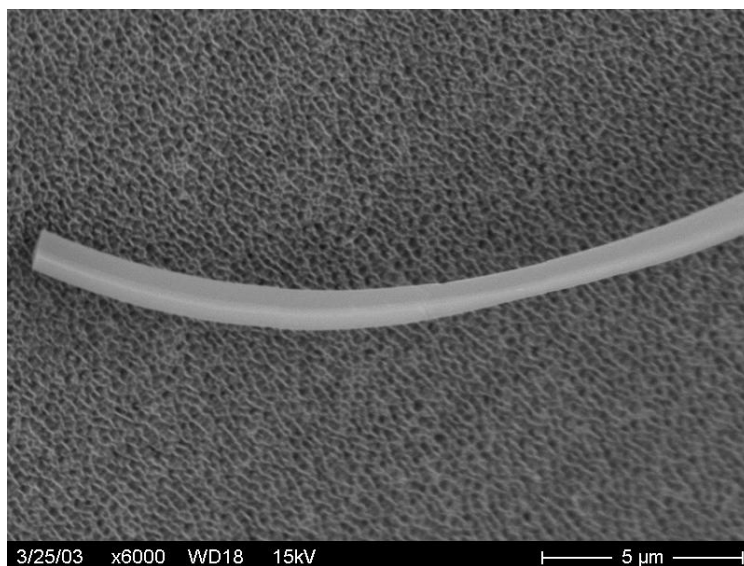


Figure 108. Co-PtOx strand measuring 953nm across (x6000 Mag.)

Figure 109 displays the right half of the polymeric formation seen in Figure 108.

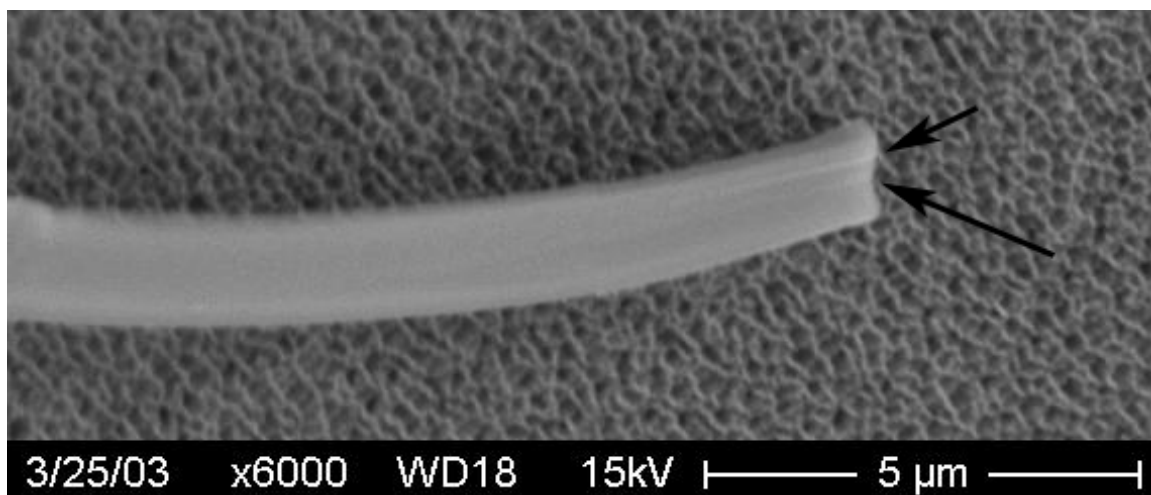


Figure 109. Right side of Co-PtOx formation consisting of three polymeric strands (x6000 Mag.)

In Figure 109, there were three individual polymeric strands that were visible. These were picked out by identifying the faint lines that made up the dividing for the

polymeric strands. These lines were visible on the edge of the polymeric formation and are indicated by the two arrows in Figure 109. Each of these strands measured around 300nm in width.

Attempts to polymerize samples of the sodium salt of bisoxalatoplatinate(2-), **3d**, through the AAO filters yielded very poor results. Although PO polymers of **3d** (Na-PtOx) were optically visible in each of the sample cells, very poorly formed polymers were visible on the surface of the AAO templates. Figure 110 shows one such attempt.

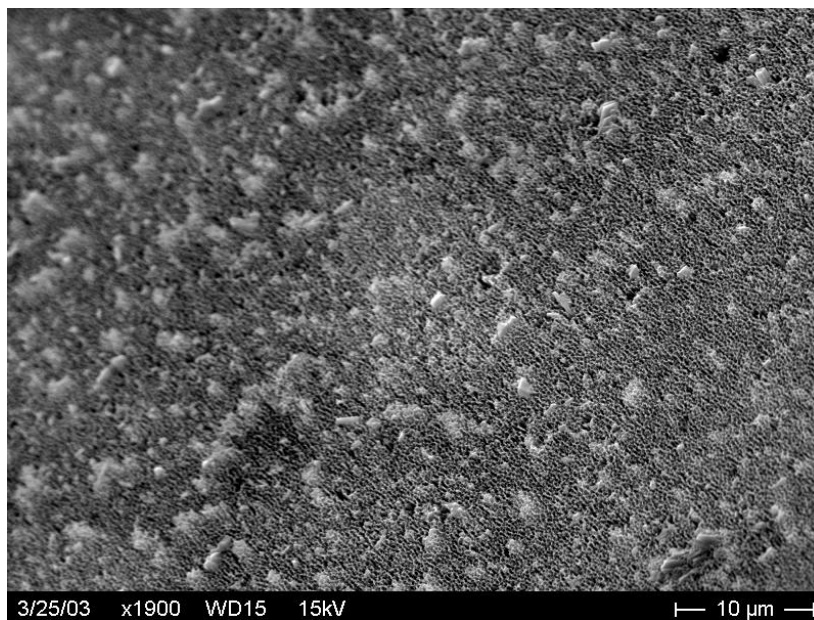


Figure 110. The surface of one attempt to polymerize a solution of **3d** through an AAO porous filter (x1900 Mag.)

The surface of the template seemed to contain a large amount of amorphous material similar to what was seen in the AAO templated polymerization of solutions of **2**. Although it appeared that a majority of the channels within the AAO template were filled with material, there was no way to determine whether the material was crystallized **3d** or

whether it was the PO polymer of that compound.

The polymerization of the zinc salt, **3p**, through the 200nm AAO templates yielded very interesting images. The AFM images of Zn-PtOx seemed to show a polymer that was much more continuous and less segmented than the K-PtOx polymers. Figure 111 shows an image of Zn-PtOx polymers formed within a 200nm AAO filter but unlike the nanopolymers previously observed; this one was nearly continuous in structure. The smoothness of the polymer seen in Figure 111 corresponds nicely with the image obtained from the AFM study. The Zn-PtOx polymers are able to form and pass through the filter but instantly recombine when in close proximity with one another.

This massive Zn-PtOx structure was the largest seen with it measuring at least 14.86 μ m long, 2.56 μ m wide at the base of the polymer where it meets the surface of the AAO template and 1.60 μ m wide across main shaft. The dimensions of the structure at its base were much different than the dimensions in the center and end of the structure. The PO polymers at the base of the formation condense into a more compact structure. The polymers at the base go from a wide but very thin formation into a formation that is nearly uniform on all sides. Polymeric structures, like the ones in Figure 111, were the only formations visible on the surface of the AAO filters when solutions of **3p** were polymerized.

Solutions of **3g**, the nickel salt of bisoxalatoplatinate(2-) yielded PO polymer formation similar in structure to what was seen with the K-PtOx PO polymers. The surface of the AAO templates was nearly barren of any PO polymer of **3g** (Ni-PtOx), much like the surface of the templates in the PO Co-PtOx polymerization experiments.

Unfortunately, very few images of the PO Ni-PtOx polymers within or on the surface of the AAO templates were captured. Every time an attempt to image any of the PO Ni-PtOx polymers, the structures were blasted off of the surface of the template. The high energy electron beam seemed to cause massive charging effects within the polymer formations which led to their destruction before any detailed images could be obtained.

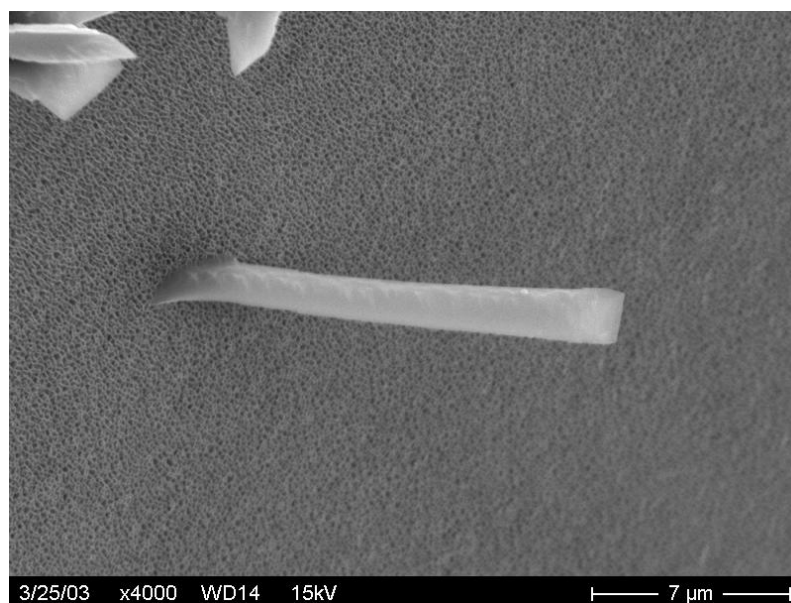


Figure 111. Massive Zn-PtOx structure seen on the surface of a 200nm porous AAO template. (x4000 Mag.)

Two images were obtained of the PO Ni-PtOx polymers on the surface of the AAO template. One image (Figure 112) was of a Ni-PtOx polymer that had been blasted off from its nanoporous channel but remained on the surface of the filter instead of being lost to the vacuum. This structure appeared to be a single strand having a width of 320nm and a length of 3.07μm, typical dimensions of what was seen in polymerizations dealing with other bisoxalatoplatinate(2-) salts.

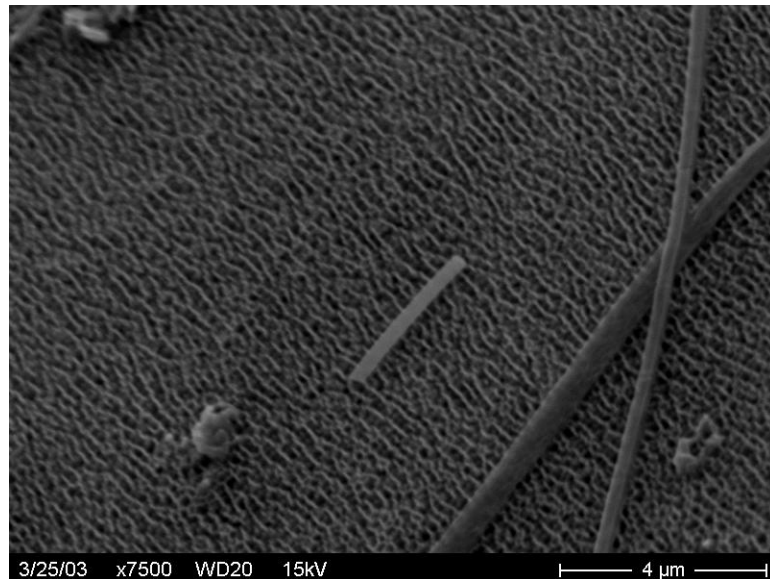


Figure 112. A PO Ni-PtOx polymer that had been blasted off the surface of an AAO polymer. (x7500 Mag.)

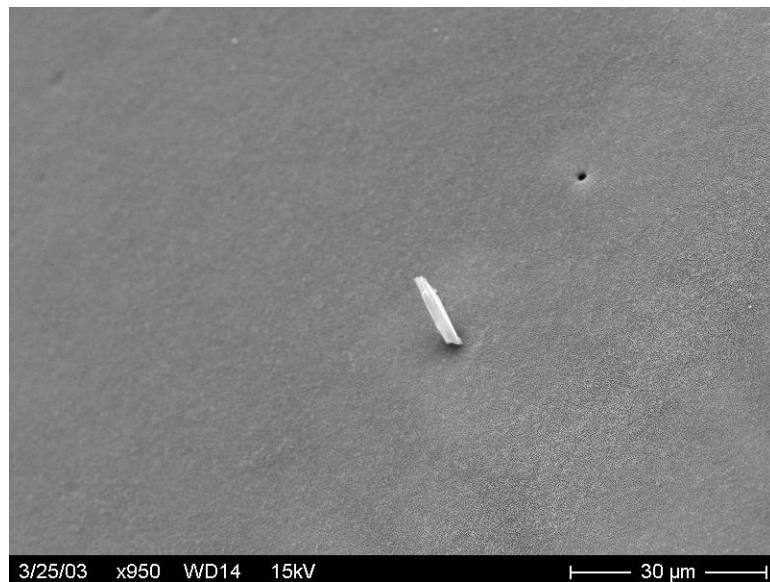


Figure 113. Ni-PtOx structure on the surface of a 200nm AAO template. This structure was later blown off of the surface due to interactions with the electron gun of the SEM (x950 Mag.)

The other image was a low magnification image of a large structure on the surface of a 200nm AAO template. The structure in Figure 113 was rather large having a height of at least 11.23 μ m and a width of 2.18 μ m.

From that image, small striations were visible on the surface of the structure and one could see multiple polymeric strands making up the complete structure. Also, the top of the structure appeared uniform and slightly textured as seen with the PO K-PtOx polymers. Unfortunately, as stated before, when the resolution was increased, the structure was pushed off of the surface by the electron beam and lost.

Templated Nanoscale Polymerization of the Magnesium and Ammonium bisoxalatoplatinate(2-) salts within 20nm channels and Their Investigation Via Scanning Electron Microscopy

The formation of the PO polymers of the nickel, zinc and cobalt salts of bisoxalatoplatinate(2-) within the 200nm porous AAO filters showed that the PO polymers were able to reduce in size and were able to navigate the nanoporous channels. Although the 200nm pores were much smaller than any templates used prior to the templated polymerization work covered in this dissertation, it was believed that the polymers should be able to form to virtually any thickness therefore, the 200nm porous AAO filters were replaced with 20nm porous AAO filters. These filters were more difficult to work with when compared to the 200nm porous filters in that the bisoxalatoplatinate(2-) solutions needed to be slowly and gently pumped through due to the 20nm porous filter's decreased pore size. The 20nm porous filters and bisoxalatoplatinate(2-) salt solutions were both added to the homebuilt electrolysis vessel in the similar fashion that had been done in all other AAO template experiments. An

electrolysis potential of 1.5V was used during all polymerizations.

SEM images of the PO polymers of the magnesium salt of the bisoxalatoplatinate(2-) **3o** (Mg-PtOx), yielded polymeric strands similar to what was seen for the K-PtOx, Co-PtOx, Ni-PtOx PO polymers that had been formed within the 200nm porous AAO filters. Figure 114 shows one image of a set of PO Mg-PtOx polymers that had formed within the 20nm channels. A large amount of amorphous material is visible next to the polymeric strands. The strands varied in diameter from 300nm up to 600nm wide.

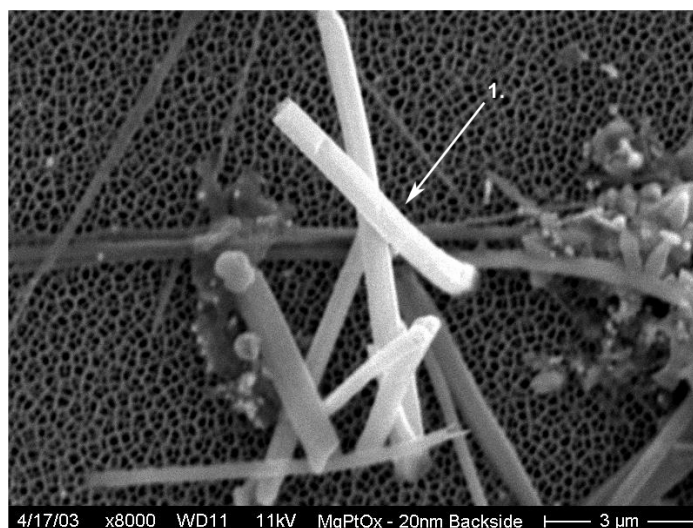


Figure 114. Mg-PtOx polymeric strands on the surface of a '20nm' porous filter (x8000 Mag)

The polymeric strand signified by the arrow labeled as '1', extended off of the surface of the AAO filter and bent over other PO polymers and various amorphous material. In Figure 115, another image of the Mg-PtOx polymers was seen.

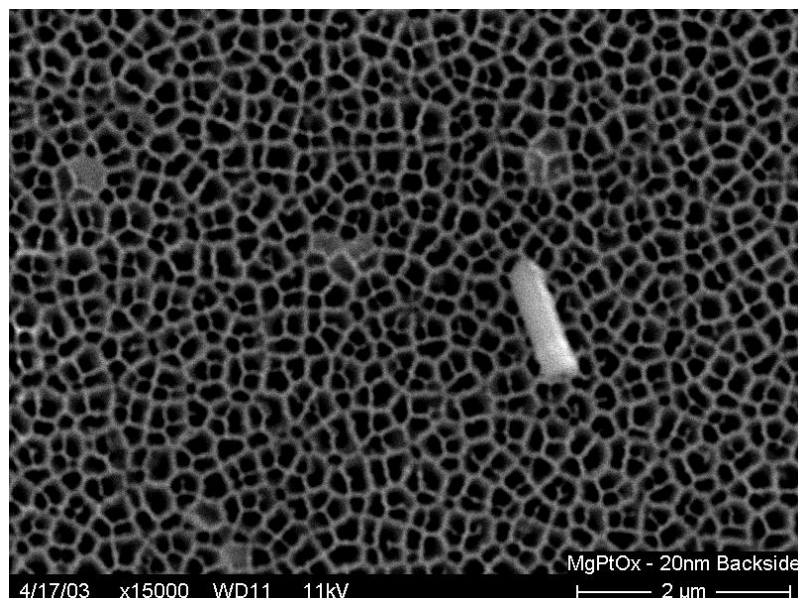


Figure 115. A single Mg-PtOx polymeric strand on a '20nm' porous filter (x15000 Mag)

This single strand was measured as having a diameter of 295nm and also appeared to be bent. All the polymer formations of Mg-PtOx were measured as having diameters roughly an order of magnitude higher than what the pore diameter of the filters was supposed to be. Upon closer inspection of the images dealing with the 20nm porous filters, it was realized that the surface of the filter appeared exactly the same as the 200nm porous filters. All the pores of the 20nm filters imaged had diameters of around 150nm to 300nm in width.

A sample of a 20nm AAO filter was split in half and alternate sides of the filter was placed on an SEM sample plate in order to be able to image both sides of the filter simultaneously. Arbitrarily, a top and bottom of the filters were chosen and imaged.

Figure 116 shows the bottom of a sample of the 20nm porous filters.

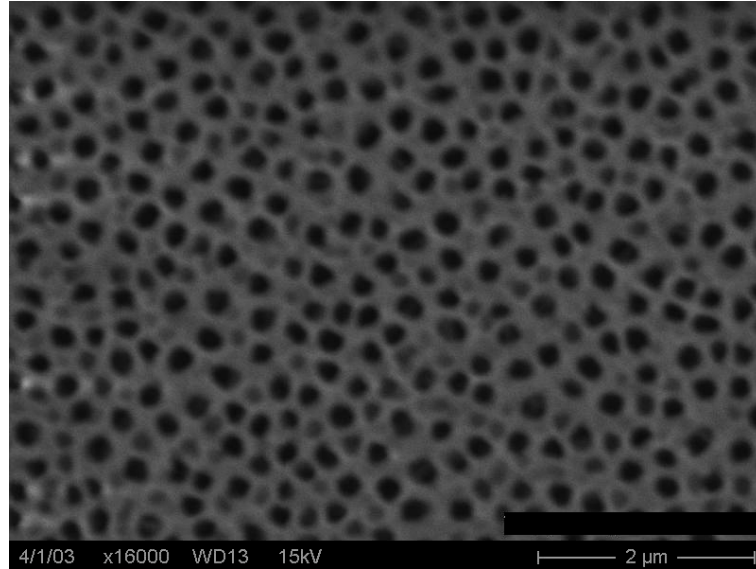


Figure 116. The ‘bottom’ of a 20nm porous filter (x16000 Mag)

The pore diameters are all around 150nm to 300nm, just like what is seen in the 200nm porous AAO filters. When the top of the 20nm porous AAO filter was imaged, the surface looked exactly like the bottom of the filter. When the electron gun was focused near the fracture point where the AAO filter had been separated in to two parts, the surface changed from the 200nm pores to one where no pores were visible. Figure 117 shows this division point.

The section of the filter shown in Figure 117 has a section where 200nm pores are clearly visible and are large enough to be imaged by the SEM. The other section is the portion that contains the 20nm pores which are too small to be seen with the SEM. After gathering further information of about the construction of these filters, it was found that the 20nm porous AAO filters had 20nm pores on only one side of the filter where the other side contained 200nm pores.

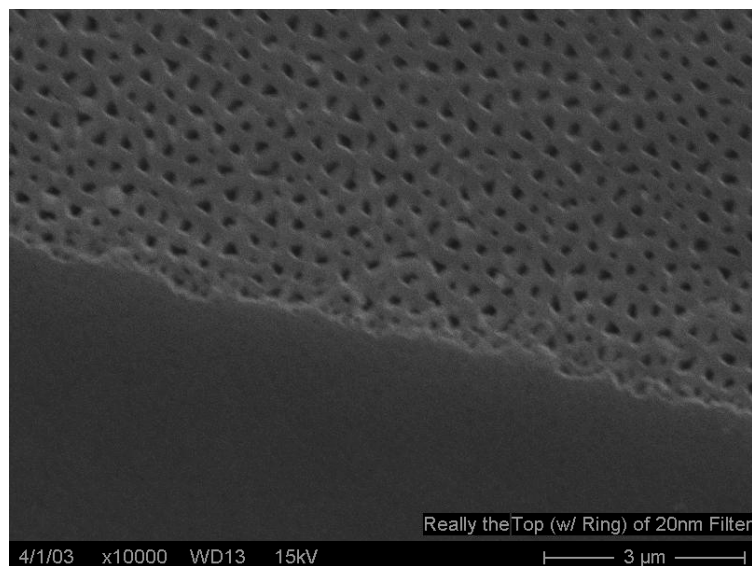


Figure 117. The ‘top’ of a 20nm porous filter (x10000 Mag)

The process used by the manufacturer (ANOTEC) uses to fabricate the 20nm porous filters involves taking a 200nm porous filter and coating one side with a material that packs on the surface of the filter. After completion of this coating process, small holes, about 20nm in diameter, remain. In actuality, any polymers exposed to these filters would have to polymerize down to fit through the 200nm channels and then reduce in diameter once again to fit through the 20nm pores. Attempts to image any PO polymers of any salts that could have extended from the 20nm porous side of the AAO filters after electrolysis yielded no images other than the bare surface of the filter except for the PO polymers of the ammonium salt of bisoxalatoplatinate(2-), **3d**.

Upon imaging the 20nm pored side of the AAO filters, the surface “lit up” with formations of the PO ammonium bisoxalatoplatinate polymers ($\text{NH}_4\text{-PtOx}$). The surface was very densely covered with the well defined $\text{NH}_4\text{-PtOx}$ PO polymers. Never before had so many PO polymeric formations been observed extending from the surface of an

AAO filter. Figure 118 shows this wide field image of the $\text{NH}_4\text{-PtOx}$ PO polymers on the surface of the 20nm pore side of an AAO filter.

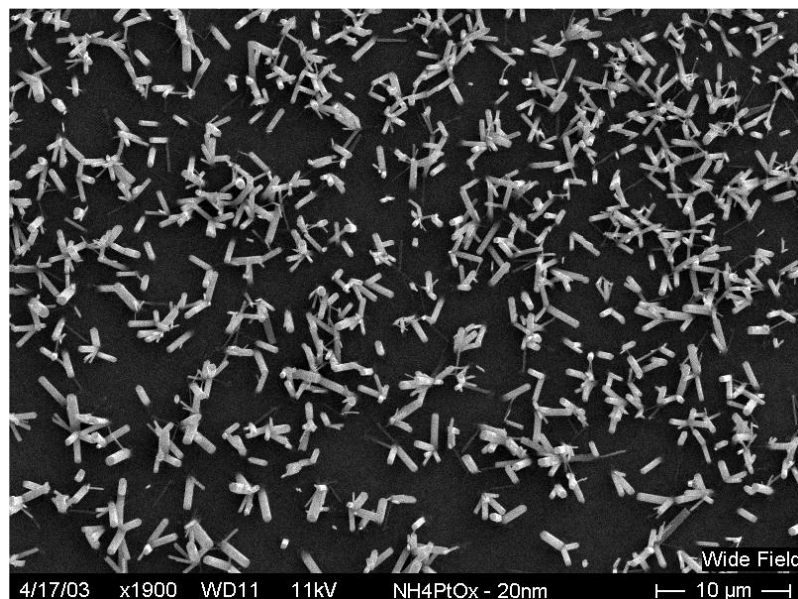


Figure 118. $\text{NH}_4\text{-PtOx}$ polymers on the surface of an AAO filter (20nm side) (x1900 Mag)

The formations of the $\text{NH}_4\text{-PtOx}$ polymers were much different in physical structure than what had been previously observed. Instead of single, polymeric strands that were associated with each other or strands that appeared to form one large, continuous formation, the PO polymers of $\text{NH}_4\text{-PtOx}$ seemed to sprout multiple large polymeric formations from a single nucleation point.

The structures appeared to form two different types of structures having two distinct diameters. Figure 119 shows a higher resolution image of the ‘field’ of $\text{NH}_4\text{-PtOx}$ PO polymers from Figure 118. This ‘field’ seemed to contain two differently sized of polymeric formations.

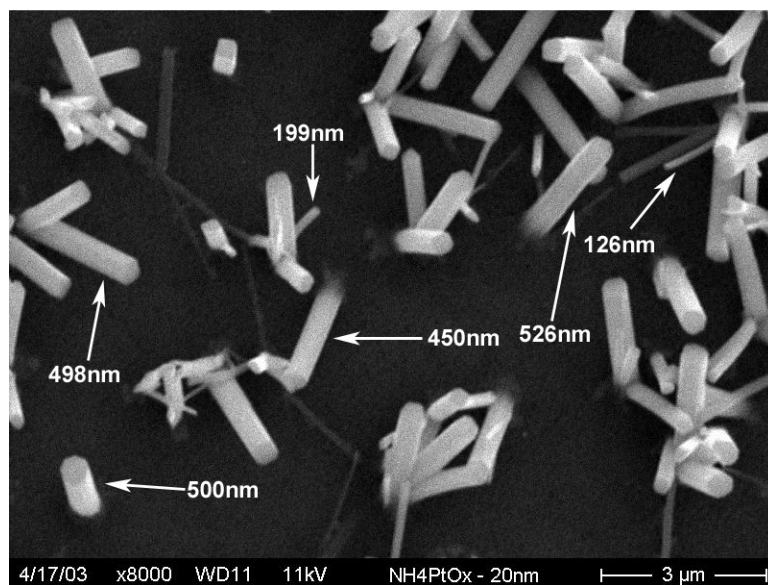


Figure 119. Magnified section of the $\text{NH}_4\text{-PtOx}$ polymers seen in Figure 118. (x8000 Mag.)

In the vast number of polymeric formations, there were formations that were around 450nm to 500nm wide and formations that were 100nm to 200nm wide. Although the PO polymers are much larger than 20nm, the still nanoscale 200nm to 500nm polymers appeared to having the plateau-like top which is characteristic for almost all the PO bisoxalatoplatinate(2-) salts imaged. Also, the surface of the polymers appeared to be smooth and not composed of individual polymers. This observation was most likely due to the lack of resolution of the SEM. If higher resolution images could have been obtained, it is believed that the surface of these polymers would appear very rough and that individual 20nm $\text{NH}_4\text{-PtOx}$ strands would have been visible.

Why there were two different sizes present was unexplainable. The reason for the massive amount of PO polymers which were literally piled on top of one another was

also difficult to understand. These two abnormalities could be explained by looking at how the PO polymers would need to behave in order to form within the AAO filters.

Rationale for the Formation of the PO polymers within the Nanoporous Channels contained within the AAO filters

It has been stated already that, for the PO polymers to form in the channels within the AAO filters, they would have to reduce in size. This reduction in size most likely occurs as the polymers enter or near the opening of the channels. Since the large polymeric formations seen in the K-PtOx, Ni-PtOx and NH₄-PtOx SEM images appeared to be composed of numerous smaller closely packed PO polymeric strands, the most likely explanation for this would be that the strands all originally came from the same polymer.

Figures 120a, 120b and 120c illustrate what most likely occurs as the polymers reach the surface of the AAO filters. As seen in Figure 120a, as the PO polymer reaches the AAO filter, only certain areas of the larger polymeric strand are available for further polymerization. Those parts of the PO polymer continue through the filter, essentially filling the pores with PO-polymer (Figure 120b). Since the rate of polymerization should be equal for all parts of the PO polymers within the AAO filter, the channels should be equally filled with PO polymer. Since the channels are usually only 20nm away from the other adjacent channels, once the PO polymer strands exit the channels (Figure 120c), they would be close enough to recombine thus lowering their overall energy of formation due to the bundling (sharing of cations) between the polymeric strands.

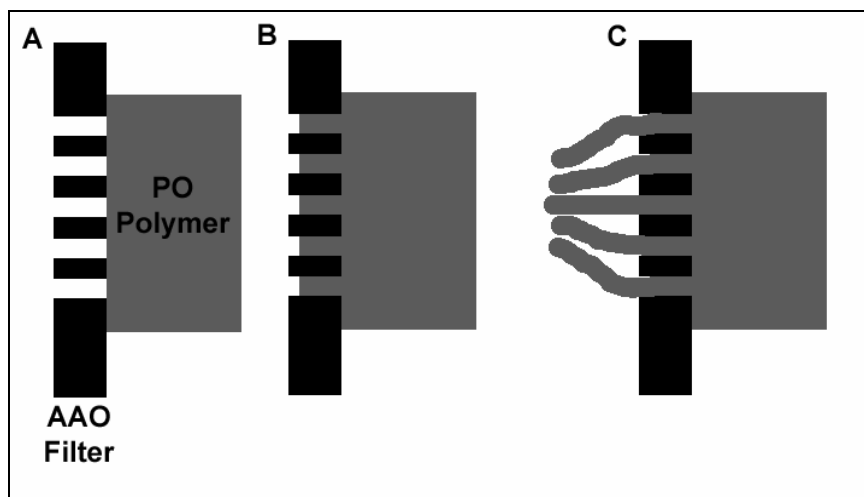


Figure 120a, b and c. The formation of the nano-PO polymers as they pass through the AAO filters.

The PO polymeric strands that were on the periphery of the larger PO formation were arcing and bending to a greater extent in order to recombine with the rest of the PO polymers which were also bending in order to congregate. The size of the parent PO polymer before it comes in contact with the anodic side of the AAO filter would dictate how many smaller, polymeric strands would be formed. Conversely, by looking at the number of PO polymeric strands within the large PO formations, the size of the original PO polymer, before it entered the AAO filter, could be approximated.

The 20nm porous filters should behave in a way similar to that of the 200nm AAO filters. The only difference was that now there was another layer with a set of even smaller channels for the polymers to pass through. The behavior of the polymeric strands within the 20nm pores is probably a bit different compared to that behavior within the 200nm channels due to the thinness of the coating used to make the 20nm pores. The thickness of the 200nm channel layer within the AAO filters is many microns wide. The

thickness of the 200nm section of the filter allows for the polymers formed within to become oriented normal to the surface of the AAO filter which was why the majority of the polymer strands are seen exiting the filters all having the same orientation. The thickness of the 20nm layer is only a small fraction of the 200nm layer. The polymer strands, as they exit the filter, are not oriented normal to the plane of the filter which would allow some of the 20nm PO strands to rebundle with its direct neighbors but not with other 20nm polymers from other 200nm pores (Figure 121). Rather than form a single 150nm to 200nm structure, some 200nm wide 20nm bundles could bend toward each other and form the larger 400nm to 500nm structures.

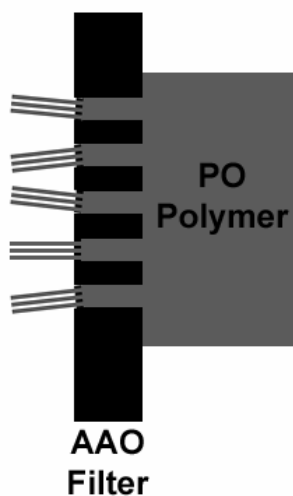


Figure 121. The formation of the structures seen in SEM images of $\text{NH}_4\text{-PtOx}$ in the 20nm porous filters.

The ability for the PO polymeric strands to distort as they exit the filter would lead to a wide range of polymers with varying diameters as seen in the SEM images of the PO $\text{NH}_4\text{-PtOx}$ polymers.

Attempts to polymerize other salts such as **3a**, **3d**, **3g** and **3h** through the 20nm porous AAO filters were made but no PO polymers were visible on the 20nm side of the templates. The lack of visible polymers did not necessarily mean that polymerization of the PO analogues of the bisoxalatoplatinate(2-) salts did not occur since the SEM used to obtain the SEM images in this dissertation had a resolution of about 60-70nm. Any single 20nm wide polymers that formed through the pores and didn't recombine into larger structures would have been 'invisible' to the SEM.

The Mobility of the Potassium and Cobalt bisoxalatoplatinate(2-) salts and Their Investigation Via Scanning Electron Microscopy

During the SEM investigation of some of the bisoxalatoplatinate(2-) salts polymerized through the 200nm porous AAO templates, the most exciting information concerning the mobility of the PO bisoxalatoplatinate(2-) polymers was discovered. It was found that some of the polymeric strands were moving during the scanning process. A polymer only appeared to have movement when the electron beam from the SEM was tightly focused on that particular strand. If the electron beam was imaging a large, wide area at low magnification, the polymers were stationary and no movement was visible.

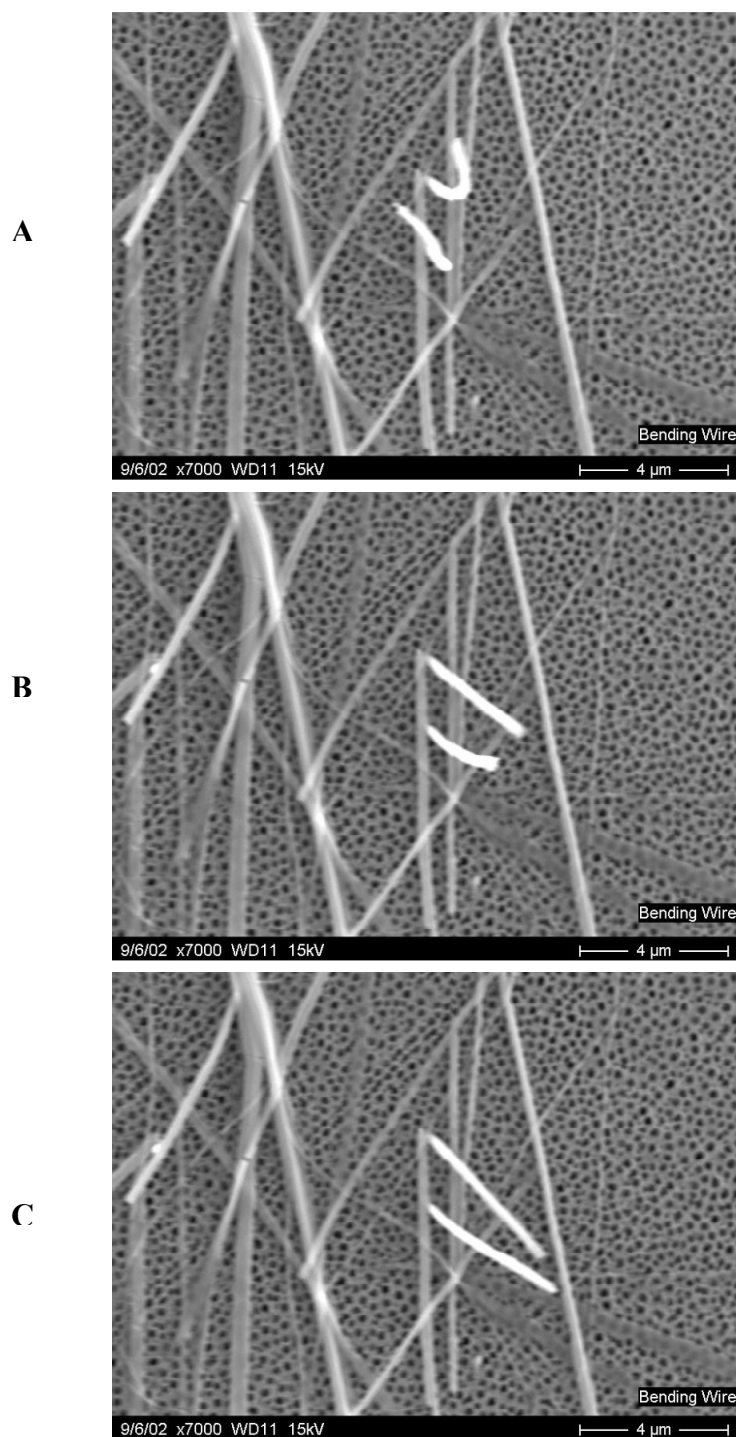
Bending of the PO polymers was observed many times before such as during the capillary experiments discussed in this dissertation, but the reason for the surprise after observing the high mobility of the PO polymer formations under the SEM was that these polymers were now bending on a microscale and nanoscale level. What made this bending even more interesting was that the PO polymer samples were quite old and had been sitting in the open atmosphere from 1 to 2 months. In past macroscale experiments,

any PO polymers that had been exposed to air for that long of a time were completely fragmented and those PO polymers that had not fragmented by that time were usually too fragile to handle. Even though these nanoscale PO polymers had been out of solution for a number of weeks, their stability and flexibility was much greater than that of the macroscale polymers. The movement of these polymers was visible in real-time but, due to limitations of the SEM hardware, only still images of the PO polymer's change in physical orientation were recorded.

Figures 122a, 122b and 122c show two single PO K-PtOx polymeric strands bending during an SEM imaging session.

The 250nm polymeric strands are seen bending 90° over a one and a half minute time period. Both polymers were seen standing normal to the surface of the AAO filter as seen in Figure 122a. As the imaging session progressed, the polymers bent and flattened out on the surface of the AAO filter. The time needed for the 4µm long polymeric strands to completely flatten out was only one minute. After the polymeric strands came to rest on the surface of the AAO filter, no further movement was seen. Another duo of polymers were visible where, instead of both the polymers ultimately coming to rest on the surface of the filter, one polymeric strand oriented itself parallel with the electron beam of the SEM (Figures 123a and 123b).

The two strands visible in Figure 123a and 123b are clearly seen orienting with and against the path of the imaging electrons used during the SEM imaging process. After the image seen in Figure ST34b was taken, no further movement from the PO polymers was visible.



Figures 122a, b and c. The bending of two PO K-PtOx Polymeric strands. The series of photos to a time lapse of the polymers bending over a 1.5 minute period.

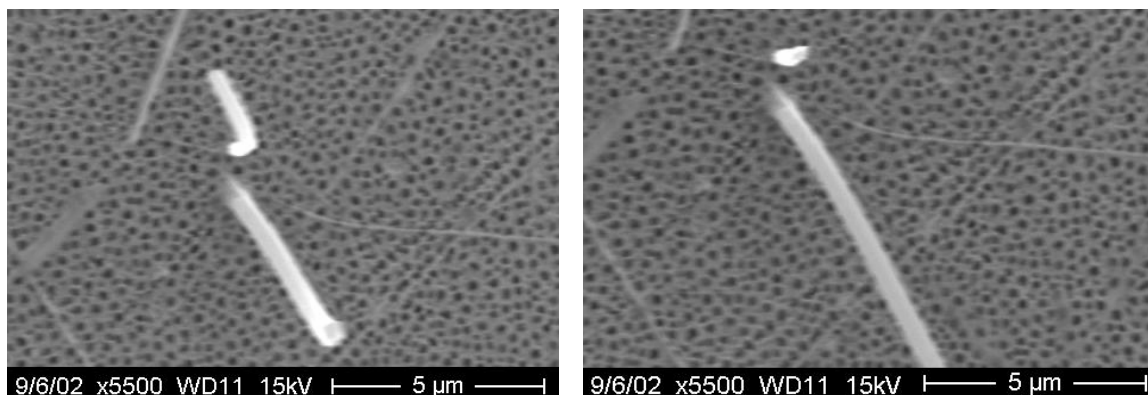


Figure 123a (left) and 123b (right). PO K-PtOx polymers bending during a one minute high resolution imaging session.

Up until this point, the only mobile polymeric strands had been those strands that were only 200nm to 300nm thick, approximately the diameter of one of the nanoporous channels. Larger structures, such as polymeric formations that were thicker than 300nm or those PO formations that contained more than one polymeric strand were never seen bending. Other PO polymer salts of bisoxalatoplatinate(2-) were found to be affected by the SEM during the imaging process. As previously stated, certain samples of the PO Ni-PtOx polymers were essentially pushed off the surface of the AAO filter by the electron beam during various imaging sessions. The most notable however, was a rather large sample of PO Co-PtOx that had exited multiple, 200nm channels of an AAO filter.

Figure 124 shows the end of a large, 1.3μm thick section of a PO Co-PtOx polymeric formation. During acquisition of this image, the large polymer bundle, which was a nearly linear polymeric formation, began curving. Because data acquisition takes a number of seconds to complete, a ‘doubly exposed’ image was seen. This formation

contained at least 3 different Co-PtOx polymeric strands but was still able to distort. After witnessing the bending and distortion of a variety of PO bisoxalatoplatinate(2-) salts, it was determined that the nanoscale polymeric strands of these compounds were much more robust than their macroscale analogues.

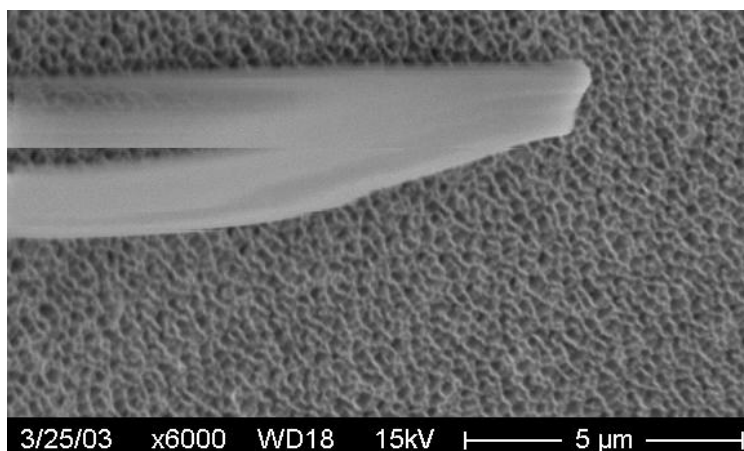


Figure 124. A 1.3 μ m thick Co-PtOx polymeric formation that bent during an image acquisition.

Why the polymers distorted when imaged via SEM at high resolution was not clearly understood. SEM imaging consists of bombarding a sample to be imaged with high energy electrons and then measuring the electrons that exit the sample and any other electrons that are ejected from the sample as well. The most likely explanation as to why the polymers distort is that the electrons from the SEM's electron gun cause ionization of polymers as well as the AAO surface around it. These ionization and charging effects would cause a reorientation of the platinum complexes within the polymers. The polymeric chains contained within the strands would begin to repel one another and the overall strand could be attracted or repelled by the surface of the AAO filter.

The reason for the bending at high resolution rather than at low resolution would be due to the fact that the polymers are bombarded by many more high energy electrons per square nanometer when imaged at a high resolution. There are probably distortions and bending that occur when the PO polymers are imaged at low resolution but they are just too subtle to witness.

Bulk Polymerization of the Manganese and Guanidinium bisoxalatoplatinate(2-) salts and Their Investigation Via Transmission Electron Microscopy (High Resolution Images)

One of the main goals of the templated growth of the PO polymers was to see how thin the polymers could possibly form. It was shown that individual polymer strands could be made to polymerize in and conform to whatever sized templates they were exposed to. No matter if the polymerization templates were macroscale or nanoscale in diameter, the PO polymers would adjust their diameter in order to pass through. During the SEM imaging of the various bulk polymerized, PO bisoxalatoplatinate(2-) salts it was noticed that the PO polymeric strands polymerized having nanoscale diameters without the use of any templates. It was thought that maybe the PO polymers could form even thinner than what had been seen while SEM imaging. The scanning electron microscope used to obtain the images in this dissertation had a limited resolution. PO polymers having diameters of 60nm or higher were visible but any formations or structures that had dimensions lower than that were not. A different higher resolution imaging technique would be needed to obtain images of even smaller polymers if they existed at all.

Transmission electron microscopy (TEM) was employed as an alternative to SEM imaging. Much like SEM, TEM also uses high energy electrons to image samples but

instead of measuring scattered electrons, the electrons that pass through the sample are collected and recorded. In order for enough electrons to be collected by the TEM, the samples to be imaged must be fairly thin as to allow enough electrons to pass through. The images are opposite in color than that of the SEM images. Instead of the dark areas being portions of a sample that contain no material and the white areas being portions of the sample that diffract the imaging electrons, the opposite is true.

The preparation of the samples is slightly different as well. Instead of coating the samples with a thin layer of conductive material, the samples are placed in solution and adhered to a very fine copper wire mesh screen. The one benefit of TEM over SEM is the fact that TEM has a theoretical resolution up to 5 picometers. Although, the theoretical resolution of 5 picometers has never been reached, images containing structures as small as 1nm are easily recognizable.

Both the PO guanidinium (Guan-PtOx) and manganese (Mn-PtOx) salts of bisoxalatoplatinate(2-) were chosen for TEM imaging. Due to the TEM's limitation concerning the need for sample to have a very small thickness, images of the polymers within the AAO filters could not be had. However, images of the bulk electrolyzed polymers could be obtained and from that it could be seen if the PO polymers naturally form having small diameters during the bulk electrolysis process.

The initial sample imaged was a small amount of bulk polymerized Guan-PtOx. Figure 125 shows the first image obtained for that sample. From the initial image obtained, it was found that the PO polymers formed smaller polymeric strands than what was previously believed. All PO polymer strands in that section of the sample grid had

diameters of 70nm or less. Conversely, the smallest PO polymer visible during SEM imaging was measured to be 70nm wide.

The polymers in Figure 125 appeared to have been fractured. This most likely occurred during the preparation of the sample for TEM imaging. No surface information about the PO polymers was had from Figure 125 due to the samples being fairly thick and of heavy metal content which limited the amount of electrons that passed through them which is why the polymeric strands appear so dark in color.

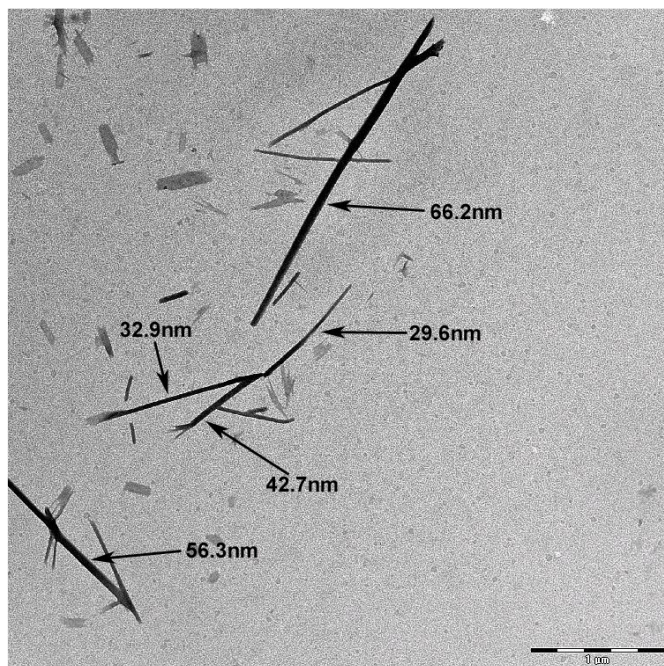


Figure 125. A sample of Guan-PtOx polymers that were visible during a TEM imaging session.

Other, lighter colored material is visible in Figure 125. It is unknown whether this material is other PO guan-PtOx polymers that are less thick in diameter or some other contaminant such as unoxidized **3f**.

From the TEM image in Figure 125, it seemed that the PO polymers formed

having very thin diameters without any outside influence. It was now realized that the PO polymers most likely had polymerized through the 20nm pores within the AAO filters but were just unimagable by the SEM. The SEM images of other PO polymers show that formations having diameters of 500nm or higher consisted of multiple PO polymeric strands having diameters of 200nm to 300nm wide. From the TEM images, these smaller strands appeared consist of many, even thinner polymeric strands. Figure 126 shows a large, single 289.5nm wide polymeric strand of the PO Guan-PtOx polymer.

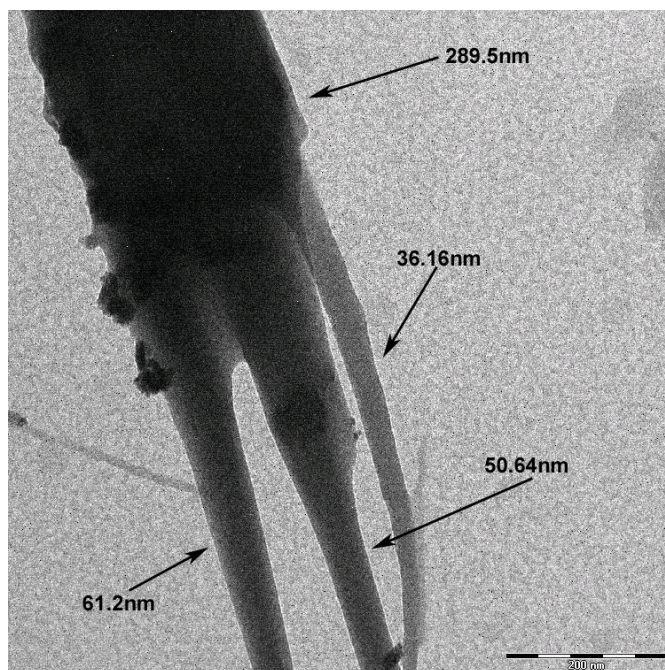


Figure 126. Guan-PtOx large strand containing smaller tendrils.

This single strand was branched into about three smaller strands having diameters ranging from 36.16nm up to 61.2nm wide. The polymeric strand having a diameter of 50.64nm was an offshoot of another, even wider polymeric strand having a diameter of nearly 75nm. The polymeric strands were poorly defined compared to the 200nm or

larger polymeric strands seen in the SEM images. The small polymers visible in the TEM images were also less uniform than their much larger parent polymeric strands. The polymeric strands seen in the SEM images were all around 250nm to 350nm wide and all had complete flat top surfaces. The smaller polymeric formations were not completely uniform in diameter and the ends of the polymeric strands seemed to polymerize down to a point a couple of nanometers wide.

In a sample of Mn-PtOx formed from the bulk polymerization process, a large polymeric formation was observed splitting into a number of smaller polymeric strands which is shown in Figure 127. The main polymeric formation showed a diameter of 308.55nm. The smaller polymeric strands were measured as having thicknesses of 42nm to 31nm wide. Some of the smaller polymeric strands actually seemed to be bundled together to form larger formations that were around 100nm to 200nm across. About 20 different 30nm to 40nm polymeric strands were found to compose the larger, 300nm polymeric formation.

Another sample of the PO Guan-PtOx polymer shown in Figure 128, contained a very large polymeric formation consisting of a number of smaller polymeric strands. This formation seemed to be less dense than the other formations that were visible in the SEM images. All the polymeric strands were below 200nm wide as well. What made this image so interesting was that a damaged section of the polymeric formation was visible which is pointed out in Figure 128.

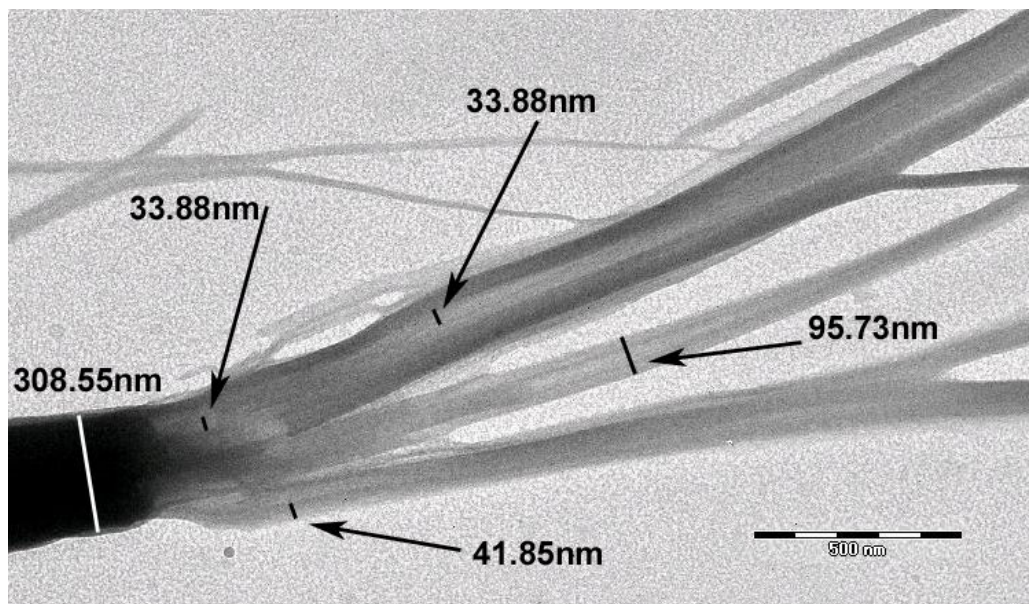


Figure 127. Mn-PtOx PO polymer formation visibly unraveling into smaller constituents.

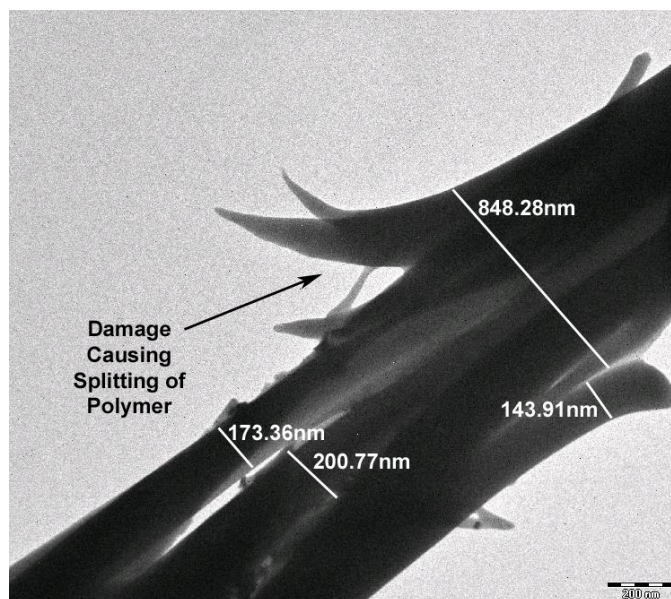


Figure 128. Guan-PtOx formation consisting of smaller Guan-PtOx strands. Damage to the main PO formation is visible .

This damaged section started off as an 185nm strand. Mishandling of the sample prior to TEM imaging seemed to have caused this section of the polymer to peel away from the main formation. Due to its increased transparency, the split section of polymer appeared to get thinner as it traveled further away from the main body of the PO Guan-PtOx formation. This image also supports the theory of the bundling of polymeric strands which form the larger PO formations seen earlier SEM images.

Of the large scale images observed during the various TEM imaging sessions the image of the partially oxidized manganese salt, Mn-PtOx, in Figure 129 yielded more data. The main structure was calculated as having a diameter of 112.4nm. This polymeric structure seemed to consist of a large majority of very thin PO polymeric strands. As pointed out in Figure 129, a large mass of what appeared to be unbound polymer strands was visible. Some of these strands appeared to still be attached to the larger polymer formation as transparent, thus thinner, polymeric strands which were visible along the sides of the main shaft of the larger polymeric formation. These thin polymers were measured as having diameters approximately 20nm to 30nm wide.

Why these polymers unraveled from the main structure is unknown but it may have to do with the fact that the polymers were placed in an aqueous solution before they were placed on the surface of the copper wire TEM sample holder. The polymers are salts which are known to decompose in water over time. Although the polymers are thought to be insoluble in water, it may just be that the polymers are slightly soluble and would begin to slowly dissociate once placed in solution.

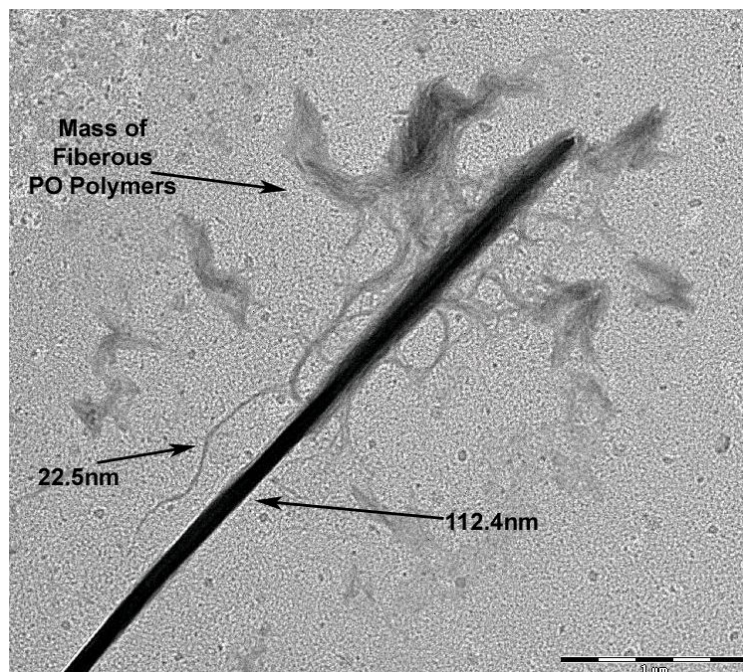


Figure 129. Mn-PtOx formation where smaller polymeric strands were seen.

Bulk Polymerization of the Manganese and Guanidinium bisoxalatoplatinate(2-) salts and Their Investigation Via Transmission Electron Microscopy (High Resolution Images)

Although the polymers imaged thus far were much smaller and thinner than what had been previously seen for those same PO polymers in past experiments, it was remembered that the main purpose for the TEM analysis of the PO polymers was to see how thin the polymers could form without any outside influence. Therefore, a search for even thinner polymers was made.

Ultra-thin PO formations were observed in both samples of Guan-PtOx and Mn-PtOx. Figure 130 shows one section of a Guan-PtOx sample that had been bulk polymerized. In this image, various sections of the polymeric formation appeared very thin due to their almost transparent appearance. A number of larger structures were observed, but amongst those formations, two very small structures were also visible.

The two formations which appeared to be branched from another, larger polymeric strand, were measured as having diameters under 5 nanometers.

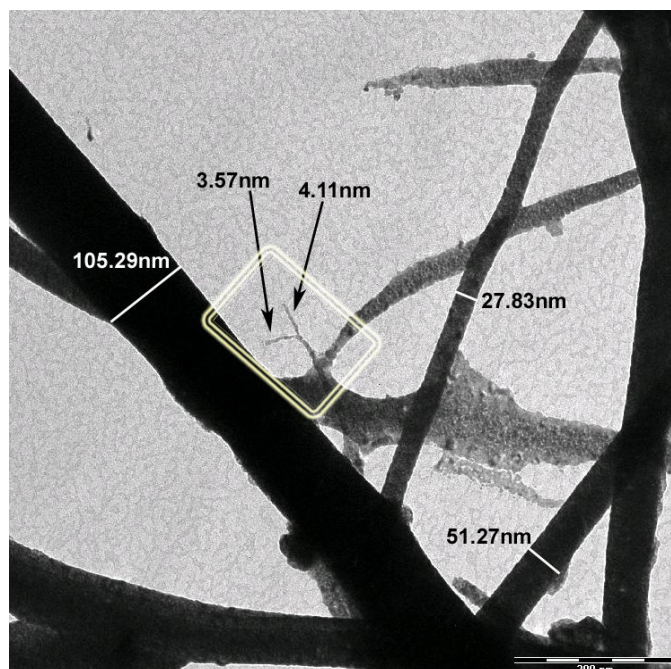


Figure 130. Guan-PtOx ultra-nanoscale formations.

The two thin polymeric formations did not seem to be the most dominant sized structures within the Guan-PtOx samples which were much larger on average. As for the Mn-PtOx samples, a large amount of ultra-thin nanopolymers were imaged.

Figure 131 shows an intertwined section of PO Mn-PtOx polymers that had formed a web shaped pattern. What was interesting about the image seen in Figure 131 was that the majority of the polymeric material was very thin. All of the ultra-thin polymeric material was very transparent, which would support the fact that the formations were all very thin. The diameters of these polymers were 10nm or less on

average. The ratio of the length versus the width of these polymeric formations was quite high and some of the polymeric formations were measured as having a length of over 600nm.

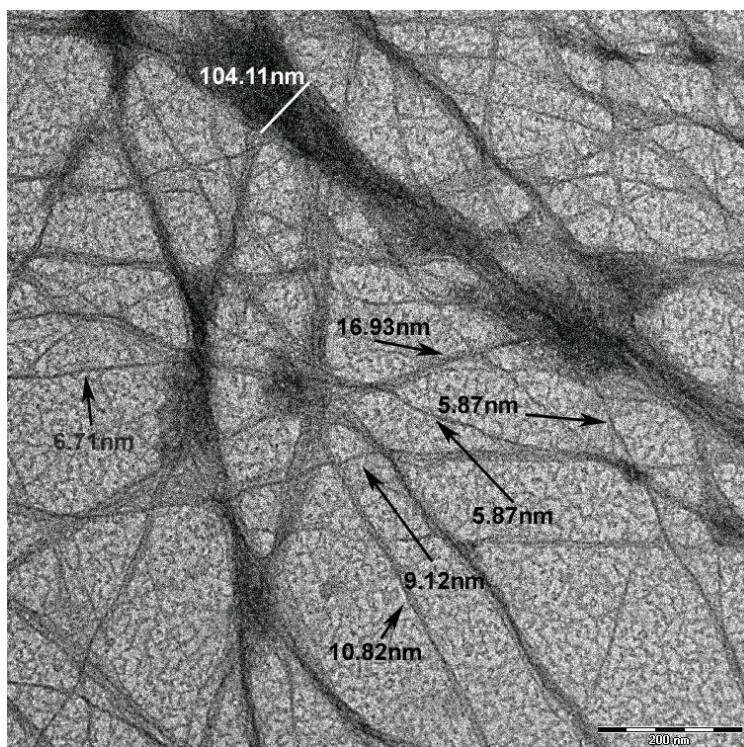


Figure 131. Mn-PtOx Ultra-thin Polymeric formations.

The TEM imaging of these very fine structures proved that the PO polymers could form having very small diameters without any outside influences. It was also shown that, with the aid of nanochanneled AAO filters, the polymeric formations could be directed to form in certain areas and the larger 200nm wide and higher polymeric formations could be purposely reduced in size. Although, it was hoped that the PO polymer formations could be polymerized so that only one platinum chain was present in the polymer, no evidence was found that supported or quenched that hope.

Calculations of the Actual Number of Platinum Atoms within the PO Polymeric Strands as seen in the SEM and TEM Images

As stated previously, it was hoped that the polymerization experiments performed and their subsequent imaging would yield polymers that contained only a single platinum chain rather than a large collection of platinum chains. Although that scale of polymerization was never reached, very fine ultra-thin polymers were formed. Even though, these polymers did not contain a single platinum chain, some rough calculations showed that the visible polymer formations contained a very limited number of individual platinum chains.

Table 21 shows the crystallographic data for the K-PtCN⁶⁶, K-PtOx⁶¹, Co-PtOx⁶⁷, Mn-PtOx³⁰, Ni-PtOx³⁰, Zn-PtOx⁶⁸ and Mg-PtOx⁶⁹ PO polymers which were studied in this dissertation via AFM, SEM and TEM. There were no crystallographic data available for the Na-PtOx, NH₄-PtOx and Guan-PtOx polymers.

PO Compound [chain axis]	Crystal System	A (Å)	B (Å)	C (Å)	α°	β°	γ°
K-PtCN [c]	Triclinic	10.360	9.303	11.832	77.57	114.74	73.64
K-PtOx [b]	Triclinic	9.749	11.403	10.694	99.54	115.81	102.32
Co-PtOx [c]	Orthorhombic	14.379	16.501	5.682	90.00	90.00	90.00
Mn-PtOx [c]	Orthorhombic	16.790	14.280	5.670	90.00	90.00	90.00
Ni-PtOx [c]	Orthorhombic	16.400	14.350	5.650	90.00	90.00	90.00
Zn-PtOx [c]	Orthorhombic	16.520	14.360	5.665	90.00	90.00	90.00
Mg-PtOx [c]	Orthorhombic	16.560	14.270	5.700	90.00	90.00	90.00
Na-PtOx	No Data Available			No Data Available			
NH ₄ -PtOx	No Data Available			No Data Available			
Guan-PtOx	No Data Available			No Data Available			

Table 21. Crystallographic Data for the PO polymers imaged via AFM, SEM and TEM.

The orthorhombic unit cells (Figure 132) for the PO polymers formed from the cobalt, manganese, nickel, zinc and magnesium salts of bisoxalatoplatinate(2-) are isostructural. A single chain of the PO PtOx anions occupies each corner of the unit cell and another full chain occupies the center of the cell. These chains run along the 'c' axis of the orthorhombic cell.

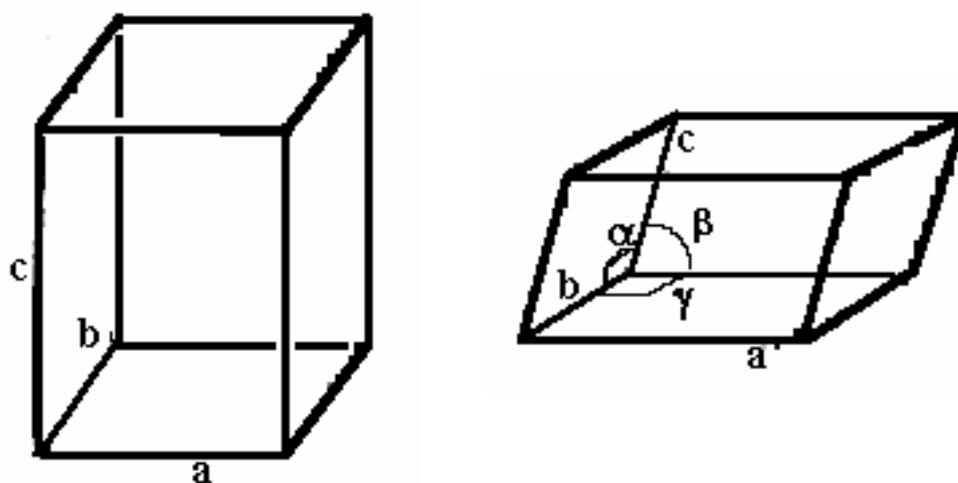


Figure 132. Orthorhombic (left) and Triclinic (right) unit cells.

The potassium salts of both the PtOx and PtCN anions have a triclinic unit cell structure where the anionic platinum chains occupied all four corners of the cell. In the case of K-PtCN, the polymers polymerized along the 'c' axis and for K-PtOx, the polymers polymerized along the 'b' axis. From the crystallographic data, the area or 'footprint' of the PO polymer's unit cells could be calculated. Using the areas calculated from the unit cells and the diameters of the polymeric formations measured, a rough

estimation of the number of individual anionic polymeric chains was calculated.

Table 22 shows the calculated values for the areas and volumes of the various PO polymer salts. Calculating the area of a surface on the orthorhombic cell consisted of multiplying the two lengths of the sides together. In this case, sides 'a' and 'b' were multiplied to give the areas. For the area of a side of a triclinic cell, the two sides had to be multiplied along with the sine of the angle between them. In the case of K-PtCN, sides A and B were multiplied along with the sine of angle gamma. For K-PtOx, sides A and C were multiplied along with the sine of angle beta.

PO Compound [chain axis]	Polymer Chains Per Unit Cell	Footprint Area (nm ²)	Volume (nm ³)
K-PtCN [c]	1	0.925	1.456
K-PtOx [b]	1	0.939	1.890
Co-PtOx [c]	2	2.373	1.348
Mn-PtOx [c]	2	2.398	1.359
Ni-PtOx [c]	2	2.353	1.330
Zn-PtOx [c]	2	2.372	1.344
Mg-PtOx [c]	2	2.363	1.347
Na-PtOx	No Data Available		
NH ₄ -PtOx	No Data Available		
Guan-PtOx	No Data Available		

Table 22. Area and Volume data for the PO polymers imaged via AFM, SEM and TEM.

Finding the exact areas for the surfaces of the PO polymers was not possible. Blurring of the SEM images yielded figures where the edges of the surfaces of the PO polymers were not well defined and as for the TEM images, the only one surface of the polymeric formations was visible. Figure 133 shows a very large and nearly square

column of K-PtOx polymer. Assuming that the top of the polymeric column was rectangular in shape, the area of that surface was found to be $608,598\text{nm}^2$. A smaller column was visible just to the right of the larger column and its square-topped surface was found to have an area of $20,023\text{nm}^2$.

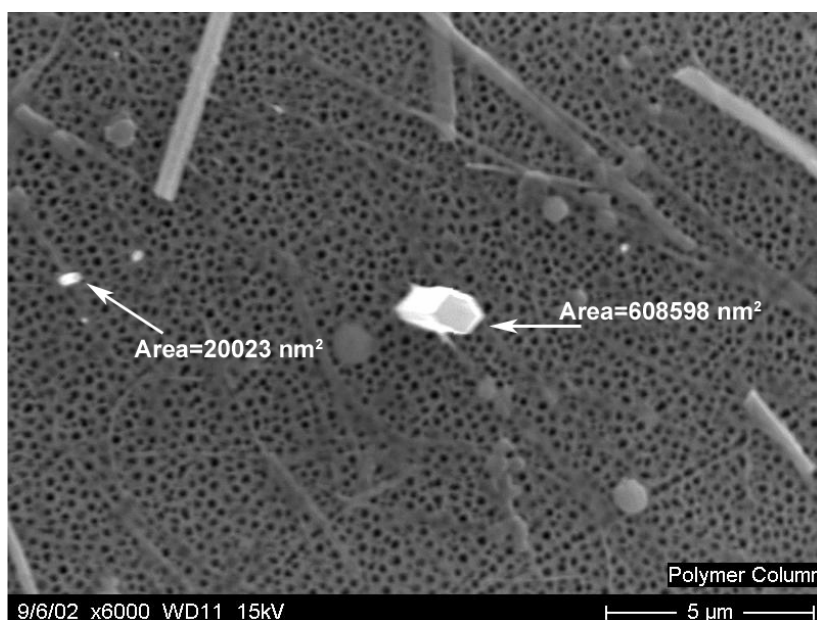


Figure 133. Large PO K-PtOx polymeric formation along with a smaller PO K-PtOx formation. Top surface areas are listed in the figure.

Simply dividing the surface area of the polymeric formations by the unit cell footprint for the corresponding PO platinum salt gave the number of individual anionic platinum chains contained within the structure. In the case of the salts containing cations other than potassium, the calculated value needed to be multiplied by two in order to account for the extra, complete polymeric chain contained within the unit cell.

The number of anionic PO bisoxalatoplatinate chains calculated for the large formation in Figure 133 was found to be 648,134. For the small formation, the number

was 21,324 anionic chains. These two polymeric formations were amongst the largest observed during the imaging sessions and contained more anionic chains than the target of a single chain.

As shown before, the majority of polymeric formations observed during the electron imaging sessions were much smaller than the structure in Figure 133. The K-PtCN polymeric formations visible in Figures 96 and 98 were not square but more circular in shape due to their formation within the AAO filters. The approximate areas of a number of these polymers were calculated, three of which are shown in Figure 134.

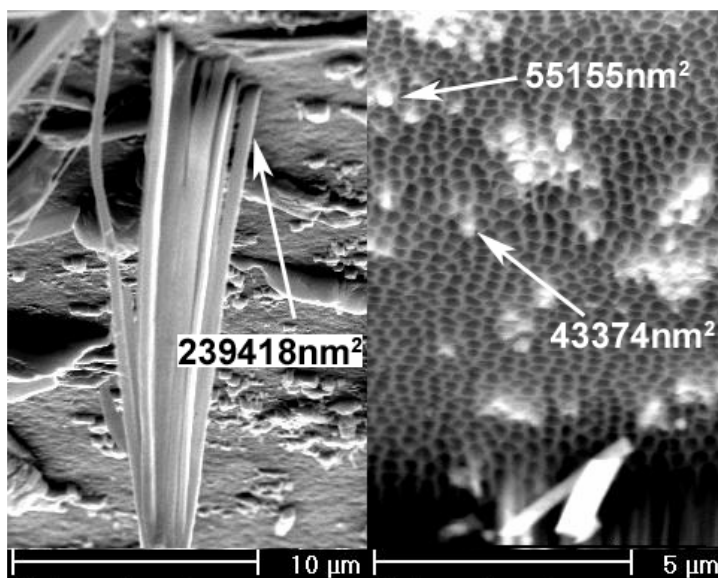


Figure 134. The polymeric formations of K-PtCN and their area calculated from the assumption that the polymers were circular in shape.

The large K-PtCN polymers observed extended off of the surface of the 200nm porous AAO filters (the left half of Figure 134) was calculated as having an area of $239,418\text{nm}^2$ and contained 258,830 individual PtCN anionic chains. The right half of Figure 134 illustrated two K-PtCN polymer formations that were still contained within

the 200nm pores. The areas of these two formations were found to be 55,155nm² and 43,374nm² which contained 59,627 and 46,891 individual PtCN anionic chains. Again, the number of anionic platinum chains was much larger than the goal of a single polymeric chain. Focusing on the other PO salts of the bisoxalatoplatinate anion, a number of the smallest formations for these salts were measured and the results for the number of anionic chain per sample are shown in Table 23.

PO Compound	Diameter of Smallest Formation (nm)	Area of Formation (nm ²)	Number of Anionic Chains
Zn-PtOx	1775	2474495	2086182
Mg-PtOx	361	102354	86626
Ni-PtOx	332	86570	73570
Co-PtOx	176	24328	20507

Table 23. The number of anionic chains per PO polymer formation.

It was calculated that the cobalt salt contained the thinnest polymeric strands. PO polymeric formations of that salt contained 20,507 individual anionic chains on average. The zinc salt was determined to contain the largest of the PO structures. The smallest of these structures contained the most having 2,086,182 individual anionic chains. Circular diameters were used for calculation the areas of the cobalt, nickel and magnesium salts whereas the area of the surface of the zinc salt was calculated as if it were square. As stated before, no crystallographic data was available for the sodium or ammonium salts of the PO PtOx formations so no calculations could be performed for those structures.

During the TEM imaging of the Guan-PtOx and Mn-PtOx PO polymers, much smaller polymeric formations were seen. These polymeric formations were also found to

contain few individual anionic chains. Since Guan-PtOx was a newly formed PO polymers, no crystallographic data was available which caused the focusing of attention on the manganese salt, Mn-PtOx. An enlargement of one of the 5.87nm Mn-PtOx strands is shown in Figure 135.

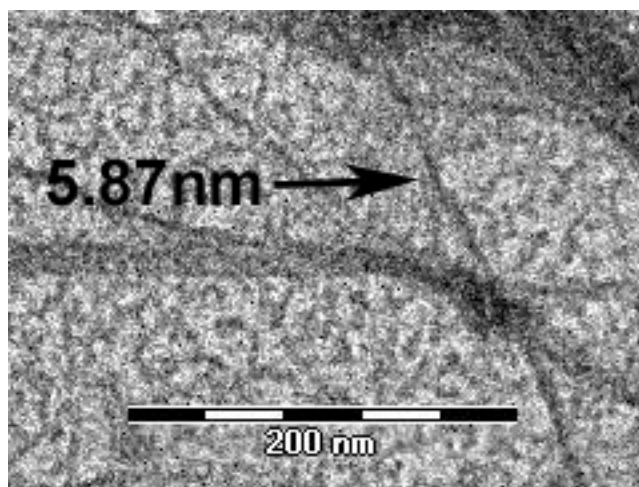


Figure 135. The smallest polymeric formation seen for all the PO platinum polymeric salts: A 5.87nm thick, Mn-PtOx strand.

This strand, which was assumed as being square in shape was measured as having a thickness of 5.87nm which would mean the area of a two dimensional slice of this polymer would be 34.46nm^2 . It was found that there would be 30 to 32 individual anionic polymeric chains within that structure.

As one can see, the goal of a single anionic platinum polymeric chain was not reached but significant progress was made from the discovery that the PO polymers formed extremely small structures having very thin diameters. Those discoveries showed that reducing the size of the PO polymers down a single anionic chain, along with the appropriate counter cation, was still a possibility.

CHAPTER 4

SUMMARY AND CONCLUSIONS

The metal-metal interactions between a variety of platinum(II) based complexes have been investigated. Based upon the findings by previous workers, it was thought that an unknown polymeric red platinum compound formed at a temperature higher than the highly studied dimeric Tetrapyrophosphitodiplatinate(2-), was in fact just a derivative of that compound. A number of structures were made based on NMR data and elemental analyses of the red compounds. The data obtained during the course of this research have shown that those structures could not be correct due to the fact that they were based on faulty assumptions concerning the NMR data. Light scattering data obtained from the red compound has shown that the compound is most likely a collection of polymeric chains with varying chain lengths. Having an impure solution of the red compound which contained many differently sized polymers would give incorrect elemental analysis results as well.

The synthesis of pyrophosphorus acid, the ligand present in the Tetrapyrophosphitodiplatinum(II) compound and also a proposed ligand thought to be present in the red compound, has been simplified and perfected to a greater extent. It was found that pyrophosphorus acid was very water sensitive and, contrary to cited references, air could be present during its synthesis or instantaneous decomposition would occur.

Pyrophosphorus acid was found to be nearly insoluble in virtually every solvent

except ether and THF, but highly reactive with a variety of alcohols. Reaction of pyrophosphorus acid with these alcohols yielded a relatively new and simple method for the synthesis of monoalkylated phosphorus acids. These monoalkylated acids could be dehydrated to form dialkylated pyrophosphorus acid and used as ligands for platinum(II), potentially making a complete set of novel platinum(II) dimeric compounds.

Further studies of platinum metal-metal interactions were obtained by studying the platinum-platinum interactions within the PO platinum polymers. The PO polymerization characteristics of various bisoxalatoplatinate(2-) and tetracyanoplatinate(2-) salts were distinguished. These polymers were formed using an electrochemical polymerization method. It was found that the polymers, when formed in bulk, would polymerize from the anode toward the cathode but never completely reach or attach to the cathode. The lack of polymer formation around the cathode was probably due to high concentrations of hydroxide anion formed at the cathodic surface.

It was found that the partially oxidized polymers formed off of virtually any conductive surface. Scanning tunneling microscopy was attempted on samples polymerized off of these various conductive surfaces but it was found that the polymers were not in the proper orientation to be imaged.

Electrolysis of the partially oxidized polymers was performed in narrow capillary tubes in order to force the polymers to form in a more uniform fashion. It was found that as the linear partially oxidized polymers formed, they were very mobile and able to transverse tight corners when distortions were made within the capillary tubes. It was found the rate a polymerization was independent of the diameter of the capillary tube

used until the diameter was decreased to 380 μ m. After that point, the polymerizations took one to two days longer to complete.

Various salts of bisoxalatoplatinate(2-) were synthesized and polymerized via electrochemical methods instead of the more common chemical oxidation method. It was during that time that the new partially oxidized guanidinium bisoxalatoplatinate polymer was formed. Also, in an attempt to enlarge the cation associated with the bisoxalatoplatinate anion, a new unoxidized salt containing potassium encased in an 18-crown-6 molecule was made, crystallized and its structure elucidated.

Atomic force microscopy was used to investigate the surface features of bulk polymerized partially oxidized salts. It was found that the large formations visible to the naked-eye were in fact made up of bundles or rope-like structures of polymeric strands. Scanning electron microscopy supported that assessment and it was found that the partially oxidized polymers synthesized from tetracyanoplatinate(2-) formed much thicker structures than those of bisoxalatoplatinate(2-).

It was found that the partially oxidized polymers self-regulate their diameters in order to pass through channels much smaller than the thickness of the polymeric strands. Anodically grown aluminum oxide filters (AAO) which contained a variety of differently sized nanochannels were used as templates for the polymerization of the partially oxidized platinum polymers. A membrane holder and electrolysis device was built in order to simplify the handling of the AAO filters and overcome issues concerning the formation of the polymers within those filters.

SEM imaging proved that the partially oxidized platinum polymers could reduce

in diameter to pass through narrow, 200nm channels as well as 20nm channels. During SEM analysis, it was found that the 'fragile' PO polymers extending from 200nm channels had a high degree of flexibility even after being exposed to air for a number of months.

It was found, with the aid of transmission electron microscopy, that the partially oxidized polymers were able to form even smaller than what had previously been thought. Polymers having diameters of 5nm and less were imaged and calculations of the number of individual anionic platinum chains were made where it was found that polymeric formations containing 42 to 43 individual platinum anionic chains were formed without any outside influence.

The possibilities in forming platinum compounds that can absorb and emit a variety of wavelengths of light, have metal or semiconductor-like properties or have differing structural properties depending on the metal-metal distance within the platinum containing complexes is very feasible and could possibly be tailored to perform such tasks.

APPENDICES

APPENDIX ACOMPLETE CRYSTALLOGRAPHIC DATA
FOR $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

<u>Data Collection</u>	
Diffractometer Used	Siemens R3m (P4 upgrade)
Radiation	MoK α (λ = 0.71073 Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2 θ Range	4 to 55 $^{\circ}$
Scan Type	2 θ - θ
Scan Speed	Constant; 10 $^{\circ}$ /min. in ω
Scan Range (ω)	0.9 $^{\circ}$ plus K α -separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	-5 $\leq$ h $\leq$ 13, -3 $\leq$ k $\leq$ 10 -28 $\leq$ l $\leq$ 28
Reflections Collected	5879
Independent Reflections	4291 (R_{int} = 0.030)
Observed Reflections	2300 ($I > 3\sigma(I)$)
Absorption Correction	Face-indexed numerical
Min./Max. Transmission	0.386 / 0.853

Table 24. Data Collection Parameters for (KC₁₂H₂₄O₆)₂Pt(C₂O₄)₂

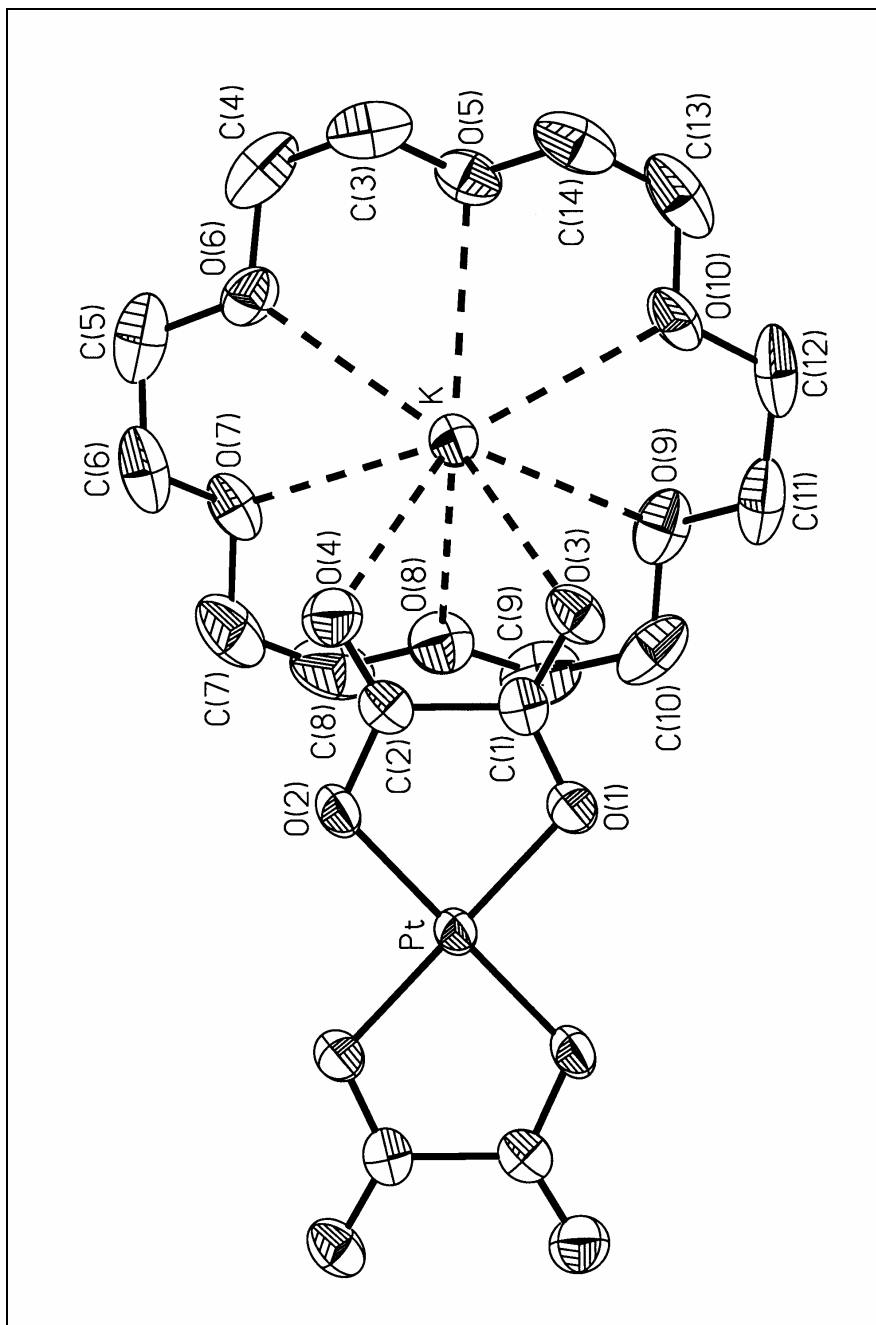


Figure 136. ORTEP Structure for $(KC_{12}H_{24}O_6)_2Pt(C_2O_4)_2$

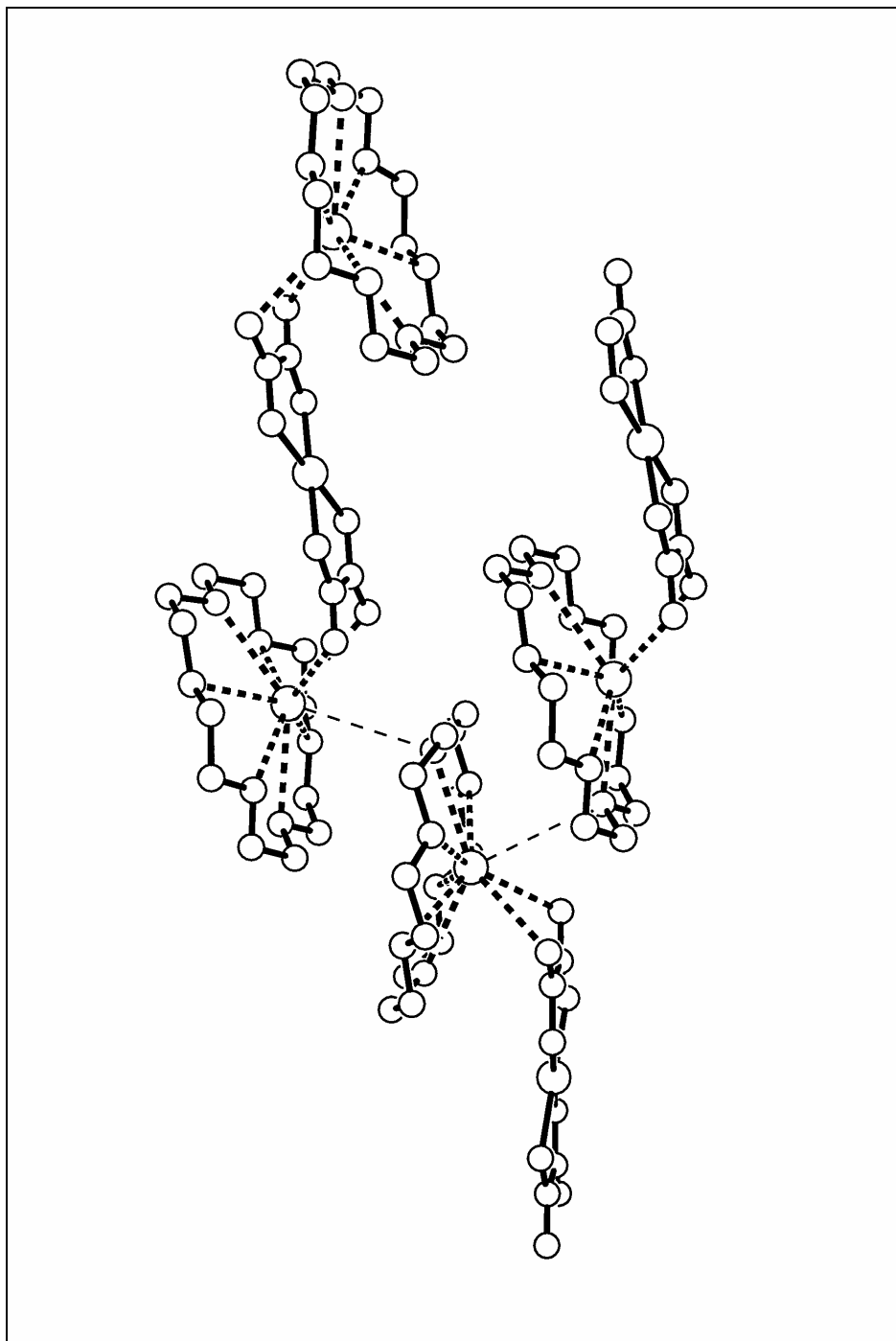


Figure 137. Unit Cell of $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

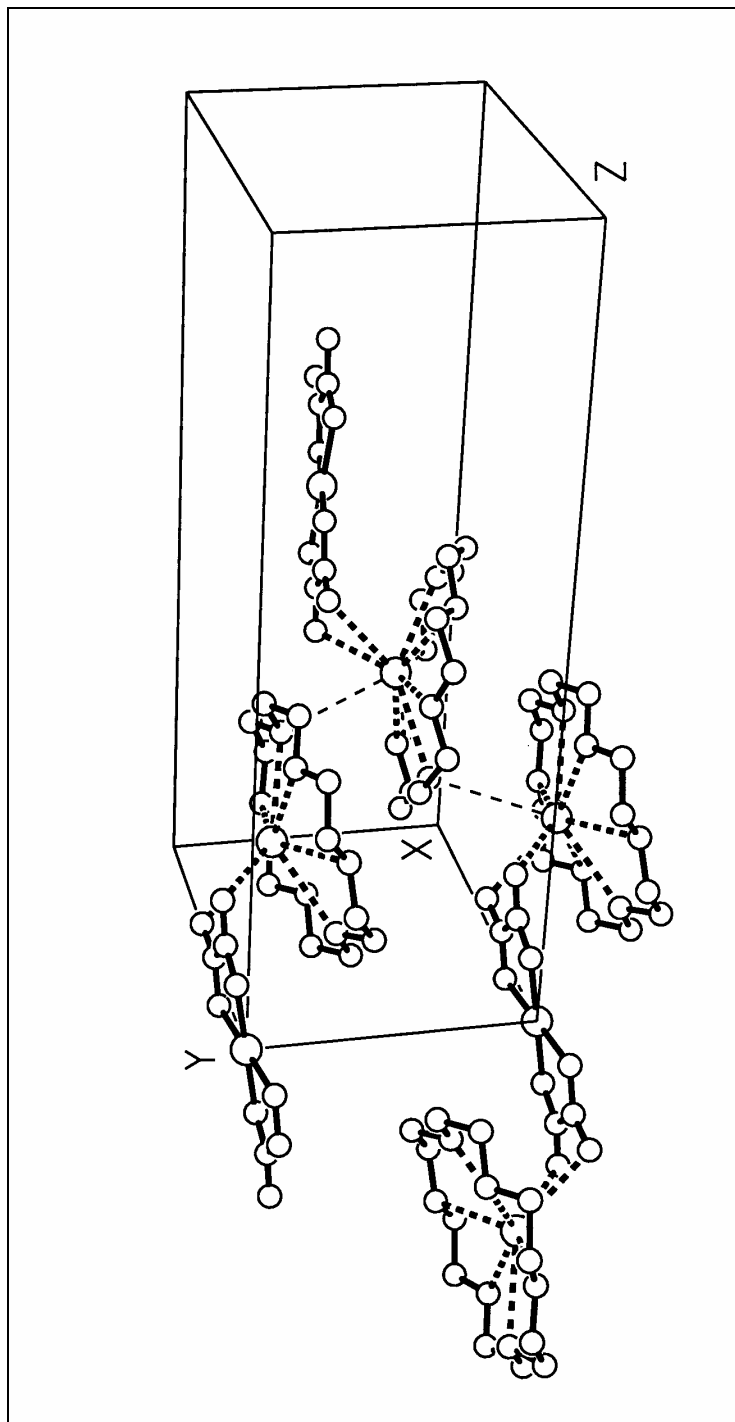


Figure 138. Unit Cell Packing for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

Solution and Refinement -----	
System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Patterson Heavy Atom
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	9 reflections excluded
Hydrogen Atoms	Riding model, common isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0015F^2$
Number of Parameters Refined	233
Final R Indices (obs. data)	R = 0.050, wR = 0.059
R Index (all data)	wR = 0.082
Goodness-of-Fit	1.03
Largest and Mean Δ/σ	Less than 0.0005
Data-to-Parameter Ratio	9.9:1
Largest Difference Peak	4.51 eÅ ⁻³
Largest Difference Hole	-1.29 eÅ ⁻³

Table 25. Solution Refinement Data for (KC₁₂H₂₄O₆)₂Pt(C₂O₄)₂

STRUCTURE DETERMINATION SUMMARY	
<u>Crystal Data</u>	
Empirical Formula	C ₂₈ H ₄₈ O ₂₀ K ₂ Pt
Color; Habit	yellow parallelepiped
Crystal size (mm)	0.02 x 0.16 x 0.22
Crystal System	Monoclinic
Space Group	P2 ₁ /c
Unit Cell Dimensions	$\underline{a}$ = 10.703(1) Å $\underline{b}$ = 7.811(1) Å $\underline{c}$ = 22.355(2) Å β = 92.493(7) ^o
Volume	1867.1(3) Å ³
Z	2
Formula weight	489.0
Density(calc.)	1.740 g/cm ³
Absorption Coefficient	4.060 mm ⁻¹
F(000)	984

Table 26. Structural Summary for (KC₁₂H₂₄O₆)₂Pt(C₂O₄)₂

Table 1. Atomic coordinates and equivalent isotropic displacement coefficients ($\text{\AA}^2$)

	x	y	z	U(eq)
K	0.3603 (2)	-0.1717 (3)	0.1778 (1)	0.041 (1)
Pt	0	0	0	0.031 (1)
O(1)	0.0088 (6)	0.036 (1)	0.0889 (3)	0.038 (3)
O(2)	0.1823 (6)	0.045 (1)	0.0077 (3)	0.038 (3)
C(1)	0.122 (1)	0.045 (1)	0.1110 (4)	0.031 (3)
C(2)	0.225 (1)	0.052 (1)	0.0638 (4)	0.033 (3)
O(3)	0.1521 (8)	0.050 (1)	0.1637 (3)	0.043 (3)
O(4)	0.3336 (7)	0.069 (1)	0.0799 (4)	0.050 (3)
O(5)	0.5409 (8)	-0.245 (1)	0.2787 (3)	0.046 (3)
C(3)	0.656 (1)	-0.171 (2)	0.2661 (6)	0.060 (5)
C(4)	0.702 (1)	-0.243 (2)	0.2108 (7)	0.060 (6)
O(6)	0.6190 (9)	-0.208 (1)	0.1606 (4)	0.044 (3)
C(5)	0.666 (1)	-0.259 (2)	0.1058 (7)	0.062 (5)
C(6)	0.566 (1)	-0.228 (2)	0.0584 (5)	0.061 (5)
O(7)	0.4643 (8)	-0.332 (1)	0.0701 (3)	0.047 (3)
C(7)	0.374 (2)	-0.328 (2)	0.0220 (5)	0.062 (5)
C(8)	0.263 (2)	-0.432 (2)	0.0377 (6)	0.069 (5)
O(8)	0.2052 (8)	-0.357 (1)	0.0883 (3)	0.050 (3)
C(9)	0.101 (1)	-0.453 (2)	0.1062 (7)	0.060 (5)
C(10)	0.041 (1)	-0.367 (2)	0.1574 (6)	0.058 (5)
O(9)	0.1264 (8)	-0.363 (1)	0.2075 (4)	0.053 (3)
C(11)	0.078 (1)	-0.270 (2)	0.2556 (6)	0.062 (5)
C(12)	0.163 (1)	-0.292 (2)	0.3088 (6)	0.059 (5)
O(10)	0.2821 (9)	-0.218 (1)	0.2972 (3)	0.047 (3)
C(13)	0.369 (2)	-0.250 (2)	0.3435 (6)	0.067 (6)
C(14)	0.492 (2)	-0.167 (2)	0.3315 (5)	0.060 (5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 27. Atomic Coordinates for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

Table 2. Bond lengths (Å)

K-O(3)	2.831 (8)	K-O(4)	2.889 (9)
K-O(5)	2.960 (8)	K-O(6)	2.827 (9)
K-O(7)	2.973 (8)	K-O(8)	2.927 (8)
K-O(9)	3.012 (9)	K-O(10)	2.855 (8)
Pt-O(1)	2.005 (6)	Pt-O(2)	1.983 (7)
O(1)-C(1)	1.29 (1)	O(2)-C(2)	1.32 (1)
C(1)-C(2)	1.56 (2)	C(1)-O(3)	1.21 (1)
C(2)-O(4)	1.21 (1)	O(5)-C(3)	1.40 (2)
O(5)-C(14)	1.45 (2)	C(3)-C(4)	1.47 (2)
C(4)-O(6)	1.43 (2)	O(6)-C(5)	1.40 (2)
C(5)-C(6)	1.49 (2)	C(6)-O(7)	1.39 (2)
O(7)-C(7)	1.41 (2)	C(7)-C(8)	1.50 (2)
C(8)-O(8)	1.44 (2)	O(8)-C(9)	1.42 (2)
C(9)-C(10)	1.50 (2)	C(10)-O(9)	1.42 (2)
O(9)-C(11)	1.41 (2)	C(11)-C(12)	1.48 (2)
C(12)-O(10)	1.43 (2)	O(10)-C(13)	1.38 (2)
C(13)-C(14)	1.50 (3)		

Table 28. Bond Lengths for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

Table 3. Bond angles ($^{\circ}$)

O(1)-Pt-O(2)	83.4(3)	O(1)-Pt-O(1A)	180
O(1)-Pt-O(2A)	96.6(3)	O(2)-Pt-O(2A)	180
Pt-O(1)-C(1)	113.0(6)	Pt-O(2)-C(2)	112.8(6)
O(1)-C(1)-C(2)	115(1)	O(1)-C(1)-O(3)	126(1)
C(2)-C(1)-O(3)	120(1)	O(2)-C(2)-C(1)	115(1)
O(2)-C(2)-O(4)	125(1)	C(1)-C(2)-O(4)	120(1)
C(3)-O(5)-C(14)	110(1)	O(5)-C(3)-C(4)	110(1)
C(3)-C(4)-O(6)	112(1)	C(4)-O(6)-C(5)	114(1)
O(6)-C(5)-C(6)	108(1)	C(5)-C(6)-O(7)	108(1)
C(6)-O(7)-C(7)	111(1)	O(7)-C(7)-C(8)	110(1)
C(7)-C(8)-O(8)	110(1)	C(8)-O(8)-C(9)	112(1)
O(8)-C(9)-C(10)	110(1)	C(9)-C(10)-O(9)	109(1)
C(10)-O(9)-C(11)	111(1)	O(9)-C(11)-C(12)	109(1)
C(11)-C(12)-O(10)	110(1)	C(12)-O(10)-C(13)	112(1)
O(10)-C(13)-C(14)	111(1)	O(5)-C(14)-C(13)	109(1)

Table 29. Bond Angles for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

Table 4. Anisotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	37 (1)	52 (2)	34 (1)	6 (1)	5 (1)	7 (1)
Pt	31 (1)	37 (1)	26 (1)	6 (1)	5 (1)	8 (1)
O (1)	41 (3)	44 (6)	30 (3)	4 (4)	3 (2)	2 (3)
O (2)	39 (3)	48 (7)	27 (3)	6 (3)	8 (3)	10 (3)
C (1)	42 (5)	13 (7)	37 (5)	3 (4)	9 (4)	0 (3)
C (2)	45 (6)	19 (6)	34 (5)	1 (4)	1 (4)	4 (3)
O (3)	60 (4)	40 (6)	31 (3)	6 (4)	4 (3)	-4 (3)
O (4)	44 (4)	53 (5)	52 (4)	-6 (4)	0 (3)	10 (4)
O (5)	59 (5)	41 (5)	38 (4)	-7 (4)	-8 (4)	0 (3)
C (3)	62 (9)	38 (8)	78 (9)	3 (7)	-25 (7)	-6 (7)
C (4)	35 (7)	37 (8)	107 (13)	-1 (6)	4 (8)	-9 (8)
O (6)	38 (5)	39 (5)	57 (6)	12 (4)	4 (4)	2 (4)
C (5)	59 (8)	41 (8)	91 (10)	3 (7)	37 (8)	4 (7)
C (6)	86 (10)	45 (8)	54 (7)	0 (8)	38 (7)	5 (6)
O (7)	69 (5)	39 (5)	33 (4)	-2 (4)	13 (4)	5 (3)
C (7)	100 (11)	53 (9)	35 (6)	17 (8)	8 (6)	-11 (6)
C (8)	92 (11)	66 (9)	49 (7)	20 (8)	-19 (7)	-26 (6)
O (8)	55 (5)	44 (5)	50 (4)	2 (4)	-2 (4)	-12 (4)
C (9)	60 (8)	41 (10)	77 (9)	-11 (6)	-14 (6)	-3 (6)
C (10)	32 (6)	42 (8)	99 (10)	-5 (6)	-1 (6)	6 (7)
O (9)	47 (5)	38 (5)	77 (6)	1 (4)	19 (4)	-1 (4)
C (11)	59 (8)	44 (8)	86 (10)	11 (7)	43 (8)	17 (7)
C (12)	78 (9)	36 (7)	68 (8)	7 (7)	51 (7)	4 (6)
O (10)	68 (7)	43 (5)	30 (4)	7 (5)	11 (4)	13 (4)
C (13)	122 (15)	41 (9)	38 (8)	22 (9)	22 (9)	8 (6)
C (14)	99 (11)	39 (8)	41 (7)	12 (8)	-12 (7)	-7 (6)

The anisotropic displacement exponent takes the form:
 $-2\pi^2 (h^2 a^{*2} U_{11} + \dots + 2hka^*b^*U_{12})$

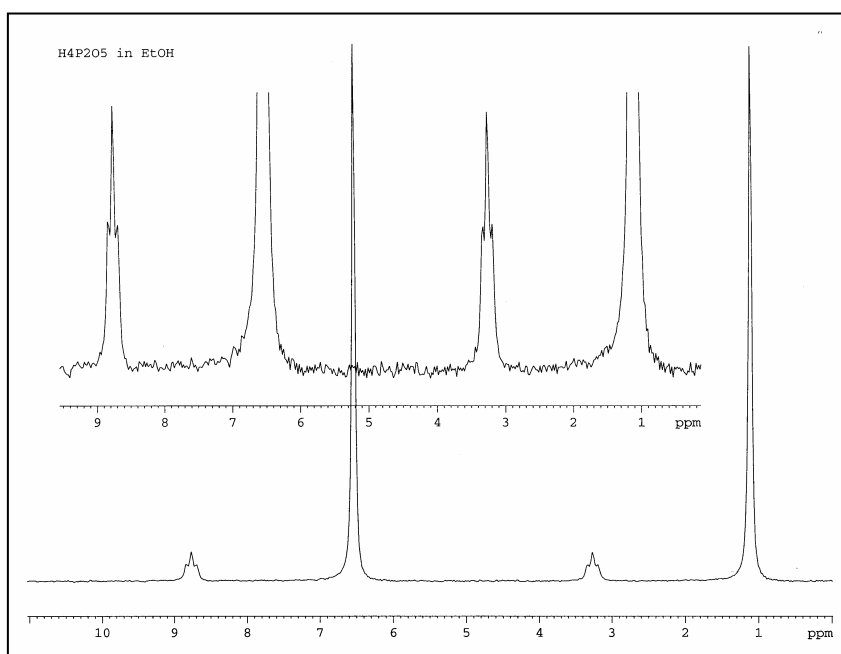
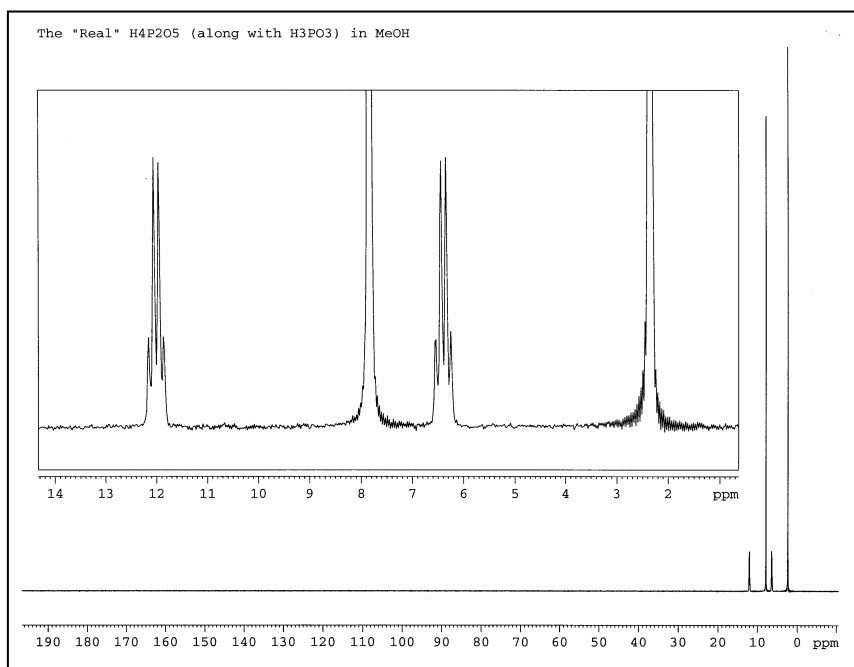
Table 30. Anisotropic Displacement Coefficients for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

Table 5. H-Atom coordinates and isotropic displacement coefficients ($\text{\AA}^2$)				
	x	y	z	U
H(3A)	0.715	-0.186	0.2990	0.068(9)
H(3B)	0.642	-0.050	0.2602	0.068(9)
H(4A)	0.710	-0.364	0.2157	0.068(9)
H(4B)	0.783	-0.196	0.2035	0.068(9)
H(5A)	0.686	-0.378	0.1072	0.068(9)
H(5B)	0.740	-0.196	0.0979	0.068(9)
H(6A)	0.597	-0.253	0.0195	0.068(9)
H(6B)	0.541	-0.110	0.0595	0.068(9)
H(7A)	0.409	-0.372	-0.0139	0.068(9)
H(7B)	0.348	-0.212	0.0149	0.068(9)
H(8A)	0.291	-0.545	0.0479	0.068(9)
H(8B)	0.203	-0.441	0.0045	0.068(9)
H(9A)	0.127	-0.566	0.1183	0.068(9)
H(9B)	0.042	-0.464	0.0727	0.068(9)
H(10A)	-0.034	-0.427	0.1674	0.068(9)
H(10B)	0.018	-0.252	0.1465	0.068(9)
H(11A)	-0.005	-0.309	0.2637	0.068(9)
H(11B)	0.074	-0.151	0.2453	0.068(9)
H(12A)	0.173	-0.412	0.3164	0.068(9)
H(12B)	0.129	-0.240	0.3433	0.068(9)
H(13A)	0.383	-0.371	0.3473	0.068(9)
H(13B)	0.340	-0.208	0.3810	0.068(9)
H(14A)	0.478	-0.048	0.3240	0.068(9)
H(14B)	0.550	-0.179	0.3652	0.068(9)

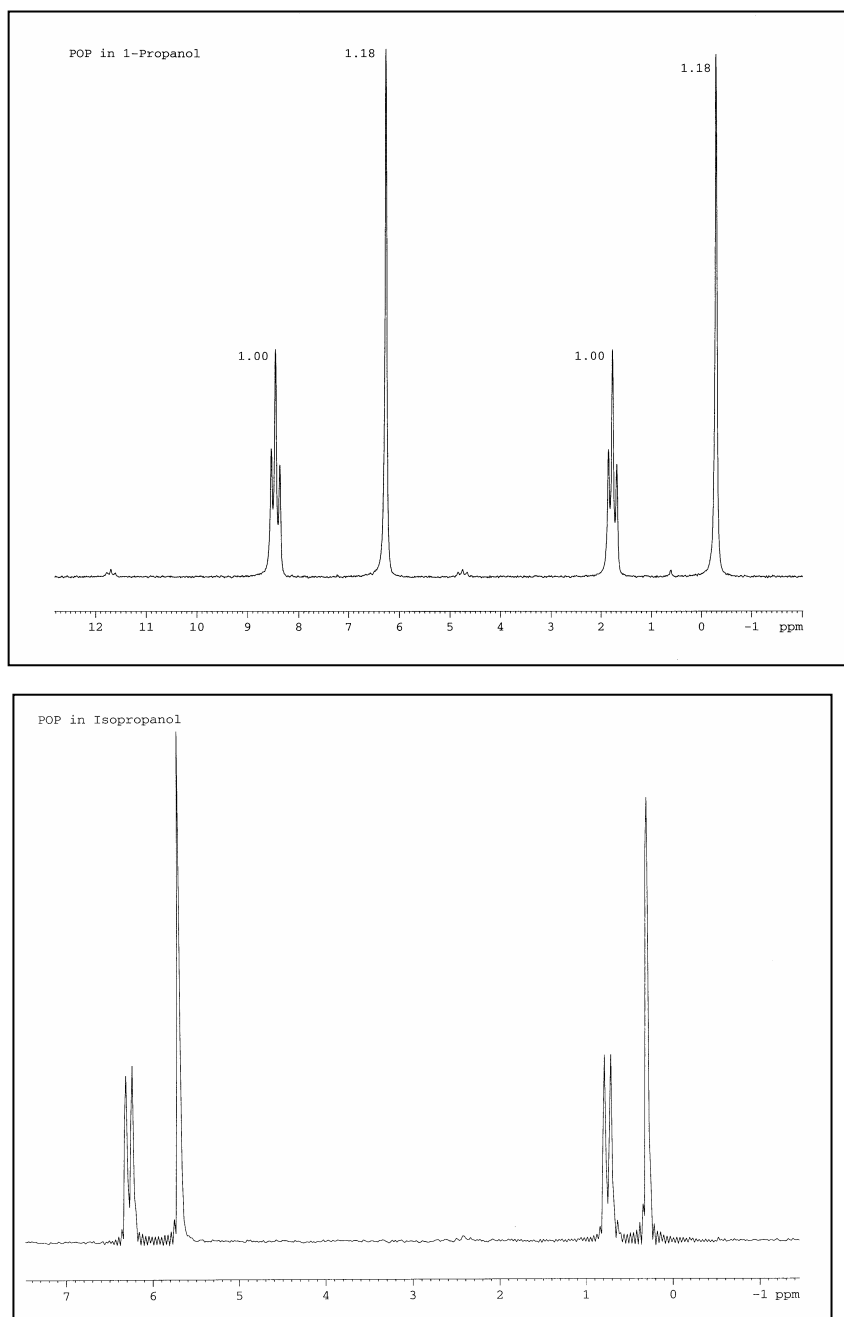
Table 31. H-Atom Coordinates for $(\text{KC}_{12}\text{H}_{24}\text{O}_6)_2\text{Pt}(\text{C}_2\text{O}_4)_2$

APPENDIX B

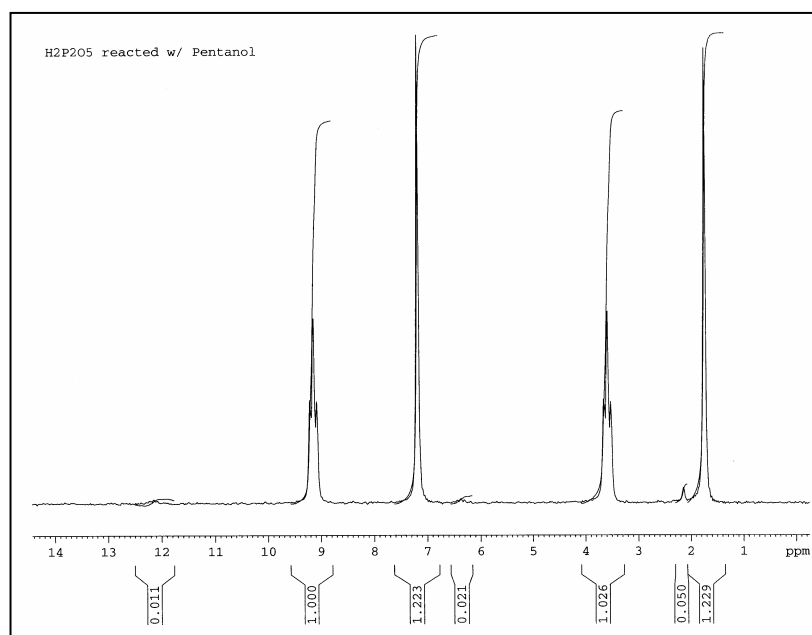
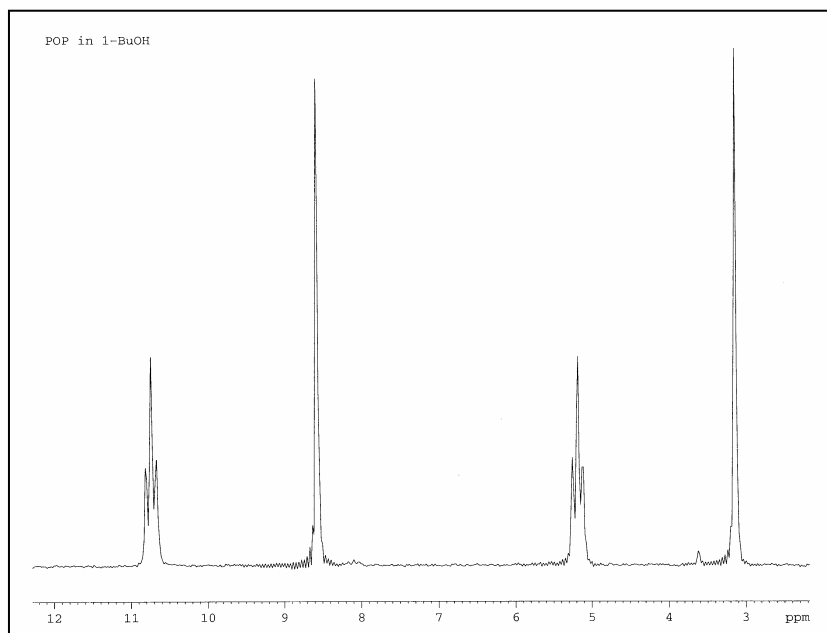
NUCLEAR MAGNETIC RESONANCE DATA OF THE REACTIONS OF
PYROPHOSPHORUS ACID WITH VARIOUS ALCOHOLS



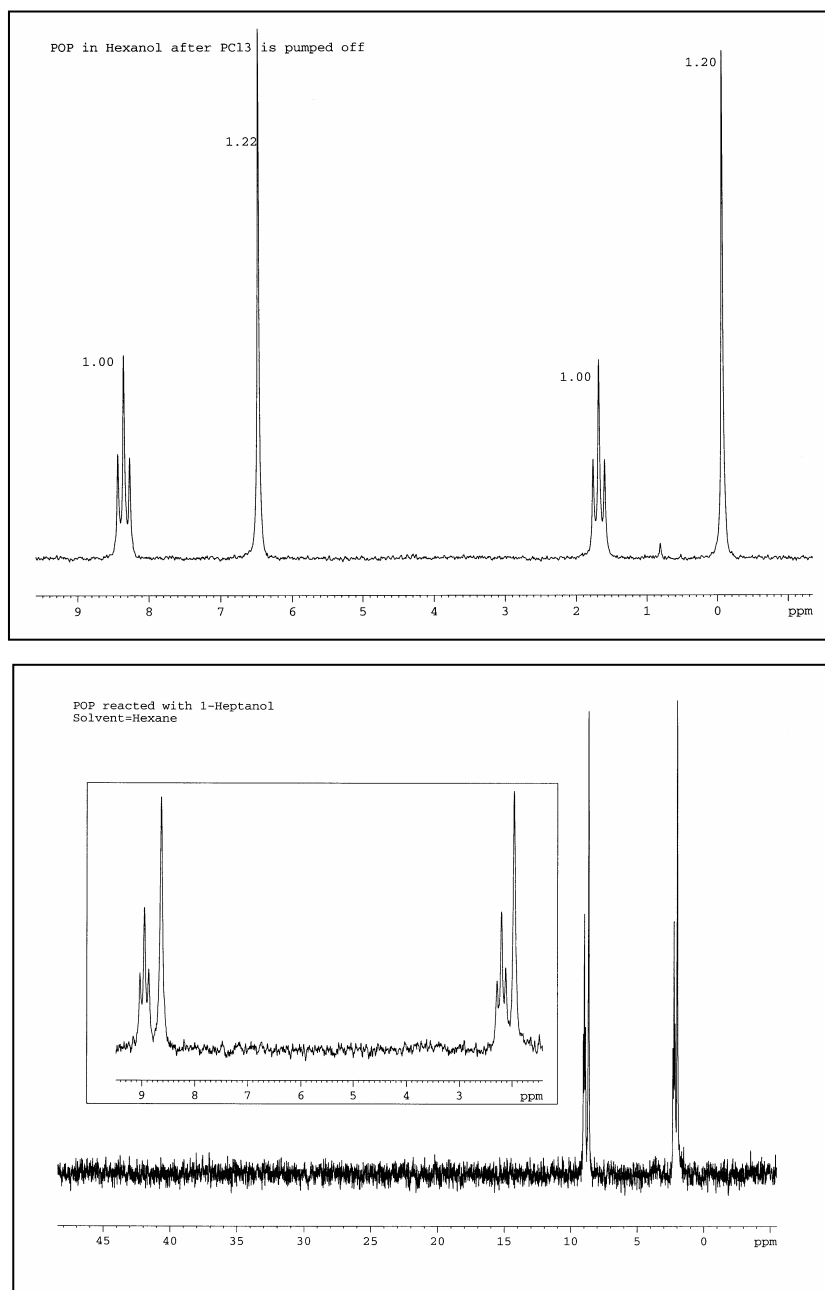
Figures 139 (Top) and 140 (Bottom): The NMR spectra of the results of the reaction of pyrophosphorus acid with methanol and ethanol respectively.



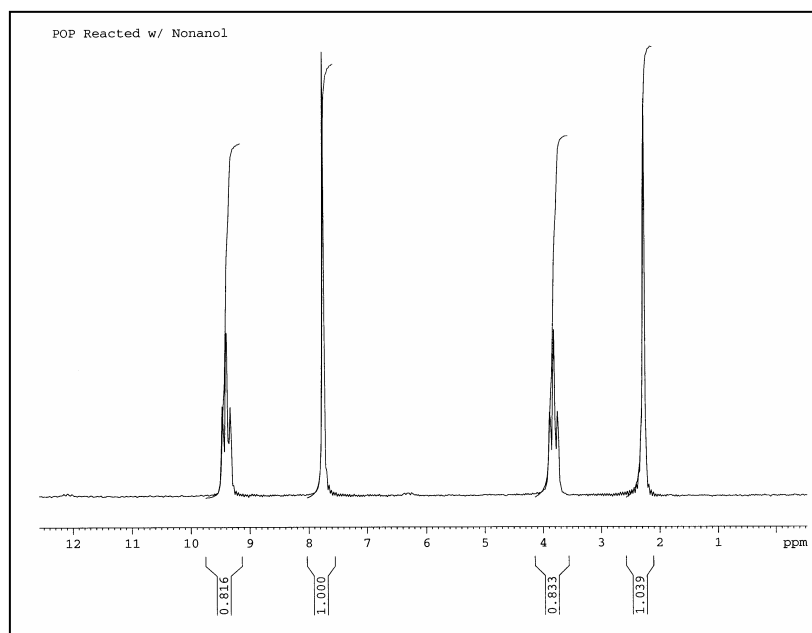
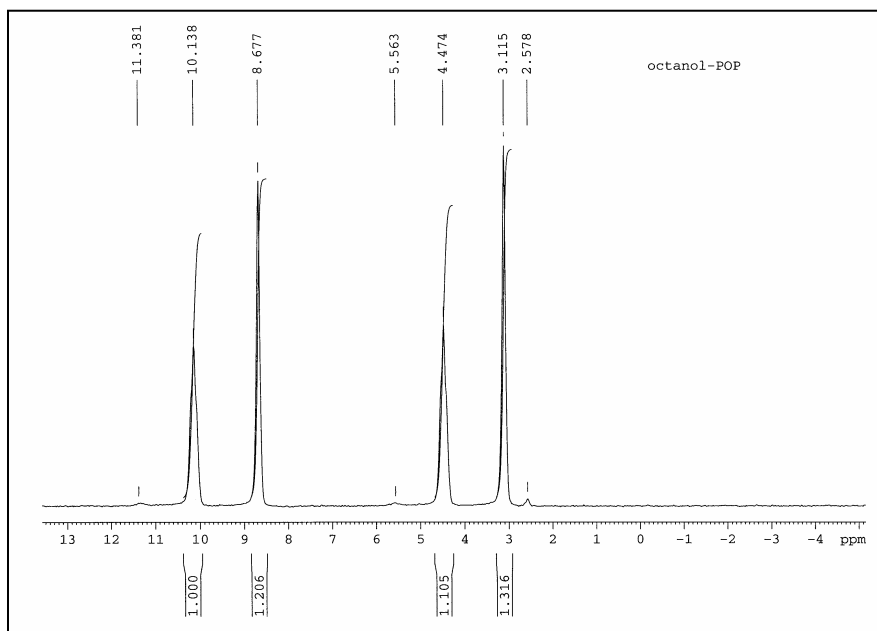
Figures 141 (Top) and 142 (Bottom): The NMR spectra of the results of the reaction of pyrophosphorus acid with 1-propanol and 2-propanol respectively.



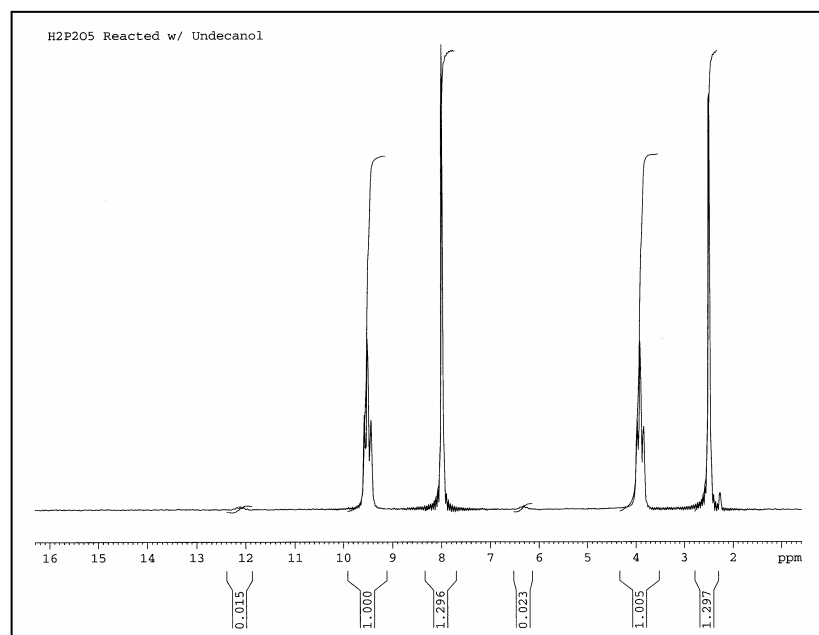
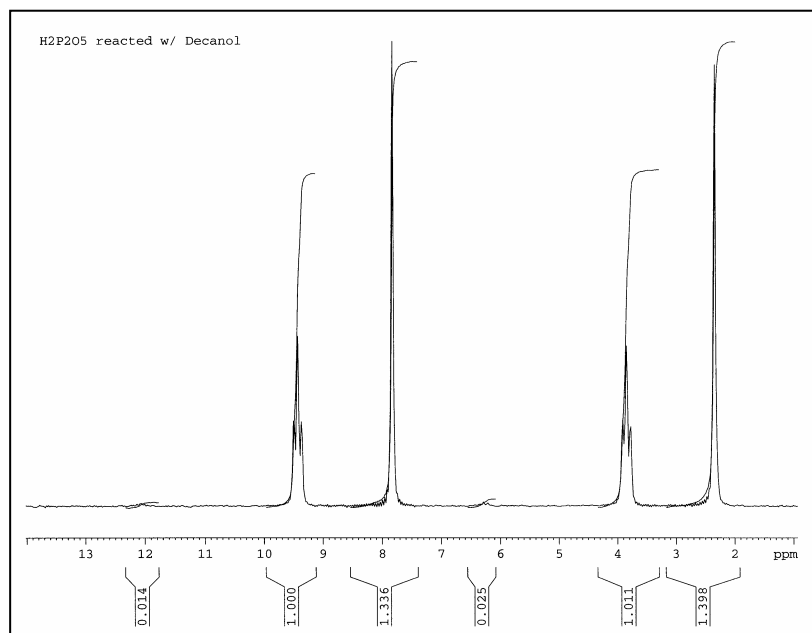
Figures 143 (Top) and 144 (Bottom): The NMR spectra of the results of the reaction of pyrophosphorus acid with 1-butanol and 1-pentanol respectively.



Figures 145 (Top) and 146 (Bottom): The NMR spectra of the results of the reaction of pyrophosphorus acid with 1-hexanol and 1-heptanol respectively.



Figures 147 (Top) and 148 (Bottom): The NMR spectra of the results of the reaction of pyrophosphorus acid with 1-octanol and 1-nonanol respectively.



Figures 149 (Top) and 150 (Bottom): The NMR spectra of the results of the reaction of pyrophosphorus acid with 1-decanol and 1-undecanol respectively.

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