



Multinuclear association of tetraethylisocyanideplatinum (II) tetracyanoplatinate (II) and the oxidized solutions of tetracyanoplatinate (II)  
by Phillip John Martellaro

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry  
Montana State University  
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Abstract:

The colors exhibited in the solid phase of the tetracyanoplatinate salts do not always exist into the solution state. The color of the solid complex is attributed to the metal-metal interaction distance. The closer the metal-metal interaction is the lower in energy the corresponding absorption band will be.

Oxidation of the tetracyanoplatinates gives numerous species in solution. Oxidized solutions result in six species that have been characterized using  $^{195}\text{Pt}$  nmr. These are the (Formula not captured by OCR), (Formula not captured by OCR) and (Formula not captured by OCR). Initial reaction solutions are a faint yellow color but when they are allowed to stand idle for at least one week a purple colored solution exists. During this time all the  $^{195}\text{Pt}$  nmr resonances are still present but in different proportions. The purple solutions are attributed to paramagnetic multi-nuclear associated species.

The double complex salt tetraethylisocyanideplatinum(II) tetracyanoplatinate(II) gives brilliant red colored solutions when concentrations are at least  $1 \times 10^{-3}\text{M}$ . The color is the result of multi-nuclear association. The species in solution at (Formula not captured by OCR) are the di-nuclear (Formula not captured by OCR) two tri-nuclear species (Formula not captured by OCR) and the tetra-nuclear (Formula not captured by OCR). The thermodynamics of the solution reveals the greater enthalpy of formation for the dinuclear and tetranuclear species. The even numbered associated species have  $C_{4v}$  symmetry and thus have a dipole moment. The net dipole results in the greater ordering of solvent. The odd numbered associated platinum species are  $D_{4h}$  and have no net dipole moment. The greater ordering in the even numbered species results in the more exothermic values of enthalpy due to bond formation with the solvent. The greater ordering of solvent for the di-nuclear and tetra-nuclear species also explains the corresponding more negative values of entropy for the even numbered species compared with the more positive entropic values of the odd numbered species.

The complexes cis-bisethylisocyanidedicyanoplatinum(II), cis-bismethyldicyanoplatinum(II) and tetra-n-butylammoniummonomethylisocyanidetricyanoplatinum(II) were structured. All three complexes contained shorter platinum-carbon bond lengths for the isocyanide compared to the cyanide. This reveals the greater  $\pi$ -acidity of the isocyanide ligand.

MULTINUCLEAR ASSOCIATION OF TETRAETHYLISOCYANIDEPLATINUM(II)  
TETRACYANOPLATINATE(II) AND THE OXIDIZED SOLUTIONS OF  
TETRACYANOPLATINATE(II)

By

Phillip John Martellaro

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APPROVAL

of a thesis submitted by

Phillip John Martellaro

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Edwin H. Abbott

Edwin H. Abbott

(Signature)

12/14/98

Date

Approved for the Department of Chemistry

David M. Dooley

David M. Dooley

(Signature)

12/17/98

Date

Approved for the College of Graduate Studies

Joseph J. Fedock

Joseph J. Fedock

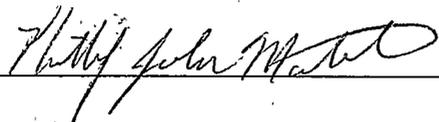
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## ABSTRACT

The colors exhibited in the solid phase of the tetracyanoplatinate salts do not always exist into the solution state. The color of the solid complex is attributed to the metal-metal interaction distance. The closer the metal-metal interaction is the lower in energy the corresponding absorption band will be.

Oxidation of the tetracyanoplatinates gives numerous species in solution. Oxidized solutions result in six species that have been characterized using  $^{195}\text{Pt}$  nmr. These are the  $\text{Pt}_3(\text{CN})_8^{2-}$ ,  $\text{Pt}_2(\text{CN})_6$ ,  $\text{Pt}_2(\text{CN})_8^{2-}$ ,  $\text{Pt}_2(\text{CN})_8(\text{H}_2\text{O})_2^{2-}$ ,  $\text{Pt}(\text{CN})_4(\text{H}_2\text{O})_2^{2-}$  and  $\text{Pt}(\text{CN})_2(\text{H}_2\text{O})_4^{2-}$ . Initial reaction solutions are a faint yellow color but when they are allowed to stand idle for at least one week a purple colored solution exists. During this time all the  $^{195}\text{Pt}$  nmr resonances are still present but in different proportions. The purple solutions are attributed to paramagnetic multi-nuclear associated species.

The double complex salt tetraethylisocyanideplatinum(II) tetracyanoplatinate(II) gives brilliant red colored solutions when concentrations are at least  $1 \times 10^{-3}\text{M}$ . The color is the result of multi-nuclear association. The species in solution at  $1 \times 10^{-3}\text{M}$  are the di-nuclear  $\text{Pt}(\text{CNC}_2\text{H}_5)_4[\text{Pt}(\text{CN})_4]$ , two tri-nuclear species  $[\text{Pt}(\text{CNC}_2\text{H}_5)_4]_2[\text{Pt}(\text{CN})_4]^{2+}$ ,  $[\text{Pt}(\text{CNC}_2\text{H}_5)_4][\text{Pt}(\text{CN})_4]_2^{2-}$  and the tetra-nuclear  $[\text{Pt}(\text{CNC}_2\text{H}_5)_4]_2[\text{Pt}(\text{CN})_4]_2$ . The thermodynamics of the solution reveals the greater enthalpy of formation for the dinuclear and tetranuclear species. The even numbered associated species have  $C_{4v}$  symmetry and thus have a dipole moment. The net dipole results in the greater ordering of solvent. The odd numbered associated platinum species are  $D_{4h}$  and have no net dipole moment. The greater ordering in the even numbered species results in the more exothermic values of enthalpy due to bond formation with the solvent. The greater ordering of solvent for the di-nuclear and tetra-nuclear species also explains the corresponding more negative values of entropy for the even numbered species compared with the more positive entropic values of the odd numbered species.

The complexes cis-bisethylisocyanidedicyanoplatinum(II), cis-bismethyldicyanoplatinum(II) and tetra-n-butylammoniummonomethylisocyanidetricyanoplatinum(II) were structured. All three complexes contained shorter platinum-carbon bond lengths for the isocyanide compared to the cyanide. This reveals the greater  $\pi$ -acidity of the isocyanide ligand.

## INTRODUCTION

Complexes with Pt-Pt Interactions

The interest and appreciation of the chemistry of metal-metal bonding originated during the middle part of this century (1 and references therein). Platinum, like other metals, exhibits two different classes of metal-metal bonding. The first class consists of molecules that contain metal atoms that are bonded directly with one another. These complexes contain no ligands that bridge between the two metal atoms. For platinum complexes this is seen in the partially oxidized tetracyanoplatinates (POTCP) as well as the platinum blues. A representation of the structural characteristics of the platinum blue complex  $\alpha$ -pyridone blue which is a dimer of the binuclear  $[(\text{NH}_3)_2\text{Pt}(\text{pyr})_2\text{Pt}(\text{HN}_3)_2]$  (**1**) and the POTCP  $\text{K}_2\text{Pt}(\text{CN})_4\text{X}_3 \cdot 3\text{H}_2\text{O}$  where X is Br (**2**) or Cl (**3**) is seen in figure 1 and 2 respectively. The POTCP is an infinite platinum-platinum bonded species whereas the platinum blues are tetraplatinum and considered finite platinum-platinum bonds. The platinum blues have been extensively studied because of their anti-tumor activity (2,3,4). Both (**1**) and (**2**) have drawn significant interest for different reasons and are formed according to equation 1.



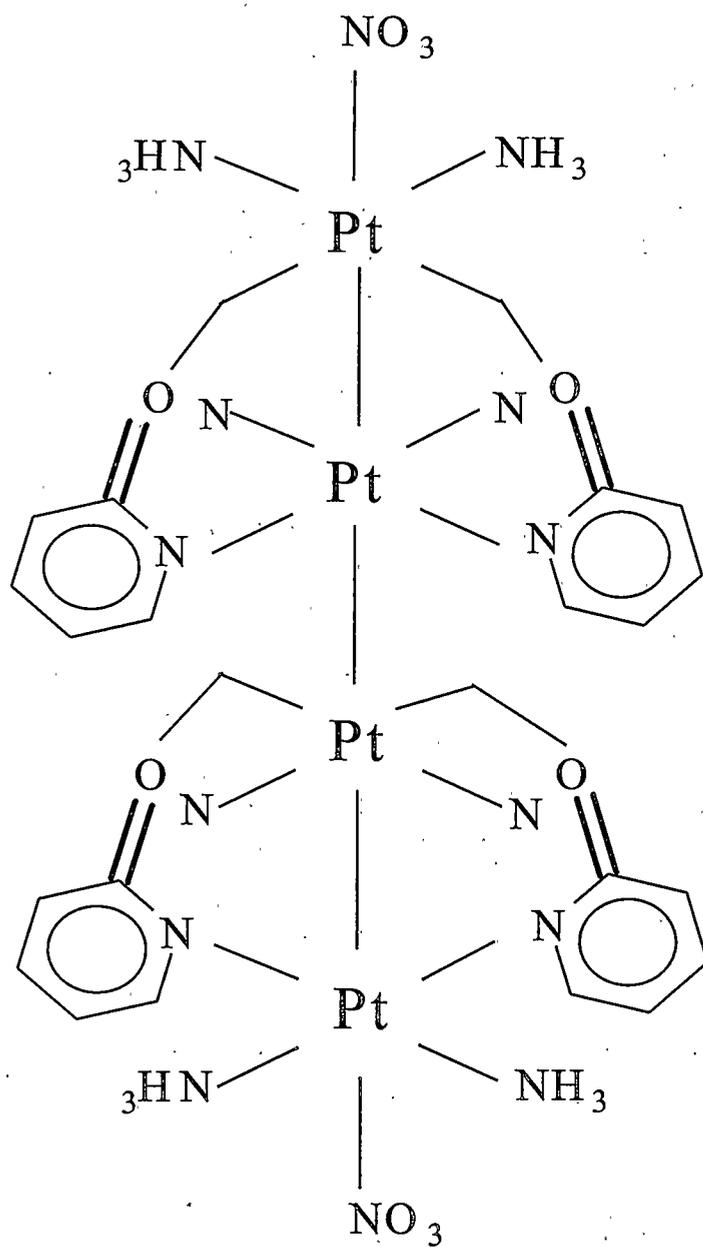
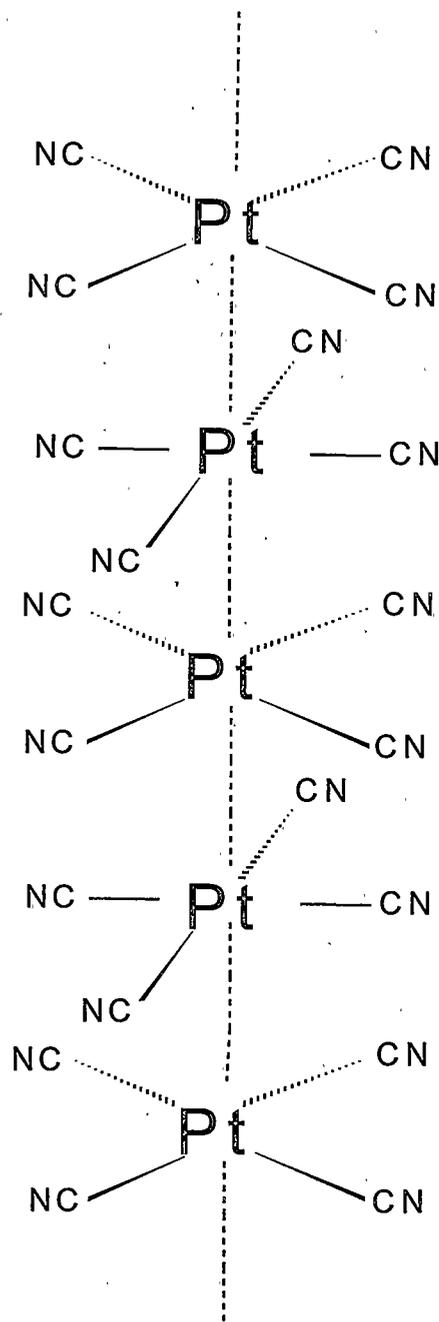


Figure 1. Depiction of the tetrameric  $\alpha$ -pyridone blue.



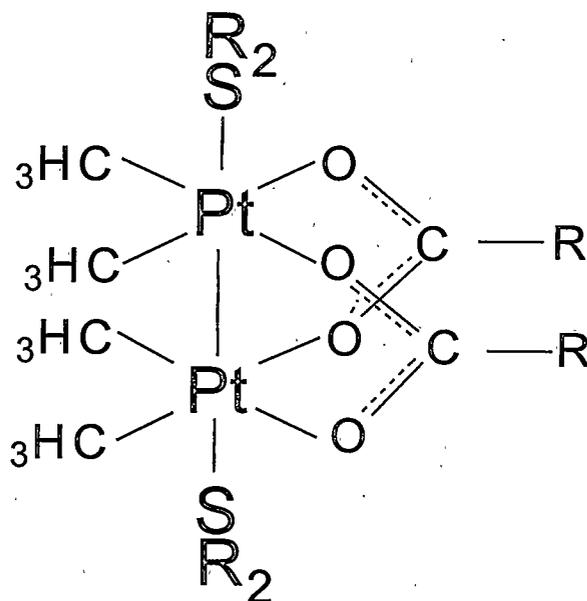
**Figure 2.** Depiction of the stacked platinum atoms in the TCP's, POTCP and DS.

The POTCP complexes have been studied for the most part because of their 1-D anisotropic physical properties. Principal among these 1-D properties is the ability for the anisotropic conduction of electricity through the Pt-Pt bonds. The  $\alpha$ -pyridone blue is also a partially oxidized (PO) compound like the POTCP. The partial oxidation (PO) is reflected in the oxidation state of these complexes being a non-integral number. The platinum atom in **(1)** is in an average oxidation state of +2.25. In the case of the **(2)** the average oxidation state of the platinum atom is +2.3. The Pt-Pt bond lengths of **(1)** are 2.774 and 2.877 Å. In **(2)** the Pt-Pt bond lengths are on the order of 2.88 Å.

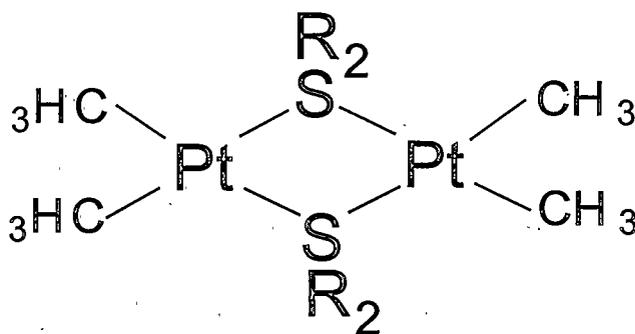
The second type of metal-metal bonded atoms are those of the bridged complexes. In this case the two metal atoms are spanned by an appropriate ligand. Figure 3 shows two examples of platinum bridged dimers. Figure 3a was one of the first Pt(III) complexes synthesized. Until recently when monomeric Pt(III) species were found the only known Pt(III) complexes were of the bridged type. The other example shown in figure 3B is the Pt(II) complex  $[\text{Pt}(\text{CH}_3)_2(\text{SR}_2)]_2$  (5). The bridged Pt(III) dimers have very short Pt-Pt bond lengths. The  $\text{H}_2[\text{Pt}_2(\mu\text{-SO}_4)_4(\text{H}_2\text{O})_2]$  shown in figure 4 has a Pt-Pt bond length of 2.466 Å (6,7). In the case of the bridged Pt(II)  $[\text{Pt}(\text{CH}_3)_2(\text{SR}_2)]_2$  the metal-metal distance is not close enough to be called a bond.

Non-bridged dimeric Pt(III) complexes have recently been observed. They have Pt-Pt bond lengths on the order of 2.7-2.8 Å. It is likely from Pt-Pt bond lengths in the Pt(III) dimers that bridging contributes to the stability of the

a)



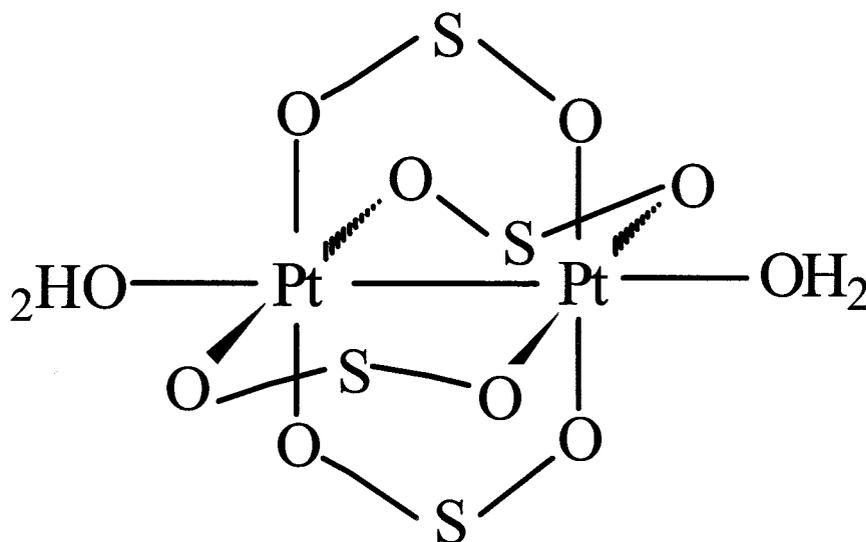
b)



**Figure 3.** a) Structure of the Pt(III)-carboxylato dimer b) Structure of the Pt(II) methyl complex

complex. These types of complexes are significant for the work described here because of the evidence that they are present in the solutions.

Also of interest to the work described here are platinum complexes that are stacked like the example in figure 2 but the platinum distances are not close enough to be considered a metal-metal bond. In these cases the platinum atoms are close enough to interact but the distances are too long for there to be any significant orbital overlap that would result in a strong covalent bond. It is generally accepted that when platinum-platinum atoms are separated by 3Å or less there is a true chemical bond between the two metal atoms.



**Figure 4** Depiction of the Pt(III) Complex  $[Pt_2(\mu-SO_4)_4(H_2O)_2]$

## The Tetracyanoplatinate(II) salts (TCP's)

### Tetracyanoplatinate(II) (TCP) in the Solid State

The solid state characteristics of both the  $\text{MPt}(\text{CN})_4$  (where  $\text{M}=\text{K}_2, \text{Na}_2, \text{Rb}_2, \text{Cs}_2, [(\text{CH}_3)_3\text{N}]_2, \text{Mg}, \text{Ca}$ ) as well as the POTCP's have been extensively studied (8-12). The TCP's were discovered nearly 150 years ago and were of interest to the early scientists because of the wide range of colors observed for the various salts of the TCP's. In the solid phase the TCP's stack with the platinum atoms on top of each other much like that of a roll of coins (Figure 2). Figure 2 can be used as the structure representation to describe both the TCP and the POTCP because the Pt-Pt stacking is identical in the two different complexes. For our purposes the only difference of significance is the Pt-Pt separations. The colors observed for the TCP's depends upon the counteraction and the content of water hydration (13). A few examples are shown in table 1.

Table 1. Pt-Pt distances and colors of TCP complexes with different cations and contents of water hydration and a few Double Complex Salts

Complex	Pt-Pt distance(Å)	Color
$\text{SrPt}(\text{CN})_4 \cdot 5 \text{H}_2\text{O}$	3.6	Colorless
$\text{SrPt}(\text{CN})_4 \cdot 3 \text{H}_2\text{O}$	3.09	Violet
$\text{MgPt}(\text{CN})_4 \cdot 7 \text{H}_2\text{O}$	3.16	Dark Red
$\text{MgPt}(\text{CN})_4 \cdot 4.5 \text{H}_2\text{O}$	3.36	Yellow
$\text{BaPt}(\text{CN})_4 \cdot 4 \text{H}_2\text{O}$	3.32	Yellow-Green
$\text{BePt}(\text{CN})_4 \cdot 2 \text{H}_2\text{O}$	3.16	Dark Red
$\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$	3.42	Yellow
$[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{Cl})_4]$	3.25	Green
$[\text{Pt}(\text{CN-iso-C}_3\text{H}_7)_4][\text{Pt}(\text{CN})_4]$	3.15	Red-Violet
$[\text{Pt}(\text{CNC}_2\text{H}_5)_4][\text{Pt}(\text{CN})_4]$	?	Bright Yellow
$[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]^*$	Varies	Varies

R= any alkylisocyanide or arylisocyanide

Referring to table 1 it can be seen that the color of the solid complexes does not change in the same direction of the absorption spectrum as the water content varies. Some salts have a red shift in their visible spectrum upon losing water in the lattice and others will have a blue shift. An example of this is the comparison of the strontium and magnesium salts of the TCP's. In the case of the strontium salt as the  $\text{H}_2\text{O}$  hydration decreases the Pt-Pt separation also decreases. The opposite is the case with the magnesium salt where a decrease in  $\text{H}_2\text{O}$  hydration causes a lengthening of the Pt-Pt separation. Since the cations and the isolated anions do not absorb in the visible region of the spectrum they cannot be the reason for the different colors observed in these complexes.

Yamada was the first to determine that there was a relationship between the color of the TCP compounds and their Pt-Pt separation (13). Yamada observed that the absorption bands of these compounds shifted to longer wavelength on

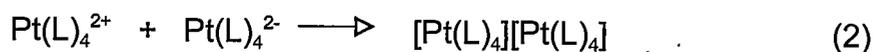
going to a shorter Pt-Pt separation. Yamada showed that the platinum-platinum separation results in the colors observed for the different cations and contents of hydration. The Pt-Pt separations of the TCP salts range from 3.09Å to 3.7Å. For the TCP's the Pt-Pt distance is usually termed as a separation because the metal-metal distance in these complexes are not close enough to constitute a metal-metal bond. In the case of the TCP's the electrostatic interactions of the ligands do not favor the atoms stacking on top of one another. This arrangement puts ligands of the same relative charge in close proximity to one another. Because of unfavorable electrostatics it is assumed the packing energies for the TCP's and their respective alkali and alkaline earth metal counter cations are responsible for the stacked structures.

#### Tetracyanoplatinate(II) in the Solution State

All of the colored solid state TCP's gives clear solutions in all solvents. The only work that studied whether there are metal-metal interactions in solution is the work by Adamson (14,15). Adamson used emission and absorption data to conclude that there is some Pt-Pt aggregation in solution. Adamson concluded that there was some Pt-Pt aggregation in solution because the absorption spectra did not obey Beers Law. There have been a few other papers dealing with the solution studies on the TCP's but these have mostly dealt with the assignment of the electronic transitions (12,16).

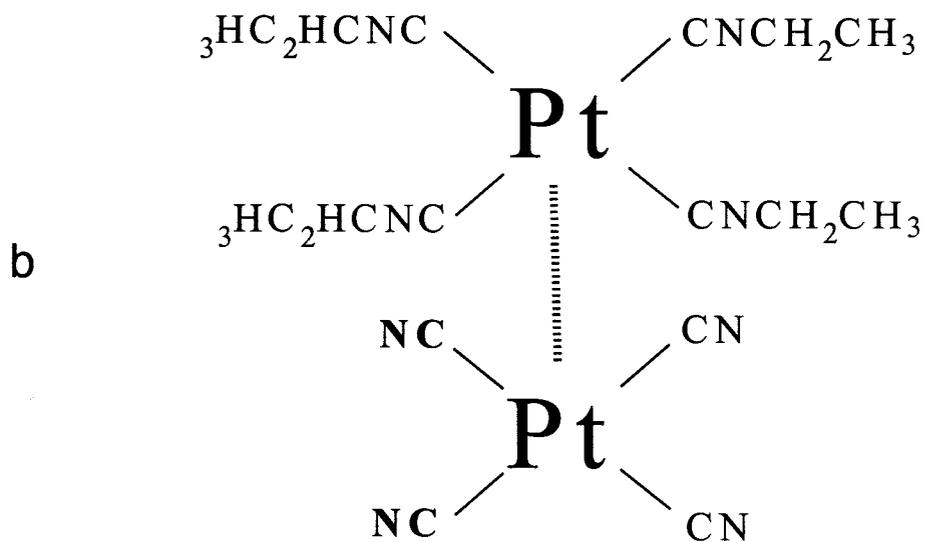
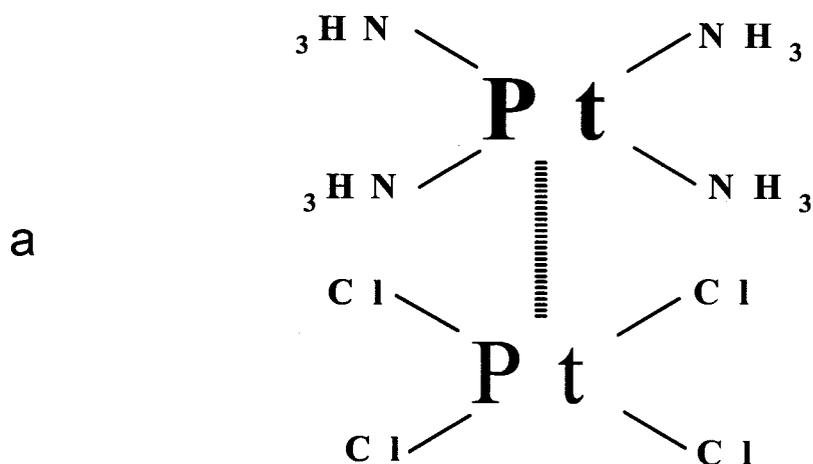
Double Salt Complexes

Included in table 1 along with the TCP's are a few representatives of the double complex salts (DS). The term double salt arises from the fact that these complexes consist of a cationic platinum complex and an anionic platinum complex. The DS complexes are formed simply by combining two oppositely charged square planar platinum complexes according to equation 2.



These compounds also stack in a similar fashion to the TCP's where the platinum atoms are on top of one another as in figure 2. In the case of the DS, this type of atom arrangement occurs for two reasons. Like the TCP's the favorable packing energies for the platinum atoms causes this type of atom arrangement, but in the case of the DS the electrostatic interactions contributes to this form of atom arrangement.

All the double complex salts contain square planar platinum(II) complexes with one metal center tetracoordinate to negatively charged ligands and the other metal center tetracoordinate to positively charged ligands. Magnus's Green salt which has the formula  $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{Cl})_4]$  (4) was described over 150 years ago but not until the middle of this



**Figure 5.** a) Depiction of Magnus Green Salt and b) the ethylisocyanidecyano double salt.

century was the structure correctly formulated (17). More recently single crystals have been obtained on more of the double complex salts (18). Because of the low solubility exhibited in most solvents it has been difficult to obtain single crystals of these complexes (19,20). The electrostatic attraction by the ligands leads to the decreased solubility of the DS compared to the TCP's. Low solubility has also prevented solution studies. Figure 5 shows the DS complexes (4) and the tetraethylisocyanideplatinum(II) tetracyanoplatinate(II)  $[\text{Pt}(\text{CNC}_2\text{H}_5)_4][\text{Pt}(\text{CN})_4]$  (5).

### Partially Oxidized Tetracyanoplatinates (POTCP)

#### Solid State Properties of the Partially Oxidized Tetracyanoplatinate(II) Complexes

When the TCP's are exposed to less than 0.5 electron equivalents of oxidant a new class of interesting compounds is formed. Partial oxidation (PO) of the Pt(II) complex results in small needle like crystals that have anywhere from a bronze sheen to a copper color sheen (8). These complexes are termed the partially oxidized tetracyanoplatinates (POTCP) because of the non-integral oxidation state of the platinum atom. The best known example of the POTCP is compound (2). PO results in the Pt-Pt separation decreasing down to 2.8Å to 2.95Å depending on the counter cation used. The decrease in the Pt-Pt

separation gives rise to 1-D physical properties. One of the most interesting properties of these complexes is the 1-D metallic conductivity that arises from delocalization of the electrons in the overlapping Pt  $5d_{z^2}$  orbitals. The shorter Pt-Pt separation in the POTCP complexes is a true metal-metal bond. When metal-metal separations are less than  $3\text{\AA}$  it is believed that there is covalent bonding between the metals. Table 2 shows the Pt-Pt bond distances for some of the POTCP.

Included in table 2 are the physical properties of two PO bisoxalatoplatinates (POBOP). The POBOP complexes are formed in a similar fashion as the POTCP's and also have nearly identical physical properties. The stacking of the platinum atoms in the POBOP's are similar to that in the POTCP complexes. This 1-D stacking and the new Pt-Pt bond give rise to the anisotropic physical properties observed in both complexes. All the known POBOP's have shorter Pt-Pt bonds than the known POTCP's. The POBOP like the POTCP have ligands that result in unfavorable electrostatic interactions. It has been suggested that the shorter Pt-Pt separations in the POBOP are the result of  $\pi$ -type interactions between the oxalate ligands (21,72).

Table 2. Bond distances of partially oxidized complexes

Complex	Oxidation #	Type	Pt-Pt $\text{\AA}$
$\text{K}_{1.75}\text{Pt}(\text{CN})_4 \cdot 1.8\text{H}_2\text{O}$	2.25	CD	2.96
$\text{K}_{1.62}\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$	2.38	CD	2.85
$\text{H}_{1.6}\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$	2.40	CD	2.80
$\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{.32} \cdot 2.6\text{H}_2\text{O}$	2.32	AD	2.88
$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{.3} \cdot 7.3\text{H}_2\text{O}$	2.30	AD	2.887
$\text{MgPt}(\text{CN})_4\text{Cl}_{.28} \cdot 7\text{H}_2\text{O}$	2.28	AD	2.985

The anisotropic properties arise because the distance between the Pt-Pt chains is upwards of 9Å. This is compared to the in-chain Pt-Pt separation which is less than 3Å for all the PO compounds. The conduction of electricity along the Pt-Pt chain is some  $10^5$  greater than perpendicular to the chain. These complexes also polarize light parallel to the chain axis.

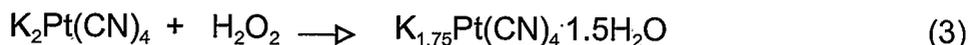
When the PO compound (2) was initially found early in this century it was formulated as a mixed complex containing five Pt(II) and one Pt(IV) molecules (22). This gives very nearly the exact stoichiometry of the PO complexes when the oxidation state is averaged over all the atoms. Five Pt(II) atoms and one Pt(IV) atom add up to a total charge of +14. If this is delocalized over all six platinum atoms the average oxidation state of each platinum would be +2.3. This is indeed the oxidation state in (2) which is the complex that was studied early in this century and described by Levy (18).

### Two Different Types of PO Compounds

For the POTCP's there are two different types of compounds that can be formed (8). These consist of the anion-deficient (AD) and the cation deficient (CD). The AD POTCP are deficient in halide ion and are found according to equation 1. They have the general formula  $K_2Pt(CN)_4X_{3.3} \cdot 2H_2O$  (where X = Br or Cl). These compounds can be made simply by mixing the Pt(II) and the corresponding trans di-halo Pt(IV) species together in a 5Pt(II):1Pt(IV) ratio in

many solvents. Upon evaporation, copper colored needles are deposited in the reaction vessel. The first evidence that the AD PO compounds were not mixed valence species was their IR spectrum. IR studies showed that the chlorine atoms were no longer bound to the platinum atom in the PO compounds (8).

The CD-POTCP is deficient in counter cation and is formed according to equation 3. The general formula for this compound is  $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$  (6).



This type of compound is formed by heating Pt(II) in the presence of hydrogen peroxide under acidic conditions. Upon slow cooling the copper colored CD-POTCP crystallizes. Table 2 indicates whether each of the PO compound are AD or CD. The CD-POTCP has also been made using electrochemical procedures (23).

Non-stoichiometry arises from the non-integral oxidation state of the platinum atom. The average oxidation number for (2) is +2.3 and for (6) +2.25. A good method for remembering the difference between the AD and the CD is that in the AD case the halide is in non-stoichiometric proportions and in the CD case the cation is in non-stoichiometric proportions. In the case of the POBOP only the CD type have been found. The most common representative of the POBOP is the  $K_{1.62}Pt(ox)_2 \cdot 2H_2O$  (7).

A term that is commonly used when referring to the PO complexes is the degree of partial oxidation (DPO). It is the measure of the amount of oxidation

that takes place. It is used as a relative correlation between the Pt-Pt bond distance and the oxidation state in the PO complexes. The above DPO's for the two POTCP are 0.3 for **(2)** and 0.24 for **(6)**. Referring to table 2 it is seen that the complex with a DPO of 0.3 compared to 0.24 has a shorter Pt-Pt bond. The DPO varies for both the AD and the CD depending upon the counter-anions and counter-cations used but the correlation always holds true that the larger the DPO the shorter is the Pt-Pt separation.

The correlation of the DPO and the Pt-Pt bond distances is also seen in the few known Pt(III) complexes. All the known Pt(III) complexes are dimeric with a Pt-Pt bond whether they are bridging or non-bridging. Whether the complex is bridging or non-bridging is irrelevant when comparing the DPO to the Pt-Pt bond distance. Because Pt(III) complexes have undergone a one electron oxidation they have a DPO of 1 and the Pt-Pt bond distances are between 2.7 and 2.8 Å for the non-bridged Pt(III) complexes (24,25). This is reduced even further for the bridged Pt(III) dimers. This is shorter than any known Pt-Pt bond distance in the POTCP and POBOP.

The oxidation state and the resulting DPO's of the PO compounds were determined using x-ray crystallographic methods. From the crystal structure all the platinum atoms are crystallographically identical. If the platinum atoms are crystallographically identical they must be in the same oxidation state. The determination of the molecular formula can be described using **(2)** as an example. In the case of **(2)** it was found that every unit cell contains two

platinum atoms. For every unit cell there is a hole for one halide atom, which gives .5 halides for every platinum atom. Only 60% of the holes that will accommodate a halide in the unit cell are occupied resulting in a total of .3 halides for every platinum atom. This gives the formula for **(2)** with a platinum oxidation state of +2.3 and a DPO of 0.3. The early hypothesis of the AD complexes like **(2)** and **(3)** being mixed valence Pt(II) and Pt(IV) species was disproved by IR methods and this was reaffirmed using crystallographic methods (11). However, the X-ray structure was needed of **(6)** to determine whether it was a mixed valence compound or not. Unlike **(2)** where there is a fairly intense IR band for the M-X there is no similar intense band for the M-OH.

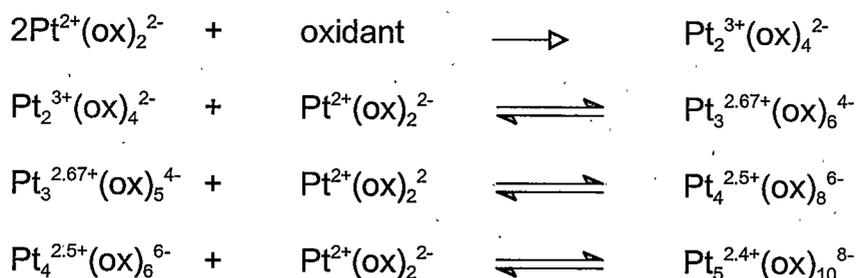
#### Solution Studies on the Partially Oxidized Compounds

The solution chemistry leading to the POTCP's is a major part of the research that is described here. The study of the solution properties of the PO compounds has not been the objective of many researchers because the 1-D solids lose their unusual anisotropic physical properties when dissolved. Additionally many of the PO compounds that form 1-D columns are not very soluble in water, although the lack of water solubility is not the case with **(6)**. The POTCP compounds do have a diminished solubility compared to the unoxidized TCP but most of the POTCP salts are still slightly soluble in water.

Partially Oxidized Bis-Oxalato Platinates Solution Chemistry

The POBOP does not give both the AD and CD form. It is only found in the CD form. The POBOP that has received the most attention to its solution behavior is (7). The solutions of the POBOP formation and their subsequent dissolution have been studied and have been shown to hold a rich solution chemistry (9,26-28). Keller proposed that the POBOP forms in a stepwise manner beginning with oxidation of the Pt(II) oxalate to give the Pt(III) dimer. This is then followed by further oligomerization until the solids precipitate out of solution as the copper colored needle like crystals. Scheme I below shows the oligomerization process proposed by Keller for the formation of the POBOP.

Scheme 1

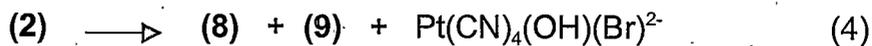


The initial step is oxidation of the Pt(II) to a dimeric Pt(III) complex. Various oxidants have been used for this first step including  $\text{Ce}^{4+}$ ,  $\text{H}_2\text{O}_2$  and  $\text{Pt}(\text{Cl})_6^{2-}$ . Three more non-integral platinum oxidation steps then follow the initial step. Each subsequent oligomer in scheme I gives a new electronic absorption

band in the visible region of the spectrum. With the addition of each platinum oxalate the absorption band is shifted to lower and lower energy. The pentamer has an overall oxidation state of +2.4. This is near the oxidation state of +2.38 that is observed in the solid crystal of (7). The crystal structure reveals that (7) is made up of repeating pentamers (8). This evidence suggests there are no multinuclear species in these solutions larger than the penta-nuclear species. Once the pentamer is formed the solubility is reduced enough to allow precipitation of (7).

#### Anion Deficient Partially Oxidized Tetracyanoplatinate Solution Chemistry

The solution chemistry of the anion-deficient (AD) POTCP is fairly limited (29). Complex (2) is made by simply combining the  $\text{Pt}(\text{CN})_4^{2-}$  (8) and the  $\text{Pt}(\text{CN})_4(\text{Br})_2^{2-}$  (9) in a 5:1 stoichiometric ratio. Saillant used UV-Visible spectroscopy to compare the solutions of the dissolved copper colored needles to the solutions of the starting materials. When the solids are dissolved in water the initial (8) and (9) are present in addition there is some of



the mixed hydrated Pt(IV) species  $\text{Pt}(\text{CN})_4(\text{Br})(\text{OH})^{2-}$  (10). When the solids are dissolved in a .1M solution of KBr it is possible to suppress the hydration which forms (10). In this case only (8) and (9) are observed.

Other studies of these solutions using  $^{195}\text{Pt}$  nmr showed similar results as Saillant (30). The  $^{195}\text{Pt}$  nmr gave singlets at -4724ppm for (8), -3573ppm for (9) and -2434ppm for (10) when (2) is dissolved in pure water. Like the UV-Visible study in solutions of .1M KBr the  $^{195}\text{Pt}$  nmr only shows two resonance's for (8) and (9).

### Cation-Deficient Partially Oxidized Tetracyanoplatinate(II) Solution Chemistry

Of all the different PO compounds the solution properties of the CD-POTCP have received the least attention. Some of this is because no colors are observed in the formation nor the dissolved solutions like the POBOP and the AD-POTCP solutions. It was of interest if the CD-POTCP forms from a Pt(IV) and a Pt(II) like that of the AD-POTCP as seen in equation 1 or if there is a more complicated process like that seen in solutions of the POBOP in scheme 1. If there are oligomers or any association of metal ions present in the formation of the CD-POTCP they do not have visible absorption bands like the POBOP because these solutions are clear like the unoxidized TCP's.

During the initial determination on the feasibility of studying these solutions it was determined that there was a Pt(IV) complex in the reaction solutions when forming the CD-POTCP using hydrogen peroxide. The Pt(IV) that exists in these solutions is of the form  $\text{Pt}(\text{CN})_4(\text{OH}_2)_2^{2-}$  (11).

(11) was described by Russian scientists and they have reported the

formation of this Pt(IV) as the potassium salt  $K_2Pt(CN)_4(OH)_2 \cdot 2H_2O$  (**11A**). The formation and isolation of pure (**11A**) was never achieved by their procedure (31). However,  $^{195}Pt$  nmr reveals that (**11**) is the dominant species present when the TCP's are oxidized with sufficient amounts of hydrogen peroxide under acidic conditions. This Pt(IV) is also the dominant species any time the conditions and oxidant used result in a larger than one electron oxidation of the TCP's.

Of considerable interest to the work described here are the reports by Levy of a purple Pt(III) crystal formed by oxidation of (**8**) with nitric acid and perhydrol (22). Purple colors are not observed in the reaction solutions when POTCP compounds are formed but when a one-electron oxidation of TCP is done, a purple color is observed after two weeks. To date there has been no characterization of any purple complexes concerning the platinumcyanides. The purple color observed in the oxidized TCP solutions is comparable to that seen in the formation of the POBOP. In the case of the POBOP it is believed this color is the result of the trimeric platinumoxalate shown in scheme I. This color is also similar to that of the platinum blues (Figure 1) which are all tetrameric and result in blue or purple colors. It may be reasonable to expect that the purple color seen in the oxidized solution of the TCP's is also a trimeric or tetrameric species. It is reasonable to compare the solution colors of the oxalates and the cyanides because the colors exhibited by these complexes are the result of Pt-Pt interaction. On the other hand one must be cautious comparing Levy's purple solid with the purple solutions because of the large difference in the Pt-Pt

interactions between the solid phase and the solutions. It would not be surprising if a purple tetramer that existed in solution gave some other color upon crystallization. For example the dimeric oxalate gives yellow solutions but it would be possible for the crystalline dimer to be purple. This is the direct result of the packing energies for these complexes. The solid phase can give drastically different Pt-Pt separation distances than the same compound in solution. Hartley concluded that the complex reported by Levy was most likely not a Pt(III) species but was a mixed valence species with stacking of Pt(II) and Pt(IV) centers (32). However, the assumptions by Hartley were made before many Pt(III) complexes had been synthesized.

Piccinin and Toussaint also reported a Pt(III) species in 1967 but their crystal structure is incomplete (33). They reported making the Pt(III) species using  $\text{HNO}_3$  to oxidize  $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$  (**8A**) to  $\text{K}_2\text{Pt}(\text{CN})_5 \cdot 3\text{H}_2\text{O}$  (**12**). The solid species reported on by Piccinin and Toussaint was reported to also be purple like that described by Levy. They also referenced Levy's 1912 paper for the synthesis of this compound.

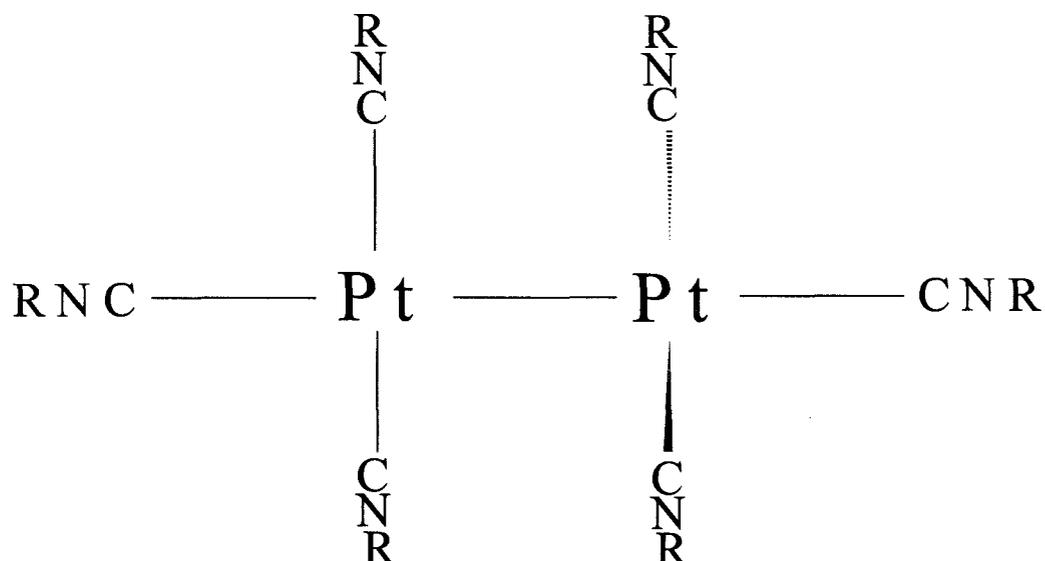
### Platinum(II) Isocyanide Complexes

#### Chemistry Effects on the Platinum Atom From the Isocyanide Ligand

Because of the highly anisotropic physical properties of the PO platinum

cyanides and oxalates, other ligands have been studied to determine if they also form complexes having similar anisotropic physical properties. Some of the interest lies with ligands that can be derivatized so the ensuing PO compound could be attached to surfaces and in essence one could make a molecular wire that can be bound to a surface. This would continue with the further miniaturization of electrical circuitry. Isocyanides are one type of ligand that can be derivatized because of the ability to alter the terminal alkyl group. To date none of the isocyanides studied have been susceptible to partial oxidation.

The isocyanides stabilize metals to a greater extent than the cyanides do in low oxidation states. This is probably due to the fact that isocyanides are fairly good reducing agents. Their stabilization of low oxidation states is apparent in the Pt(I) species  $[\text{Pt}(\text{CNC}_2\text{H}_5)_6][\text{BF}_4]_2$  (**13**). (**13**) has a Pt-Pt separation of 2.583Å. The crystal structure has been solved for the Pt(I) methyl isocyanide  $[\text{Pt}(\text{CNCH}_3)_6][\text{BF}_4]_2$  (**14**) and the crystal structure of the ethyl isocyanide is described in this thesis (34,35). This species has some unique characteristics. It is one of the few stable Pt(I) species that has been characterized by  $^{195}\text{Pt}$  nmr,  $^1\text{H}$  nmr and x-ray crystallography. Its stability is also unique because of the unsaturation at the metal centers. The structure of these complexes is seen in figure 5. A good overview of isocyanides can be found in the references listed and all those therein (75,76).



**Figure 6.** Depiction of the Pt(I) unsaturated isocyanide complexes.

The result of the unsaturation is that there is a ligand along what would be the metal-metal bonding axis. This Pt(I) species contains a Pt-Pt bond that is shorter than any of the dimeric Pt(III) that have been found. It is also shorter than all the known bridged Pt(III) complexes except for the one used in figure 4. Cyanides on the other hand form stable complexes in high (+4) oxidation states.

Molecular orbital (MO) considerations that are described later indicate that removal of electrons from the  $dz^2$  orbitals in Pt(II) complexes is necessary to form strong metal-metal bonds. The Pt(I) isocyanide mentioned above is a special

case where there is unsaturation at the metal that makes the metal-metal bond possible. The higher the oxidation state of a metal-metal bonded complex the shorter this bond will be. Removal of electrons the antibonding orbital would give a higher bond order. Finding isocyanides that will allow the metal to undergo partial oxidation has not been done. To date there are no known platinum isocyanides that exist in oxidation states higher than +2. Because the isocyanides prefer to be in lower oxidation states it is unlikely without altering the substituents on the isocyanide to get the platinum to oxidize.

Isocyanide ligands are also susceptible to nucleophilic attack when coordinated to a metal-although most organic solvents are poor enough nucleophiles they result in the rate of nucleophilic attack being very slow. The rate of attack is sufficiently slow enough in acetonitrile that it does not impede the solution studies of these complexes. In acetonitrile at 25°C one usually has up to one hour before any significant changes are seen in the UV-Visible absorbance of the isocyanides. When the isocyanides are dissolved in water at 25°C there are changes seen in the UV-Visible spectrum after 30 minutes. If the solution studies are done as low as 7°C there are no changes in the spectrum after 2 hours. The mechanism for the nucleophilic attack on the isocyanide by water has been studied and described by Balch (36,37). The UV-Visible studies done here were done within 15 minutes of dissolution and this showed no degradation of the ethyl isocyanides.

## Vapochromic Double Salts

### Solid State Properties of the Vapochromic Double Salts

One interesting property associated with the isocyanide complexes when they are combined with the TCP's is the resulting vapochromic properties of the resulting DS. Vapochromism is the ability of these complexes to change color when exposed to solvent vapors. The vapochromic properties in these solid complexes give changes in the color of the complex when exposed to volatile organic compounds (VOC's) (38,39). The color change observed is reversed when the solvent is removed from the presence of the isocyanide complex. The most useful vapochromic complex for the detection of VOC's are of the type  $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]$  (where  $\text{R} = \text{C}_6\text{H}_4\text{-C}_n\text{H}_{n+1}$   $n > 5$ ) (Figure 7). The first vapochromic complexes contained tetracyanopalladate as the anion (37). These complexes are potentially useful for both environmental and industrial detection of VOC's. In most cases the eye can see the change in color of the vapochromic solid. The magnitude of the shift is different for the various solvents when exposed to a vapochromic complex as is shown in table 3.



**Figure 7.** Arylisocyanideplatinum(II) tetracyanoplatinate(II) vapochromic complex.

Table 3. Absorption for solid state films of I when exposed to VOC's

Solvent	Absorption max(nm)	Shift(nm)
None	548	
MeOH	544	-4
EtOH	554	6
2-PrOH	554	6
Et <sub>2</sub> O	558	10
CH <sub>3</sub> CN	559	11
Hexanes	561	13
Acetone	562	14
Benzene	567	19
CH <sub>2</sub> Cl <sub>2</sub>	569	21
CHCl <sub>3</sub>	578	30

For the vapochromic complexes to be effective as environmental sensors for VOC's they must be insoluble in the solvents that they will be exposed to yet still change color when exposed to the solvents being investigated.

### Solution State Properties of the Double Complex Salts

Our interest lies with double complex salts like those that exhibit vapochromic properties but are soluble in either aqueous or organic media. As with most of our research we are interested in investigating which species exhibit metal-metal bonding in solution. It is believed that the metal-metal interaction in the solid phase is the cause of the extensive colors exhibited in these double complex salts much like the colors of the TCP salts. In the case of the TCP salts when they are exposed or depleted of water a color change occurs. The change in the content of water hydration disrupts the lattice resulting in a different Pt-Pt separation and hence a different color. To have the ability to alter the vapochromic complexes for environmental uses or the electrical properties of the POTCP it is of significant importance to understand the solutions leading up to the solid state products.

Our solution studies were carried out on the tetraethylisocyanide tetracyanoplatinum  $[\text{Pt}(\text{CNC}_2\text{H}_5)_4][\text{Pt}(\text{CN})_4]$  (5) double complex salt because of its slight solubility in acetonitrile and high solubility in water. This solubility allows us to study the metal-metal interaction in solution. The ethylisocyanide double complex salt does possess vapochromic properties like the aryl isocyanides. It gives a change in color from yellow to red when exposed to water vapor but because of its solubility in water it begins to dissolve. This ethylisocyanide complex is not favorable for practical use as a vapochromic compound for two

reasons. The ethylisocyanide complex only shows vapochromism towards water and it is soluble in this solvent. Secondly there is no demand for the detection of water vapor. However this complex does have vapochromic properties and it is easily made. These reasons make it a useful example of these complexes to study the metal-metal interactions in the solution state.

### Mixed Cyanide/Isocyanide Platinum(II) Complexes

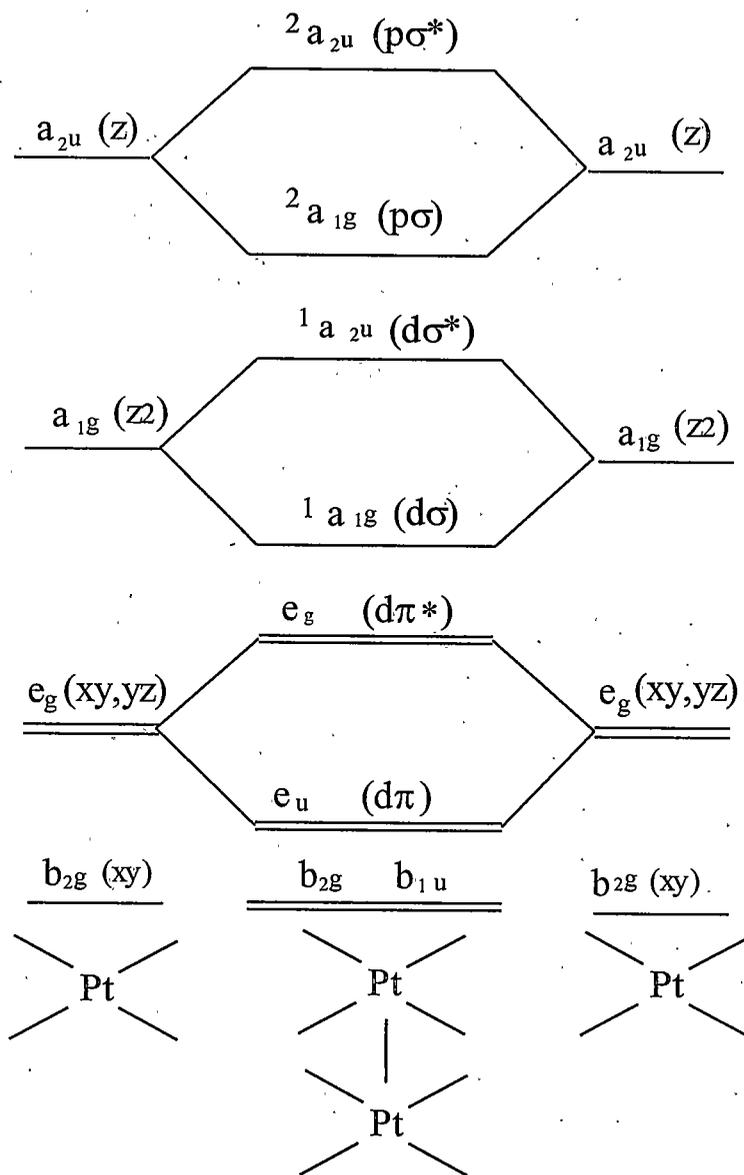
In addition to the tetrakisocyanideplatinum(II) complexes Isci and Mason assigned the electronic spectra for bismethyldicyanoplatinum(II) and bisethylidicyanoplatinum(II) (57). These complexes have received no attention beyond the work of Isci and Mason. The crystal structures have been solved for the two mixed complexes and described here. The bond lengths of the mixed complexes have been analyzed and attempts have been made to position the two strong field ligands in respect to their position in the spectrochemical series. Isci and Mason made suggestions that the CNR was in fact a slightly stronger  $\pi$ -acids than the  $\text{CN}^-$  ligand. The crystal structures of the bisisocyanidedicyano complexes are studied and conclusions are made on the  $\pi$ -acid strengths of the two ligands.

A similar complex to the mixed isocyano/cyano is the cis- $\text{Pt}(\text{CH}_3)_2(\text{CNCH}_3)_2$  that was studied by Pudaphat (41). The few known

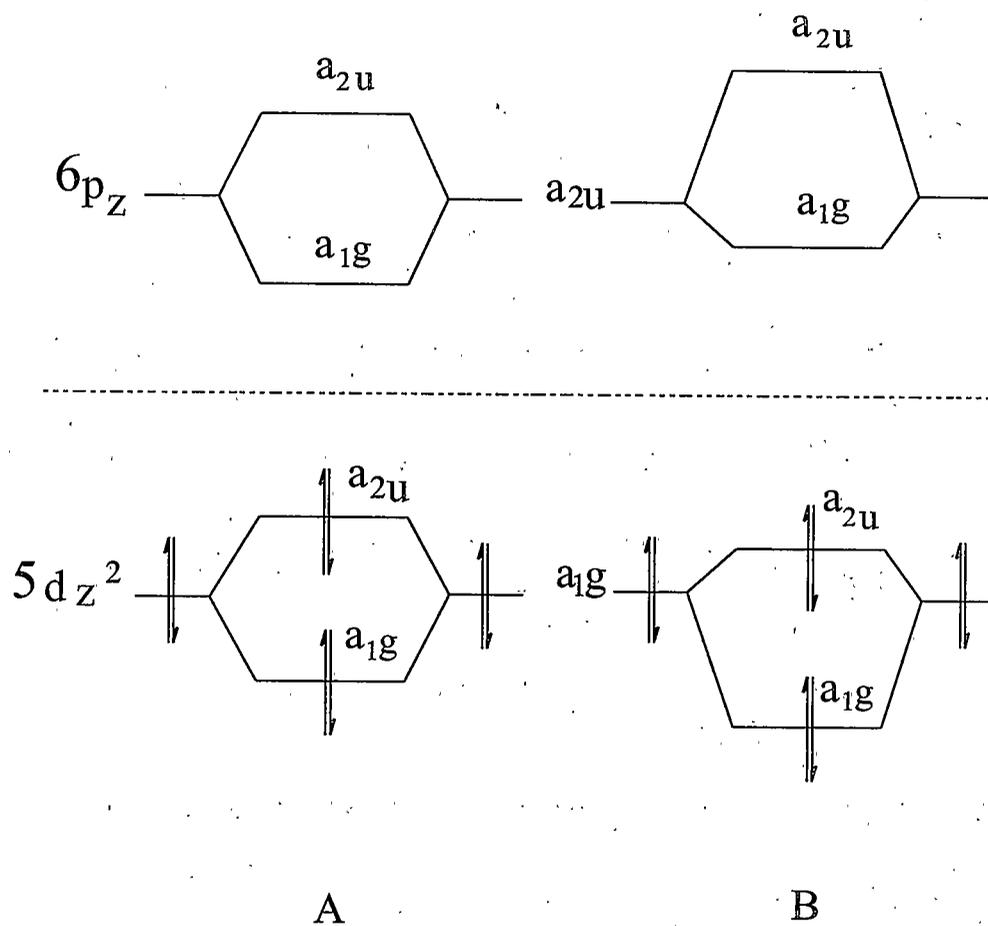
(bisisocyanide)(biscyano/bismethyl) platinum(II) complexes containing the three strong field ligands CNR, CN<sup>-</sup> and CH<sub>3</sub> all give the cis arrangement. The complexes structured here may give some information on the small differences that exist between the ligands in regard to the thermodynamic cis/trans-influence.

### Bonding Descriptions for the Pt-Pt Complexes

An appreciation of the molecular orbital bonding descriptions for metal-metal complexes is helpful in the understanding of the chemistry involved with these complexes. All the Pt(II) TCP's are d<sup>8</sup> square planar complexes. Figure 8 shows a simplified MO sketch for the interaction of two platinum atoms. Figure 9 expands the view of figure 8 to only include the HOMO and LUMO of two interacting platinum complexes. The MO diagram would suggest there is no metal-metal interaction for the complex since the a<sub>1g</sub> and a\*<sub>2u</sub> are both full and thus there would be no net bonding interaction (figure 9A). However the a<sub>1g</sub> and a<sub>2u</sub> derived from dz<sup>2</sup> orbitals are lowered in energy compared to the a<sub>1g</sub> and a<sub>2u</sub> that are derived from p<sub>z</sub> orbitals (9,42). This repelling arises because the a<sub>1g</sub> and a<sub>2u</sub> are non-degenerate molecular orbitals that are of similar symmetry. This results in a net bonding energy for the TCP's as shown in figure 9B. Krogmann and Gray have termed this as a configuration interaction. The configuration interaction gives a small net bonding interaction in the TCP's and this is evident



**Figure 8.** Simplified MO sketch of two interacting square planar platinum complexes.



**Figure 9.** a) Two platinum atoms interacting giving no net bonding interaction b) two platinum atoms interacting with a "configuration interaction" resulting in a net bonding interaction for the two platinum atoms.

in the Pt-Pt distances which are all greater than 3Å. As the configuration interaction becomes larger the resulting Pt-Pt separation is shorter. The electronic transition energy moves to lower energy the larger that the configuration interaction is (13).

A similar treatment for metal-metal interactions was done by Mann et. al. (73,74). The favorable metal-metal interactions of the dinuclear tetraphenylisocyaniderhodium(I) was rationalized with a molecular orbital depiction that is identical to the treatment shown in figure 9. The symmetry between the platinum and the rhodium species is the same so the molecular orbital treatment would be identical. The rhodium isocyanides give similar solid state complexes as the platinum cyanides where there is metal-metal interactions in both the platinum and rhodium cases with the metal-metal distances greater than 3Å. The major difference between the two systems is in the solution properties. The rhodium complexes give metal-metal association into the solution state where the platinum cyanides only give association in oxidized solutions and when mixed with a planar counter-cation.

One would expect a resulting stabilization of a Pt-Pt complex if electrons were effectively removed from the  $\sigma^*$  orbital. This is the case in the POTCP's. It is more appropriate to view these complexes in a MO band model. Figure 10 shows the band model of a POTCP platinum chain complex. Figure 11 is the band model for a chain of Pt(II). In figure 10 it is seen that upon PO the removal of electrons from bands that are mostly antibonding in character causes a net

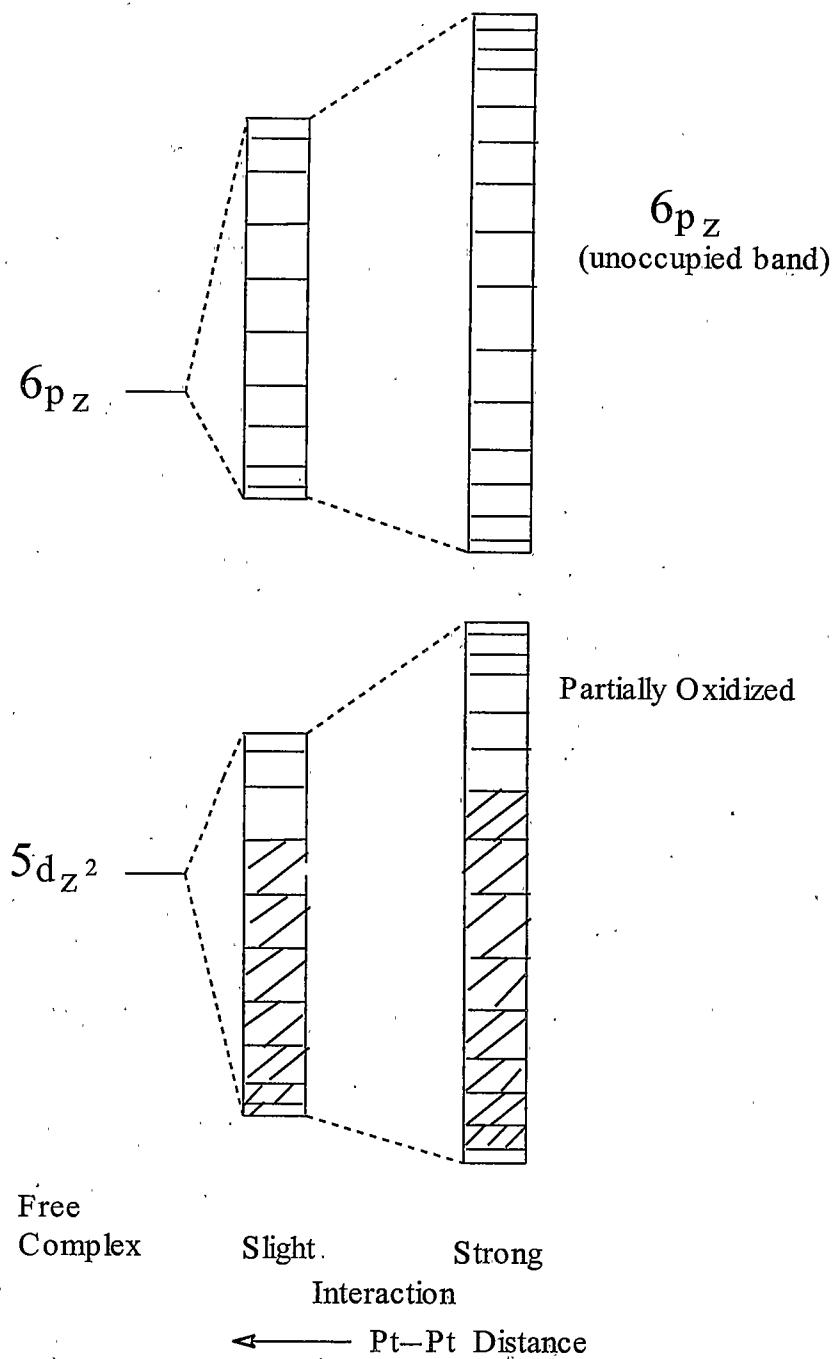


Figure 10. Band model for the POTCP chain compounds.

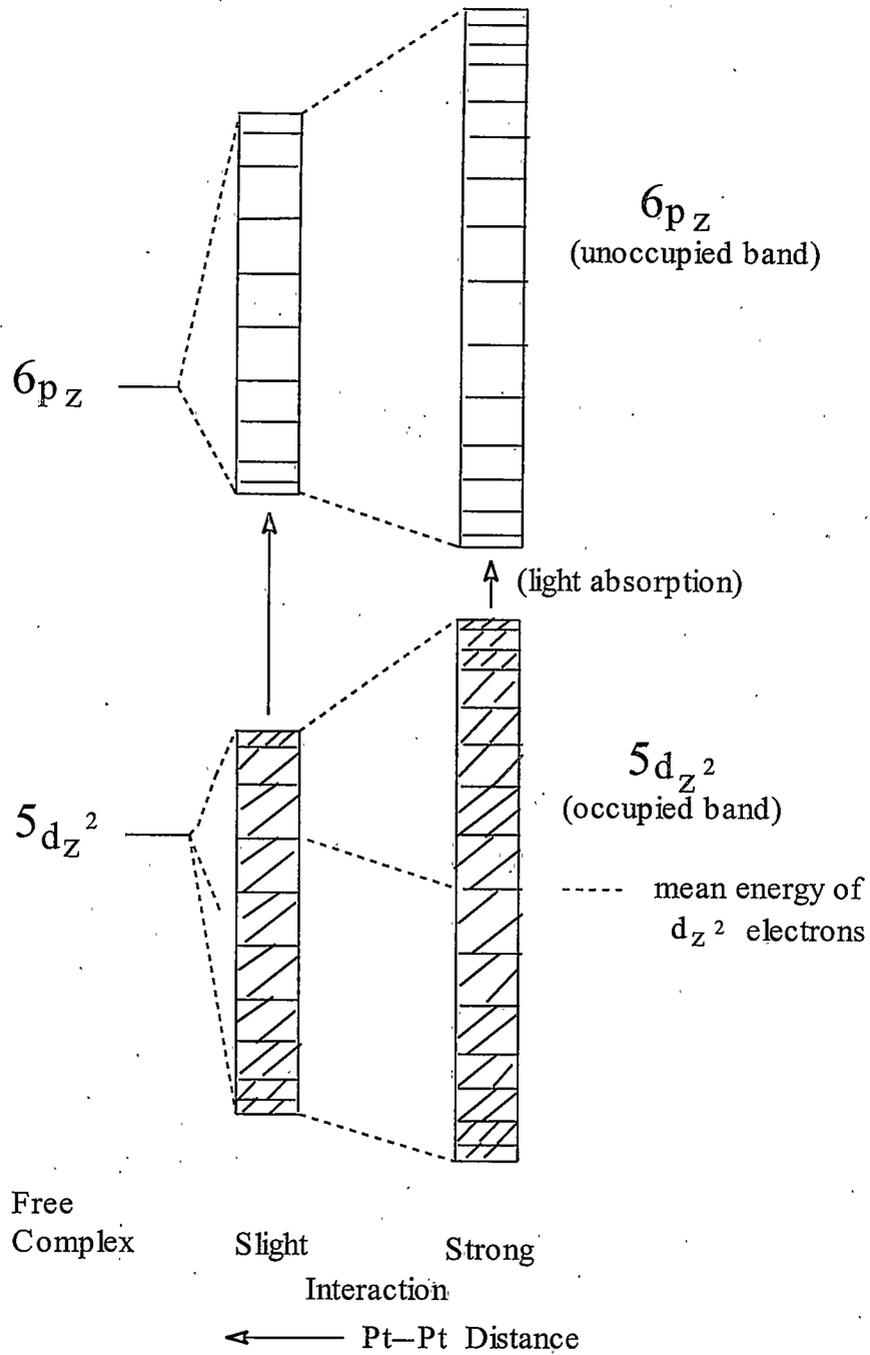


Figure 11. Band model of a chain of platinum(II) compounds.

stabilization and thus a shorter Pt-Pt bond. This is correlated with the DPO described earlier where the more electrons that are removed the lower in energy the molecule becomes and the shorter the Pt-Pt bond.

It would seem logical from the MO depiction in figure 9 that one would be able to suggest the inherent stability of the dimeric Pt(III) complexes. The dimeric Pt(III) complexes have  $d^7$  electron configurations giving a total of 14 electrons to accommodate on the correlation diagram. When describing this on the MO diagram it would appear the Pt(III) dimers should be more stable than the POTCP complexes. Only needing to fill 14 electrons on the MO diagram would result in a much more energetically favorable bonding situation than the POTCP. There must be larger electronic effects that take precedence causing the Pt(III) dimers to not be all that common. However, the few that exist do have shorter Pt-Pt separations, which is what the MO diagrams suggest.

### $^{195}\text{Pt}$ Nuclear Magnetic Resonance

$^{195}\text{Pt}$  nmr spectroscopy gives us a powerful tool to probe the solution chemistry of the TCP's and their partially oxidized compounds. The  $^{195}\text{Pt}$  chemical shift affords us useful information on the species present in solution. The chemical shift is dependent on both the ligands surrounding the platinum atom and the oxidation state of the metal. Although there is overlap of where the

different oxidation states of Pt occur in the spectrum, the oxidation state of the Pt species can be nearly assigned by where the chemical shift occurs in the spectrum assuming there is some knowledge of the ligands attached to platinum.

The one bond coupling constants are also indicative of the oxidation state of the platinum complex. This can be useful when the oxidation state of different species in solution are unknown. On going to a higher oxidation state the couplings decrease due to less s character involved in the bonding. In the case of square planar platinum(II) complexes the hybridization is  $dsp^2$  which has a 25% s character. Octahedral platinum(IV) complexes on the other hand are  $d^2sp^3$  which correlates with only about a 17% s character. The  $^1J_{Pt-C}$  in the platinum cyanides are on the order of 250Hz smaller for the Pt(IV) species than their Pt(II) counterparts (43,44).

Unfortunately any species present in solution that are monomeric Pt(III) can not be detected because they are paramagnetic. However, if the Pt(III) species exist as a dimeric Pt(III) species or any even numbered multinuclear species they are then diamagnetic and nmr detectable. Broad peaks of greater than 200Hz in width generally give a good indication that metal-metal associated species are present in the solution. The broadening of dimers occurs for two reasons. The first is that these complexes have higher molecular weights compared to their monomer counterparts. This results in a slower tumbling rate and a broader signal. Secondly the Pt(III) dimers have faster relaxation times which also causes broadening of the resonance.

The chemical shift range for  $^{195}\text{Pt}$  spans about 15,000ppm. The slightest change of the electronic influences surrounding the platinum atom result in a change in its chemical shift. In some cases exchange of only a single ligand on a platinum complex can result in a chemical shift change of up to 1000ppm. The  $^{195}\text{Pt}$  chemical shifts of hundreds of various complexes can be found in the reviews done by Pregosin (43,44).

The substituents surrounding the Pt nucleus can be determined with near certainty by the  $^{195}\text{Pt}$  chemical shift using comparative methods (43,44). For example in the case of oxidation where two oxygen atoms are added to the platinum center the chemical shift observed for the new complex can be compared to other well known oxidation's where two coordinated oxygen atoms are added to the Pt nucleus. The comparative method is described in great detail later in this thesis.

## EXPERIMENTAL METHODS

Preparation of Compounds

Starting Materials  $\text{K}_2\text{Pt}(\text{Cl})_4$  (**15**) was obtained from Alfa Aesar and used without further purification. KCN was obtained from J.T. Baker and used without further purification. The monopersulfate compound Oxone<sup>TM</sup> was also obtained from Aldrich and used without further purification. The 99+%  $\text{K}^{13}\text{CN}$  and the 30% solution of hydrogen peroxide were obtained from Aldrich chemical and used without further purification. Tetra-butylhydrogen peroxide was obtained from Fisher scientific and used without further purification. All alkylating agents including methyl iodide, ethyl iodide,  $[(\text{C}_2\text{H}_5)_3\text{O}][\text{BF}_4]$  and  $[(\text{CH}_3)_3\text{O}][\text{BF}_4]$  were obtained from Aldrich and used without further purification. The  $\text{Cs}_2\text{SO}_4$  and the tetra-n-butylammonium chloride were obtained from Aldrich Chemical and the  $\text{BaSO}_4$  was obtained from J.T. Baker Co. and were used without further purification. Anhydrous  $\text{CH}_2\text{Cl}_2$  was obtained by distillation over  $\text{P}_2\text{O}_5$ .

Preparation of  $\text{MPt}(\text{CN})_4 \cdot \text{XH}_2\text{O}$  (M=Ba,  $\text{K}_2$ ,  $\text{Na}_2$ ,  $\text{Cs}_2$ , [t-n-butylN]<sub>2</sub>) (**8A-8D**) The  $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$  (**8A**) was made by adding a slightly greater than 4 mole equivalents of KCN to a concentrated solution of (**15**) and allowed to stir for one

hour. The reaction was dried and brought back up in a minimal amount of warm water (50°C) and placed over a NaCl ice bath. The crystals were then washed, filtered with a little cold water and collected from a fine porosity fritted filter. It is necessary to repeat the crystallization process at least four times to obtain about 96% of the TCP.

$\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  (**8B**) was prepared by addition of a small excess of barium chloride to a fairly concentrated solution of compound (**8A**), resulting in a green solid precipitating out of the solution immediately (22). The green solid was collected over a fine fritted filter. Re-dissolving the collected green solid in warm water (60°C) and then cooling over an ice bath results in bright yellow needle like crystals of the form (**8B**). The yield obtained for the Ba salt by way of the K salt was 91.4%.

$\text{Na}_2\text{Pt}(\text{CN})_4$  (**8C**) was prepared by ion exchange. A concentrated solution of (**8A**) was prepared in water and ran through a Dowex 50W-8X  $\text{Na}^+$  charged cation exchange resin. Compound (**8C**) was collected from the ion-exchange column and dried. No further purification was carried out.

$\text{Cs}_2\text{Pt}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$  (**8D**) was prepared by the method of Mafly et al. (19) 4.0g of (**8C**) was dissolved in 14.5ml of hot  $\text{H}_2\text{O}$  (75°C), to this was added 1 eq of  $\text{Cs}_2(\text{SO}_4)$  (2.86g). An immediate white precipitate of  $\text{BaSO}_4$  results. The reaction was stirred for 30 minutes then the  $\text{BaSO}_4$  was filtered off over a fine fritted filter. The  $\text{BaSO}_4$  was washed 3 times with warm water, the filtrate was then dried and brought back up in a minimal amount of hot water and cooled

over a NaCl ice bath. The resulting white crystals were filtered off and washed with cold water. The recrystallization was repeated 3 more time on the filtrate obtaining a 89% yield.

(t-n-butylN)<sub>2</sub>Pt(CN)<sub>4</sub> (**8E**) This was prepared similar to the literature method with small modifications (45). 4.0g of (**8A**) were dissolved up in 10ml of water in a separation funnel. A stoichiometric amount of the tetra-n-butylammonium chloride was added to the solution of (**8A**). The resulting mixture was then extracted 3 times with CH<sub>2</sub>Cl<sub>2</sub>. The collected organic phase was dried over MgSO<sub>4</sub> and then the solution was dried on vacuo. Recovery of platinum salt = 95%.

Preparation of K<sub>2</sub>Pt(ox)<sub>2</sub> (**16**) The complex was prepared by the method of Krogmann and Dodel using K<sub>2</sub>Pt(Cl)<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (17,19).

Preparation of K<sub>2</sub>Pt(ox)(CN)<sub>2</sub> (**17**) .2g of K<sub>2</sub>Pt(ox)<sub>2</sub> (**16**) was dissolved in 5ml of distilled water and heated to 55°C. To this was added .054g (2mole eq.) of K<sup>13</sup>CN. The mixture was stirred for one hour holding the temperature at 55°C and then dried. The solid after drying contained a mixture of yellow and red. The <sup>195</sup>Pt nmr indicated three different species present in different concentrations. Pt(ox)<sub>2</sub><sup>2-</sup> (-525ppm) << Pt(CN)<sub>4</sub><sup>2-</sup> (Pentet with <sup>1</sup>J<sub>Pt-C</sub>=1029Hz) < Pt(ox)(CN)<sub>2</sub><sup>2-</sup> (triplet with <sup>1</sup>J<sub>Pt-C</sub>=1195Hz). The <sup>13</sup>C spectrum shows a 1:4:1 triplet at 125ppm for the Pt(CN)<sub>4</sub><sup>2-</sup> and a 1:6:1 triplet at 131.5ppm for the mixed ligand species. Attempts



















































































































































































































































































































































































