



Studies of the solution chemistry in the oxidation reaction to produce the one-dimensional partially oxidized bis (oxalato) platinate polymers
by Barbara Jo Keller

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:

When acidic aqueous solutions of bis(oxalato)platinate(II), $[\text{Pt}(\text{Ox})_2]^{2-}$, are subjected to oxidation, polymeric chains of the partially oxidized bis(oxalato)platinate salts form. These polymeric chains are one-dimensional conductors with metal-metal bonded platinum atoms. Examination of the solution chemistry involved in this polymerization reaction has been studied. Four distinct solution species have been identified. The average Pt oxidation states in each of these four species are (formula not captured in OCR), respectively. The four species have been assigned chemical formulae. A reaction scheme has been proposed to explain the solution chemistry that occurs to produce each of the four solution species and finally, the polymer itself. The Pt^{3+} species has been investigated with ^{195}Pt NMR and UV-Vis spectroscopies and been determined to be a dimeric Pt^{3+} complex, (formula not captured in OCR). An extinction coefficient for the (formula not captured in OCR) complex absorbing at 426 nm has been determined. Verification of this extinction coefficient came from the UV-Vis absorbance data obtained of a solution of polymer, (formula not captured in OCR), dissolved in H_2O . An extinction coefficient and a formation constant for the (formula not captured in OCR)- complex absorbing at 510 nm were determined. The observance of consistent formation constants under various reaction conditions support the proposed reaction scheme. The dissolution of the polymer also confirmed the presence of the dimeric Pt^{3+} species through UV-Vis spectroscopy and ^{195}Pt NMR spectroscopy. Base titrations of the dissolved polymer were utilized to determine pK_a values for the dimeric Pt^{3+} complex, (formula not captured in OCR) The values are $\text{pK}_{a1} = 3.9$ and $\text{pK}_{a2} = 5.2$. The role of the acid in the polymerization reaction was investigated. pH measurements confirmed that each of the four solution species have different proton requirements. Ranges of proton requirements have been determined for each of the four solution species. In addition, FT-IR spectroscopy has confirmed that protonation of the carbonyl group on the oxalate ligand is occurring. Finally, attempts were made to oxidize bis(malonato)platinate(II), (formula not captured in OCR) to form a partially oxidized bis(malonato)platinate polymer. The attempts were unsuccessful due to the instability of the dimeric Pt^{3+} malonate complex.

STUDIES OF THE SOLUTION CHEMISTRY IN THE OXIDATION REACTION
TO PRODUCE THE ONE-DIMENSIONAL PARTIALLY OXIDIZED
BIS(OXALATO)PLATINATE POLYMERS

by

Barbara Jo Keller

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ABSTRACT

When acidic aqueous solutions of bis(oxalato)platinate(II), $[\text{Pt}(\text{ox})_2]^{2-}$, are subjected to oxidation, polymeric chains of the partially oxidized bis(oxalato)platinate salts form. These polymeric chains are one-dimensional conductors with metal-metal bonded platinum atoms. Examination of the solution chemistry involved in this polymerization reaction has been studied. Four distinct solution species have been identified. The average Pt oxidation states in each of these four species are Pt^{3+} , $\text{Pt}^{2.67+}$, $\text{Pt}^{2.5+}$ and $\text{Pt}^{2.4+}$, respectively. The four species have been assigned chemical formulae. A reaction scheme has been proposed to explain the solution chemistry that occurs to produce each of the four solution species and finally, the polymer itself. The Pt^{3+} species has been investigated with ^{195}Pt NMR and UV-Vis spectroscopies and been determined to be a dimeric Pt^{3+} complex, $[\text{Pt}(\text{ox})_2]_2^{2-}$. An extinction coefficient for the $[\text{Pt}(\text{ox})_2]_2^{2-}$ complex absorbing at 426 nm has been determined. Verification of this extinction coefficient came from the UV-Vis absorbance data obtained of a solution of polymer, $\text{K}_{1.6}[\text{Pt}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$, dissolved in H_2O . An extinction coefficient and a formation constant for the $[\text{Pt}^{2.67+}(\text{ox})_2]_3^{4-}$ complex absorbing at 510 nm were determined. The observance of consistent formation constants under various reaction conditions support the proposed reaction scheme. The dissolution of the polymer also confirmed the presence of the dimeric Pt^{3+} species through UV-Vis spectroscopy and ^{195}Pt NMR spectroscopy. Base titrations of the dissolved polymer were utilized to determine pK_a values for the dimeric Pt^{3+} complex, $[\text{Pt}^{3+}(\text{ox})_2(\text{OH}_2)]_2^{2-}$. The values are $\text{pK}_{a1} = 3.9$ and $\text{pK}_{a2} = 5.2$. The role of the acid in the polymerization reaction was investigated. pH measurements confirmed that each of the four solution species have different proton requirements. Ranges of proton requirements have been determined for each of the four solution species. In addition, FT-IR spectroscopy has confirmed that protonation of the carbonyl group on the oxalate ligand is occurring. Finally, attempts were made to oxidize bis(malonato)platinate(II), $[\text{Pt}(\text{mal})_2]^{2-}$, to form a partially oxidized bis(malonato)platinate polymer. The attempts were unsuccessful due to the instability of the dimeric Pt^{3+} malonate complex.

INTRODUCTION

The interest in the one-dimensional partially oxidized platinum complexes has recently increased dramatically. These materials exhibit unique electrical properties in that they conduct electricity in one direction along the Pt-Pt metal chain that extends down the backbone of these materials. It appears that conditions can be found whereby chain length can be controlled. If so, these new polymers could lead to new materials with unique electrical properties. It may also be possible, in the future, to form electrical circuits via chemical reactions and thereby provide an entry into the further miniaturization of electrical circuitry.

To date, only two types of one-dimensional partially oxidized platinum materials have been characterized; the linear chain bis(oxalato)platinate salts and the linear chain tetracyanoplatinate salts (1). A possible third type, partially oxidized bis(squarato)platinate has been reported by Toftlund *et al.* (2, 3) although relatively little has been done to characterize this complex. The properties of these materials in solution have received relatively little attention. This is not surprising since dissolution of the one-dimensional polymeric chains breaks up the chains into much smaller segments which do not necessarily possess the unique properties associated with the long chains. Since metal-metal bonds are quite stable it is reasonable to assume that they will persist in solution. The extent to which they persist, however, is unknown. The colors of the solutions from which these one-dimensional platinum complexes precipitate suggest that a complex

array of materials are present in both the formation of the polymer and in the dissolution of the polymer. A study of these solution species, then, could possibly provide great insight into the reactions that occur in the polymer formation. The purpose of this study is to investigate the solution reactions leading to the formation of the partially oxidized bis(oxalato)platinate salts. It is hoped that an understanding of the solution chemistry will eventually lead to ways of controlling the polymerization and thus initiate the formation of electrical circuits via chemical reactions.

Description of Pt Metal-Metal Bond Formation

Dimeric Pt Complexes

The interaction of d orbitals plays the dominant role in transition metal bonding. Platinum is no exception to this. The electronic interaction between two metal atoms is directly related to the amount of d orbital overlap between the two metal atoms. A large metal overlap will delocalize the individual metal orbitals (MO's) such that new unique molecular orbitals will occur. When only two metal atoms are interacting a metal-metal dimer is the result. Two types of metal-metal bonded dimers are known. In one type the metals are bonded directly to each other and bridged by an appropriate ligand along the metal-metal axis. Examples of this type include $K_2[Pt_2(\mu-SO_4)_4(H_2O)_2]$ (9) and $K_2[Pt_2(\mu-HPO_4)_4(H_2O)_2]$ (16). In

the second type the metals are directly bonded to each other but there is no bridging of ligands. An example of this type is $[\text{Pt}_2\text{Cl}_6(\text{NH}=\text{C}(\text{OH})\text{C}(\text{CH}_3)_3)_4]$ (30). It is the direct bonding without bridging ligands that is of interest in this work since the partially oxidized bis(oxalato)platinate polymer contains many metal-metal bonds but no apparent bridging ligands.

A simplified MO diagram shown in Figure 1 can be utilized to depict the interaction of the two platinum atoms in a dimeric species (4). This MO is the result of two platinum atoms in square planar complexes approaching each other along the z-axis. The d_{z^2} orbitals combine directly to form d_{σ} and d_{σ^*} bonding and antibonding molecular orbitals. The d_{xz} and d_{yz} orbitals combine to form two degenerate d_{π} bonding and d_{π^*} antibonding molecular orbitals. The d_{xy} orbitals form two degenerate d_{δ} bonding and d_{δ^*} antibonding molecular orbitals. The $d_{x^2-y^2}$ orbital interactions are not depicted in the MO diagram. These orbitals interact with the ligands of the square planar complex to form σ bonds and the relative energy is much lower than any of the other d orbitals. The antibonding orbital, $d_{x^2-y^2^*}$, will be a d_{δ} orbital. It can be seen then, using this simple MO, that two transition metals must have less than sixteen electrons total in their combined d orbitals to form a metal-metal bond. The Pt(II) atoms in the square planar complexes have a d^8 configuration. In order for Pt(II) complexes to form metal-metal bonded structures, they must undergo oxidation. In dimeric Pt complexes, each Pt(II) must lose one electron before metal-metal bonding can occur.

This simple MO for the dimeric complex has the disadvantage that it does

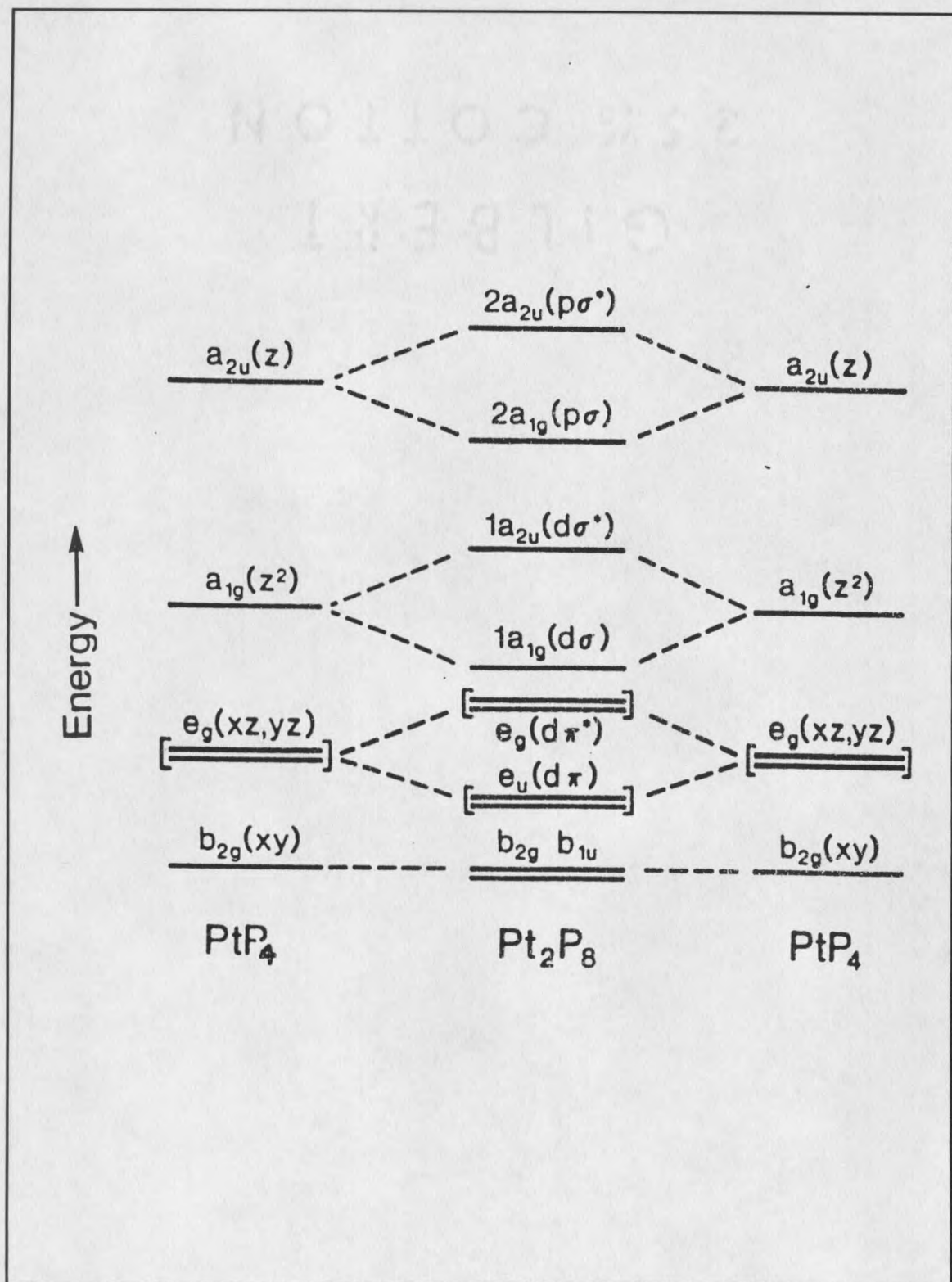


Figure 1. A simplified MO depicting the interaction of two platinum atoms (4).

not show the configuration interaction of the two adjacent complex platinum nuclei. An MO depicting this interaction is shown in Figure 2 (5). As shown before, the two $5d_{z^2}$ atomic orbitals have split to form bonding and antibonding orbitals, a_{1g} and a_{2u} . The $6p_z$ atomic orbitals have also split to form bonding and antibonding orbitals, a_{1g} and a_{2u} . The symmetry of the molecular orbitals is the same in both cases. Since nondegenerate MO's of the same symmetry "repel" each other a configuration interaction occurs and the resultant MO is depicted in Figure 2b (5). The MO's derived from the $5d_{z^2}$ orbitals obtain some p character, and those derived from the $6p_z$ orbitals acquire some d character. It is of interest then that two Pt(II) atoms could interact somewhat with each other, even though their d orbitals are filled, due to configuration interaction.

Polynuclear Platinum Complexes

When more than two platinum atoms are joined together in a single complex the MO's retain the same general splitting pattern as depicted in Figures 1 and 2 only the number of MO's obtained is increased. When a chain of platinum atoms is involved band theory is commonly used to describe the electron configurations. As more and more platinum atoms are added to the chain the number of bands become larger and larger. Figure 3 depicts the MO of a chain complex. The shorter the distance between atoms, the broader the band becomes and the shorter is the distance between the highest occupied level in the d_{z^2} band and the

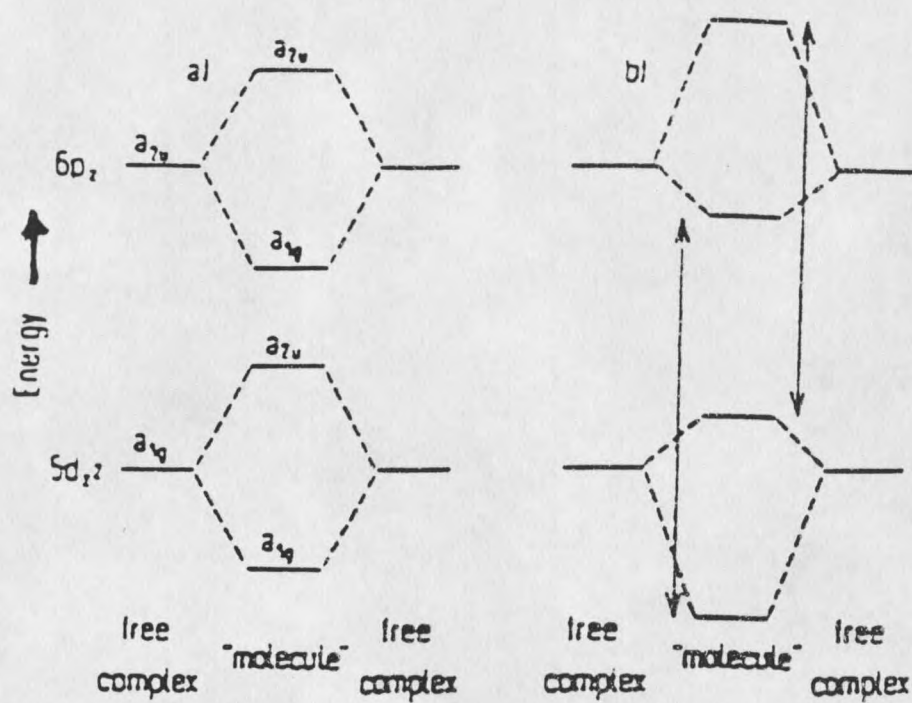


Figure 2. MO depicting configuration interaction of a dimeric Pt complex (5).

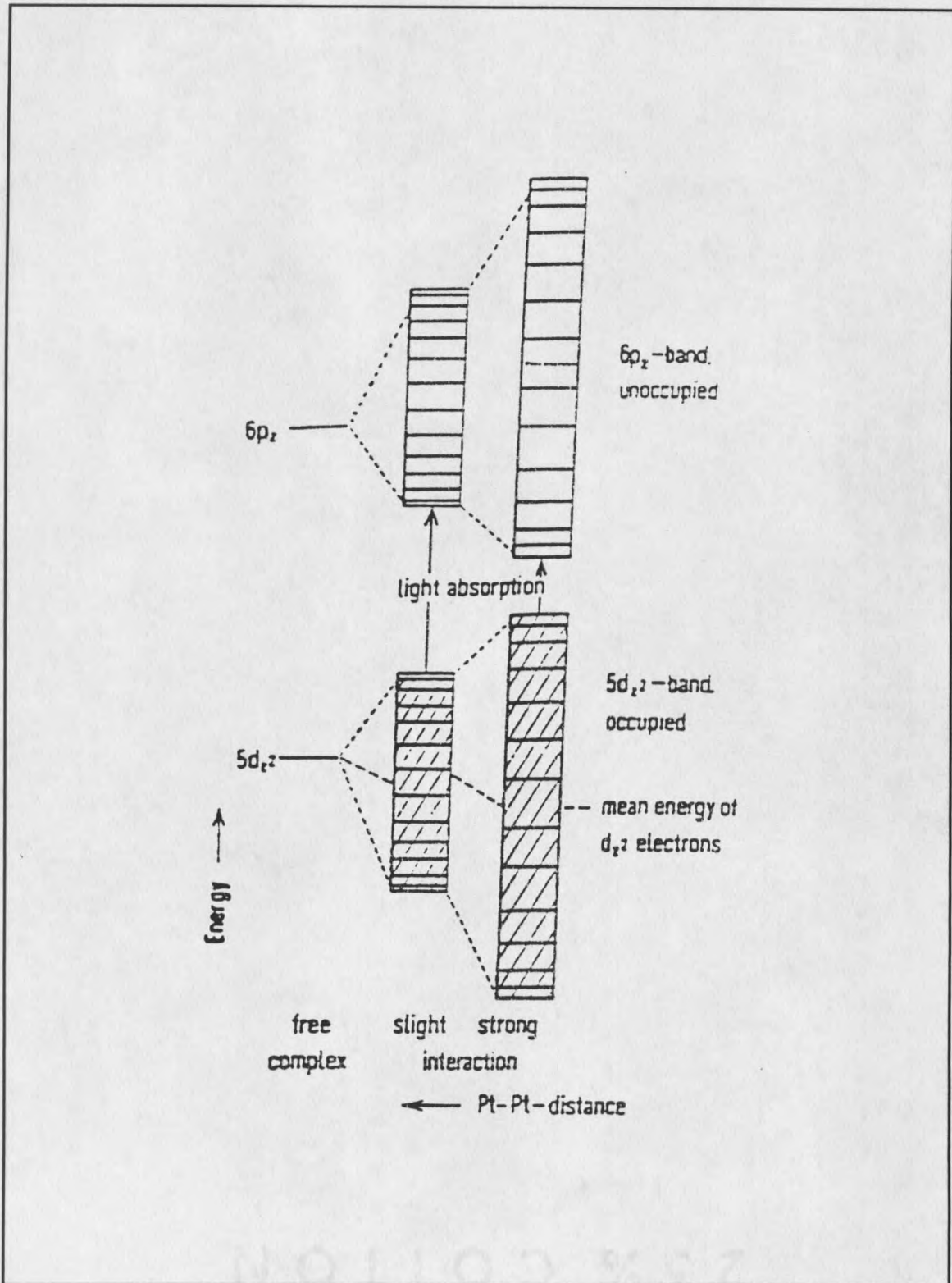


Figure 3. MO of a platinum chain complex complex (5).

lowest unoccupied level in the p_z band. The shorter the distance between Pt atoms, the smaller is the energy required to promote an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

Partially Oxidized Chain Complexes

The d_{z^2} orbital is filled in Pt(II) ions. A chain of Pt(II) ions then would have a filled d_{z^2} band. If multiple Pt(II) atoms are brought together in a chain then metal-metal bonding would not be expected to occur since the bonding and antibonding orbitals are filled. Even if configuration interaction is considered (Figure 4) the upper orbitals of this band would have an antibonding effect on the chain, since these are situated above the d_{z^2} level of the free complex. Strengthening the bonding in the chain could be achieved by removing electrons from the filled orbitals. Figure 4 shows how the Pt-Pt distance decreases (and therefore the strength of the metal-metal bond increases) as electrons are removed (5). The partially oxidized complexes of Pt undergo just such an oxidation as described here. The average oxidation state of the Pt in these complexes is nonintegral.

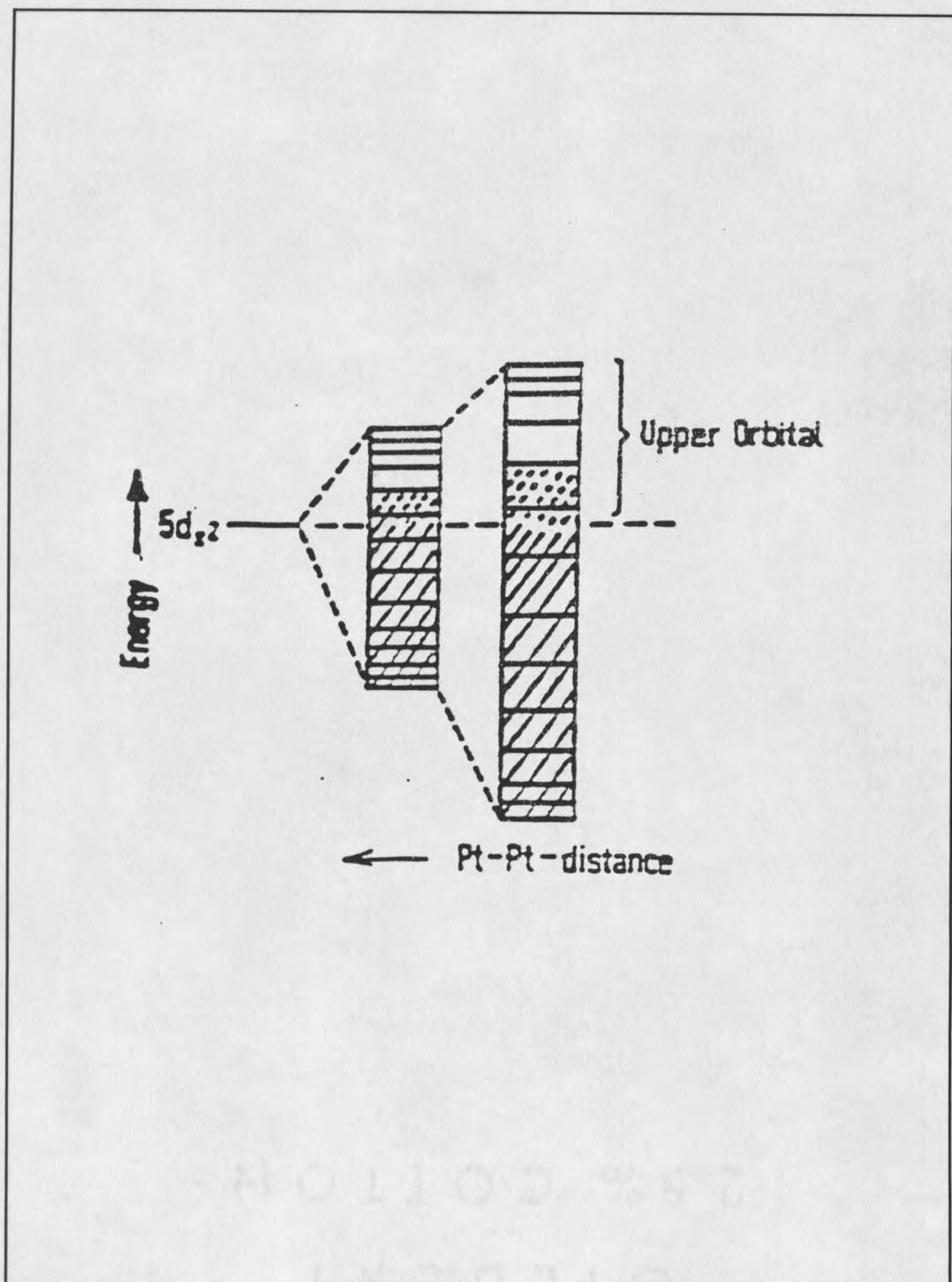


Figure 4. MO of the partially oxidized platinum chain complexes (5).

Mononuclear Platinum(III) Complexes

Mononuclear platinum(III) complexes, in which the formal oxidation state of the platinum metal center is +3, are rare. The first complex of this type to be fully characterized is $(\text{NH}_4)[\text{Pt}^{\text{III}}(\text{C}_6\text{Cl}_5)_4]$ (6). It is prepared by adding Cl_2 or Br_2 (dissolved in CCl_4) to a solution of $(\text{NH}_4)_2[\text{Pt}^{\text{II}}(\text{C}_6\text{Cl}_5)_4]$. This complex is paramagnetic since the platinum has a d^7 electron configuration. Figure 5 shows the crystal structure of this blue complex. The molecule has a square planar geometry, and the closest Pt-Pt distance is 9.7 Å. Since the molecule is paramagnetic no ^{195}Pt NMR resonances are observed. One other mononuclear Pt(III) complex that has been reported is $[\text{Pt}^{\text{III}}\text{L}_2]$ where L = 1,4,7-triazacyclononane (7). This complex is formed by room temperature oxidation of $[\text{Pt}^{\text{II}}\text{L}_2]$ where L = 1,4,7-triazacyclononane at 0.5V under nitrogen in acetonitrile. This complex is also paramagnetic. Finally, Boucher *et al.* have reported the complex $[\text{Pt}^{\text{III}}(\text{diamsar})]^{3+}$ where diamsar = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (8). This complex is generated by the γ -radiolysis of $[\text{Pt}^{\text{IV}}(\text{diamsar})]^{4+}$ at 77K. Other mononuclear platinum(III) complexes have been reported but exist only as short-lived transients in various reactions.

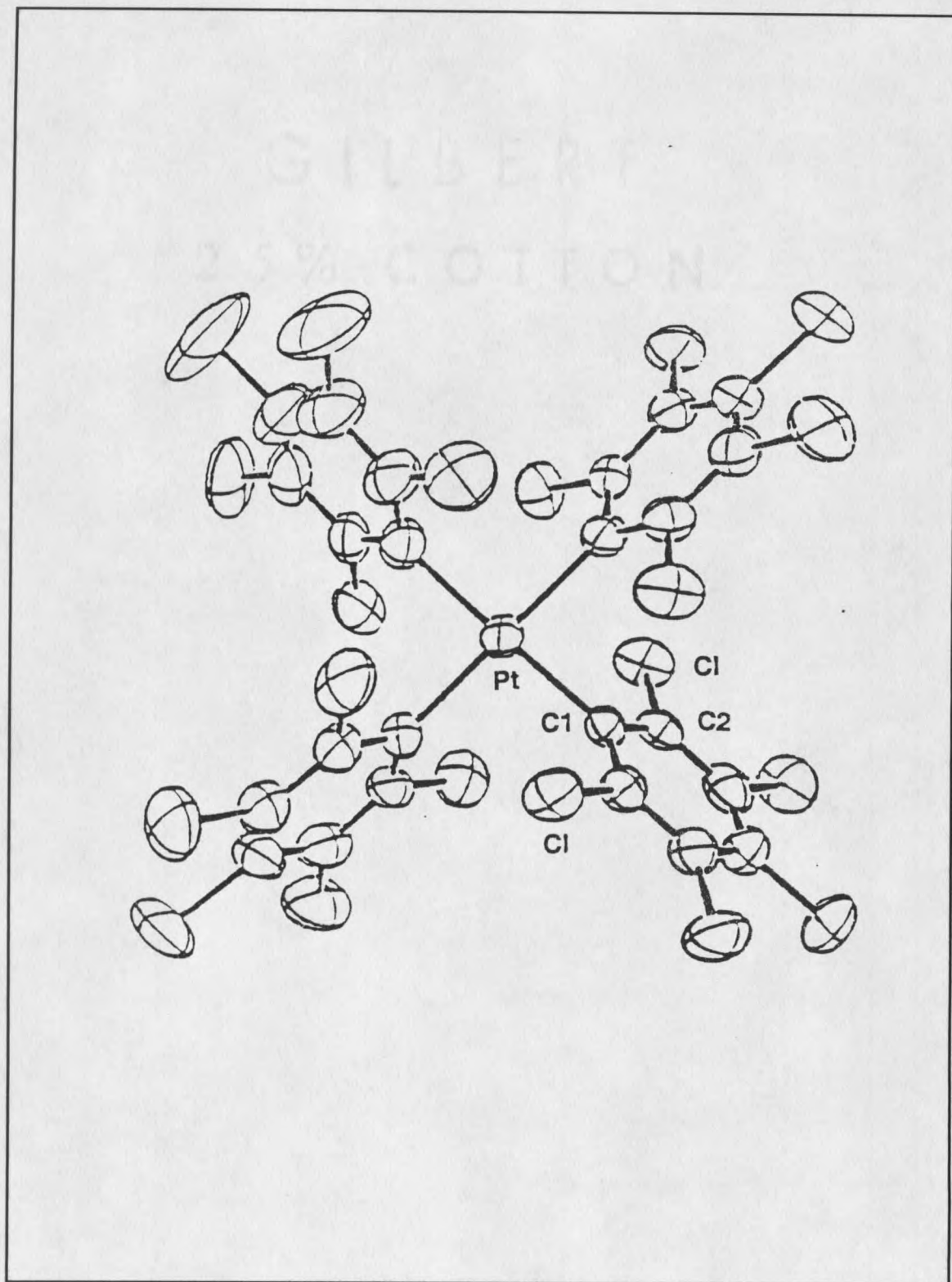


Figure 5. Crystal structure of $[\text{Pt}^{\text{III}}(\text{C}_6\text{Cl}_5)_4]^-$ (6).

Dimeric Platinum(III) Complexes

Bridged ComplexesPlatinum(III) Sulfates

The tetra- μ -sulfato complex, $K_2[Pt_2(\mu-SO_4)_4(H_2O)_2]$, was the first diplatinum(III) complex to be characterized using X-ray crystallography (9). Figure 6 show the structure of this complex. This compound is prepared by reacting $K_2[Pt(NO_2)_4]$ with sulfuric acid. Potentiometric titrations have shown that the platinum metal centers are in an oxidation state (+3). X-ray crystallographic studies have shown that this compound contains two Pt(III) centers metal-metal bonded with a bond distance of 2.466 Å. The Pt centers are bridged by four sulfates in a "lantern" structure. Work by Appleton et. al. has shown that the axial Pt-OH₂ bonds in this complex are labile to ligand substitution due to the high *trans* effect of the metal-metal bond (10). Raman spectra show a $\nu(Pt-Pt)$ between 150-236 cm⁻¹ (11, 12, 13). The electronic spectra of the diaqua, dibromo, dichloro derivatives contain an intense band at 220nm which has been assigned to the metal-metal $\sigma \rightarrow \sigma^*$ transition (12, 13). The complex is diamagnetic since the individual platinum atoms, which are d⁷, have formed a metal-metal bond resulting in an orbital scheme of $\sigma^2\pi^4\delta^2\delta^*\pi^4$. NMR data were obtained by Appleton *et al.* (10) on $[Pt_2(\mu-SO_4)_4XY]^{n-}$ where the axial ligands, X and Y, included H₂O, CN⁻, NH₃,

