



Spectroscopic investigation of di- $\mu$ -hydroxo bridged platinum complexes  
by John Raymond Marvin

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 various Pt(II) complexes, coordinated in a cis fashion by certain monodentate sulfoxide and phosphane ligands, undergo hydrolysis, an extremely acidic (pH  $\sim$  1.5-2.5) solution results. These hydrolysis reactions are accompanied by the formation of di- and occasionally tri-hydroxo bridged complexes which exist in equilibrium with the monomers at these low pH values. For the sulfoxide complexes, rapid scrambling of the sulfoxide ligands occurs between the two homodimeric forms in solution. The phosphane ligands, in contrast, appear to be considerably more substitutionally inert.

When monodentate sulfoxides are replaced by the bidentate sulfoxide ligand CH<sub>3</sub>-S(O)-CH<sub>2</sub>CH<sub>2</sub>-S(O)-CH<sub>3</sub> (MSE), hydrolysis is followed by the formation of a complex mixture of products postulated to have a polymeric structure with the MSE ligand in a bridging role.

Heterodimeric structures were obtained when two different monomeric diaqua complexes containing neutral monodentate phosphane ligands were reacted in aqueous solution. Only the monomeric substitution product was observed when one of the monomers contained an anionic ligand (e.g. oxalate). A series of heterodimeric complexes containing the Pt(PMe<sub>3</sub>)<sub>2</sub> fragment were systematically synthesized incorporating neutral nitrogen and sulfur donor ligands.

A novel network silver complex was obtained and characterized. This structure was initially formed as a result of the incomplete removal of Ag(I) ion used to assist in abstraction of chloride ion from the Pt(II) starting material. A crystal structure was acquired which shows the MSE ligand in a bridging mode.

Attempts to determine the acid dissociation constants of the monomeric diaqua complexes by potentiometric titration revealed a titration curve with only a single apparent inflection point, possibly indicating overlapping pK<sub>a</sub> values. NMR titration of the trimethylphosphane system, plotting <sup>1</sup>H chemical shift vs. pH, revealed, two abrupt transitions which were associated with the pK<sub>a</sub>'s of the coordinated water ligands giving values of 6.5 and 9.6 for pK<sub>a1</sub> and pK<sub>a2</sub> respectively. The sum of these pK's was compared with the sum of the dimer formation (K<sub>f</sub>) and dissociation (K<sub>a</sub>) constants which had also been determined by NMR methods. K<sub>f</sub> was found to be  $2.701 \pm 0.050$  and K<sub>d</sub> was found to be  $22.008 \pm 0.059$ .

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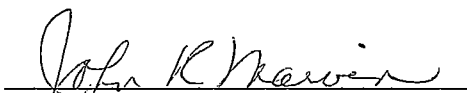
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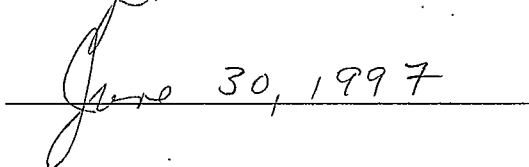
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## ABSTRACT

When various Pt(II) complexes, coordinated in a *cis* fashion by certain monodentate sulfoxide and phosphane ligands, undergo hydrolysis, an extremely acidic (pH  $\sim$  1.5-2.5) solution results. These hydrolysis reactions are accompanied by the formation of di- and occasionally tri-hydroxo bridged complexes which exist in equilibrium with the monomers at these low pH values. For the sulfoxide complexes, rapid scrambling of the sulfoxide ligands occurs between the two homodimeric forms in solution. The phosphane ligands, in contrast, appear to be considerably more substitutionally inert.

When monodentate sulfoxides are replaced by the bidentate sulfoxide ligand  $\text{CH}_3\text{-S(O)-CH}_2\text{CH}_2\text{-S(O)-CH}_3$  (MSE), hydrolysis is followed by the formation of a complex mixture of products postulated to have a polymeric structure with the MSE ligand in a bridging role.

Heterodimeric structures were obtained when two different monomeric diaqua complexes containing neutral monodentate phosphane ligands were reacted in aqueous solution. Only the monomeric substitution product was observed when one of the monomers contained an anionic ligand (e.g. oxalate). A series of heterodimeric complexes containing the  $\text{Pt(PMe}_3)_2$  fragment were systematically synthesized incorporating neutral nitrogen and sulfur donor ligands.

A novel network silver complex was obtained and characterized. This structure was initially formed as a result of the incomplete removal of Ag(I) ion used to assist in abstraction of chloride ion from the Pt(II) starting material. A crystal structure was acquired which shows the MSE ligand in a bridging mode.

Attempts to determine the acid dissociation constants of the monomeric diaqua complexes by potentiometric titration revealed a titration curve with only a single apparent inflection point, possibly indicating overlapping  $\text{pK}_a$  values. NMR titration of the trimethylphosphane system, plotting  $^1\text{H}$  chemical shift vs. pH, revealed two abrupt transitions which were associated with the  $\text{pK}_a$ 's of the coordinated water ligands giving values of 6.5 and 9.6 for  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  respectively. The sum of these  $\text{pK}'$ s was compared with the sum of the dimer formation ( $K_f$ ) and dissociation ( $K_d$ ) constants which had also been determined by NMR methods.  $K_f$  was found to be  $2.701 \pm 0.050$  and  $K_d$  was found to be  $22.008 \pm 0.059$ .

## INTRODUCTION

The formation of larger and ever more complex structures from simpler precursors has long been one of the primary goals of the synthetic chemist. Until recently, success in this endeavor has belonged almost exclusively to the field of organic chemistry and, although the vast array of carbon chains and rings can hardly be expected to be matched by transition metals, a great deal of progress has been made in the last few years towards increasingly more complex and functional structures containing multiple metal atoms and metal-metal bonds. In the case of carbon, the enormous diversity of structures can be explained in part by the modest size of the carbon atom and its ability to form robust multiple bonds in small molecules. In the words of one eminent chemist, "Carbon does everything well and nothing to extreme" (1).

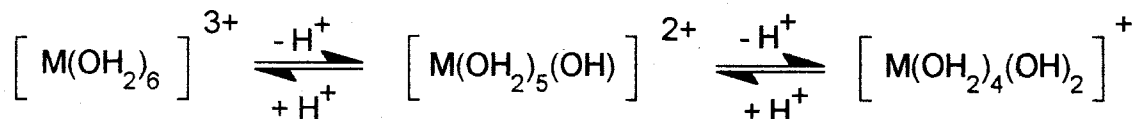
The chemistry of transition metals on the other hand is dominated by the availability of partially filled *d* orbitals. From the time of Werner at the beginning of the century up until the early 1960's, the properties of transition metal complexes were accounted for entirely in terms of individual metal atoms surrounded by a primary coordination sphere of ligands (2). It was not until the first experiments postulating the existence of a metal-metal bond were reported that the Wernerian concept of transition metal chemistry had to be modified to include a whole new class of

compounds, now referred to as metal cluster compounds. Clusters have since been defined as "a finite group of metal atoms that are held together mainly or at least to a significant extent, by bonds directly between metal atoms, even though some non-metal atoms may also be intimately associated with the cluster" (3). It should be emphasized that this definition specifically excludes complexes in which several metal atoms are held together exclusively by bridging ligands.

#### General Phenomenon of Metal Ion Hydrolysis

In the context of the preceding definition, the current work has focused on a specific class of di- $\mu$ -hydroxobridged compounds with a view towards using these species as building blocks for more complex structures. The creation of metal-metal bonds through oxidation of these complexes is expected to be a logical extension of this work but was of only secondary importance to understanding the fundamental chemistry surrounding the formation and reactivity of these dimers and higher oligomers. Because there were no specific "target" complexes in mind at the outset, each experiment was guided by the results of the previous one in an effort to find appropriate ligands with which to study the hydrolysis and polymerization reactions of the monomeric species.

It has long been known that metal ions undergo extensive and often complicated hydrolysis reactions in aqueous solution. Investigations into these species goes back to the pioneering work of N. Bjerrum (4) into the hydrolysis of chromium(III) and the introduction of the concept of "aquo acidity" introduced by Werner and Pfeffer (5, 6). This process can be described as in Figure 1 which depicts the rapid and reversible hydrolysis of mononuclear species of a tri-positive metal ion such as Al(III) or Fe(III).

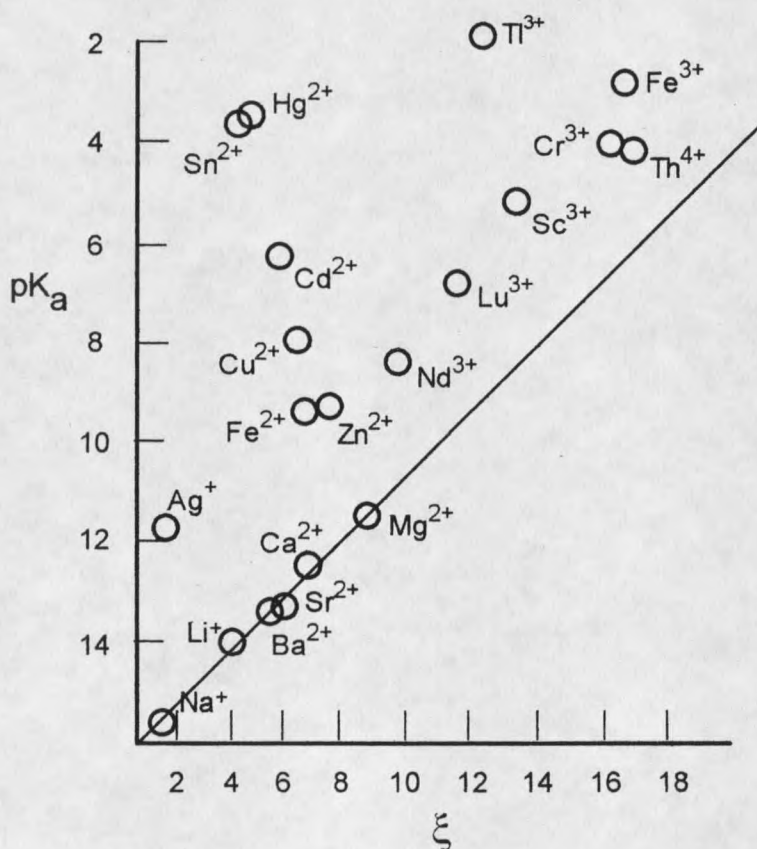


**Figure 1.** General reaction scheme for the hydrolysis of an aquated metal cation.

The relative strengths of aqua acids have been rationalized in terms of an ionic model which treats the metal ion as a hard sphere with radius  $r$ , and  $z$  units of positive charge (7). This model predicts that the acidity of the water in the primary coordination sphere of the metal cation should increase as the value of  $r$  decreases and as the charge on the metal increases, roughly paralleling the value of the electrostatic parameter given by Equation 1.

**Equation 1**  $\xi = z^2 / (r + d)$

where  $d$  is the diameter of the water molecule. This model works well for those metals from groups I and II of the periodic table that normally form ionic solids, but significant deviations are seen for many transition metals due to the departure from purely ionic interactions, as shown in Figure 2.



**Figure 2.** Plot of  $pK_a$  vs. electrostatic parameter ( $\xi$ ) for some metal cations (7).

As the positive charge of the metal ion becomes delocalized over the entire complex, corresponding to a greater degree of covalent character, the proton of the coordinated water is repelled more strongly, resulting in a lower value of  $pK_a$ . Although it is probably not safe to extend this reasoning to other metals of the second and third row transition series, it is reasonable to expect that any factors which influence the charge distribution on a metal atom will affect the acidity of coordinated water molecules. Even for metals which do not adhere to this ionic model, the positive charge of the metal ion appears to stabilize the conjugate base of coordinated protic acids (8). The  $pK_a$ 's for some coordinated protic ligands are given in Table 1 (8, 9).

It has also been firmly established that many hydrolysis reactions are accompanied by polymerization, leading to complex and poorly characterized products. Well known examples include the formation of  $\mu$ -hydroxo and  $\mu$ -oxo iron(III) species at intermediate pH. After initial formation of a hydroxo bridge, the  $pK_a$  of the bridging hydroxide group is reduced considerably ( $pK_a=6$ ) by coordination to not just one, but two metal atoms. These metal activated deprotonation reactions are not only important in inorganic systems but also have been postulated as important first steps in some metalloenzyme systems (8). Early studies often failed to recognize these polymerization reactions, resulting in erroneous conclusions concerning formation constants of hydrolysis products.

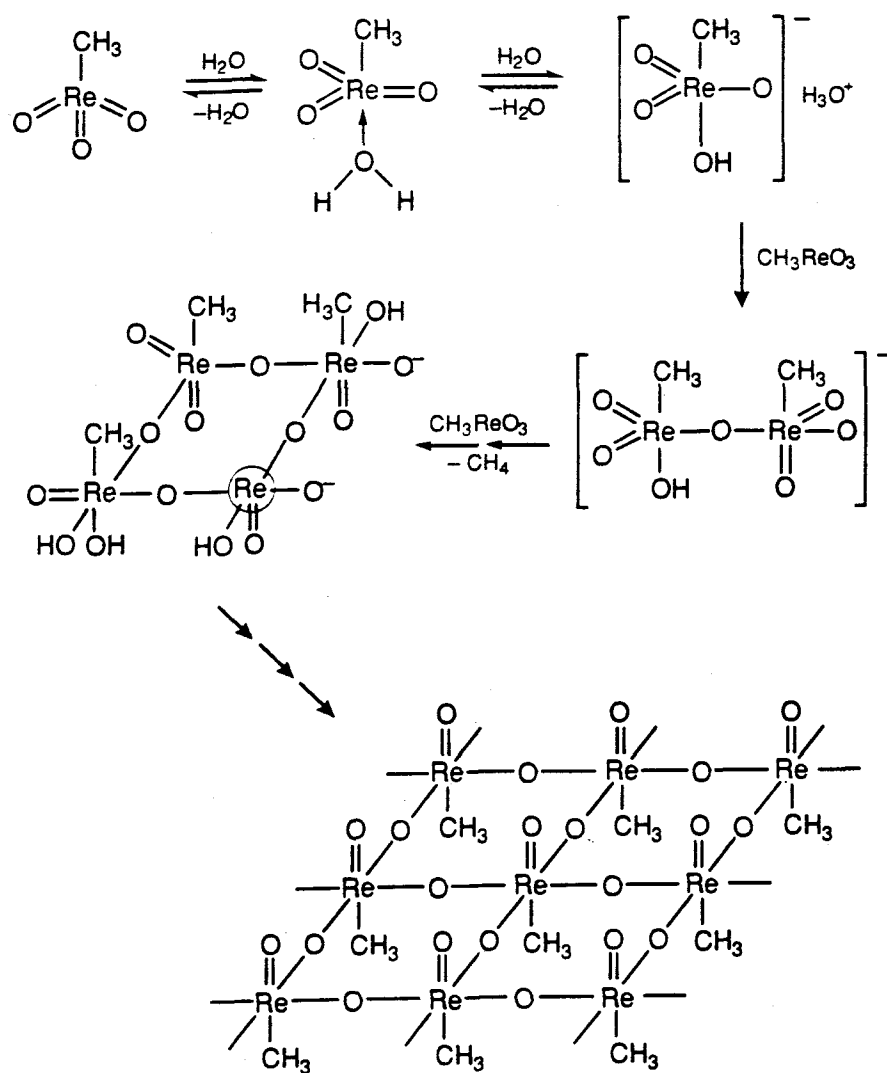
**Table 1.**  $pK_a$  values for some coordinated protic ligands for the reaction  
 $[MLH]^n \rightleftharpoons [ML]^{n-1} + H^+$  (8, 9)

| Metal            | Metal<br>Charge/Radius <sup>a</sup> | Ligand           | $pK_{a1}$  |
|------------------|-------------------------------------|------------------|------------|
| ----             |                                     | H <sub>2</sub> O | 14.0       |
| Na <sup>+</sup>  | 1.0                                 | H <sub>2</sub> O | negligible |
| Li <sup>+</sup>  | 1.5                                 | H <sub>2</sub> O | 13.7       |
| Ca <sup>2+</sup> | 2.1                                 | H <sub>2</sub> O | 13.4       |
| Mg <sup>2+</sup> | 3.1                                 | H <sub>2</sub> O | 11.4       |
| Zn <sup>2+</sup> | 2.7                                 | H <sub>2</sub> O | 10.0       |
| Cu <sup>2+</sup> | 2.8                                 | H <sub>2</sub> O | 10.7       |
| Al <sup>3+</sup> | 6.7                                 | H <sub>2</sub> O | 5.0        |
| Cr <sup>3+</sup> | 4.8                                 | H <sub>2</sub> O | 4.0        |
| Fe <sup>3+</sup> | 4.7                                 | H <sub>2</sub> O | 2.7        |
| ----             |                                     | NH <sub>3</sub>  | 35.0       |
| Cu <sup>2+</sup> | 2.8                                 | NH <sub>3</sub>  | 30.7       |
| Ni <sup>2+</sup> | ----                                | NH <sub>3</sub>  | 32.2       |
| Co <sup>2+</sup> | ----                                | NH <sub>3</sub>  | 32.9       |

a) Relative to Na<sup>+</sup> = 1

An elegant example of polymerization involving the formation of  $\mu$ -oxo bridges has recently been demonstrated by Herrmann et al. (10). Figure 3 shows a simplified reaction scheme for the spontaneous "self assembly" of methyltrioxorhenium monomers to form a three dimensional polymeric rhenium complex. This complex is reported to

have a metallic sheen similar to graphite and exhibits electrical conductivity in the solid state.

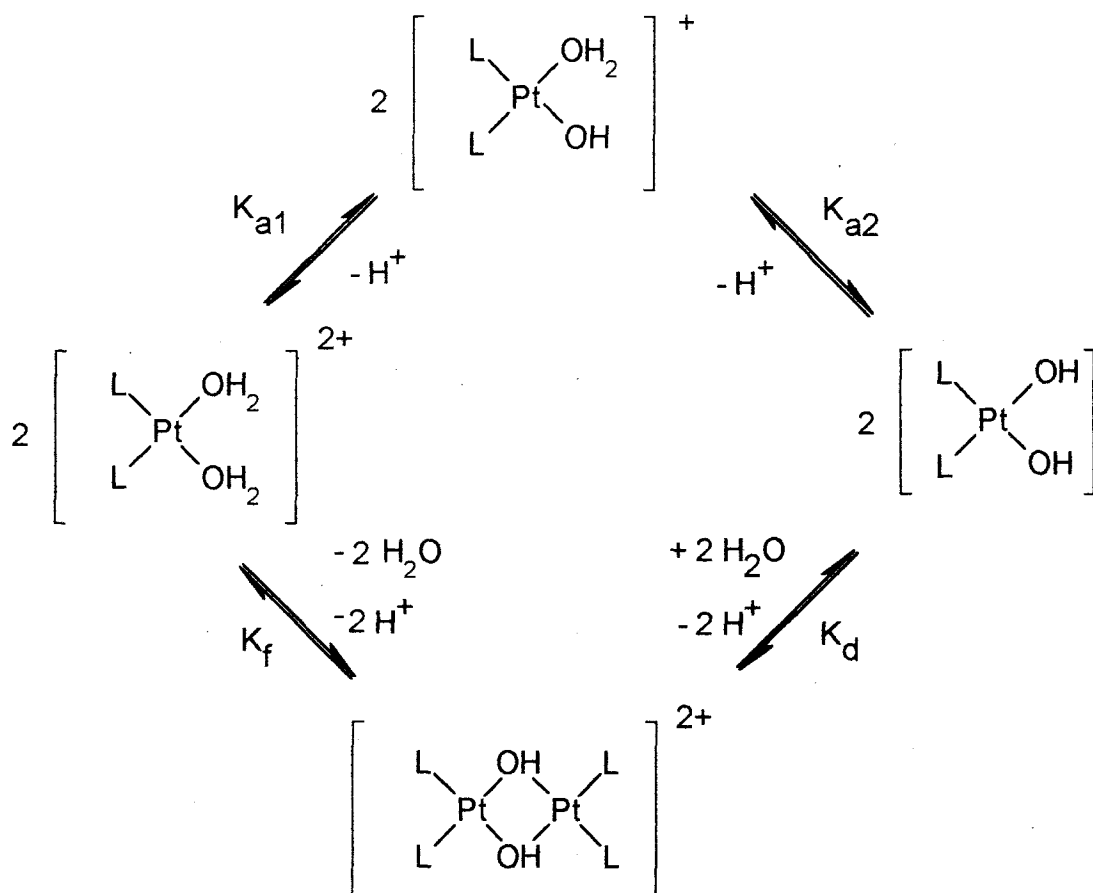


**Figure 3.** Hydrolysis and polymerization of methyltrioxorhenium (10).

### Statement of Objectives

#### Hydrolysis of 2<sup>nd</sup> and 3<sup>rd</sup> Row Platinum Group Metals

The work presented here grew out of the observation that when Pt(II) is coordinated by certain sulfoxide or phosphane ligands, hydrolysis and deprotonation of the aqua ligands results in the formation of di- $\mu$ -hydroxo-bisplatinum(II) species, even under strongly acidic conditions (11, 12, 13). We have been interested in exploiting the marked tendency of these Pt(II) complexes to polymerize in acidic solution to develop methods for the systematic preparation of polymeric Pt(II) complexes and the oxidized Pt(IV) counterparts. The following therefore represents fundamental research into the formation of hydroxo bridged complexes and their equilibrium distribution as a function of pH. Of particular importance was determining the driving force behind these reactions, whether they were simply a result of the low  $pK_a$ 's of the coordinated waters in the monomeric hydrolysis products or whether there was some inherently greater thermodynamic stability conferred on the dimer as compared with the monomer. This last property is reflected in the values of the formation ( $K_f$ ) and dissociation ( $K_d$ ) constants shown in Figure 4 below.



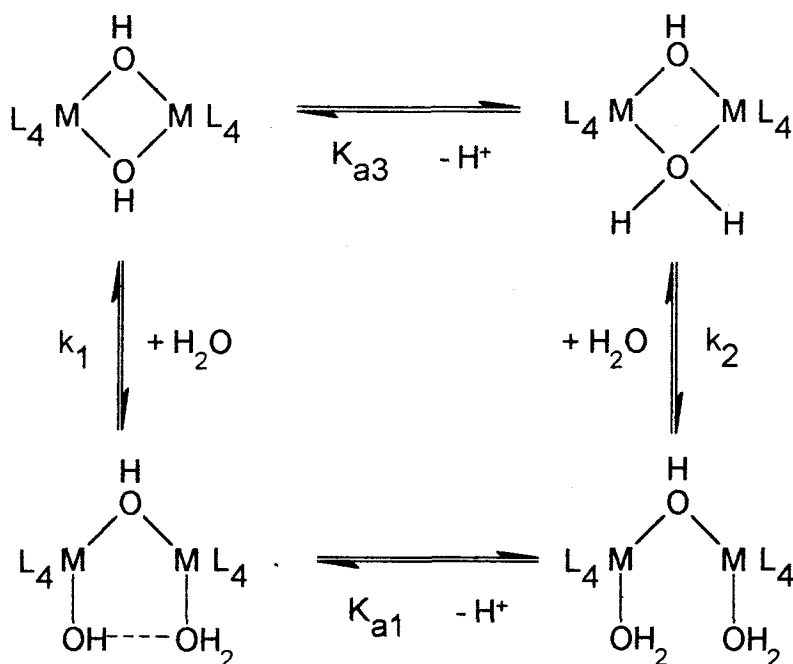
**Figure 4.** Relationship between  $K_f$ ,  $K_d$ ,  $K_{a1}$  and  $K_{a2}$  for dihydroxo bridged dimers.

As can be seen, the net reaction, starting with the *cis*-diaqua complex, releases two equivalents of water and two protons. Although the detailed mechanism is uncertain, the first step is thought to involve the deprotonation of one of the coordinated waters to form the aqua hydroxo complex. This singly charged cationic

species now has one highly nucleophilic ligand in hydroxide ion and one weakly nucleophilic leaving group in water. Dimer formation then simply requires two of these fragments to come together in the proper orientation, followed by release of the remaining water ligands. Other studies done on similar systems also provide strong evidence to suggest that the mono-deprotonated monomer is the reactive species in dimer formation at near neutral pH (15). At lower pH however, mechanistic studies indicate that the diaqua monomer also makes a substantial contribution to dimer formation (16). Any proposed mechanism for the formation of these dimeric species should be consistent with the established mechanisms for other square planar coordination complexes which normally involves the formation of a five coordinate intermediate (17).

It is useful to compare the mechanism for dimer formation in these four coordinate species with the fairly well established mechanism for hydroxo bridge formation in octahedral six coordinate complexes of other platinum group metals. These systems lend themselves to studies of this kind due in part to the much slower reaction times, with half-lives for the hydrolysis of dibridged Ir(III) amine and ammine complexes ranging from 60 to  $9 \times 10^6$  seconds (18). Figure 5 shows the proposed reaction scheme for the equilibrium between mono- and dinuclear M(III) species (19). These reactions are thought to involve a well defined monohydroxo bridged intermediate shown in the figure. It has been postulated that a major stabilizing influence can be conferred on this intermediate by the hydrogen bonding interaction

shown between the singly coordinated water and hydroxo group of the aqua-hydroxo species.



**Figure 5.** Reaction scheme for the equilibria between dinuclear mono- and dihydroxo-bridged species of Cr(II), Rh(III) and Ir(III). The dashed line indicates a hydrogen bonding interaction. (After Ref. 19)

The existence of this interaction has been confirmed in the solid state by X-ray diffraction data of the Ir(en) complex and is demonstrated in solution by examining the acid strength of mono- and dinuclear species (20). Mono-hydroxo bridged species of sufficient lifetime to be observed by NMR methods have also been postulated for several Pt(II) amine systems (21, 22, 23). Because the nonbonded distances between

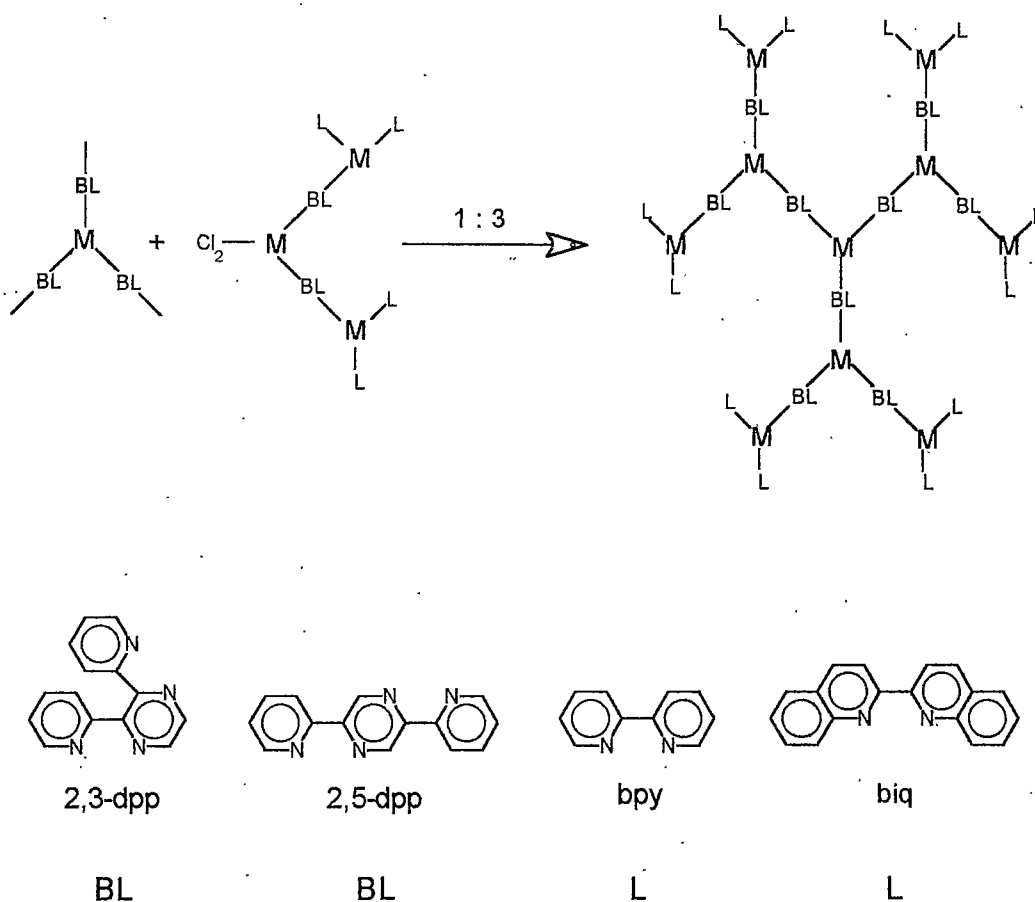
the aqua and hydroxo ligands should be comparable in four coordinate square planar and six coordinate octahedral geometries, it is reasonable to expect that the same sort of stabilizing interaction may exist in square planar Pt(II) complexes.

Because these reactions are inherently pH dependent, the majority of our work was restricted to species which were at least partially water soluble. Many sulfoxide and several trialkylphosphane ligands form water soluble ionic complexes when coordinated to platinum and were therefore well suited to these investigations. Platinum was additionally convenient for this study due its favorable magnetic properties and intermediate reaction rates.

#### Practical Applications of the Research

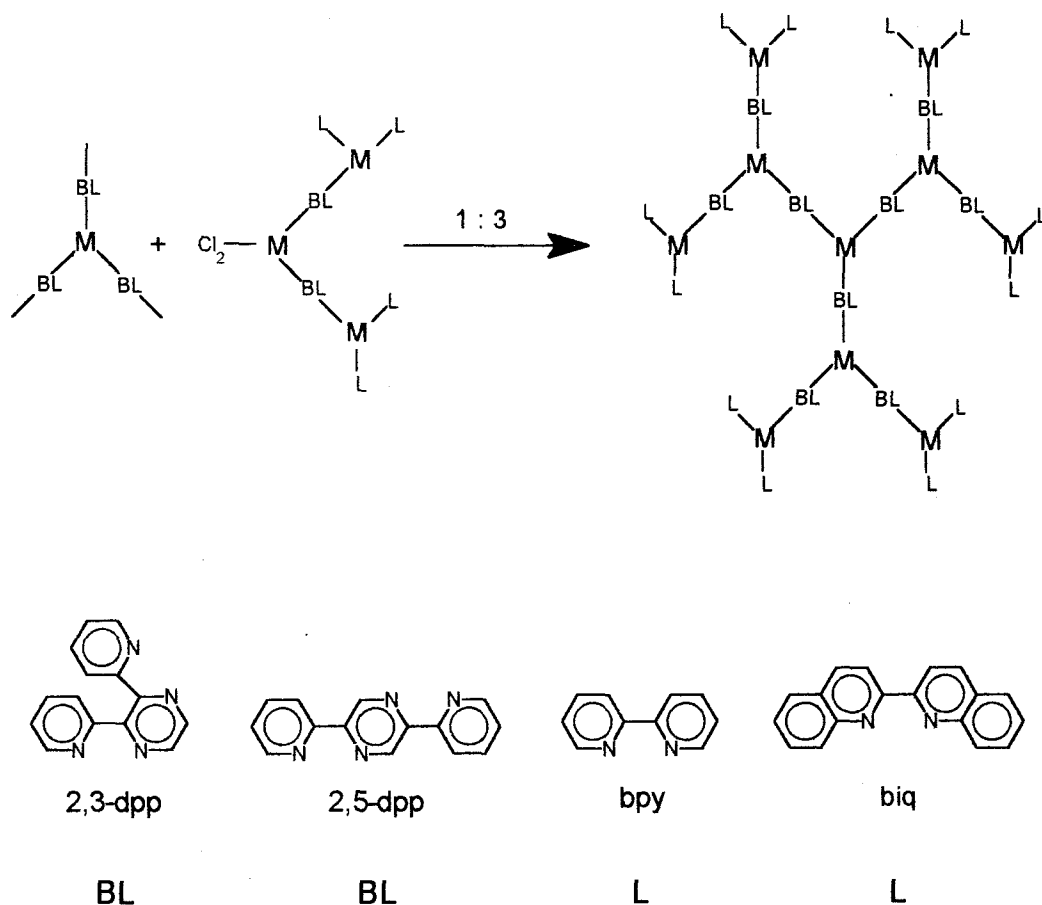
Although the work presented here has concentrated on the basic synthesis and spectroscopic characterization of di- $\mu$ -hydroxo bridged complexes, fundamental research into polymerization reactions of this type are important for several reasons. The following briefly examines some of the possible practical applications of this work by discussing several synthetic strategies in which complex structures with very specific chemical and physical properties are "assembled" from two or more smaller fragments.

The systematic design and synthesis of "molecules with function" has recently emerged as an efficient route for more advanced materials applications involving transition metals.



**Figure 6:** Schematic Diagram of the Structure Directed Synthesis of a High Nuclearity Metal Complex Using Complexes as Both "Metal" and "Ligand" (M = Ru or Os). The bridging (BL) and terminal (L) ligands used are also shown (24).

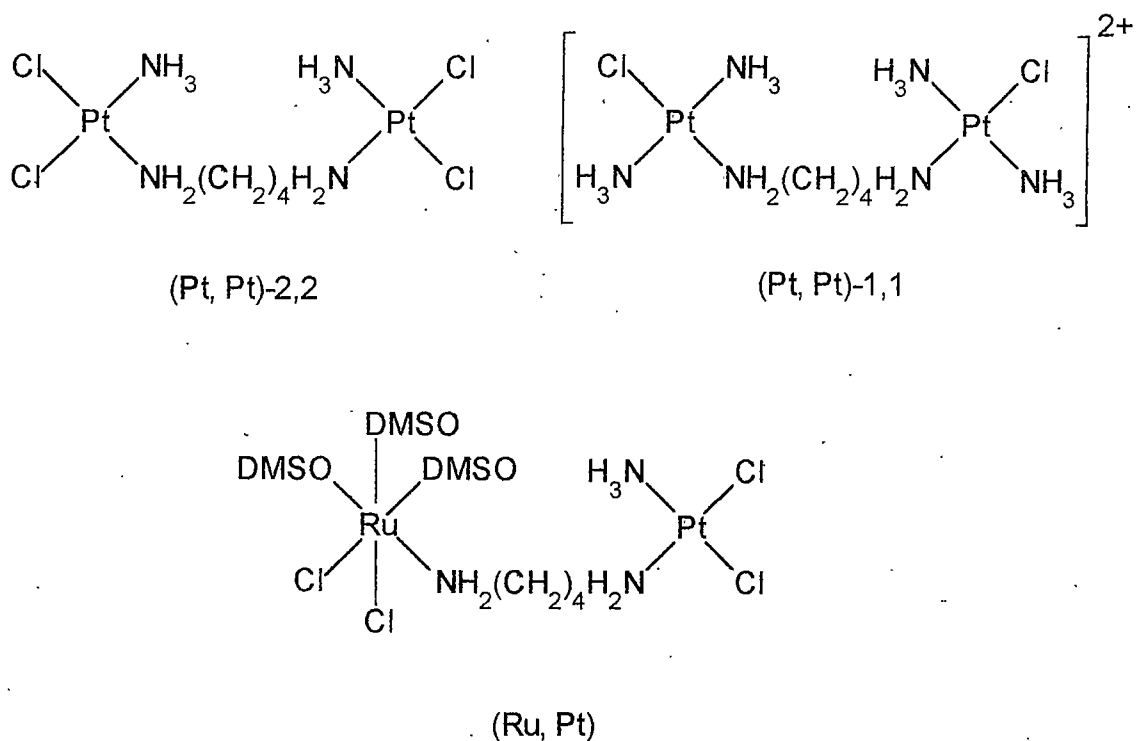
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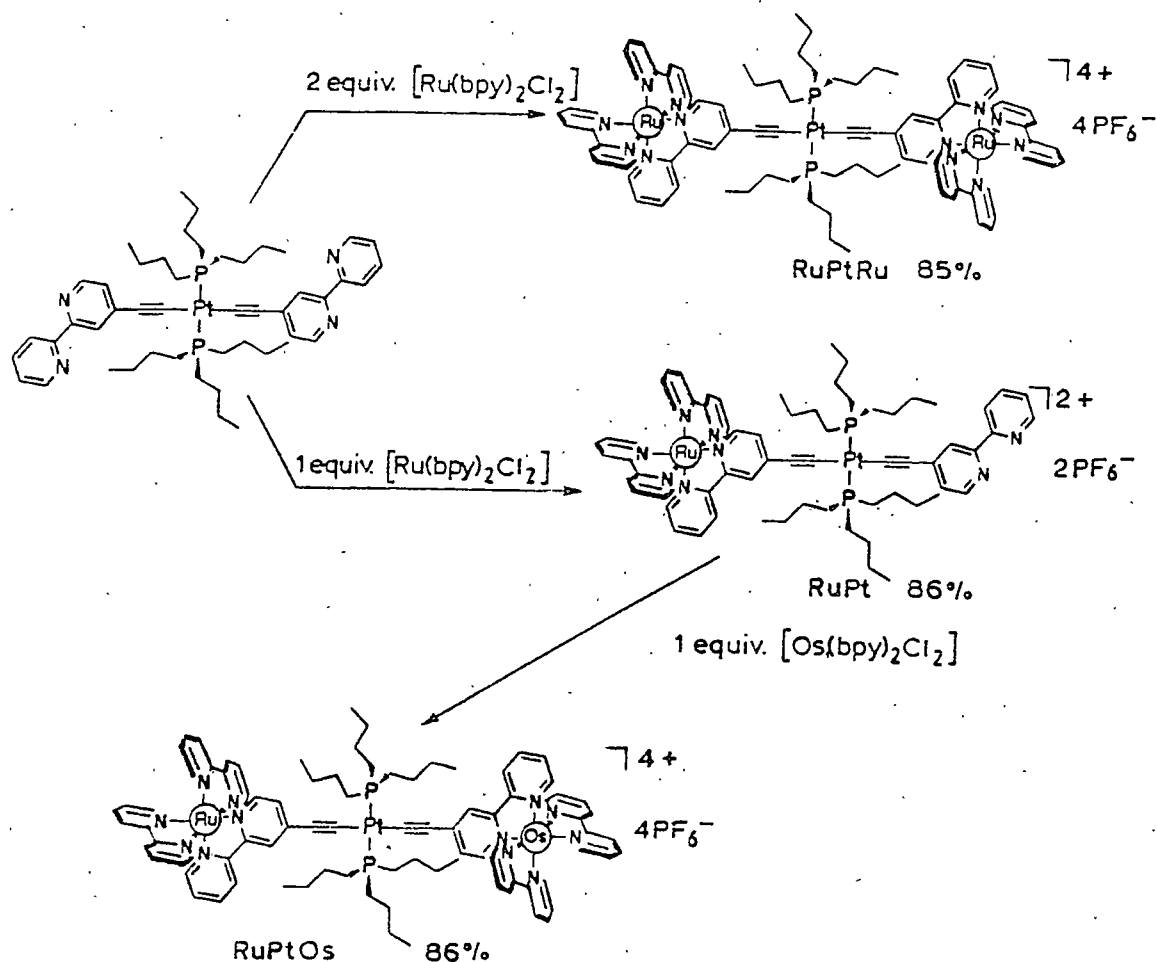
This strategy makes extensive use of multinuclear complexes as both "metal" and "ligand" and is exemplified by the synthesis of a host of closely related ruthenium complexes which can be systematically designed to possess a wide range of redox and luminescence properties (24). An example of this so called "structure directed synthesis" is shown in Figure 6. In the example shown, chloride provides a labile ligand on the metal atom. If this ligand is hydrolyzed by the addition of a silver salt, a free coordination site exists which is available to the "ligand" complexes. Only a few examples of this approach have been reported for platinum, including the homo- and heterodimeric complexes shown in Figure 7 (25). In this case, the synthesis of these complexes is accomplished by reacting a "precursor" Pt complex with a potentially bidentate amine ligand followed by reaction of the free functionality with a target complex (25). The potential of these complexes as potent second generation anti-tumor agents is discussed below.

A final example of the use of the structure directed approach applied to platinum group metals is seen in the elegant synthesis of bi- and tri-metallic complexes with the potential for applications in molecular circuitry. Figure 8 shows the synthetic use of alkynyl-bipyridine derivatives of Pt(II) as substrates for the addition of ruthenium and/or osmium fragments, resulting in a polymetallic species which shows unique electrical and luminescence properties (26). A brief discussion of molecular wires in the context of partially oxidized and mixed valence platinum complexes is given below.



**Figure 7.** Bimetallic bridged structures formed by reaction of "precursor" and "target" complexes (25).

These examples serve to illustrate the tremendous potential of using polynuclear transition metal species as building blocks for structures with unique physical and chemical properties. It was one of the major goals of this research to determine whether di- $\mu$ -hydroxo bridged Pt complexes, with their inherent propensity toward polymer formation, and the availability of two free coordination sites at low pH, could be used in a similar fashion.



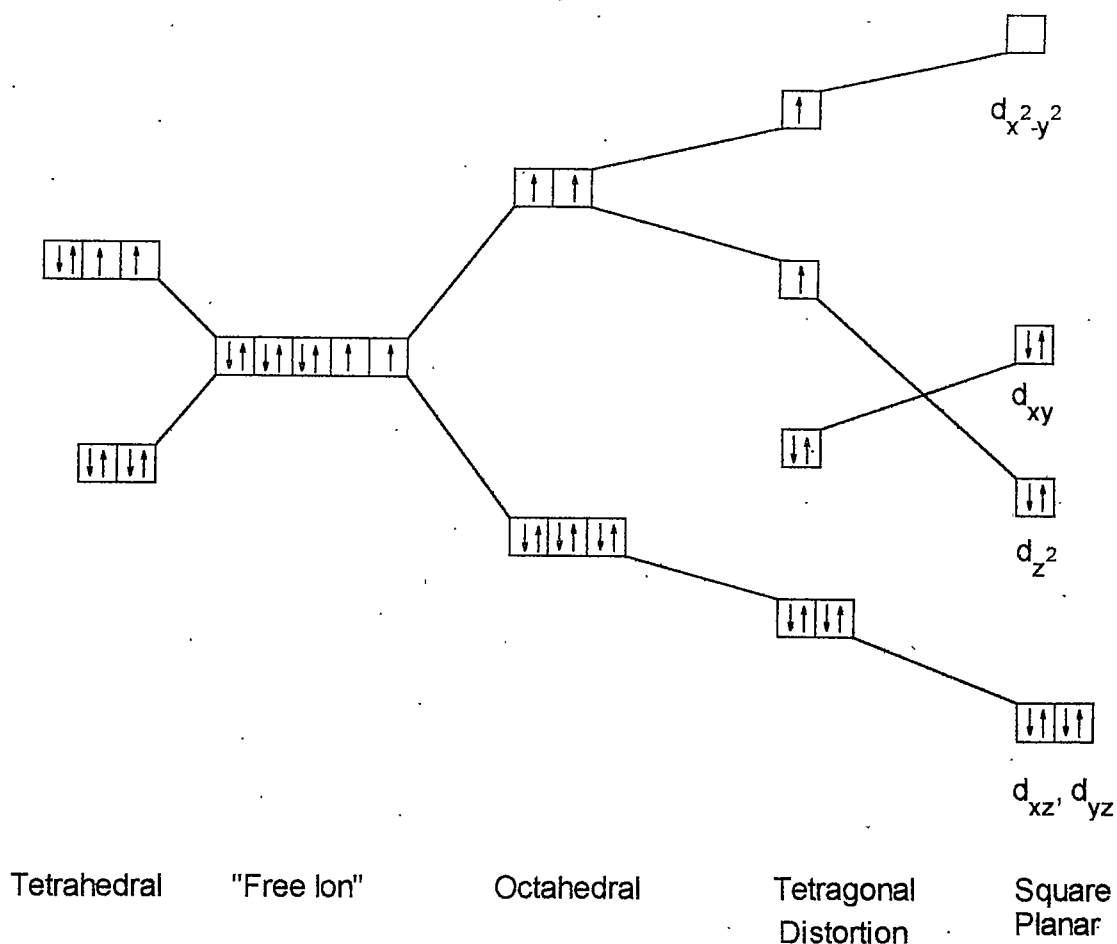
**Figure 8.** General reaction scheme for the formation of high nuclearity polymetallic complexes (26).

### Partially Oxidized and Mixed Valence Complexes

The chemical properties of a transition metal complex can be dramatically altered by oxidation of the metal center. Until recently, the chemistry of platinum has been dominated by the two most stable oxidation states, +2 and +4. Platinum(II) almost invariably forms four coordinate square planar complexes typical of the other  $d^8$

metals including Rh(I), Ir(I), Pd(II) and Au(III) (6). A few five coordinate Pt(II) species are known, including a proposed tri- $\mu$ -hydroxobridged dimer (27). These five coordinate species are of interest because of the structural information they may provide concerning the transition states for associative substitution reactions of square planar complexes. As mentioned previously, these reactions normally proceed through five coordinate trigonal bipyramidal intermediates (17). For first row  $d^8$  metals such as Ni(II), tetrahedral complexes are formed with the weaker field ligands such as chloride and bromide, whereas square planar complexes are formed with strong field  $\pi$  donor ligands such as  $CN^-$  (28). The square planar configuration is favored over tetrahedral or octahedral geometry in this case due to the increased ligand field stabilization energy. This behavior can be explained using simple crystal field theory by appealing to the energy level diagram shown in Figure 9.

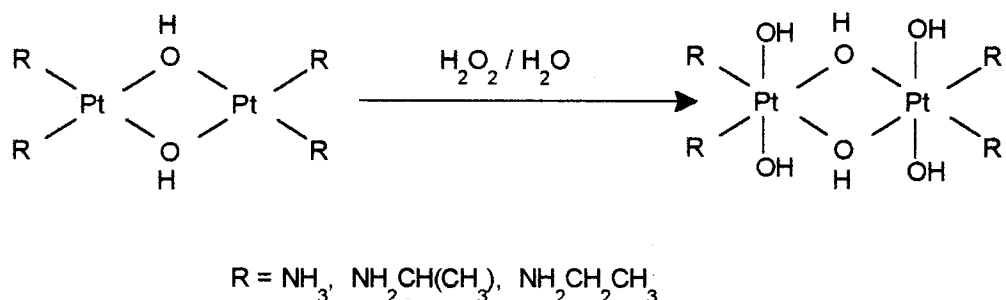
This diagram shows the ligand field splitting for tetrahedral, octahedral and square planar  $d^8$  complexes as well as the tetragonal distortion representing the transition from octahedral to square planar geometry (29). In this diagram, the overall energy of the system can be lowered by pairing electrons in the  $d_{xy}$  orbital as the geometry moves from octahedral to square planar.



**Figure 9.** Ligand field splitting for hypothetical tetrahedral, octahedral and square planar  $d^8$  coordination geometries (After Ref. 29).

Oxidation of Pt(II) to Pt(IV). Oxidation to the substitutionally inert Pt(IV) state can be accomplished by a variety of oxidizing agents. For the dimeric complexes being considered here, formation of the Pt(II) species followed by oxidation of one or both of the metal atoms could serve to lock the ligands in place, and would represent a significant step in being able to manipulate the reactivity of the dimer fragment. Only

one example of this type of reaction has been reported in the literature (30) (Figure 10). Hydrogen peroxide has also been shown to be effective at oxidizing *bis*-oxalato Pt(II) to the Pt(IV) *trans* dihydroxo complex. The mechanism for that reaction has been determined by  $^{195}\text{Pt}$  NMR studies using isotopically labeled  $\text{H}_2\text{O}$  (31).

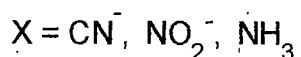
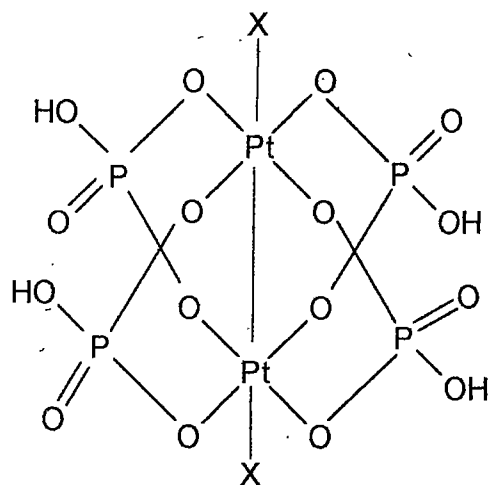


**Figure 10.** Oxidation of Pt(II) dimer with hydrogen peroxide (30 ).

Other oxidizing agents have also been successfully utilized for the oxidation of Pt(II) species, including cerium (IV), chlorine, bromine, monopersulfate ion and Pt(IV) (32, 33, 34, 35). Two electron oxidation with halogens normally produces the corresponding *trans* dihalo Pt(IV) species but also may result in halogen substitution on the more labile Pt(II) species if the reaction is carried out in aqueous solution. Because molecular chlorine disproportionates in aqueous solution, parallel oxidation by  $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{OCl}^-$  always occurs, the relative importance of each species being a

function of pH and concentration of free chloride. Details of reactions involving oxidation of monomeric and dimeric Pt(II) complexes pertinent to this investigation are discussed more fully in the Results and Discussion Section below.

The intermediate oxidation state of Pt(III) plays an important role in the formation of metal-metal bonded complexes and partially oxidized linear chain conductors. These octahedral  $d^7$  complexes are substitutionally labile as well as being paramagnetic due to the unpaired electrons in the  $d_{xy}$  orbital. One of the most intensively studied classes of dimeric Pt(III) species is exemplified by the bridged pyrophosphito complex shown in Figure 11. In this structure, the metal  $p_z$ - $p_z$  and  $d_z^2$ - $d_z^2$  orbitals interact along the Pt-Pt axis to form a single metal-metal bond (36). A very important fundamental difference exists between the bridging geometry of this complex and the di- $\mu$ -hydroxo bridges discussed in this thesis. In the case of  $[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4]^{2-}$  the three atom span and the tetrahedral geometry around the interdonor oxygen atom create a face to face orientation of the  $\text{PtO}_4$  units, thereby allowing the  $d_z^2$  orbitals on each platinum atom to interact. Bonded Pt-Pt distances in these diplatinum (III,III) complexes range from 2.716 Å to 2.760 Å depending on the axial ligand, X (2). This range can be compared with the non-bonded Pt--Pt distance in di- $\mu$ -hydroxo bridged complexes which are all greater than 3 Å.



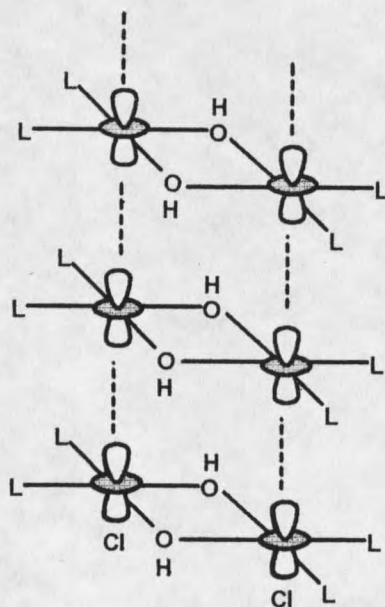
**Figure 11.** Pyrophosphito bridged Pt(III) dimer (36).

It remains to be seen whether Pt-Pt bonds can be induced to form upon one electron oxidation of these dimeric species. The oxidation of mono- and dimeric Pt(II) sulfoxide and phosphane complexes is discussed more fully in the Results and Discussion section.

Although the individual  $d^7$  metal centers are paramagnetic due to a single unpaired electron, polymer formation results in an overall diamagnetic " $d^{14}$ " complex which can be studied by nuclear magnetic resonance spectroscopy. Chemical shifts have been reported for these complexes and appear to lie roughly midway between the

corresponding +2 and +4 shift values (37, 38). In the area of advanced materials applications, platinum has long been known to form partially oxidized linear chain complexes which exhibit electrical conductivity along the metal-metal bond axis (38).

Practical applications of these one dimensional conductors include the growing interest in molecular circuitry. Although they have not yet been demonstrated, bridged structures may also be expected to stack given the proper ligands (Figure 12). These structures may in fact gain some degree of stability by the formation of hydrogen bonding between the bridging hydroxide groups.



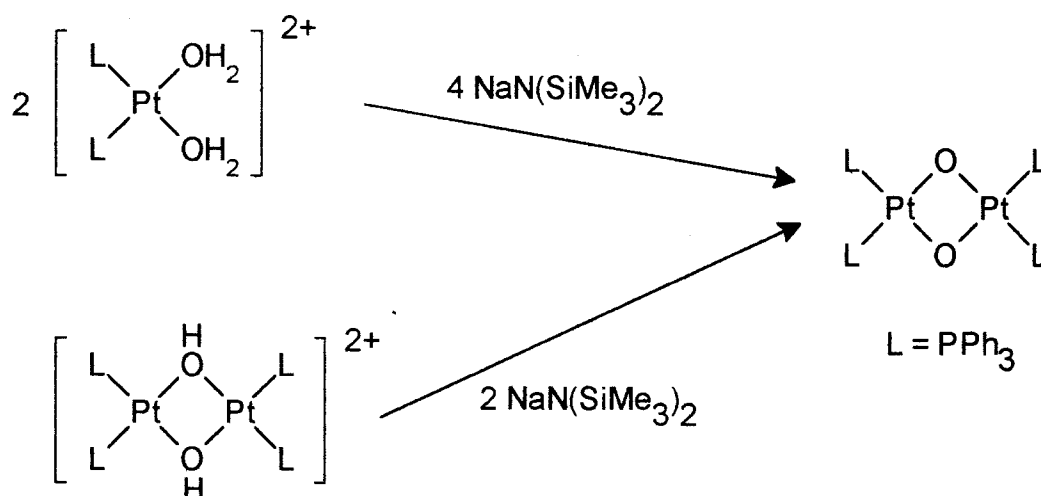
**Figure 12.** Hypothetical structure of stacked complex formed by partial oxidation of dihydroxo bridged platinum (II) dimers.

This stacking interaction, which was first investigated by Krogmann using the oxalate salts, has also been demonstrated for other ligands including cyanide although the solution chemistry of these polymeric species remains only partially understood (38). A few examples have recently been reported which demonstrate the feasibility of using chemical systems to form molecular circuitry including an entirely organic "molecular wire" anchored by a sulfur atom to a gold surface (39). So far, it appears that those ligands which tend to form stacked, linear chain conductors, do not form hydroxo bridged dimers and vice versa. Clearly, ligand properties such as nucleophilicity and steric bulk play important roles in the formation and stability of each of these types of complex.

#### Models for Homogenous Catalysis

A second area where fundamental research on these dimeric complexes becomes important is in the study of model systems for homogenous catalysis. As stated earlier, coordination of two metal centers to a bridging hydroxide ligand renders the remaining proton much more acidic than it would otherwise be. For di- $\mu$ -hydroxo bridged systems containing electron withdrawing triphenylphosphane groups, treatment with strong base in non aqueous solution results in deprotonation of the bridging hydroxo group to yield the di- $\mu$ -oxo species (40). These, together with the corresponding amido and imido analogs have been the subject of a recent investigation

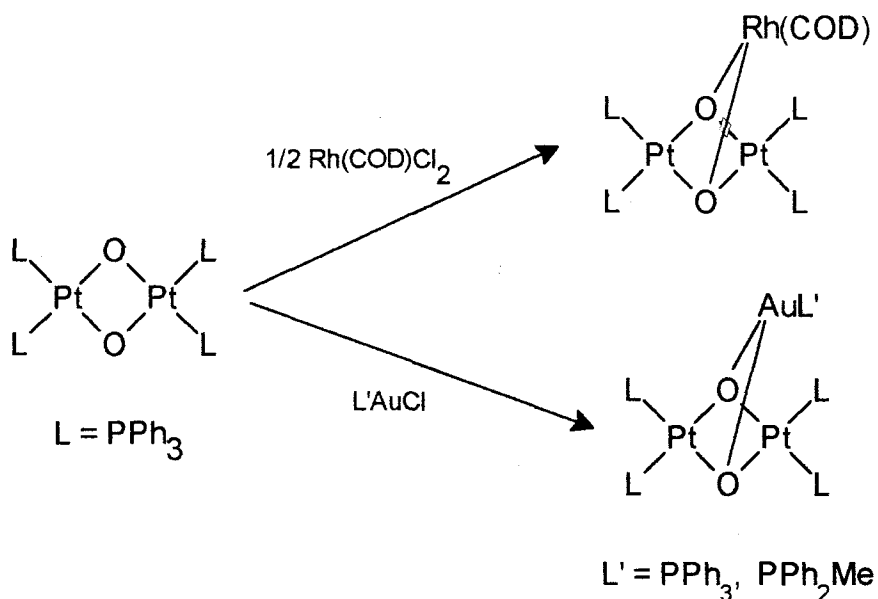
aimed at developing possible models for homogenous catalysis (40, 41). Although the majority of the complexes studied in that work were prepared with phenyl substituted phosphane ligands which rendered them insoluble in water, the synthesis of many of them involved di- $\mu$ -hydroxo bridged Pt(II) species as either reagents, intermediates or products. A typical example of one of these reactions is shown in Figure 13.



**Figure 13.** Formation of a di- $\mu$ -oxo complex by treatment of aqua or hydroxo species with strong base (41).

These complexes provide an excellent example of the stability of oxygen as a bridging atom for late transition metal species as predicted by simple molecular orbital considerations. This point is developed more fully below.

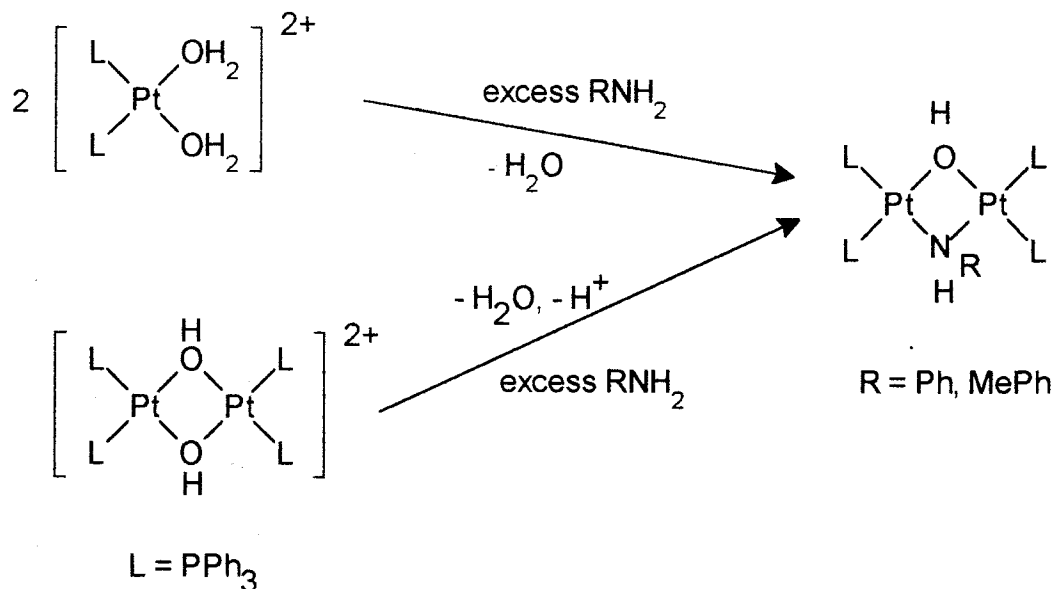
Once the di- $\mu$ -oxo complex is formed, the Lewis basicity of the bridging oxygen atoms can be exploited to form bimetallic  $\mu_3$  heterometallic clusters as shown in Figure 14.



**Figure 14.** Synthetic applications of di- $\mu$ -oxo bridged Pt(II) dimers (41).

Although most of the  $\mu$ -oxo compounds studied were highly water sensitive, the basicity of the oxo bridges has opened up a whole new route for the synthesis of both homo and hetero-metallic complexes with potential catalytic applications which require, or are more efficient with, two different metal centers.

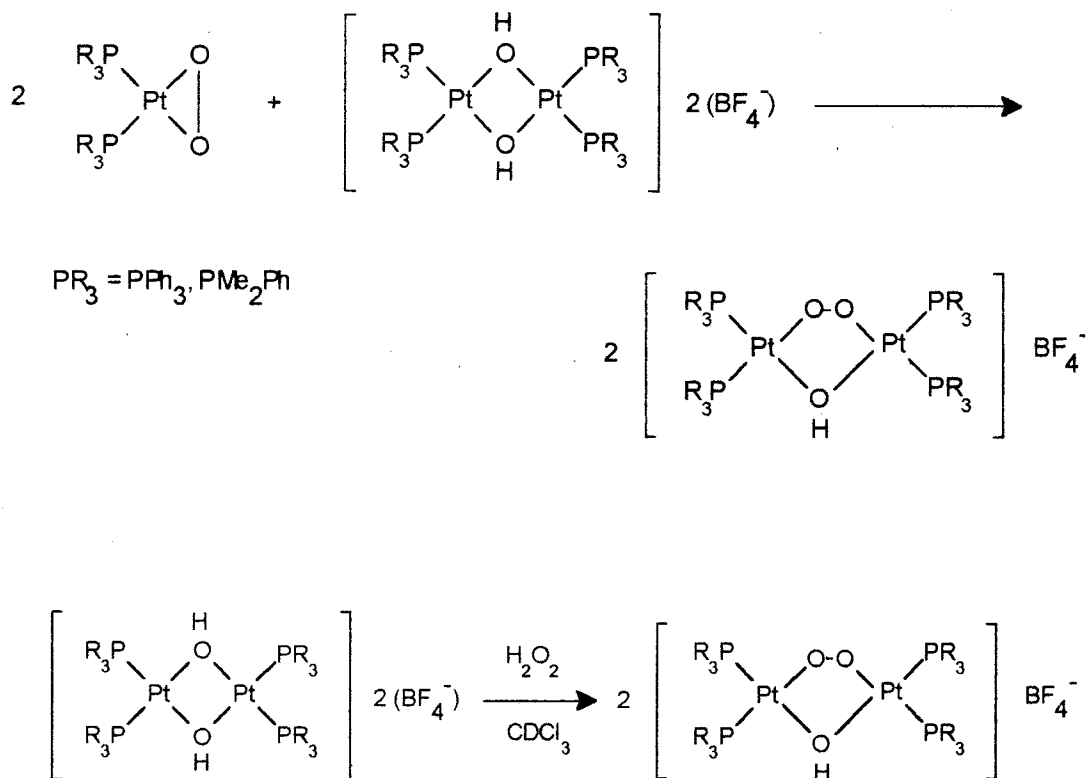
The imido complexes are formed by reaction of an imide with either the di- $\mu$ -hydroxo bridged species or with the diaqua monomer, as shown in Figure 15.



**Figure 15.** Imide bridge substitution (41).

Because the imido group is both isoelectronic and isostructural with the oxo group these two bridged species show similar chemical properties (41). It is of mechanistic interest that the imido group ends up in a bridging role rather than in a terminal position having displaced one of the phosphane ligands.

In addition to the  $\mu$ -oxo complexes just discussed, dibridged species have also found use in the synthesis of mixed bridge  $\mu$ -oxo,  $\mu$ -peroxo complexes as shown in Figure 16 (42).



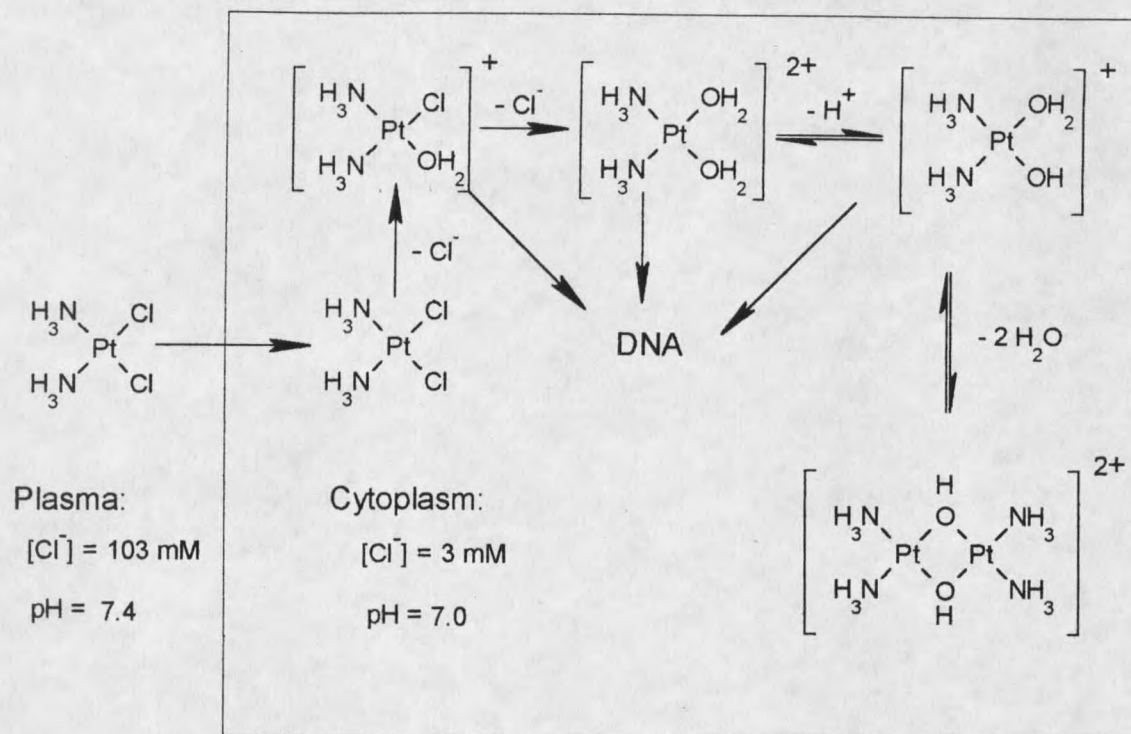
**Figure 16.** Formation of mixed hydroxo-, peroxo- bridged complexes by oxidation of di- $\mu$ -hydroxo bridged dimers (42).

### Biologically Active Metal Complexes

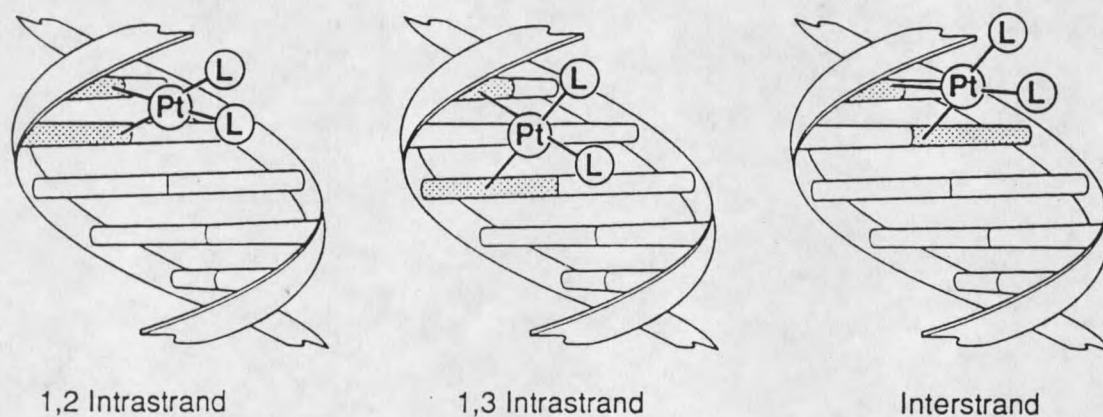
Yet another area with close ties to these polymeric and hydroxobridged platinum complexes is that of biologically active anti-tumor agents. With the discovery of the anti-tumor activity of *cis*-diamminedichloroplatinum(II) or cisplatin, by

Rosenberg (43) in 1965, the number of studies done on hydroxo bridged dimers of the platinum group metals grew enormously. Early interest in these species was centered around the observation that in the case of cisplatin, the dimer species was the stable form under physiological conditions of pH and chloride concentration, and that this dimer appeared to be responsible for some of the toxic side effects of cisplatin treatment. Figure 17 shows the probable fate of cisplatin after being introduced into the bloodstream. Although the precise mode of action of the monomeric aquachloro or diaqua complexes has not been firmly established, there is strong evidence to suggest that formation of an adduct with DNA is the crucial step. A crystal structure of double stranded DNA containing the major adduct of cisplatin has recently been obtained (44).

For double stranded DNA, it has been proposed that adduct formation can occur as either inter- or intra-strand cross linking as shown in Figure 18. Formation of these crosslinks is thought to interfere with the replication process of tumor cell DNA (8).



**Figure 17.** Fate of cisplatin after entering the bloodstream.



**Figure 18.** Formation of cross-links in double stranded DNA by *cis*-platinum complexes (46).

Early on in the investigation of anti-tumor agents, attempts were made to form a list of general structure-activity relationships (SARs) for these complexes in order to provide a rational guide for the design of more potent "second generation" drugs. At present, these SARs include the following (45):

- 1) A *cis* geometry is required with the general formula *cis*-PtX<sub>2</sub>(amine)<sub>2</sub> for Pt(II) compounds and *cis*-PtX<sub>2</sub>Y<sub>2</sub>(amine)<sub>2</sub> for Pt(IV) compounds.
- 2) The X ligand should be an anion with intermediate binding strength such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, citrate, oxalate, etc.
- 3) The amine ligands should possess at least one NH moiety, necessary for hydrogen bonding interactions with DNA.

Chloride has been the ligand of choice in many of these complexes due to the large difference in free chloride ion concentration between the plasma and the cytoplasm as well as the fairly low *trans* effect of Cl<sup>-</sup> compared with the other halogens. This ligand also serves to maintain electrical neutrality of the complex, an essential requirement for passive diffusion across the cell membrane (8). With continued research however, compounds are being discovered which violate many of these SARs. Until very recently for example, it was generally assumed that only *cis* complexes would show any significant biological activity. In the case of cisplatin, this does appear to be the case. However, several *trans* complexes (Table 2) are now being tested (46). Many of these contain planar aromatic ligands such as pyridine or bipyridine, and it is

thought that these may act either by forming interstrand DNA cross links, as with the *cis* complexes, or by acting as intercalating agents (46).

Although all transition metal complexes tested so far for their anti-cancer properties necessarily have some degree of toxicity associated with them, it has been found that in not all cases is the higher molecular weight polymer the toxic agent (15). In contrast to the known toxicity of the ammine dimer, the ethylenediamine dimer seems to be less toxic than the monomer. Table 2 lists some of the platinum group complexes relevant to this work and currently under investigation for potential chemotherapeutic value.

**Table 2.** Partial listing of platinum group metals currently in use or being tested for anti-tumor activity (46).

|                                                                                  |                                                                  |
|----------------------------------------------------------------------------------|------------------------------------------------------------------|
| $\text{PtCl}_2(\text{NH}_3)$                                                     | <i>trans</i> - $\text{PtCl}_2(\text{NH}_3)(\text{quin})^c$       |
| $\text{PtCl}_2(\text{en})$                                                       | <i>trans</i> - $\text{PtCl}(\text{py})(\text{RR}'\text{SO})^d$   |
| <i>cis</i> - $\text{PtCl}_2(\text{iso-C}_3\text{H}_7\text{NH}_2)_2(\text{OH})_2$ | <i>trans</i> - $\text{PtCl}_2(\text{RR}'\text{SO})(\text{quin})$ |
| <i>cis</i> - $\text{Pt}(\text{NH}_3)_2(\text{CBDCA})^a$                          | <i>fac</i> - $\text{Ru}(\text{NH}_3)_3\text{Cl}_3$               |
| <i>cis</i> - $\text{Pt}(\text{mal})(1,2\text{-dach})^b$                          | <i>cis</i> - $[\text{Ru}(\text{NH}_3)\text{Cl}_2]\text{Cl}$      |
| <i>cis</i> - $\text{Pt}(\text{SO}_4)(\text{OH})(1,2\text{-dach})$                | <i>cis</i> - $\text{RuCl}_2(\text{dmsO})_4$                      |
| <i>trans</i> - $\text{PtCl}_2(\text{py})_2$                                      | $\text{Ru}(\text{bipy})_2\text{ox}$                              |

a) CBDCA = cyclobutanedicarboxylic acid b) dach = diaminocyclohexane

c) quin = quinoline d) R= Me R'=Me, Ph, Bz, Tol

The dinuclear Pt,Pt and Pt,Ru complexes discussed earlier (Figure 7) are currently being investigated for their anti tumor activity and have been found to cause a 250 fold increase in the number of intrastrand cross-links compared with cisplatin (25). By introducing a different metal atom, such as Ru, into the complex, the two ends now have distinctly different steric properties. This feature, as well as the difference in reaction rate for the two metals, may make the heterodimeric complex more specific, and therefore more selective, in its binding to particular DNA sequences.

It should be emphasized that although the current research is not directly concerned with discovering or developing these agents. The wealth of fundamental knowledge concerning the synthesis, reactivity and characterization simply serves as a useful comparison for the properties which this research seeks to exploit in using related complexes as building blocks for more complex structures.

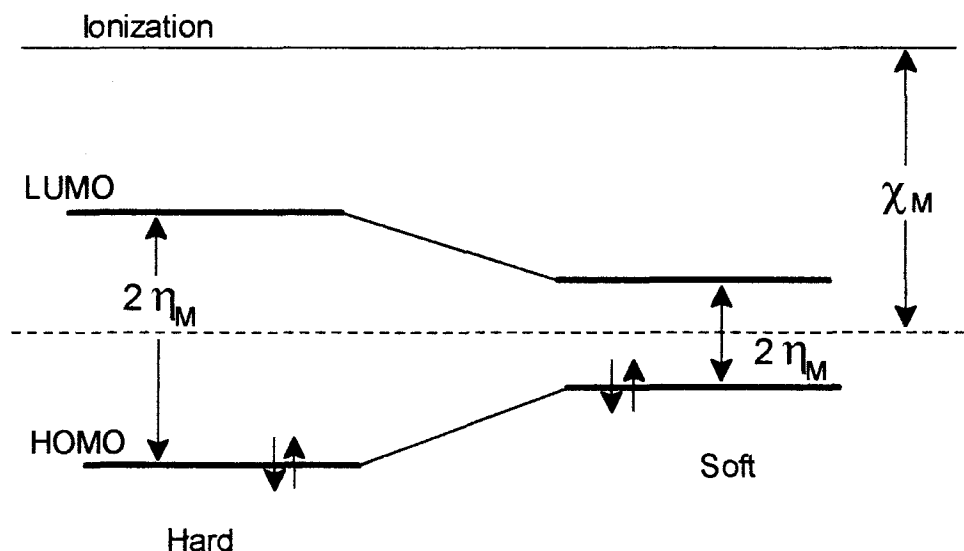
#### Structural Features and Proposed Mechanism of Formation of $\mu$ -hydroxo Bridged Platinum Complexes

For complexes containing ambidentate ligands such as sulfoxides, the theory of Hard and Soft Acids and Bases is expected to play a role in the eventual mode of coordination of these ligands. This theory, introduced originally by Dewar, Chatt and Davies and later expanded on by Pearson (47), is based on empirical observations of formation constants ( $K_f$ ) of metal ions with halogen ligands.

Both Pt(II) and Pt(IV) are formally classified as soft acids while most sulfur donor ligands including  $R_2S$ ,  $RSH$  and  $RS^-$  are classified as soft bases (48). The terms hard and soft refer to the polarizability of the atom, molecule or ion in question. A quantitative definition has been applied to atomic hardness by Equation 2 below.

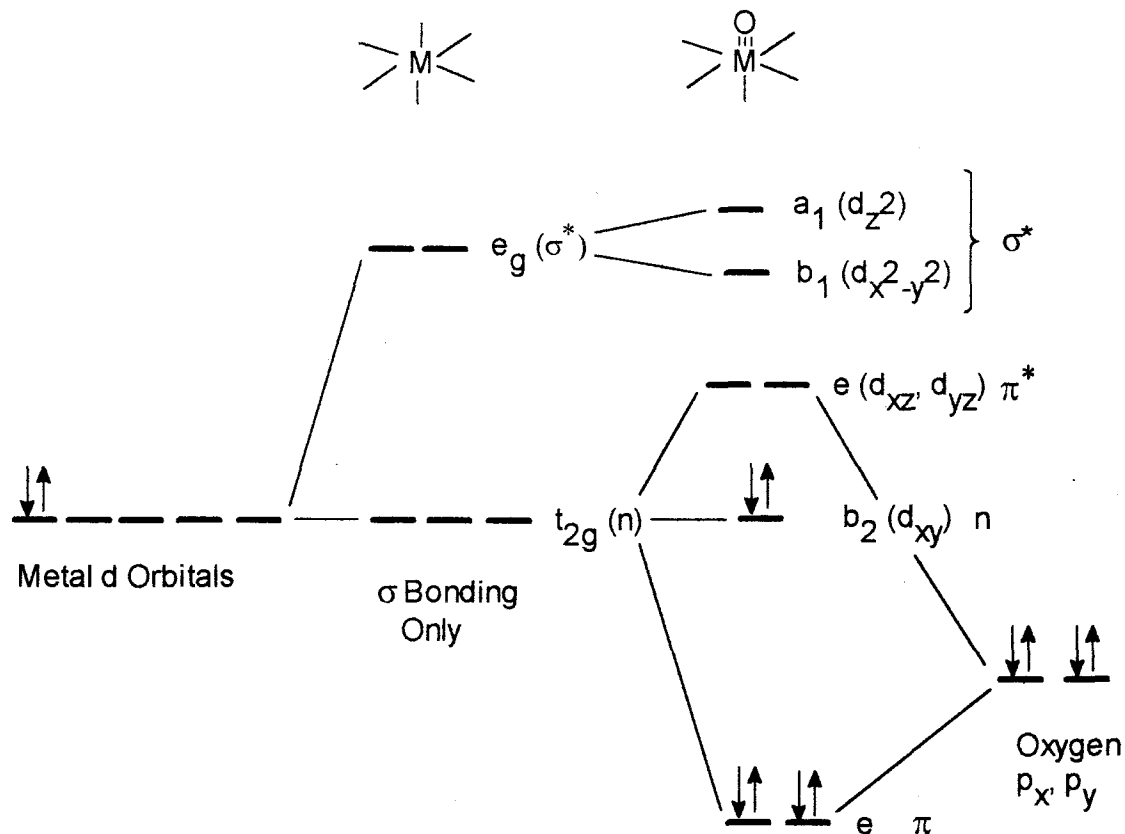
**Equation 2**       $\eta = 1/2 (I - E_a)$       I = ionization energy  
E = electron affinity

Molecular polarizability ( $\eta_M$ ) is most easily envisioned by appealing to the simplified molecular orbital diagram shown in Figure 19 (7).



**Figure 19.** Frontier orbital diagram showing the relative HOMO and LUMO energy separation for hard and soft acids and bases (After ref. 7).

Both  $O^{2-}$  and  $OH^-$  are formally classified as hard bases. It is therefore somewhat surprising that these ligands form such robust bonds between two soft platinum centers. Some appreciation for the bridging role of  $OH^-$  in these complexes can be found by examining the periodic distribution of transition metals that form terminal oxo complexes. These complexes are invariably formed by metals in higher oxidation states, from vanadium to osmium, there being virtually no examples of terminal oxo complexes in the cobalt, nickel and copper triads. For these metals, the only stable oxo species utilize these ligands in a bridging role (49). This behavior has been explained by noting that in order to form stable metal-ligand  $\pi$  bonds, utilizing the lone electron pairs on  $O^{2-}$  (or  $OH^-$ ), at least one of the d orbitals of  $\pi$  symmetry must be empty. For the early transition metals, this condition is often satisfied. For the later metals, from cobalt to copper however, the ligand lone pairs populate  $\pi$  antibonding orbitals which tends to destabilize the bonding interaction. Figure 20 illustrates this concept for octahedral mono-oxo, as well as the isoelectronic imido complexes (50). In this diagram, up to two d electrons can be accommodated without populating the  $\pi^*$  antibonding orbitals. An example of a stable complex with three terminal oxo ligands is seen in the methyltrioxorhenium species mentioned previously (Figure 3). In this case, rhenium is in its highest oxidation state of +7 which gives it a  $d^0$  electron configuration.



**Figure 20.** Partial molecular orbital diagram for metal-oxygen  $\sigma$  and  $\pi$  bonding (50).

For square planar  $d^8$  Pt(II), terminal oxo complexes are not known because there are no empty d orbitals of  $\pi$  symmetry on the metal. Only by adapting a bridging role can the *Pt-O* bond become stable. This same basic reasoning can also be applied to hydroxo species although the basicity of oxygen would now be moderated by the presence of a hydrogen atom.

As mentioned previously, several qualitative proposals have been advanced regarding the mechanism of dimer formation (15, 16). As with the octahedral Ir(III) case, deprotonation of at least one of the coordinated waters appears to be a critical first step in dimer formation. One of the primary goals of this research therefore was to determine the  $pK_a$ 's for one or both of these ligands. These  $pK$  values have been determined for only a few diaqua Pt(II) species using various techniques (51, 52) and most recently by NMR (53) and are given in Table 3. In addition to the other factors mentioned previously, the acidity of coordinated water appears to depend on the position in the trans influence series of the ligand *trans* to the water undergoing deprotonation, with the value of  $pK_a$  increasing as the ligand moves higher in the trans influence series (54, 55). This trend is reflected in the few  $pK_a$  values known (Table 3) and the empirical ordering of ligands based on numerous studies. The trans influence series of several nitrogen, phosphorus and sulfur donor ligands has been determined by comparing the Pt-Cl bond distance for complexes of the type  $PtCl_2LL'$  in the solid state (46) and by comparing NMR coupling constants in solution (54). This study placed sulfides and *S* bound sulfoxides above  $NH_3$  and below phosphanes in the series. These results would suggest that the  $pK_a$ 's for the deprotonation of the first water in complexes with *S* and *P* donor ligands in the trans position should be less than 5 or 6.

**Table 3.** Platinum complexes for which the  $pK_a$ 's of coordinated waters have been determined.

| Complex                                                                                          | Solvent          | $pK_{a1}$ | $pK_{a2}$ | Temp. °C | Method | Ref. |
|--------------------------------------------------------------------------------------------------|------------------|-----------|-----------|----------|--------|------|
| <i>cis</i> -[Pt(NH <sub>3</sub> )(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>                 | H <sub>2</sub> O | 5.93      | 7.87      | 5        | NMR    | 22   |
| <i>cis</i> -[Pt(NH <sub>3</sub> )(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>                 | H <sub>2</sub> O | 5.6       | 7.3       | 20       | Pot.   | 52   |
| <i>trans</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> | H <sub>2</sub> O | 4.35      | 7.40      | 25       | NMR    | 54   |
| [Pt(H <sub>2</sub> O)(NH <sub>3</sub> ) <sub>3</sub> ] <sup>2+</sup>                             | H <sub>2</sub> O | 6.37      | ----      | 25       | NMR    | 22   |
| [Pt(en)(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>                                           | H <sub>2</sub> O | 5.8       | 7.6       | 25       | Pot.   | 51   |
| [Pt(dien)(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>                                         | H <sub>2</sub> O | 6.53      | ----      | 23       | Pot.   | 51   |
| [Pt( <i>trans</i> -dach)(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>                          | H <sub>2</sub> O | 6.14      | 7.56      | 25       | Pot.   | 15   |
| [Pt( <i>trans</i> -dach)(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>                          | D <sub>2</sub> O | 6.48      | 8.08      | 25       | Pot.   | 15   |
| <i>trans</i> -[PtCl(H <sub>2</sub> O)(NH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>             | H <sub>2</sub> O | 5.63      | ----      | 25       | NMR    | 54   |
| [Pt(NO <sub>2</sub> ) <sub>3</sub> (H <sub>2</sub> O)] <sup>-</sup>                              | H <sub>2</sub> O | 5.32      | ----      | 25       | NMR    | 56   |
| [Pt(OH <sub>2</sub> ) <sub>4</sub> ] <sup>2+</sup>                                               | H <sub>2</sub> O | > 2       | ----      | ----     | ----   | 57   |
| <i>trans</i> -Pt(ox) <sub>2</sub> (OH) <sub>2</sub>                                              | H <sub>2</sub> O | 2.3       | 2.83      | 25       | Pot.   | 58   |

Appleton et al. have determined the  $pK_a$ 's for *trans*-[Pt(OH<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and *trans*-[Pt(Cl(OH<sub>2</sub>)(NH<sub>3</sub>)]<sup>2+</sup> complexes and have compared these values with the corresponding *cis* complexes (59). In both cases, the *trans* complexes had significantly lower values for  $pK_{a1}$ . From this and other results, they concluded that the difference was due to the *trans* influence between NH<sub>3</sub> and H<sub>2</sub>O. Specifically, they postulated that because the *trans* influence of H<sub>2</sub>O is rather weak, the oxygen of the water

molecule bound *trans* to it would be bound more strongly to platinum. The net effect is to transfer electronic charge towards the metal and away from the hydrogen atoms, leaving them with an increased positive charge. This explanation is entirely consistent with that suggested for the acidity of aqua acids discussed earlier.

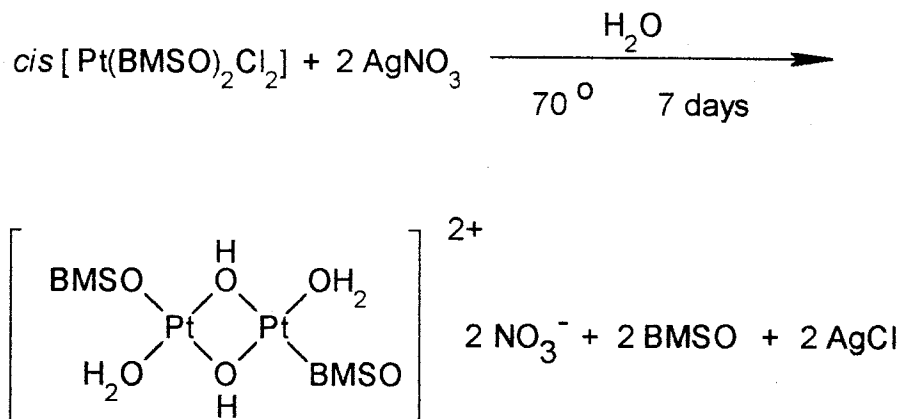
The last entry in Table 3 is of particular interest, being the only Pt(IV) complex in the list. The considerably lower  $pK_a$ 's are consistent with the higher positive charge density on the metal as discussed in connection with metal ion hydrolysis in general and are also consistent with the smaller *trans* influence of water compared with oxalate. Both the *cis* and the *trans* species have been studied by plotting pH against  $^{195}\text{Pt}$  chemical shift (31). Whereas the *trans* isomer exhibits a fairly large chemical shift change between pH 2 and 10, the *cis* isomer remains virtually constant. This behavior has yet to be fully explained but may simply indicate that the shielding effects upon deprotonation of coordinated water are not nearly as dramatic as in the *trans* isomer.

#### Homo- and Heterodimeric Pt(II) Sulfoxide Complexes

More recently, square planar  $d^8$  platinum and palladium complexes containing other than nitrogen donor ligands have been found to undergo the same type of dimerization reactions. The current research has focused almost exclusively on sulfur and phosphorus donors due to the original interest in using dimethylsulfoxide as a ligand.

Monodentate bis-sulfoxide platinum (II) complexes. Sulfoxides readily coordinate platinum(II). Both *S*- and *O*-bonded cases are known but it would seem that *S*-bonding is preferred in the absence of steric constraints (60). Thus, it has been noted that two sulfoxides readily coordinate Pt(II) to form *cis*-di-*S*-sulfoxo fragments (61). These fragments have the remarkable property of forming di- $\mu$ -hydroxo-bisplatinum(II) species under strongly acidic conditions. This contrasts with the more familiar *cis*-bis amine complexes which form bridged species only in neutral and mildly basic solutions. As would be anticipated, other factors such as temperature, concentration, ionic strength and even the counterion can all have an appreciable effect on species distribution as a function of pH (62, 63, 64).

Rochon et al. have studied the solution behavior of several platinum(II) complexes with monodentate sulfoxide ligands (11, 12). For ethylmethyl sulfoxide and diisopropyl sulfoxide, dihydroxo bridged dimers are formed upon silver assisted removal of chloride in aqueous solution, with a resulting pH of 1-2, suggesting considerable hydrolysis of the monomeric diaqua complex. In the case of dibenzyl sulfoxide, the complex shown in Figure 21 is formed, presumably due to steric hinderance caused by the bulky benzyl groups (65).



BMSO = benzylmethylsulfoxide

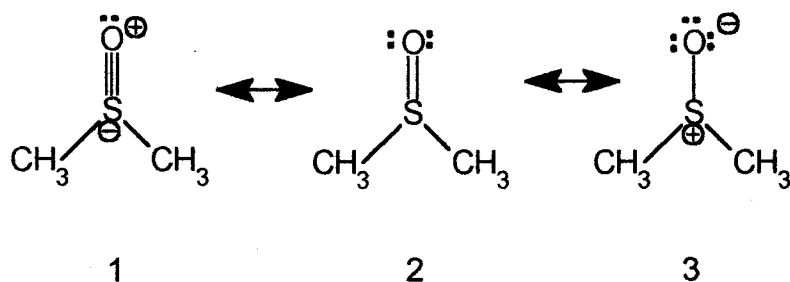
**Figure 21.** Hydrolysis and dimerization reaction for Pt complexes coordinated by bulky sulfoxide ligands.

Only after one of the sulfoxide ligands has been hydrolyzed does the formation of the dimer proceed. This would account for the longer reaction time and more extreme reaction conditions compared with less sterically demanding sulfoxide ligands.

We have been interested in exploiting the strong tendency of sulfoxo platinum(II) complexes to polymerize in acidic solution to develop methods for the systematic preparation of polymeric platinum(II) complexes. As has been previously discussed, pH plays an extremely important role in the species distribution in these systems.

Two *cis* sulfoxides are known to exert a considerable labilizing effect on one another in square planar  $d^8$  complexes (66, 67). This *cis* effect is paralleled by a

moderate *trans* effect for sulfoxides but is otherwise contrary to the observation that strong *trans* directing ligands are also highly nucleophilic (68). This combination of high *trans* effect and poor nucleophilicity is also seen in ethylene (69). It has been proposed, in the case of sulfoxides, to be due to the polarity of the sulfinyl group, which serves to impart a small positive charge to the sulfur atom (70). The difference in Pauling electronegativity between sulfur and oxygen is significant (0.86 Debye). This effect can be seen most easily by inspection of the resonance forms of DMSO in Figure 22. It has been suggested that the initial bond formed between platinum and a sulfoxide ligand is through the oxygen atom of the sulfinyl group, or that an olefinic type bond, involving the double bond between sulfur and oxygen, may exist in the five coordinate intermediate, thus explaining the similarity to ethylene (70).



**Figure 22.** Resonance forms of dimethylsulfoxide.

Although not entirely unreasonable, preferential bonding through oxygen rather than sulfur would seem to violate the Hard-Soft Acid-Base (HSAB) theory.

Steric factors also have a very strong influence on the rate of reaction and on product outcome. Although Pd(II) normally reacts some  $10^4$  -  $10^6$  times faster than an analogous Pt(II) species, it has been shown that by coordinating bulky ligands to the metal, it is possible to sterically "tune" a Pd complex to react at rates comparable to Pt (71).

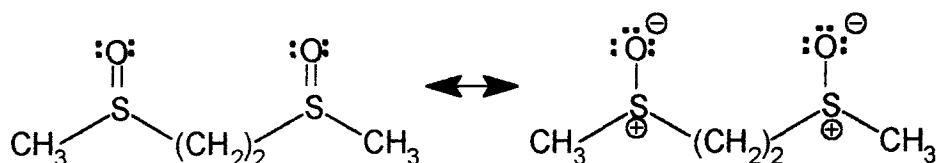
The interplay of steric and electronic factors in determining coordination geometry around square planar Pt(II) complexes is well illustrated by the formation of the tetrakis DMSO complex. In this case, two of the sulfoxide ligands are coordinated through sulfur while the other two are coordinated through oxygen. It has been suggested that steric interactions are responsible for this configuration (72). This hypothesis is supported by a study of the reactivity of sulfoxides towards the tetrachloroplatinate ion (67). These results show that the second order rate constant for the substitution of chloride by a series of sulfoxide ligands is determined by the steric bulk of the ligand rather than the difference in inductive effect. An alternative explanation for the mixed coordination mode may be that the presence of two soft ligands leads to a diminished preference for further substitution of soft bases by reducing the polarizability of the metal atom. This so called antisymbiotic effect has been experimentally demonstrated for a series of soft metal-ligand interactions and can be rationalized by noting that "two soft ligands in mutual *trans* positions will have a destabilizing effect on each other when attached to soft metal atoms" (73). This

follows from the fact that ligands having a large *trans* influence are invariably soft bases.

### Bidentate Sulfur Donor Ligands

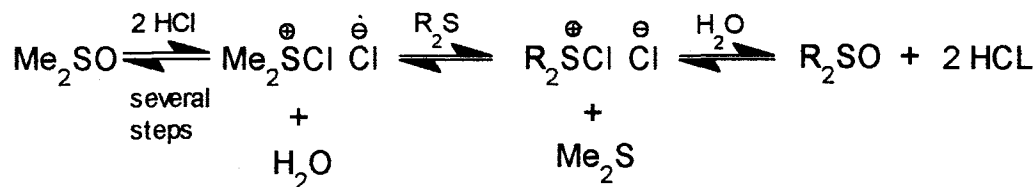
Bidentate sulfoxide and thioether ligands also form stable complexes with the platinum group metals and in many cases exhibit similar spectroscopic and chemical properties with the monodentate counterparts (74).

These compounds can be considered to be formed from two alkyl sulfide or sulfoxide fragments with a hydrocarbon link between the "methyl" groups. Due to the conformational rigidity imposed by the interdonor linkage, configurational isomers are formed on coordination to metal ions. One of the simplest sulfoxides of this type is 1,2-bis(methylsulfinyl)ethane (MSE). Two resonance structures of the *meso* form are shown in Figure 23.



**Figure 23.** Two resonance forms of *meso*-1,2-bis(methylsulfinyl)ethane.

The synthesis of this compound has been accomplished by several different methods. Oxidation of the parent disulfide with hydrogen peroxide or sodium periodate inevitably results in formation of the overoxidized sulfone (75). Overoxidation can be avoided by the method developed by Hull and Madden involving the HCl catalyzed transfer of oxygen from DMSO to dithiahexane (76). Because mechanistically similar reactions may be involved in the metal ion mediated deoxygenation of coordinated sulfoxide ligands, the proposed series of steps is worth discussing at this point. A common intermediate in the transfer of oxygen to sulfides appears to be the halosulfonium ion shown in Figure 24 below.

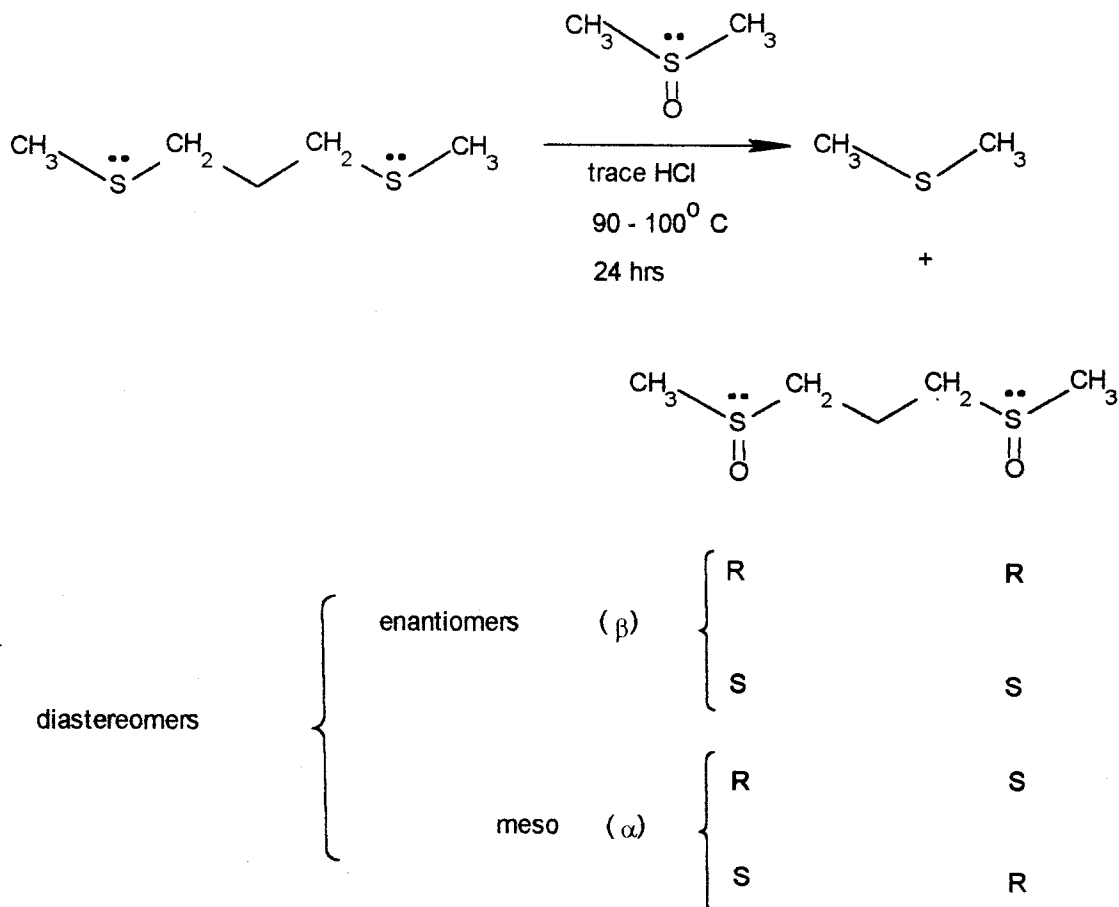


**Figure 24.** Proposed scheme for HCl catalyzed transfer of oxygen to an organic sulfide (77).

In the absence of a sulfide substrate, this intermediate can react further to form one of several products depending on the nature of the alkyl groups (77). Aside from reduction to the corresponding sulfide, several decomposition products as well as products formed by the cleavage of the *C-S* bond have also been identified. These

include halogenated alkylsulfides, alkyl halides and methanesulfonic acid thioalkyl esters (78). Cleavage of the  $C-S$  bond may be important in explaining the products of oxidation reactions of coordinated ligands using molecular chlorine in aqueous solution. This general topic of oxidation reactions of monomeric and dimeric  $Pt(II)$  complexes is treated more fully below.

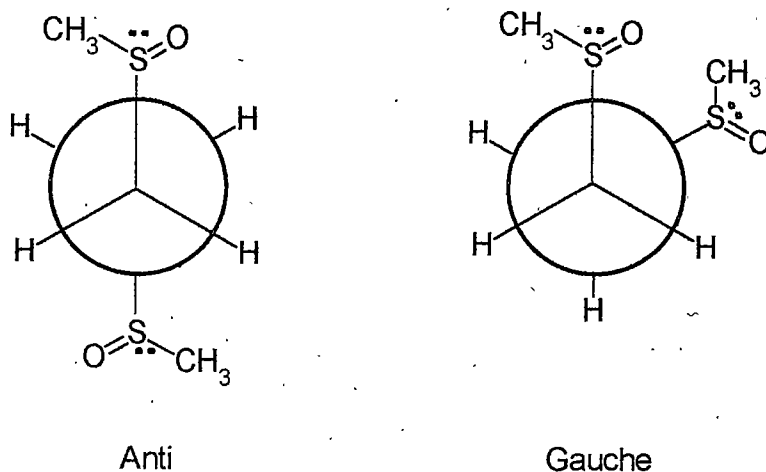
Because the sulfur atoms are chiral, MSE can exist as the *meso*-form and a *d,l* pair of enantiomers, as shown in Figure 25. It has long been recognized that disulfoxides of general formula  $RSO(CH_2)_nOSR$  can exist as diastereomers due to the presence of two chiral sulfur centers. In 1927, Bell and Bennett (75) first synthesized the compound for  $n = 2$ ,  $R = CH_3$  by oxidizing the corresponding disulfide with hydrogen peroxide. Although they were able to separate the diastereomers by repeated fractional crystallization, they were unable to assign absolute configuration around the sulfur atoms and designated them simply as the  $\alpha$  ( $\alpha$ ) and  $\beta$  ( $\beta$ ) forms based on melting point. Some forty years later, interest in the donor properties of these compounds toward metal ions resulted in the synthesis and spectroscopic characterization of several first row transition metal complexes as well as those of  $Pt$  and  $Pd$  (60). Based on IR evidence, it was determined that as expected from the HSAB theory for an ambidentate ligand containing both sulfur and oxygen, the "harder" first row metals all coordinated through oxygen while the "softer" platinum group metals, barring steric constraints, coordinated through sulfur.



**Figure 25.** Introduction of chirality by transfer of oxygen from a sulfoxide to a symmetrical disulfide.

Even with this additional structural information, the problem of diastereomeric assignment of the ligand still remained. In the following year, Louw and Nieuwenhuys (79) claimed to have resolved the issue for disulphoxides of  $n=1$  and 2 by oxidizing the parent disulfide or its racemic monosulfoxide with (1S)-(+)-percamphoric acid followed by fractional crystallization to yield the optically active  $\alpha$

and optically inactive  $\beta$  forms. They thus concluded that the higher melting  $\alpha$  form was the racemic mixture and the lower melting  $\beta$  form was the *meso* compound. Several years later, a crystal structure of the  $\alpha$  form was published by Svinning, Mo and Brunn (80) suggesting that the earlier assignment was incorrect and that the "alpha" form was in fact the *meso* compound. Curiously, no mention was made of the previous assignment. Additional work by other groups has since confirmed the crystallographic assignment of 1,2-bis-(methylsulfinyl)ethane as well as a number of other related disulfoxides (81). More recently, NMR has been used in an attempt to determine stereochemistry of these and related complexes (82). In the case of MSE, the chirality around the sulfur atoms renders the methylene protons magnetically non-equivalent. This can be seen by looking at the Newman projections shown in Figure 26.



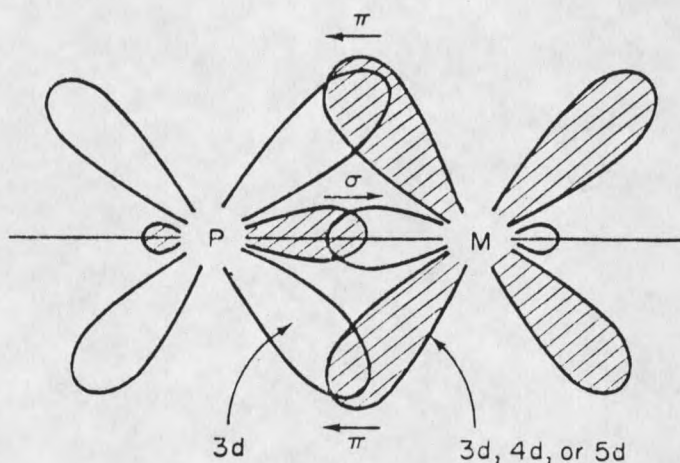
**Figure 26.** Newman projection of *meso*-MSE.

This magnetic non-equivalence results in an AA'BB' splitting pattern in the  $^1\text{H}$  NMR spectrum for both the *meso* and *d,l* forms of the ligand. Because both configurations of MSE show the same splitting pattern, it was not possible to use this criteria for stereochemical assignment. Further investigation into these and similar compounds however has shown that in many cases, for the symmetrical *meso* form, the AA'BB' splitting collapses into an  $A_4$  pattern (82).

For compounds of the general formula  $\text{R-S(O)-CH}_2\text{-CH}_2\text{-(O)S-R'}$ , diastereomeric *threo* and *erythro* forms are possible. In particular, it was found that when R and R' were aryl groups, the *meso* form showed a sharp singlet in the  $^1\text{H}$  NMR spectrum whereas the *d,l* enantiomeric pair showed the complex AA'BB' multiplet expected on theoretical grounds. Variable temperature experiments ruled out a significant contribution from intramolecular self association and demonstrated a fairly low barrier to bond rotation. The role of the solvent in the appearance of the spectrum is demonstrated by the variable temperature study of the diaryl compound with  $\text{R}=2\text{-carbomethoxyphenyl}$ . Between  $39^\circ$  and  $59^\circ$  C, in deuteriochloroform, the ethano region gives only a sharp singlet in the  $^1\text{H}$  NMR spectrum, whereas below  $39^\circ$  C, the complex splitting pattern reappears. Due to these incompletely understood results, NMR remains an inconclusive method for determination of stereochemistry for compounds of this type.

### Monodentate Platinum(II) Phosphane Complexes

Phosphane donor ligands in general and alkyl phosphanes in particular have long been known to be excellent ligands for Pt(II) (83, 84). The stability of the *Pt-P* bond has been explained in terms of the  $\sigma$  and  $\pi$  bonding interactions between these atoms, as shown in Figure 27.

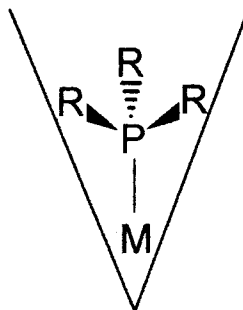


**Figure 27.** Sigma and pi interactions between  $d^8$  platinum(II) and phosphorus (83).

Considerable controversy has surrounded the relative importance of these  $\sigma$  and  $\pi$  type interactions. It was originally believed that donation of electron density from the partially filled metal *d* orbitals into the vacant *3d* orbital on phosphorus, the so called back bonding, made a major contribution to the affinity of phosphorus ligands for

"soft" metals such as platinum (85). Subsequent  $^{31}\text{P}$  NMR studies looking at the  $\text{Pt-P}$  coupling constants for a series of phosphorus ligands suggests that it is in fact the very strong  $\sigma$  donor capability of phosphorus that makes these bonds so robust (84). This conclusion was based on the observation that the ratio of the coupling constant for the *cis* and *trans* complexes is virtually the same for  $\text{Pt(II)}$  and  $\text{Pt(IV)}$  complexes.

As with sulfoxides, the chemistry of metal phosphane complexes is largely dominated by the steric interactions of the phosphane ligands in the primary coordination sphere of the metal (86). This aspect of phosphane chemistry has been intensively investigated by Tolman who proposed the formulation of a "cone angle" parameter which can be used as a measure of the steric bulk of various phosphane ligands (87). This cone just encloses the van der Waals radii of the ligand atoms over all rotational orientations around the metal-phosphorus bond axis. Figure 28 shows how this parameter is measured and Table 4 lists a range of phosphane ligand cone angles.



**Figure 28.** Illustration of the cone angle for phosphane ligands (After ref. 86).

**Table 4.** Phosphane ligand cone angles (86).

| Ligand                                         | Cone Angle (°) | Ligand                                                            | Cone Angle (°) |
|------------------------------------------------|----------------|-------------------------------------------------------------------|----------------|
| PH <sub>3</sub>                                | 87             | PH <sub>2</sub> Ph                                                | 101            |
| P(OCH <sub>2</sub> ) <sub>3</sub> CR           | 101            | PF <sub>3</sub>                                                   | 104            |
| P(OMe) <sub>3</sub>                            | 107            | PMe <sub>3</sub>                                                  | 118            |
| PMe <sub>2</sub> Ph                            | 122            | Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> | 123            |
| PEt <sub>3</sub>                               | 132            | PPh <sub>3</sub>                                                  | 145            |
| PPh <sub>2</sub> ( <i>t</i> -Bu)               | 157            | PCy <sub>3</sub>                                                  | 170            |
| PPh( <i>t</i> -Bu) <sub>2</sub>                | 170            | P( <i>t</i> -Bu) <sub>3</sub>                                     | 182            |
| P(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> | 184            | P(mesityl) <sub>3</sub>                                           | 212            |

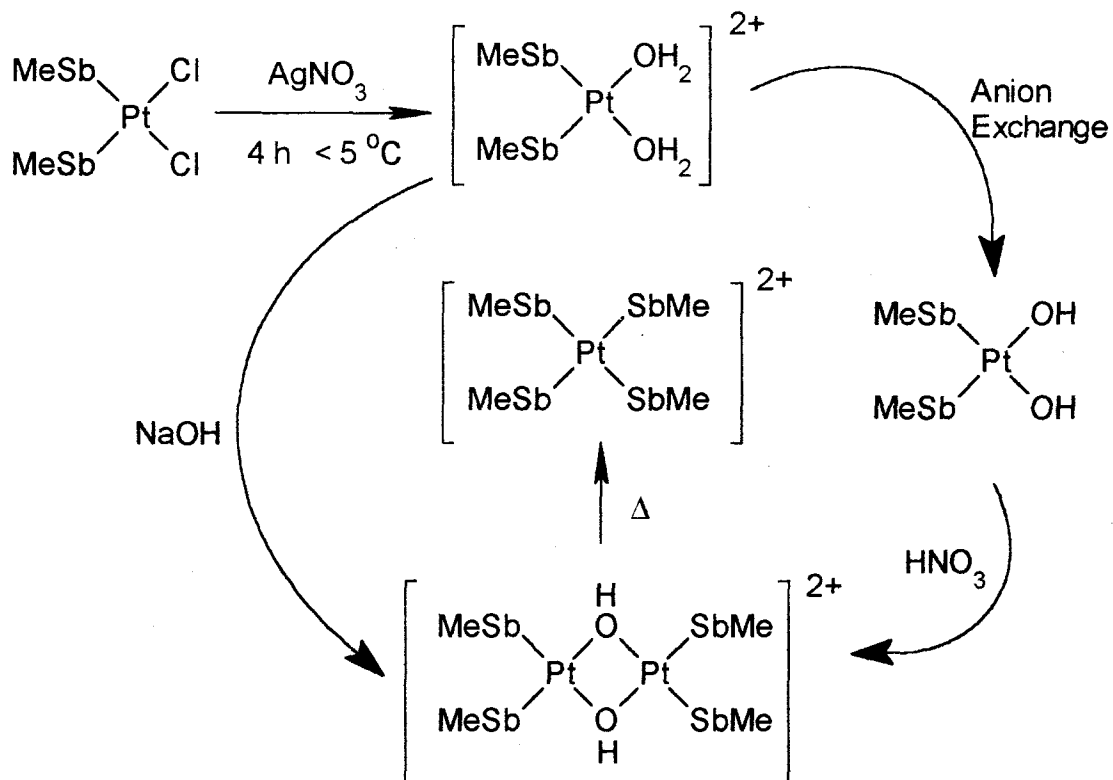
Two immediate effects of this steric interaction are that bulky phosphane ligands with large cone angles tend to bind *trans* to one another and to increase the rate of substitution reactions proceeding by a dissociative pathway (88). Distortions from idealized coordination geometry are also thought to be a result of steric interaction and can often lead to enhanced lability of phosphane ligands. An example of this is seen in Wilkinson's catalyst, RhCl(PPh<sub>3</sub>)<sub>3</sub>. In this complex, Rh(I) has a d<sup>8</sup> electron configuration and therefore normally adopts a square planar geometry. Distortion of this plane is thought to account for the effectiveness of this complex as a hydrogenation catalyst by labilizing one of the phosphane ligands leading to eventual ligand dissociation, a key step in the proposed catalytic mechanism (86).

Interest in transition metal phosphane complexes has mainly been centered around their use as catalysts (84). More recently however, a growing number of investigations are being conducted in attempts to develop biologically active metal-phosphane complexes analogous to the metal amines currently being used in cancer therapy. Clearly, one of the principle requirements for agents of this type is a moderate solubility in an aqueous medium. When trimethyl phosphane is used as a ligand for the synthesis of the type of di- $\mu$ -hydroxo bridged species discussed above for sulfoxides, the complexes become extremely water soluble. We have taken advantage of this solubility to form a number of mixed ligand dimers containing the  $\text{Pt}(\text{PMe}_3)_2$  fragment. Because of the hydrophobic nature of alkyl groups in general, trialkyl phosphane complexes are not normally considered very water soluble (89). *cis*- $\text{Pt}(\text{PMe}_3)_2\text{Cl}_2$  for example is only soluble to the extent of about  $10^{-5} \text{ mol dm}^3$  in aqueous solution (90).

#### Ligands With Other Group 15 Donor Atoms

Although much less well studied, the heavier group 15 elements show similar steric repulsive interactions, with the trend in donor atoms being  $\text{P} < \text{As} < \text{Sb} < \text{Bi}$  (84). Interestingly, di- $\mu$ -hydroxo bridged  $\text{Pt}(\text{II})$  species containing these ligands have recently been reported (91). These complexes are formed using the same general procedure as for the corresponding phosphane species but appear to have a much lower thermal stability. If subjected to only moderate temperatures ( $80^\circ\text{C}$ ) for short periods,

the dimers decompose or undergo intramolecular rearrangement to form the tetrakis stibine complex as shown in Figure 29.



**Figure 29.** Formation and thermal decomposition of Di- $\mu$ -hydroxo bridged Pt(II) stibane dimers (91).

As expected from the steric considerations discussed above, the crystal structure of the  $[\text{Pt}(\text{SbMe}_3)_4]^{2+}$  ion shows a distorted square planar arrangement around Pt (91).

### Reactions of Coordinated Ligands

Finally, some mention should be made of the variety of reactions that can occur on coordinated ligands. Because one of the primary objectives of this research was to explore the feasibility of using oligomeric bridged complexes as building blocks for more complex structures, the ability to modify the chemical properties of coordinated ligands is of fundamental importance. For sulfoxide ligands, this area has only recently been investigated (78). In particular, it was found that the reactivity of coordinated monodentate sulfoxides is significantly different than that of the free ligand. This reactivity is due in part to the difference in bond length of the sulfinyl group in *S* and *O* bonded ligands. Deoxygenation of the sulfinyl group has been observed with a variety of reagents. Although we did not actively investigate reactions of this type, a crystal structure was obtained which suggested that a carbon-carbon bond had been broken in a bidentate sulfoxide ligand. Clearly, this is an area which deserves more attention in these systems.

## Spectroscopy

### Nuclear Magnetic Resonance Spectroscopy

Virtually all of the platinum containing complexes in this investigation were studied by  $^{195}\text{Pt}$  NMR spectroscopy.  $^{195}\text{Pt}$  nuclear magnetic resonance is an attractive technique for the study of polynuclear platinum complexes.  $^{195}\text{Pt}$  chemical shifts are extremely sensitive to chemical environment and afford an opportunity to distinguish Pt atoms in complex molecules (92). This sensitivity can be explained in part by considering the relative contributions to the shielding constant ( $\sigma$ ) of a heavy atom such as platinum. This constant is comprised of two main terms as shown in equation 3 (93).

**Equation 3.**

$$\sigma_{\text{total}} = \sigma_p + \sigma_d$$

In this equation,  $\sigma_p$  and  $\sigma_d$  are the diamagnetic and paramagnetic contributions to the total shielding constant respectively. The terms paramagnetic and diamagnetic as used here do not refer to the presence or absence of unpaired electrons but rather to the free circulation of electrons about the nucleus (diamagnetic) or the hinderance to that circulation (paramagnetic) caused by the presence of other electrons or nuclei in the molecule (94). For most heavy nuclei such as  $^{195}\text{Pt}$ ,  $\text{Co}^{59}$  and  $^{103}\text{Rh}$ , the paramagnetic

term dominates the shielding interaction and has been evaluated for  $^{195}\text{Pt}$  (95) (Equation 4).

$$\text{Equation 4. } \sigma_p = (-e^2 h^2 / 2 m^2 c^2) \langle r^{-3} \rangle C_{a1g}^2 [8 C_{a2g}^2 \Delta E_A^{-1} + 4 C_{eg}^2 \Delta E_E^{-1}]$$

In this equation,  $\langle r^{-3} \rangle$  is an average over the radial  $5d$  functions used as a basis set;  $C_{eg}$ ,  $C_{a1g}$ , and  $C_{a2g}$  are the coefficients of the corresponding  $d$  orbitals in the molecular orbitals of platinum; and  $\Delta E$  terms are differences in energies between highest occupied and lowest unoccupied orbitals accessible for one electron transitions. Equation 4 reflects the relative importance the difference in energy of the various molecular orbitals and has led to an attempt to correlate chemical shifts of these nuclei with UV-Vis data based on the  $e_g \leftarrow t_{2g}$  transitions (96). The energy separation ( $\Delta E$ ) is fairly small for  $d^6$  Pt(IV) complexes leading to a large contribution from the inverse dependence on this term. The correlation is not nearly so good for Pt(II) species however, limiting the usefulness of this method for predicting chemical shifts (97).

An excellent example of the power of  $^{195}\text{Pt}$  NMR is the assignment of all sixteen isotopomers of a Pt cluster complex with direct metal-metal bonding (92). Coupling constants range from 5450 Hz to 7700 Hz and the distinctive splitting pattern of natural abundance Pt allow these assignments to be made unambiguously.

With the wealth of information on chemical shifts and coupling constants for  $^{195}\text{Pt}$  complexes, several trends have emerged which were used extensively in assigning

spectra. The first of these concerns the resonance frequency of the various oxidation states of platinum. Due to the decreased shielding from the six *d* electrons, Pt(IV) almost always resonates downfield of the analogous Pt(II) species, which in turn resonate downfield of Pt(0) (37). Notable exceptions to this general trend is seen in certain Pt(II) and (IV) iodides and this may reflect the increase in covalent character of the *Pt-I* bond over Cl and Br.

Another trend that has emerged from this and other studies of dimeric complexes is that there is normally seen a downfield shift of 300 - 400 ppm on going from the diaqua monomer to a di- $\mu$ -bridged species. This shift is thought to be caused by the strain imposed by the four membered Pt-OH-Pt-OH ring (11). Consistent with this observation is the assignment of a hydroxo bridged cyclic trimer peak located 15 ppm to higher field of the dimer due to the decreased strain of a six membered ring. All of these factors were extremely useful in assigning resonances for new complexes formed in this work and are discussed more fully at the appropriate time in the Results and Discussion section below.

## EXPERIMENTAL

### Instrumental Methods

#### Nuclear Magnetic Resonance Spectroscopy

$^1\text{H}$  NMR spectra were acquired on Bruker WM250, AC300, AM500 FT spectrometers operating at 5.85 T, 7.02 T or 11.7 T respectively, or on the upgraded AVANCE DPX-250 or DRX-300 versions of these instruments using the same magnets at virtually identical field strengths. Chemical shifts were referenced to the residual solvent peak or to dioxane for pH titrations.

$^{195}\text{Pt}$  NMR spectra were obtained on Bruker WM250 or DPX250 spectrometers equipped with a 10 mm broadband probe (WM250) or 10 mm platinum specific probe (DPX250). Spectra were normally  $^1\text{H}$  decoupled and referenced to an external standard of 0.1 M  $\text{Na}_2\text{PtCl}_6$ . Shifts to higher field are negative. For samples run in non-deuterated solvents, the lock signal was provided by a concentric insert tube containing  $\text{D}_2\text{O}$ . Temperature control was achieved by a B-VT 1000 variable temperature unit and is accurate to within  $\pm 1^\circ\text{C}$ . For increased resolution or for samples with limited solubility, temperatures were elevated to slow the relaxation times somewhat and enhance the resolution. At times, resolution was further enhanced by Gaussian multiplication. Typical acquisition parameters are given in Table 5.

**Table 5.** Typical acquisition parameters for  $^{195}\text{Pt}$  NMR spectra.

| Parameter                     | WM250                 | AM500                 | DPX250        |
|-------------------------------|-----------------------|-----------------------|---------------|
| Spectrometer Frequency (MHz)  | 53.518                | 107.036               | 53.770        |
| Sweep Width (Hz)              | 50,000                | 125,000               | 125,000       |
| Pulse Width ( $\mu\text{s}$ ) | 30 ( $50^\circ$ tilt) | 10 ( $60^\circ$ tilt) | 10            |
| Relaxation Delay (s)          | 0.00                  | 0.00                  | 0.00          |
| Number of Scans               | 64 - $10^3$ K         | 64 - $10^3$ K         | 64 - $10^3$ K |
| Time Domain Size              | 4 K                   | 4 K                   | 4K            |
| Spectrum Size                 | 4 - 16 K              | 4 - 16 K              | 8 - 64 K      |

**Table 6.** Typical acquisition parameters for  $^{31}\text{P}$  NMR spectra.

| Parameter                     | WM250     | AM500     | DPX300 |
|-------------------------------|-----------|-----------|--------|
| Spectrometer Frequency (MHz)  | 101.255   | 202.458   |        |
| Sweep Width (Hz)              | 42000     | 83000     |        |
| Pulse Width ( $\mu\text{s}$ ) | 18.0      | 12.0      |        |
| Relaxation Delay (s)          | 1.0 - 2.5 | 0.5 - 2.5 |        |
| Number of Scans               | 1 - 64 K  | 1 - 64 K  |        |
| Time Domain Size              | 32 K      | 32 K      |        |
| Spectrum Size                 | 64 K      | 64 K      |        |

$^{31}\text{P}$  NMR spectra were acquired on Bruker WM250, AM250 or DPX300 spectrometers. Proton decoupling was achieved by broadband (WM250, AM500) or

composite pulse (DPX300) decoupling using a WALZ-16 pulse sequence. Chemical shifts are referenced to  $\text{PPh}_3$  in  $\text{CDCl}_3$  at 0.0 ppm with negative values upfield from this resonance. Temperature control was achieved as for the other nuclei. Low temperatures were achieved by controlled boil off of liquid nitrogen around the NMR tube. Typical acquisition parameters are given in Table 6.

$^{13}\text{C}$  NMR spectra were acquired on Bruker AC300 and DPX300 spectrometers. Typical acquisition parameters are given in Table 7.

**Table 7.** Typical acquisition parameters for  $^{13}\text{C}$  NMR spectra.

| Parameter                     | AC300        | DPX250   | DRX300       |
|-------------------------------|--------------|----------|--------------|
| Spectrometer Frequency (MHz)  | 75.469       | 62.902   | 75.476       |
| Sweep Width (Hz)              | 20,000       | 4400     | 10 - 20 K    |
| Pulse Width ( $\mu\text{s}$ ) | 5.5          | 10.0     | 6.0          |
| Relaxation Delay (s)          | 2.0          | 2.0      | 2.0          |
| Number of Scans               | 400 - 16,000 | 1 - 14 K | 400 - 16,000 |
| Time Domain Size              | 32 K         | 16 K     | 16 K         |
| Spectrum Size                 | 32 - 64 K    | 32 K     | 16 - 32 K    |

### Infrared Spectroscopy

Mid IR spectra from  $4000\text{ cm}^{-1}$  -  $400\text{ cm}^{-1}$  were recorded on a Bruker IFS20 FT spectrometer. Solid samples were prepared as KBr pellets or as Nujol mulls between NaCl plates. Far IR spectra below  $400\text{ cm}^{-1}$  were recorded on a Bruker IFS120 FT spectrometer as either polyethylene pellets or in Nujol between polyethylene plates.

### Ultraviolet-Visible Spectroscopy

UV-Vis spectra were recorded on a Hewlett Packard HP8452A diode array spectrophotometer. Solutions were typically  $10^{-3}$  -  $10^{-4}$  M and were run in 0.1 or 1.0 cm quartz cells.

### pH Measurements and Melting Point Determination

pH measurements were made with a Radiometer PHM64 Research pH meter with an Ag/AgCl combination electrode calibrated with pH 1.09, 4.00, 7.00 and 10.00 buffer solutions. Melting points were taken on a Multi-temp II melting point apparatus and are uncorrected.

### Preparation of Starting Complexes

Abbreviations: DMSO = dimethylsulfoxide, DESO = diethylsulfoxide, TMSO = tetramethylenesulfoxide, EMSO = ethylmethylsulfoxide, MSE = 1,2-bis-methylsulfinylethane, dth = 2,4-dithiahexane (1,2-bis-methylthioethane), DES = diethylsulfide, dach = diaminocyclohexane, en = ethylenediamine, ox = oxalate.

$\text{AgNO}_3$  (Aldrich) and  $\text{K}_2\text{PtCl}_4$  (Johnson-Matthey) were used as supplied. DMSO and TMSO (Aldrich) were stored over Linde 4A molecular sieves and used without further purification. DESO was prepared by the periodate oxidation of diethylsulfide according to literature methods (97) and vacuum distilled prior to use.

cis-dichlorobis(dimethylsulfoxide)platinum (II) was synthesized according to literature methods (11).

di- $\mu$ -hydroxobis(dimethylsulfoxide)platinum (II) nitrate. This complex as well as the other dihydroxo bridged species in this thesis were synthesized via the silver assisted hydrolysis of chloride ions from the corresponding dichloro complexes by the method of Rochon et al. (11). All of the reactions which resulted in the formation of silver chloride were run in the dark to prevent photo induced reduction of silver (I) and concomitant oxidation and degradation of platinum complexes. In most cases, the complex was not isolated as a solid but was used as formed in solution. The sulfate,

trifluoromethanesulfonate, and tetrafluoroborate salts of this and other dimeric cationic complexes were prepared similarly using the corresponding silver salt. For sulfate salts, NMR data suggest that sulfate is coordinated to Pt(II) to form mono- or di-substituted  $\text{SO}_4$  species in solution. These results are discussed fully in the Results and Discussion below. The pH of these solutions was adjusted with NaOH, KOH, NaOD, DCl or  $\text{CF}_3\text{SO}_3\text{D}$  to shift the monomer dimer equilibrium to the desired point for subsequent reactions.

Dichloro(*trans*-1,2-diaminocyclohexane)platinum (II) and Di- $\mu$ -hydroxobis(*trans*-diaminocyclohexane)platinum (II) nitrate were prepared according to literature methods (15).

Dichloroethylenediamineplatinum (II) was prepared according to literature methods (51)

*meso*-1,2-bis(methylsulfinyl)ethane was prepared according to the method of Hull et al. using the HCl catalyzed transfer of oxygen from DMSO to 1,2-bis(methylthio)ethane (77). Three recrystallizations from ethanol yielded 4.2 g (34.9 % yield) of pure  $\alpha$  isomer (MP 171-174 °C, lit. 169-170°C). Purity was also checked by  $\{^1\text{H}\}^{13}\text{C}$  NMR.

Silver(I)-trimethylphosphane adduct. This complex was synthesized by literature methods (99) and used in one method of preparation of *cis*-Pt(en)Cl<sub>2</sub>. In our hands,

this product always produced a small quantity of dark material, presumed to be metallic silver, when dissolved in water. The use of this "intermediate" in the synthesis of the Pt complex was therefore discontinued in favor of the original literature preparation.

Silver(I)meso-1,2-bis(methylsulfinyl)ethane trifluoromethanesulfonate was formed in one method by adding 0.138 g (0.894 mmol) of the  $\alpha$  isomer of MSE to 10 ml (1.0 mmol) of an aqueous solution of silver trifluoromethanesulfonate, allowing the solution to stir for ~ 1 hour followed by reducing the volume of the solution to ~ 3 ml under reduced pressure and allowing the solution to stand. If this solution was placed in a vacuum desiccator under reduced pressure, crystals of compound formed within 12 hours.

Tetraaquaplatinum (II) perchlorate was prepared as described by Elding (57).  $^{195}\text{Pt}$  NMR was used to check for the presence of any residual chloro species and the known UV-Vis absorption peak at 274 nm ( $56.5 \text{ cm}^{-1} \text{ M}^{-1}$ ) was used to determine the total platinum concentration of the stock solution. This solution was stored under argon at 4° C between uses.

Cis-dichlorobis(trimethylphosphane)platinum(II) was prepared by two different literature methods with slight modifications to each one (52). For each method, trimethylphosphane was added as a 1.0 M solution in tetrahydrofuran (THF). Rather than simply heating for twenty minutes at 100 °C, the  $[\text{Pt}(\text{PMe}_3)_4]^{2+} [\text{PtCl}_4]^{2-}$  complex

ion which initially formed was refluxed for three to four hours in order to effect complete rearrangement to the *cis*-dichloro species. The crude product in each case was recrystallized once from a 1,2-dichloroethane / dichloromethane 1:1 solution.

Dichlorobipyridilplatinum(II) and di- $\mu$ -hydroxo-bis-bipyridilplatinum(II) nitrate were prepared according to literature methods (99).

Dichloro-1,2-bis(methylthio)ethaneplatinum(II) was prepared by reacting  $K_2PtCl_4$  with 1,2-bis(methylthio)ethane in a solution of . The greenish-yellow precipitate was filtered on a sintered glass filter and washed with 3 x 5 ml cold water, 5 ml ethanol, and 5 ml diethyl ether, and dried in vacuo over Dreirite.

Dichloro- $\alpha$ -1,2-bis(methylsulfinyl)ethaneplatinum(II) was prepared by reaction of  $K_2PtCl_4$  with  $\alpha$ -1,2-bis(methylsulfinyl)ethane in water. The red solution was stirred for 18 to 24 hours and the off-white precipitate filtered on a sintered glass filter, washed with 3 x 5 ml cold water, 5 ml ethanol and 5 ml diethyl ether and dried in vacuo over Dreirite. Typical yields were between 85-90 %. The dibromo- and diiodo- complexes were formed by adding 10 equivalents KBr or KI respectively to the reaction mixture.

Dichloro- $\beta$ -1,2-bis(methylsulfinyl)ethaneplatinum(II) was prepared in an analogous manner using  $\beta$ -1,2-bis(methylsulfinyl)ethane.

Dichloro-1,2-bis(methylthio)ethanepalladium(II) was synthesized in a similar fashion to the analogous platinum complex starting with  $\text{PdCl}_2$ .

Cis-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) was synthesized according to literature methods (100). Early reports on the products of this synthesis indicated that a mixture of *cis* and *trans* isomers are formed in solution and that *cis* / *trans* isomerization is photo induced. No attempt was made to rigorously exclude light during the preparation of this compound. The use of this complex and its photochemical behavior is addressed in the Results and Discussion section below.

## RESULTS AND DISCUSSION

The following section presents the major results of this research in roughly the order in which they were obtained. Because there were no specific "target" complexes in mind at the outset, each set of experiments was based largely on the results of the previous ones. Discussion of pertinent literature is also included where such discussion serves to further elucidate the interpretation of these results.

### Monodentate Platinum(II) Sulfoxide Complexes

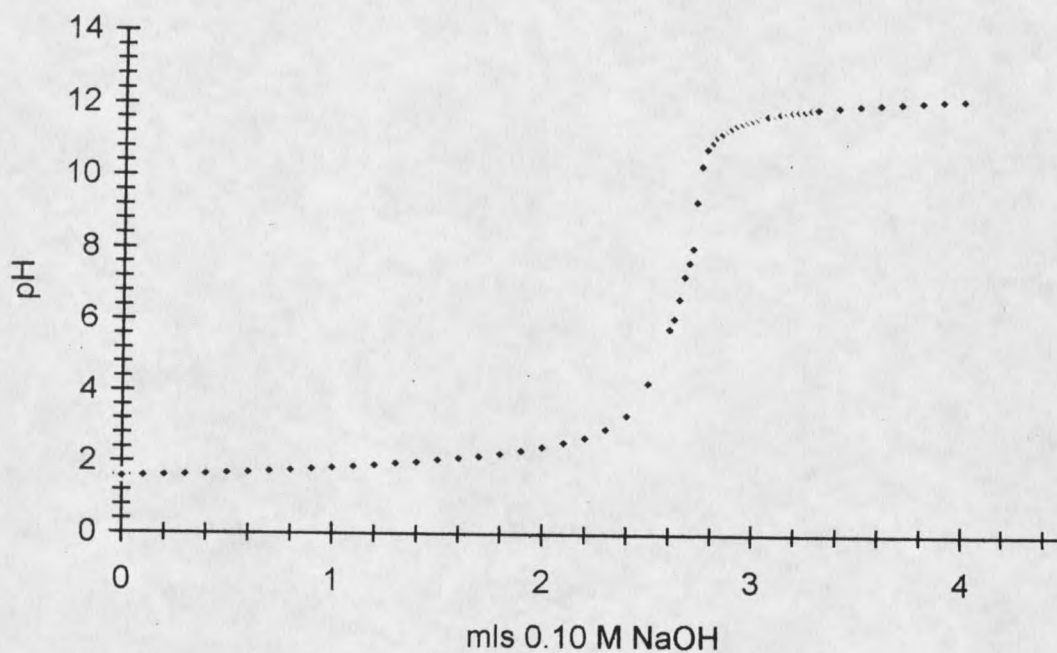
#### Potentiometric Titration of $[\text{Pt}(\text{DMSO})_2(\text{OH}_2)_2] (\text{NO}_3)_2$ (1)

Rochon and coworkers have studied the formation of a number of di- $\mu$ -hydroxo-bis(sulfoxide)platinum(II) complexes and have reported that they form in acidic solution (65). Because pH plays such an important role in the formation and species distribution of the hydroxo bridged complexes being investigated, one of the primary goals of this research was to determine the acid dissociation constants ( $K_a$ 's) of the coordinated water ligands in the diaqua monomers.

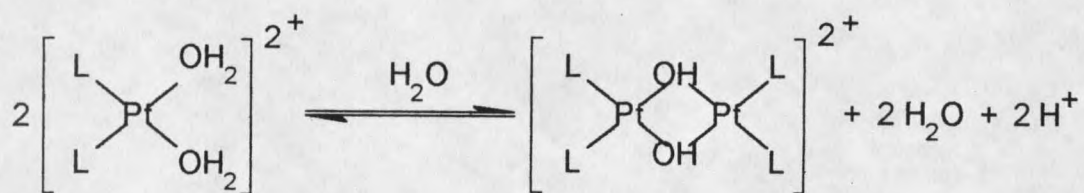
Initial attempts to determine the  $pK_a$ 's for complexes of the type *cis*- $[\text{PtL}_2(\text{OH}_2)_2]^{2+}$  where L is a monodentate sulfoxide ligand included potentiometric titrations of the monomer species, plotting pH vs. volume of added acid or base. This

technique has been used by several groups to determine the  $pK_a$ 's of the analogous *cis*-diammine and related complexes (51, 52). The values obtained in that study compare well with values obtained more recently using NMR methods, although results obtained by direct titration such as this have been treated with caution due to the inevitable formation of dimer or higher polymeric species at moderate to high pH levels (54).

Figure 30 shows the titration curve generated by titrating a solution of *cis*-[Pt(DMSO)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (1) with 0.10 M NaOH. A single inflection point is clearly visible at around 2.6 ml added base. The presence of only one inflection point presumably indicates overlapping of the two ionizations expected due to the presence of two coordinated water ligands. Overlapping  $pK$ 's such as this have been successfully treated for other systems including those involving complex polymerization reactions (22). During the course of the titration, it was observed that between pH 5.8 and 9.4, the pH would jump up by two to three pH units with the addition of base but then almost immediately begin to fall again until a steady reading was reached after approximately five minutes. This behavior would seem to indicate that a reaction was occurring to liberate protons which subsequently reacted with the added base. These observations in this pH range are consistent with the formation of a dibridged species which does in fact release two equivalents of protons, as shown in Figure 31. The qualitative appearance of this curve is similar to that for the *cis*-diamine system, which was generated using NMR methods, yielding the values  $pK_{a1} = 5.37$  and  $pK_{a2} = 7.21$  (53).

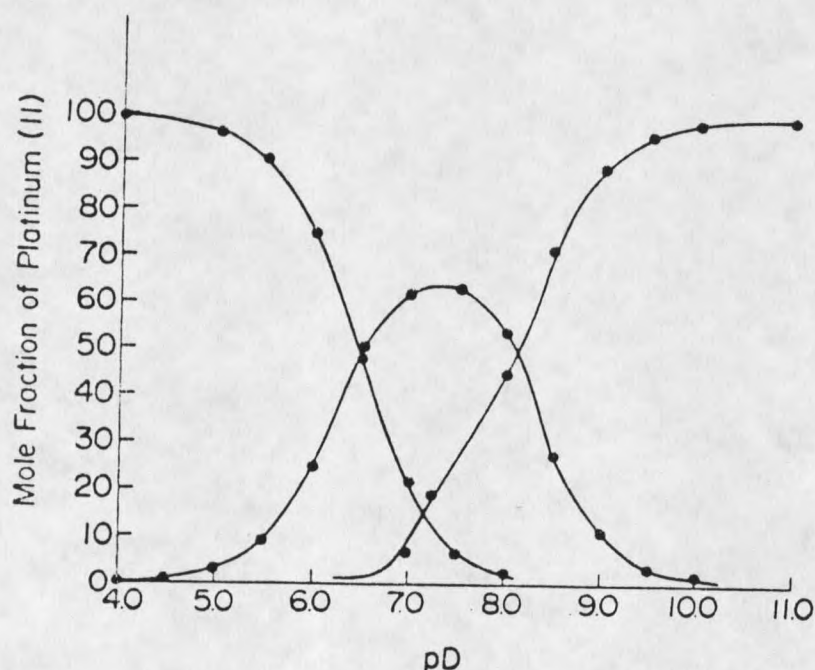


**Figure 30.** Titration of a solution of **1** with 0.10 M NaOH.



**Figure 31.** Dimerization scheme showing the liberation of two equivalents of  $\text{H}_2\text{O}$  and  $\text{H}^+$ .

The distribution of diaqua monomer and dihydroxo bridged dimer as a function of pH appears to contrast sharply with that for the diaminocyclohexane (dach) case for which the species distribution of the monomeric forms has been determined using experimental  $pK_a$  values (15). Figure 32 shows the results of that work based on NMR measurements of a solution with an initial concentration of diaqua monomer of 0.05 M. Due to the nature of the monomer-dimer equilibrium expression, concentration is very important in these systems. The pH dependence on concentrations of solutions following hydrolysis of chloride the ligands indicates that deprotonation has already occurred to a significant extent. Increasing the total Pt concentration always shifts the equilibrium towards dimer formation.



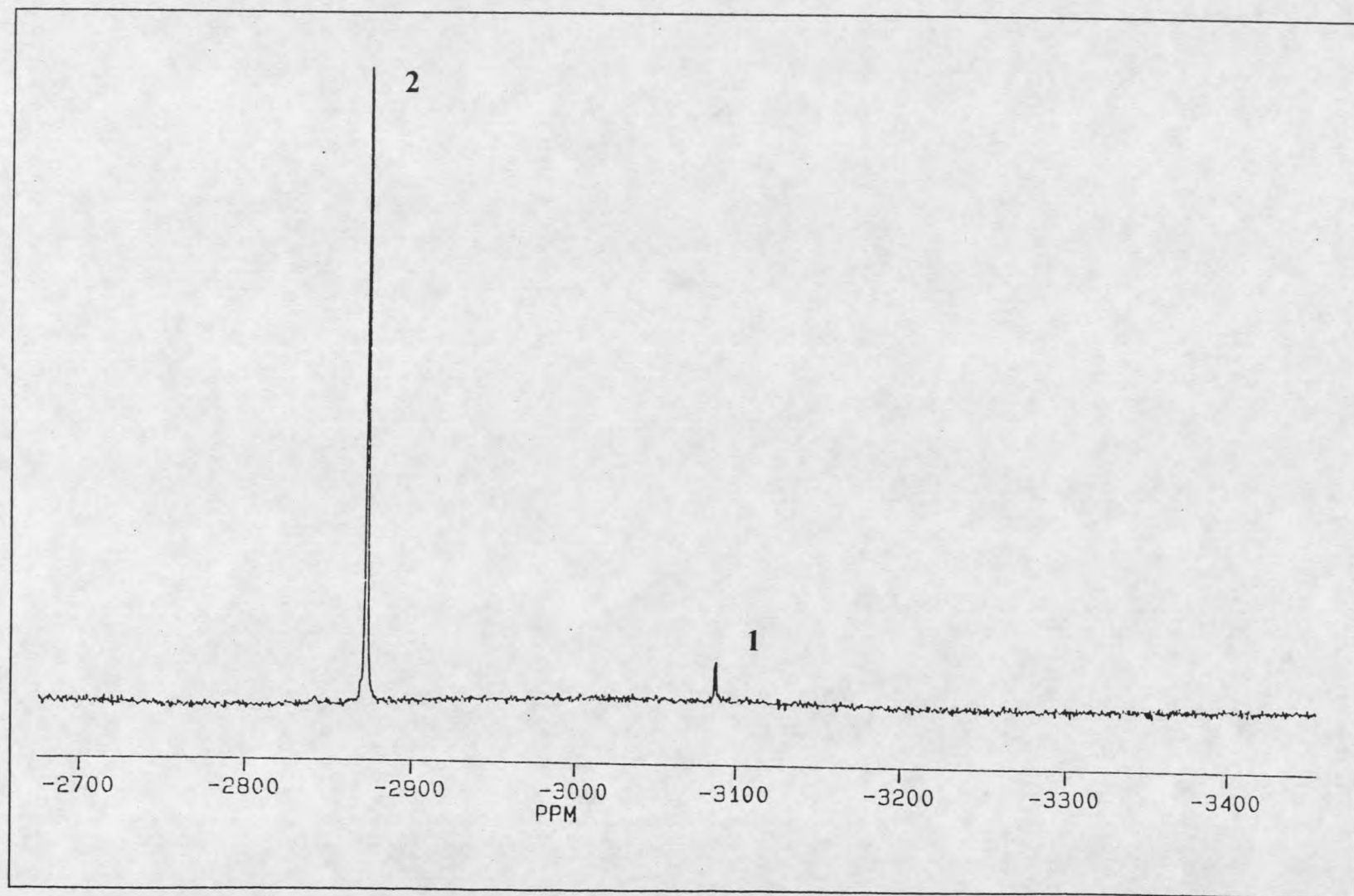
**Figure 32.** Species distribution as a function of pD for the  $cis$ -[Pt(dach)(OH<sub>2</sub>)]<sup>2+</sup> system (pD = pH + 0.4) (15).

It can be seen in Figure 32 that the only species present below pH 4 is the diaqua monomer at this concentration. This is in contrast to the DMSO case where the predominate species is present as the dimer at pH's as low as 2, as shown in the  $^{195}\text{Pt}$  NMR spectrum in Figure 33.

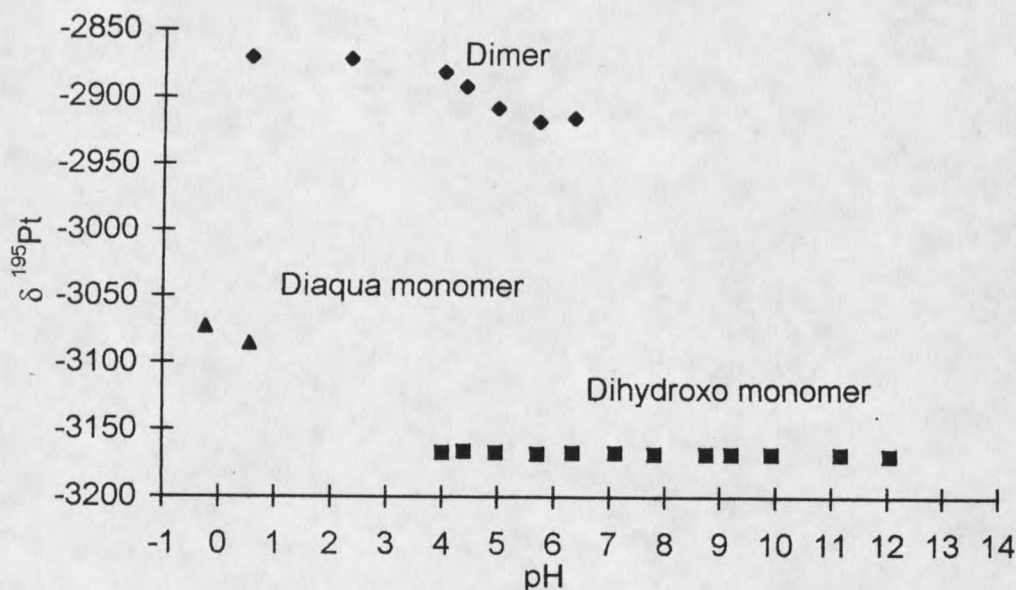
#### $^{195}\text{Pt}$ NMR Titration of $\text{Pt}(\text{DMSO})_2(\text{OH}_2)_2(\text{NO}_3)_2$ (1)

In a second attempt to determine the values of  $\text{pK}_a$  in these complexes, a titration was performed plotting  $^{195}\text{Pt}$  chemical shift vs. pH. Because  $^{195}\text{Pt}$  chemical shifts are so sensitive to the environment of the Pt atom, a plot of  $\delta \text{ Pt}$  vs. pH may be expected to yield a titration curve similar to that used to determine the  $\text{pK}$ 's in the *cis* diammine case in which pH was plotted vs.  $\delta \text{ }^{15}\text{N}$  (53). It was soon realized however that due to the very low pH at which dimerization occurred, the monomer peak could not be followed through the entire titration range at the concentrations required to obtain a Pt spectrum in a reasonable amount of time.

Figure 34 illustrates the pH dependence of  $^{195}\text{Pt}$  chemical shifts in solutions of *cis*-bis(dimethylsulfoxide)platinum(II) complexes. The aqua complex is observed at -3086 ppm and exists only below pH 1 at concentrations of ~0.15 M. A chemical shift of about -3000 ppm is characteristic of a Pt(II) complex where Pt is bound to two sulfurs and two oxygens. A new resonance appears near -2870 ppm as the pH is raised above 1. It dominates the spectrum between pH 1 and pH 7.



**Figure 33.**  $^{195}\text{Pt}$  NMR spectrum of an equilibrium mixture of *cis*- $[\text{Pt}(\text{DMSO})(\text{OH}_2)]^{2+}$  and  $[\text{Pt}(\text{DMSO})_2(\mu\text{-OH})]_2^{2+}$ .



**Figure 34.** Plot of  $^{195}\text{Pt}$  chemical shift versus pH for a  $\sim 0.15$  M solution of 1.

This resonance is best assigned to di- $\mu$ -hydroxo-bis(dimethylsulfoxide)platinum(II)-nitrate (2). The downfield shift of ca. 200 ppm relative to diaqua-bis(dimethylsulfoxide)platinum(II) is consistent with the formation of the four membered, hydroxo bridged ring (63). Proof that this is a binuclear complex comes from the spectra of the unsymmetrical mixed ligand complexes discussed below. Above pH 7, this complex is hydrolyzed to *cis*-dihydroxo-bis(dimethylsulfoxide)platinum(II). Its resonance persists to pH 12. The chemical shift of the dimer is not constant over the pH range where it is observed. Figure 34 shows that there is a 45 ppm difference between its chemical shift at the lowest and highest pH. A distinct inflection is

observed at pH 4.2. Its sigmoidal shape suggests a pH dependent equilibrium which is rapid on the NMR timescale. Two possible explanations were considered and rejected. A pH of 4.2 corresponds to the lowest pH at which the dihydroxo monomer appears and is consistent with the base hydrolysis of one of the hydroxo bridges. It may be postulated that the breaking of one of bridges relieves some of the strain of the four membered ring, causing an upfield shift of  $\sim 45$  ppm. However, conversion to a monobridged complex at ca. pH 4.2 was considered and rejected because it seems unlikely to be rapid on the NMR timescale. Another possibility is that one of the hydroxo bridges is being deprotonated to form an oxo, hydroxo bridged dimer. Such a structure has precedent in a novel Pt(II) compound synthesized recently by Sharp et.al.(40). In that case, deprotonation was achieved by addition of the  $\text{Li}^+$  or  $\text{Na}^+$  salt of  $\text{N}(\text{SiMe}_3)_2$  in THF, resulting in a highly basic di- $\mu$ -oxo bridged compound which regenerates the hydroxo complex in the presence of water. It therefore seems unlikely that deprotonation of the hydroxo bridges would occur at such low pH in aqueous solution. Although this particular titration involved the nitrate salt of the dimer, analogous results were obtained using the sulfate, triflate and tetrafluoroborate salts. The triflate and tetrafluoroborate ions are generally thought to be noncoordinating in aqueous solution although there are reports that at least for some metal cations, the triflate ion is a better ligand than water in non-aqueous organic solvents (102). It has been suggested that silver salts of the conjugate base of a weak acid such as  $\text{F}^-$  may promote dimer formation by assisting in the deprotonation step following initial

hydrolysis of the chloride ligands (103). At least one group has claimed that the choice of counter-ion has an influence on the equilibrium distribution of monomer and dimer species (63) and we have also seen some evidence for this although the effect appears to be small. Sulfate is known to coordinate to platinum(II) to some extent (54) and we have seen some NMR evidence to indicate that monodentate sulfate species may be present in solution at low to moderate pH when this counter-ion is used.

Because the DMSO methyl protons would not exchange with solvent, it was felt that  $^1\text{H}$  NMR, although not nearly as sensitive to changes in structure, could afford a suitable probe of the monomer-dimer equilibrium. The increased receptivity of  $^1\text{H}$  over  $^{195}\text{Pt}$  would allow a much lower total concentration to be used, thereby shifting the equilibrium in favor of the monomer. A major disadvantage of using such dilute solutions was that hydrolysis of the monomeric aqua complex occurred, resulting in free DMSO in solution and the formation of the triaqua species. Although this result was not completely unexpected considering the known strong *cis* effect of *S* bound DMSO, it did preclude the use of this method for determining the  $\text{pK}_a$ 's of the coordinated waters and set the stage for the next set of experiments concerning the formation of mixed ligand sulfoxide ligands.

### Formation of Heterodimeric Monodentate Sulfoxide Complexes

Because we had an interest in synthesizing heterodimeric bridged complexes of platinum(II), that is, hydroxobridged complexes where each Pt atom is coordinated by different ligands, other monodentate sulfoxide ligands were selected from literature preparations. Rochon et al. have shown that "less" bulky monodentate sulfoxides such as EMSO and TMSO all react similarly following silver assisted hydrolysis of the chloride ligands (65). Presumably due to steric constraints, the "bulkier" ligands formed somewhat different complexes (Fig. 21) and then only at considerably reduced rates or under more extreme reaction conditions. Table 8 lists the  $^{195}\text{Pt}$  NMR data for the diaqua and di- $\mu$ -hydroxo bridged sulfoxide complexes used in this study.

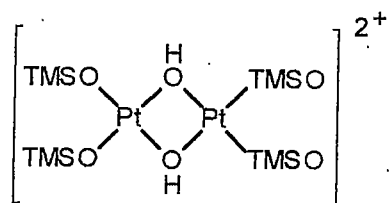
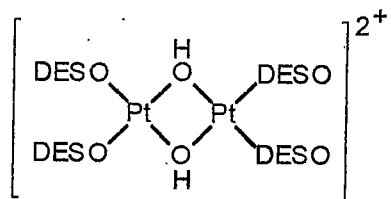
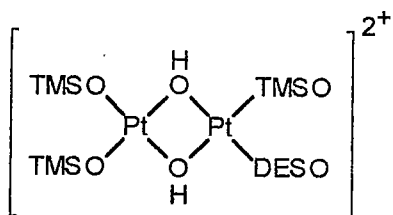
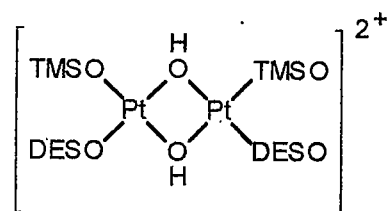
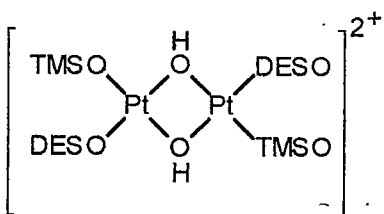
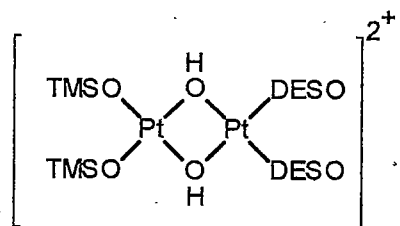
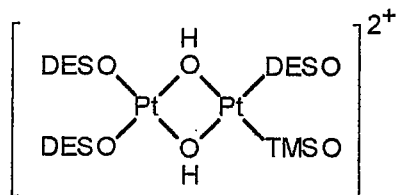
Addition of a mono sulfoxide ligand like DESO to solutions of  $[\text{Pt}(\text{TMSO})_2(\mu\text{-OH})]_2^{2+}$  (5) would be expected to produce an equilibrium distribution of the species depicted in Figure 35. These two sulfoxide dimers were chosen because the respective homodimers have the largest chemical shift separation of the monodentate sulfoxides known to form hydroxo bridged dimers (Table 8), thus resulting in greater peak separation within each group. Figure 36 is the  $^{195}\text{Pt}$  NMR spectrum of an equilibrium mixture of equimolar 5 and 6. Equilibrium is established rapidly among the possible binuclear species and all of the expected mixed ligand dimeric species are observed within twenty minutes. Table 9 presents the spectral assignments of the resonances.

**Table 8.**  $^{195}\text{Pt}$  chemical shifts for monodentate sulfoxide monomer and dimer complexes.

| # | Complex                                            | $\delta \text{ Pt}$ (ppm) | Ref.      |
|---|----------------------------------------------------|---------------------------|-----------|
| 1 | $[\text{Pt}(\text{DMSO})_2(\text{OH}_2)_2]^{2+}$   | -3086 <sup>a</sup>        | This work |
| 2 | $[\text{Pt}(\text{DMSO})_2(\mu\text{-OH})]_2^{2+}$ | -2870 <sup>a</sup>        | "         |
| 3 | $\text{Pt}(\text{DMSO})_2(\text{OH})_2$            | -3170                     | "         |
| 4 | $[\text{Pt}(\text{TMSO})_2(\text{OH}_2)_2]^{2+}$   | -3015 <sup>c</sup>        | "         |
| 5 | $[\text{Pt}(\text{TMSO})_2(\mu\text{-OH})]_2^{2+}$ | -2813 <sup>a</sup>        | "         |
| 6 | $[\text{Pt}(\text{DESO})_2(\mu\text{-OH})]_2^{2+}$ | -2912 <sup>a</sup>        | "         |
| 7 | $[\text{Pt}(\text{EMSO})_2(\text{OH}_2)_2]^{2+}$   | -3146 <sup>b</sup>        | 11        |
| 8 | $[\text{Pt}(\text{EMSO})_2(\mu\text{-OH})]_2^{2+}$ | -2887 <sup>b</sup>        | 11        |
| 9 | $\text{Pt}(\text{EMSO})_2(\text{OH})_2$            | -3213                     | 11        |

a)  $\text{NO}_3^-$  counterion b)  $\text{SO}_4^{2-}$  counterion c)  $\text{CF}_3\text{SO}_3^-$  counterion

Because the complexes of interest in this work often contain two or more magnetically non-equivalent platinum atoms, it is essential to have a firm theoretical understanding of the appearance of the NMR spectra for these species in solution. Resonances in these spectra represent a superposition of a singlet and a doublet as shown in Figure

**5****6****10****11****12****14****13**

**Figure 35.** Species present in an equilibrium mixture of **5** and **6**.

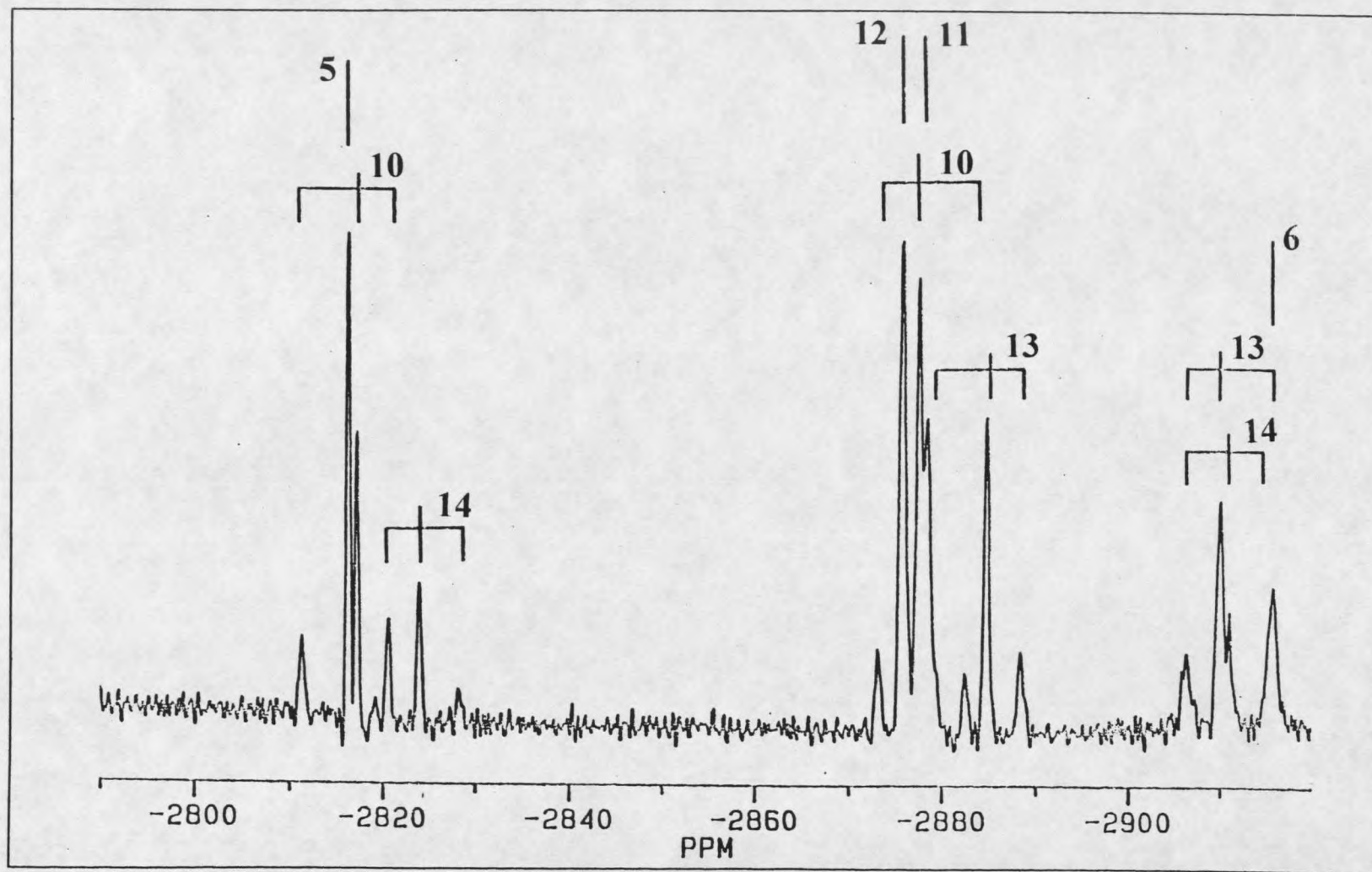


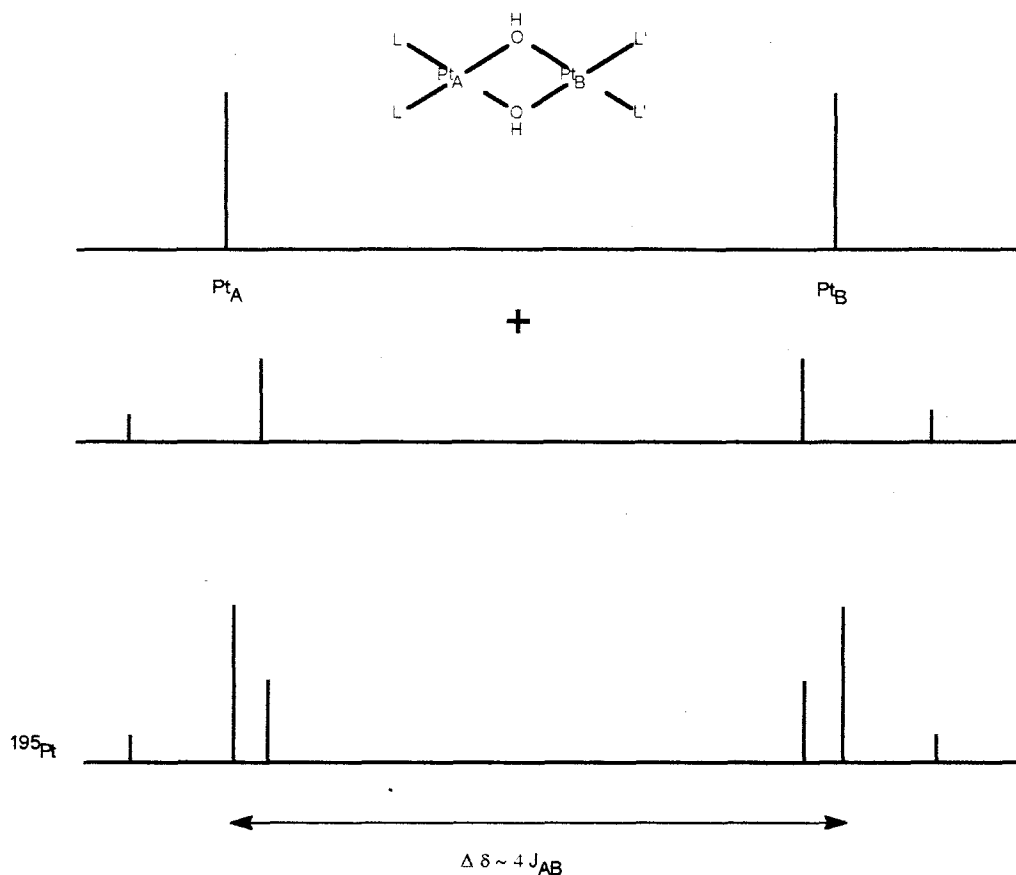
Figure 36.  $^{195}\text{Pt}$  NMR spectrum of an equilibrium mixture of equimolar 5 and 6.

In this figure, the ratio of chemical shift difference ( $\Delta \delta$ ) to coupling constant ( $J_{AB}$ ) has been arbitrarily set to  $\sim 4$ . As this ratio becomes smaller, the inner satellites of each resonance increase in intensity and move closer to the main singlet peak, while the outer satellites decrease in intensity and move away from the main singlet peak.

This so called leaning of the multiplets is identical to that seen in second order coupled  $^1\text{H}$  NMR spectra. The resulting asymmetry of these resonances provides definitive proof for the presence of multiple Pt atoms and was crucial to the unambiguous assignment of coupled sets of peaks.

**Table 9.** Chemical shifts and coupling constants for all di- $\mu$ -hydroxo bridged binuclear complexes formed at equilibrium in aqueous solution for TMSO and DESO. Structures of the compounds appear in Figure 35. pH = 1.8  
Concentrations  $\sim 0.16$  M.

| #  | Complex                                                                                                             | $\delta_{\text{Pt}}$<br>(ppm) <sup>a</sup> | $^2J_{\text{Pt-Pt}}$<br>( $\pm 12$ Hz) |
|----|---------------------------------------------------------------------------------------------------------------------|--------------------------------------------|----------------------------------------|
| 5  | $[\text{Pt}(\text{TMSO})_2(\mu\text{-OH})]_2^{2+}$ <sup>b</sup>                                                     | -2813                                      |                                        |
| 6  | $[\text{Pt}(\text{DESO})_2(\mu\text{-OH})]_2^{2+}$                                                                  | -2912                                      |                                        |
| 10 | $[(\text{TMSO})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{TMSO})(\text{DESO})]^{2+}$                               | -2814<br>-2871                             | 491                                    |
| 11 | <i>sym-cis</i> - $[(\text{TMSO})(\text{DESO})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{TMSO})(\text{DESO})]^{2+}$   | -2870                                      |                                        |
| 12 | <i>sym-trans</i> - $[(\text{TMSO})(\text{DESO})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{TMSO})(\text{DESO})]^{2+}$ | -2874                                      |                                        |
| 13 | $[(\text{TMSO})(\text{DESO})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{DESO})_2]^{2+}$                               | -2880<br>-2905                             | 465                                    |
| 14 | $[(\text{TMSO})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{DESO})_2]^{2+}$                                          | -2822<br>-2910                             | 483                                    |



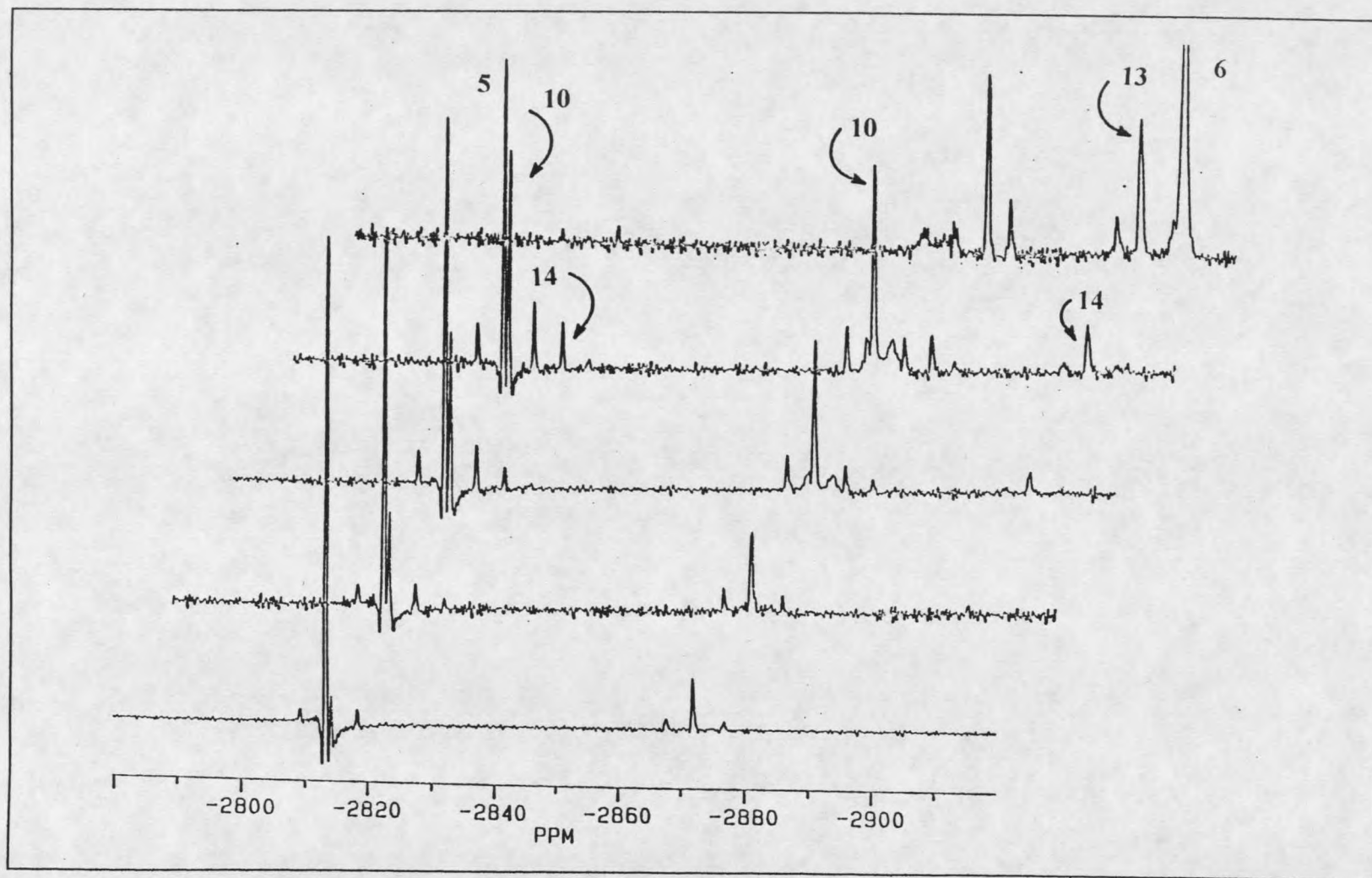
**Figure 37.** Diagrammatic illustration of the superposition of singlet and doublet spectra seen in J coupled  $^{195}\text{Pt}$  NMR spectra.

Based on the preceding discussion, resonances are readily assigned to the various binuclear species. For the unsymmetrical complexes, each platinum appears as three resonances, a singlet and an unsymmetrical doublet. The singlet corresponds to the case where the other platinum atom in the complex has no spin (66.2 %). A doublet flanks it, arising from the case where the other platinum is  $^{195}\text{Pt}$  with a spin of  $1/2$  (33.8 %). The doublet always appears as the A part of an AB pattern since the

chemical shift difference is only five to ten times greater than the coupling constant. Referring to either Table 9 or Figure 36, it is noted that the resonances form three groups, one group for each of the fragments  $\text{Pt}(\text{TMSO})_2$ ,  $\text{Pt}(\text{TMSO})(\text{DESO})$ , and  $\text{Pt}(\text{DESO})_2$ . In the  $\text{Pt}(\text{TMSO})_2$  group, there is a singlet for the symmetrical dinuclear complex **4** and two doublets, one where  $\text{Pt}(\text{TMSO})_2$  is bridged to a  $\text{Pt}(\text{TMSO})(\text{DESO})$  group (**10**) and the other where it is bridged to a  $\text{Pt}(\text{DESO})_2$  group (**14**). The same is true for the  $\text{Pt}(\text{DESO})_2$  region, although in this case it was difficult to make peak assignments due to the broad, overlapping resonances. The broadening of these peaks is most likely a direct reflection of the slower tumbling time of the molecule as TMSO is replaced by DESO. Peak assignments in this region were made by the standard addition method discussed below. In the  $\text{Pt}(\text{TMSO})(\text{DESO})$  region there are two symmetrical complexes, *sym-cis* (**11**) and *sym-trans* (**12**), and there are two doublets, one coupled to the  $\text{Pt}(\text{TMSO})_2$  group (**10**) and the other coupled to the  $\text{Pt}(\text{DESO})_2$  group (**13**). The asymmetry of the AB pattern gives the chemical shift of the coupled fragment (**104**) and was crucial to assigning resonances where one or both of the doublets was obscured by other peaks. Confirmation comes from matching up the coupling constants for the multiplets in the different groups.

### Standard Addition of DESO

Further confirmation was achieved by starting with a pure TMSO system and making standard additions of DESO to it. A separate solution of **4** (0.091 M) was prepared as described above. A standard addition of ~20 mol% DESO was made and the  $^{195}\text{Pt}$  spectrum acquired. This was repeated until a total of ~320 mol% DESO had been added at which time the downfield resonances due to the bis-TMSO fragments had all but disappeared. At low DESO concentrations the complexes with  $\text{Pt}(\text{TMSO})(\text{DESO})$  fragments dominate those with  $\text{Pt}(\text{DESO})_2$  fragments (Figure 38). With the first addition of DESO, the resonance due to **10** is apparent as a small peak at -2814 ppm, 0.88 ppm upfield from the intense TMSO homodimer resonance of **5**. The coupled set of resonances centered at -2872 ppm, representing the Pt fragment with one TMSO and one DESO ligand also becomes apparent. Assignments can be made with certainty since the coupling constants observed in the two fragments of any heterodimer must be identical. With continued additions of DESO, the peaks in the far upfield group begin to appear, representing the Pt fragment with two coordinated DESO ligands, until at ~320 mol% DESO, this group of peaks becomes dominant. To check the reversibility of the reaction, TMSO was added to the final mixture resulting in the reappearance of the downfield peaks. In neither of the methods mentioned above was it possible to unambiguously assign the peaks due to isomers **11** and **12**. Assignments were made in this case based on the observation by Fakley et.al. that in a



**Figure 38.**  $^{195}\text{Pt}$  NMR of standard additions of 20, 40, 60, 80 and 325 mol% DESO to a solution of **5**. For unsymmetrical complexes, only the most intense central peak is labeled.

closely related di- $\mu$ -hydroxo phosphine dimer, the *sym-trans* structure becomes predominate as the size of the ligand increases (105). The more intense of the two singlet peaks of the TMSO-DESO fragments was therefore assigned to structure 12.

When solutions of 5 and 6 are combined, a statistical formation of the seven dinuclear complexes might be anticipated. For equal initial concentrations of the two mononuclear precursors, the relative abundance of each isomer is expected to follow a binomial distribution giving peak intensities of 1:4:6:6:6:4:1 for isomers 5, 10, 11, 12, 13, 14, 6 respectively. Although it was not possible to accurately integrate the individual peaks, the qualitative appearance of Figure 36 suggests a non-statistical distribution. It seems reasonable to assume that ligand steric effects may play some part in determining the equilibrium distribution of species. In some cases, these steric effects may play an indirect role by affecting the O-Pt-O angle and therefore the match-up between the two dimer fragments. Table 10 lists the homodimeric complexes for which crystallographic data is available. This concept of matching "bite" distance is taken up again in the context of the formation and stability of heterodimeric complexes involving the Pt(PMe<sub>3</sub>)<sub>2</sub> fragment. To the best of our knowledge, a crystal structure is available only for 5 so a direct comparison of that angle is not possible at this time (106).

The rapid scrambling of sulfoxide ligands among the dimeric complexes can be rationalized as mentioned above by the known strong *cis* influence of sulfoxides. This effect, which pertains to the influence on bond strength of the two ligands in a *cis* position to the ligand in question has been much less well documented than the *trans*

influence and is generally regarded as being less important in terms of product outcome although there are cases where it seems to exert a comparable effect.

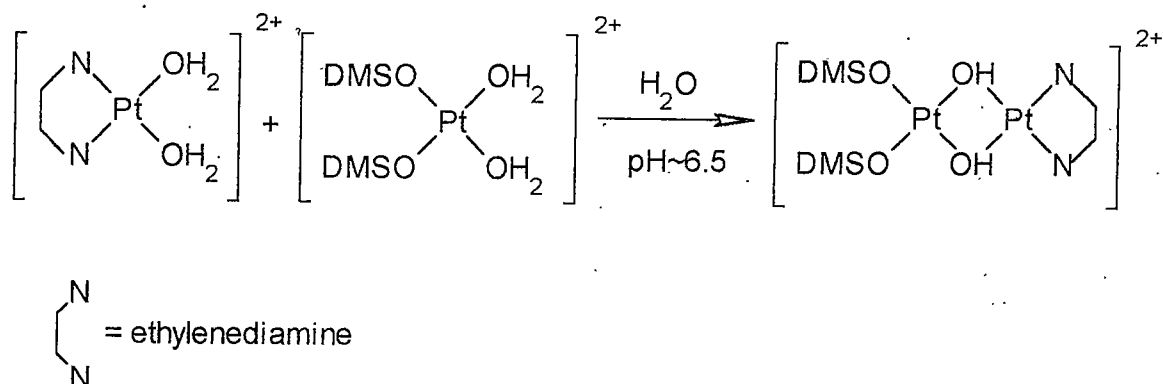
**Table 10.** Selected bond angles and distances for monodentate, di- $\mu$ -hydroxobridged dimeric platinum complexes (46).

| Complex                                                                                                                 | Pt--Pt (Å) | O-Pt-O ( $^{\circ}$ ) | Pt-O-Pt ( $^{\circ}$ ) |
|-------------------------------------------------------------------------------------------------------------------------|------------|-----------------------|------------------------|
| [Pt(NH <sub>3</sub> ) <sub>2</sub> (OH)] <sub>2</sub> 2 NO <sub>3</sub>                                                 | 3.085(1)   | 81.3(4)               | 98.7(4)                |
| K <sub>2</sub> [Pt(NO <sub>2</sub> ) <sub>2</sub> (OH)] • 3/2 H <sub>2</sub> O                                          | 3.167(1)   | 81(1)                 | 99(1)                  |
| [Pt(C <sub>4</sub> H <sub>8</sub> SO) <sub>2</sub> (OH)] <sub>2</sub> 2 NO <sub>3</sub>                                 | 3.137(3)   | 80.0(2)               | 100.0(3)               |
| [Pt(dmso) <sub>2</sub> (OH)] <sub>2</sub> 2 (ClO <sub>4</sub> )                                                         | 3.145(3)   | 79.6(4)               | 100.4(4)               |
| [Pt(NH <sub>3</sub> ) <sub>2</sub> (OH)] <sub>2</sub> 2 CO <sub>3</sub> • 2 H <sub>2</sub> O                            | 3.104(1)   | 81.9(5)               | 98.8(5)                |
| [Pt(dmso) <sub>2</sub> (OH)] <sub>2</sub> 2 BF <sub>4</sub>                                                             | 3.144(1)   | 80.0(6)               | 100.0(6)               |
| [PtCl(dmso)(OH)] <sub>2</sub>                                                                                           | 3.0496(9)  | 79.5(4)               | 96.1(5)                |
| [Pt(dmso) <sub>2</sub> (OH)] <sub>2</sub> 2 CF <sub>3</sub> SO <sub>3</sub>                                             | 3.1417(9)  | 81.0(4)               | 99.0(4)                |
| (NBu <sub>4</sub> ) <sub>2</sub> [Pt(C <sub>6</sub> F <sub>5</sub> )(OH)] <sub>2</sub>                                  | 3.211(1)   | 78.6(5)               | 101.4(6)               |
| [Pt(PMe <sub>3</sub> ) <sub>2</sub> (OH)] <sub>2</sub> 2 NO <sub>3</sub>                                                | 3.261(1)   | 75.9(4)               | 104.1(4)               |
| [Pt(dppf) <sub>2</sub> (OH)] <sub>2</sub> 2 BF <sub>4</sub><br>• 2 CH <sub>2</sub> Cl <sub>2</sub> • 2 H <sub>2</sub> O | 3.227(1)   | 79.4(4)               | 100.6(7)               |
| [Pt(PEt <sub>3</sub> ) <sub>2</sub> (OH)] <sub>2</sub> 2 BF <sub>4</sub>                                                | 3.121(1)   | 79.4(6)               | 92(2)                  |
| [Pt(N,N-Me <sub>2</sub> en)( $\mu$ -OH)] <sub>2</sub> 2 NO <sub>3</sub>                                                 |            | 79.1(6)               | 101.0(6)               |
| [Pt(dmso) <sub>2</sub> ( $\mu$ -OH)] <sub>2</sub> [Pt(ox) <sub>2</sub> (OH) <sub>2</sub> ]                              | 3.123(2)   | 79.8(9)               | 100.2(9)               |

### Formation of Heterodimeric Complexes With Other Donor Atoms

Based on the results of the preceding experiments with monodentate sulfoxides, it was clear that the lability of these ligands would make it very difficult to control the product outcome in mixed ligand dimers. The next set of experiments therefore was designed to introduce a less labile ligand onto one end of the dimeric unit, thus preventing the rapid exchange of ligands between coordination sites.

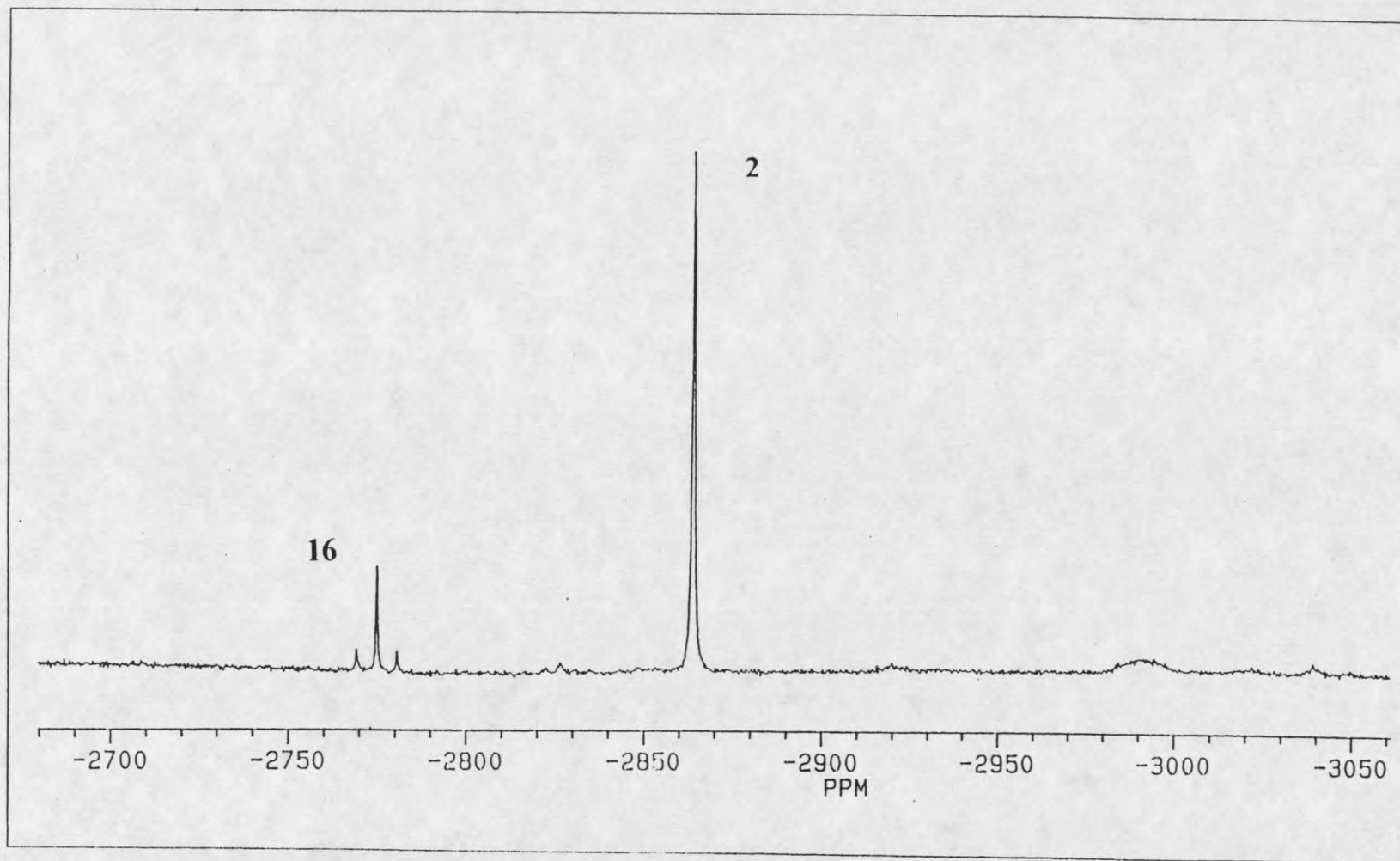
Nitrogen Donor Complexes. Because many nitrogen donor ligands are known to form dihydroxo bridged homodimeric species, these ligands were used in the investigations into the formation of heterodimeric Pt(II) complexes containing more than one type of donor atom. Complexes of this type are important because the presence of different functionality's allow for both steric and electronic tuning of each end of the dimeric structure, resulting in different reactivities. When equimolar amounts of *cis*-[Pt(en(OH)<sub>2</sub>]<sup>2+</sup> (**15**) and (**1**) are combined and the pH of the resulting solution adjusted to pH ~ 6.5 with 3 M KOH, <sup>195</sup>Pt NMR reveals the presence of the heterodimeric complex di-μ-hydroxo-bis(dimethylsulfoxide)ethylenediamine platinum(II) (**16**) shown in Figure 39 as well as the homodimeric complexes for each ligand.



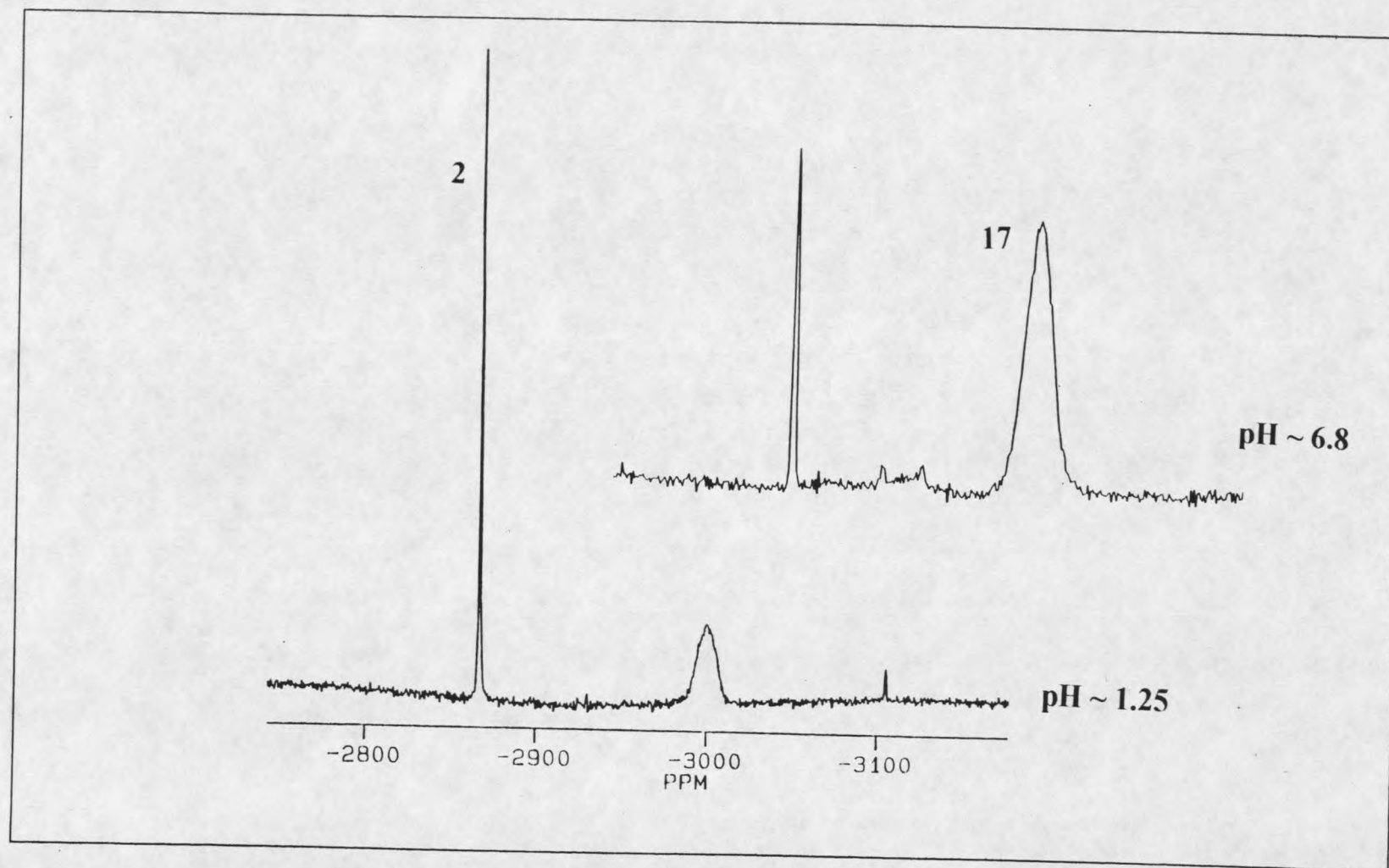
**Figure 39.** Reaction scheme for the formation of the heterodimeric bridged complex containing both sulfur and nitrogen donor atoms.

A near neutral pH was chosen for this reaction because of the known predominance of dimer species in solution for the Pt(en) system (51). The formation of heterodimers of the type shown in Figure 39 is unambiguously demonstrated by the 1:4:1 splitting pattern of Pt satellites discussed in the introduction. Figure 40 shows the  $^{195}\text{Pt}$  NMR spectrum in the region of the  $\text{Pt}(\text{DMSO})_2$  fragment. The dominant peak at -2863 ppm has previously been assigned to **2** and the smaller set of peaks centered around -2775 ppm can be assigned to the DMSO bound heterodimeric Pt center of **16** based on the presence of Pt satellites with  $^2J_{\text{Pt-Pt}}$  of 605 Hz. The downfield shift of  $\sim 90$  ppm is consistent with the substitution of an *S* donor with an *N* donor ligand, in this case the chelating ethylenediamine ligand, on the distant Pt fragment. The peaks corresponding to the heterodimeric Pt fragment coordinated by ethylenediamine as well as the ethylenediamine homodimer resonance are much further downfield around -1512

and -1788 ppm respectively. These downfield peaks are all broadened due to coupling to quadrupolar  $^{14}\text{N}$  nuclei. The Pt satellites are therefore obscured by the main resonance. It is of theoretical interest that the two resonances corresponding to the heterodimeric species are both shifted downfield of the corresponding homodimer species. This behavior is in contrast to that seen for the monodentate sulfoxide cases discussed previously in which the heterodimeric fragments lie between the corresponding homodimer resonance. It is also in contrast to the results obtained for some bidentate heterodimeric thioether complexes discussed below. Also noticeable in Figure 40 is a very small broad peak around -2995 ppm. This peak was subsequently shown to be the substitution product  $[\text{Pten}(\text{DMSO})_2]^{2+}$ . Attempts to prepare the heterodimer by direct substitution of ethylenediamine for two of the DMSO ligands in **2** were unsuccessful. When one equivalent en (based on Pt) was added to a solution of **2** at pH  $\sim 1.25$ , no sign of a peak assignable to **16** was seen. Rather, a broad peak at -3000 ppm, 33 ppm upfield of **2** appeared (Figure 41). When the pH of the solution was raised to  $\sim 6.8$ , this peak increased in intensity at the expense of **2**. The broad nature of this peak clearly indicates that Pt is coordinated directly to an  $^{14}\text{N}$  nucleus and the resonance frequency is consistent with two sulfur and two nitrogen donor ligands. This peak is therefore assigned to  $[\text{Pten}(\text{DMSO})_2]^{2+}$  (**17**).



**Figure 40.**  $^{195}\text{Pt}$  NMR spectrum for the reaction of **2** and **16** in the  $\text{Pt}(\text{DMSO})_2$  region. pH  $\sim$  1.25

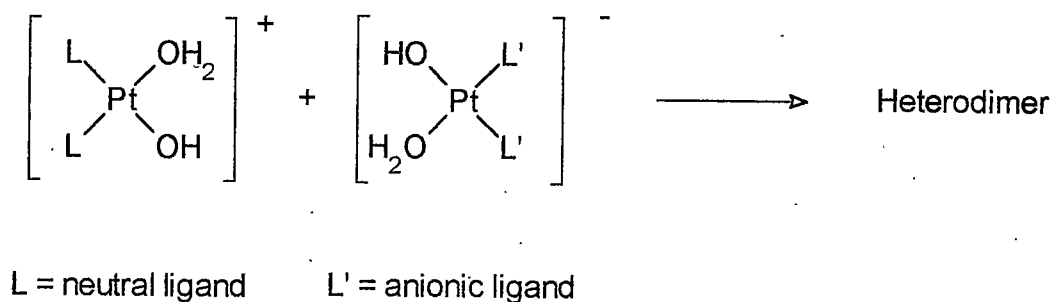


**Figure 41.**  $^{195}\text{Pt}$  NMR spectrum for the reaction of **2** and 1 eq. ethylenediamine in the  $\text{Pt}(\text{DMSO})_2$  region. After mixing, the pH was raised from ~ 1.25 to ~ 6.8.

The formation of this complex indicates that the ethylenediamine ligand is cleaving the hydroxo bridges and substituting for hydroxide or is coordinating to the small fraction of diaqua monomer complex in solution, slowly shifting the equilibrium away from the dimer.

Oxygen Donor Ligands. Reactions of the type shown in Figure 42 are important because they involve the formation of dimeric bridged complexes from one cationic and one anionic Pt(II) fragment.

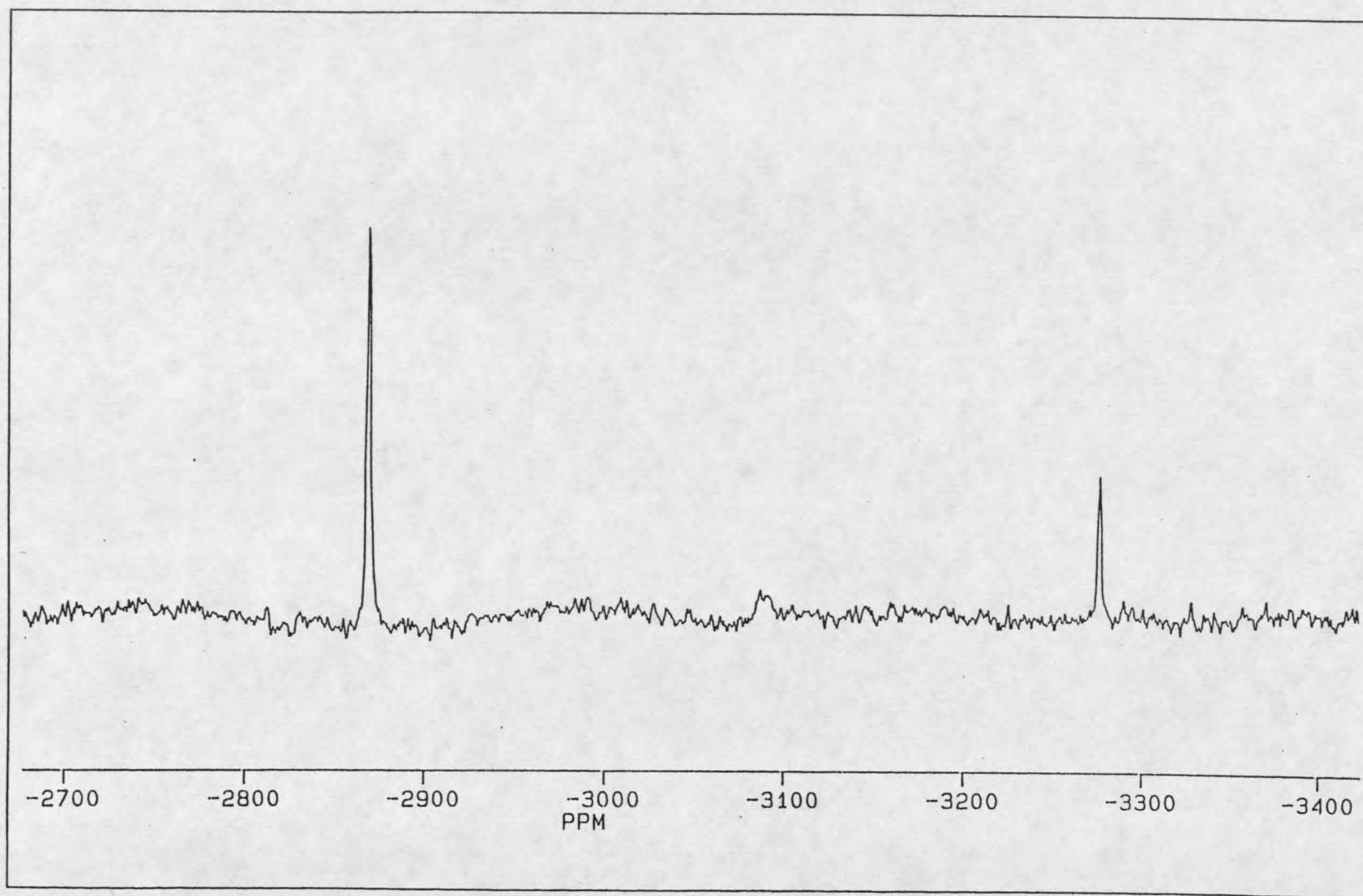
It was felt that two fragments of opposite charge such as these may show an enhanced tendency to dimerize due to the coulombic interaction between them. Among the oxygen donor ligands, oxalate was chosen because of its well known propensity for forming stacked complexes from the anionic bis-oxalato monomers (31).



**Figure 42.** Utilization of coulombic interaction to form a heterodimeric structure from one anionic and one cationic fragment.

Di- $\mu$ -hydroxobridged homodimeric Pt oxalates have not previously been reported and attempts to prepare them in this laboratory have so far been unsuccessful

$\text{Pt}(\text{ox})(\text{OH}_2)_2$  was prepared in solution by the  $\text{Ag}(\text{I})$  assisted hydrolysis of the dichloride complex.  $^{195}\text{Pt}$  NMR verified this to be the major species in solution ( $\delta \text{ Pt} = 336 \text{ ppm}$ ) with a minor contribution from  $[\text{Pt}(\text{Ox})(\text{OxH-O})\text{Cl}]^{2-}$  ( $\delta \text{ Pt} = -601 \text{ ppm}$ ) in which a second oxalate ligand is monodentate. These assignments had been previously made during an investigation into the synthesis of partially oxidized one-dimensional complexes (31). The complexes were not isolated but the solution combined with a roughly equimolar solution of **1**. The pH of the resulting solution was adjusted to  $\sim 6.3$  with 1 M NaOH during which time the color changed from clear to deep yellow. Figure 43 shows the  $^{195}\text{Pt}$  NMR spectrum of this solution in the  $\text{Pt}(\text{DMSO})_2$  region. While monitoring the resonance for **2**, a new peak appeared  $\sim 400 \text{ ppm}$  upfield at  $-3276 \text{ ppm}$ . This peak, which showed no sign of  $J_{\text{Pt-Pt}}$  coupling was tentatively assigned to the neutral complex  $\text{Pt}(\text{DMSO})_2(\text{Ox})$  (**18**) based on the proximity to the known resonance for  $\text{Pt}(\text{DMSO})(\text{OH})_2$  (**3**) and the observation that five membered chelate rings generally cause an upfield shift of  $\sim 200 \text{ ppm}$ . The weak intensity of the peak can be explained by the insoluble nature of most neutral platinum complexes in aqueous solution. Support for this assignment came from an X-ray analysis of crystals which formed in both the NMR tube and the reaction vessel within several days.



**Figure 43.**  $^{195}\text{Pt}$  NMR spectrum of the reaction of **1** with an equilibrium mixture of Pt(oxalate) species; pH = 6.3.

Interestingly, the crystals from the two different vessels showed different packing arrangements as well as two different unit cells. Figures 44 and 45 show the ORTEP plots for these two isostructural complexes.

Packing arrangements are shown in Figure 46 and 47. For **18a**, the DMSO ligands are stacked one over another along the crystallographic *a* axis and for **18b**, the DMSO ligands are turned 180 degrees to eclipse the oxalate ring. The bond distances and angles are virtually identical for the two structures (Table 11).

Although the oxalate ligand does coordinate strongly to platinum(II) despite oxygen being a hard base, no sign of the oxalate homodimer or oxalate-DMSO heterodimer was observed. It is of considerable interest that only one dimer containing an anionic ligand has been characterized (Table 10). Electron distribution and charge clearly seem to be important factors governing the formation and stability of these di-bridged complexes.

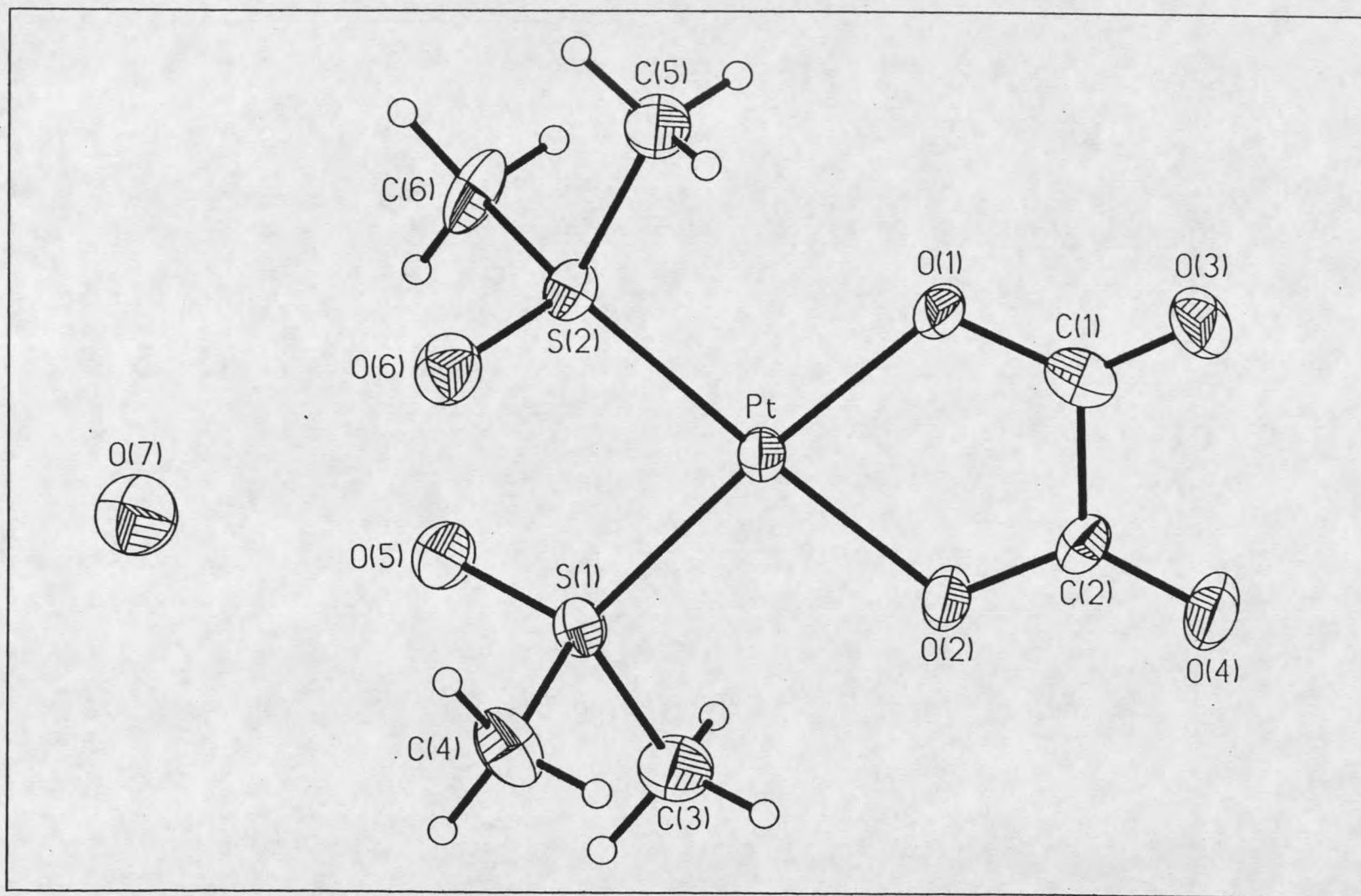


Figure 44. ORTEP plot for 18a.

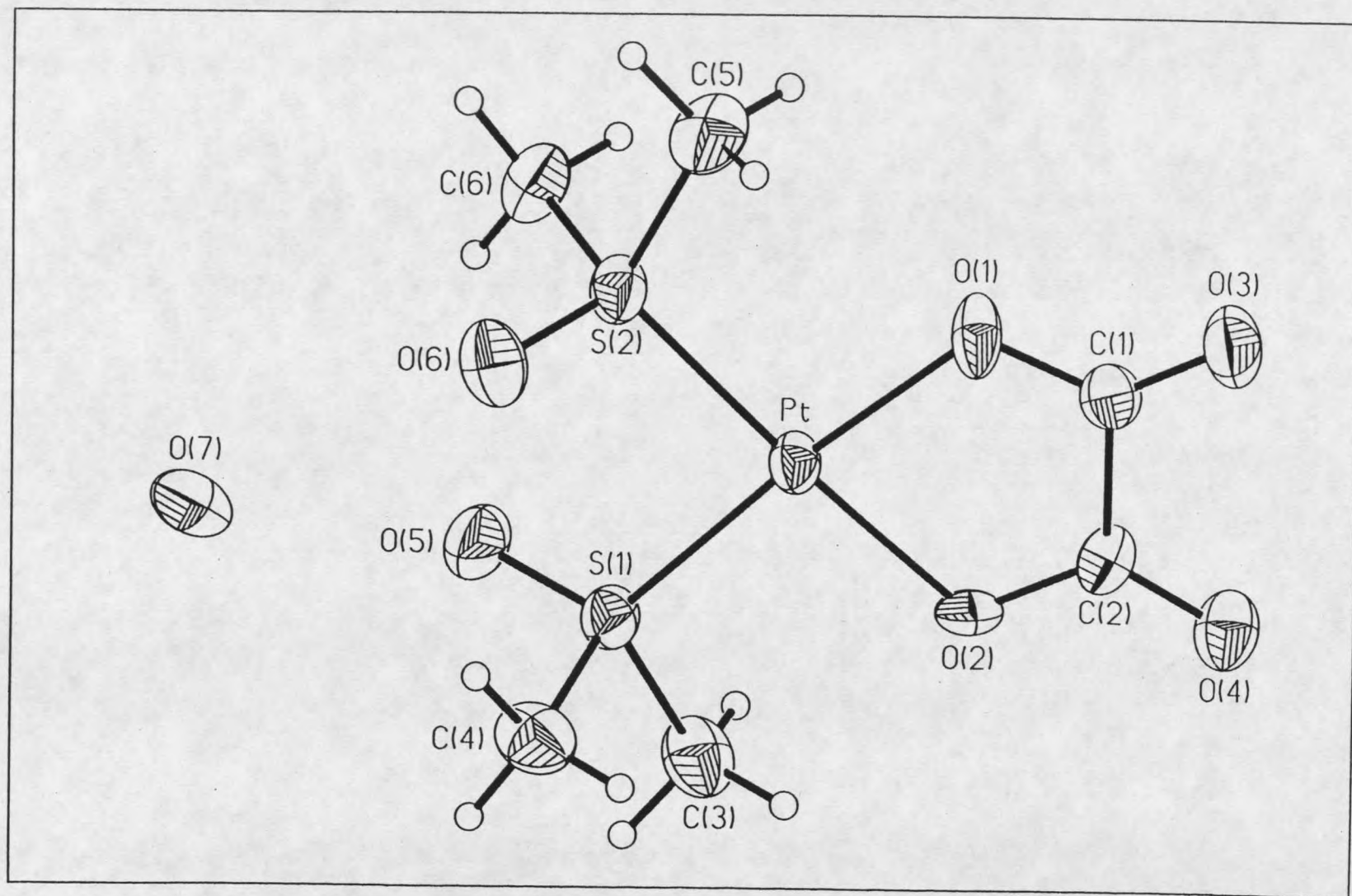


Figure 45. ORTEP plot for 18b.

**Table 11.** Crystallographic data for **18a** and **18b**.

| Parameter                               | <b>18a</b>                                             | <b>18b</b>                                             |
|-----------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| Formula                                 | $\text{C}_6\text{H}_{14}\text{O}_7\text{S}_2\text{Pt}$ | $\text{C}_6\text{H}_{14}\text{O}_7\text{S}_2\text{Pt}$ |
| Formula weight                          | 457.37                                                 | 457.37                                                 |
| Space group                             | $P2_1 / c$                                             | $P2_1 / n$                                             |
| Temperature °C                          | 27                                                     | 27                                                     |
| a (Å)                                   | 6.467(1)                                               | 8.452(2)                                               |
| b (Å)                                   | 15.945(3)                                              | 15.603(3)                                              |
| c (Å)                                   | 12.148(2)                                              | 9.106(2)                                               |
| $\alpha$ (°)                            | 90                                                     | 90                                                     |
| $\beta$ (°)                             | 100.67(3)                                              | 91.78(3)                                               |
| $\gamma$ (°)                            | 90                                                     | 90                                                     |
| Cell Volume (Å <sup>3</sup> )           | 1230.96(87)                                            | 1200.18(64)                                            |
| Z                                       | 4                                                      | 4                                                      |
| $R_w$ (F <sub>o</sub> )                 | 0.0456                                                 | 0.0337                                                 |
| R (F <sub>o</sub> )                     | 0.0496                                                 | 0.0399                                                 |
| $\lambda$ (Å)                           | 0.07107                                                | 0.07107                                                |
| $\rho$ (g cm <sup>-3</sup> ) calculated | 2.305                                                  | 2.282                                                  |
| $\mu$ (mm <sup>-1</sup> )               | 11.75                                                  | 12.05                                                  |
| Transmission factor range               | 0.365 - 0.454                                          | 0.250 - 0.306                                          |
| F (000)                                 | 864                                                    | 864                                                    |
| Unique reflections                      | 4444                                                   | 5273                                                   |
| Observed reflections                    | 1675                                                   | 2560                                                   |
| Number of parameters                    | 146                                                    | 146                                                    |
| Goodness of fit                         | 1.097                                                  | 1.158                                                  |
| Scan mode                               | $\theta / 2\theta$                                     | $\theta / 2\theta$                                     |

**Table 12.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\times 10^3$ ) for *cis*-bis(dimethylsulfoxide)oxalatoplatinum(II) hydrate (**18a**).

| Atom | x/a       | y/b      | z/c      | $U_{eq}$ |
|------|-----------|----------|----------|----------|
| Pt   | 2254(1)   | 861(1)   | 3558(1)  | 26(1)    |
| O(1) | 3178(18)  | 1226(6)  | 5168(8)  | 34(4)    |
| O(2) | 1925(17)  | -267(6)  | 4303(9)  | 31(4)    |
| C(1) | 3181(26)  | 663(10)  | 5908(13) | 31(6)    |
| C(2) | 2470(24)  | -227(10) | 5393(12) | 27(5)    |
| O(3) | 3605(20)  | 740(7)   | 6900(9)  | 44(4)    |
| O(4) | 2425(17)  | -835(7)  | 5999(9)  | 40(4)    |
| S(1) | 1160(7)   | 345(3)   | 1851(3)  | 31(1)    |
| O(5) | 2231(22)  | 637(8)   | 942(10)  | 49(5)    |
| C(3) | 1214(29)  | -761(11) | 1912(13) | 44(6)    |
| C(4) | -1518(28) | 529(11)  | 1447(15) | 45(6)    |
| S(2) | 2598(7)   | 2131(3)  | 2882(3)  | 30(1)    |
| O(6) | 685(17)   | 2439(8)  | 2139(9)  | 41(4)    |
| C(5) | 3376(32)  | 2846(10) | 3975(14) | 47(7)    |
| C(6) | 4783(29)  | 2173(11) | 2195(14) | 43(6)    |
| O(7) | -1415(18) | 2528(9)  | -114(9)  | 55(5)    |

**Table 13.** Bond lengths for *cis*-bis(dimethylsulfoxide)oxalatoplatinum(II) hydrate (**18a**).

| Bond    | Length (Å) | Bond      | Length (Å) |
|---------|------------|-----------|------------|
| Pt-O(1) | 2.022(9)   | C(2)-O(4) | 1.221(19)  |
| Pt-O(2) | 2.042(10)  | S(1)-O(5) | 1.482(14)  |
| Pt-S(1) | 2.222(4)   | S(1)-C(3) | 1.765(18)  |

**Table 13** (cont.)

|           |           |           |           |
|-----------|-----------|-----------|-----------|
| Pt-S(2)   | 2.213(4)  | S(1)-C(4) | 1.735(18) |
| O(1)-C(1) | 1.27(19)  | S(2)-O(6) | 1.474(11) |
| O(2)-C(2) | 1.307(17) | S(2)-C(5) | 1.751(17) |
| C(1)-C(2) | 1.584(21) | S(2)-C(6) | 1.77(20)  |
| C(1)-O(3) | 1.192(19) |           |           |

**Table 14.** Bond angles and standard deviations for  
*cis*-bis(dimethylsulfoxide)oxalatoplatinum(II) hydrate (**18a**).

| Atoms          | Angle (°) | Atoms          | Angle (°) |
|----------------|-----------|----------------|-----------|
| O(1)-Pt-O(2)   | 82.4(2)   | C(1)-C(2)-O(4) | 119.6(7)  |
| O(1)-Pt-S(1)   | 175.5(2)  | Pt-S(1)-O(5)   | 116.1(3)  |
| O(2)-Pt-S(1)   | 93.3(2)   | Pt-S(1)-C(3)   | 108.8(3)  |
| O(1)-Pt-S(2)   | 93.4(2)   | O(5)-S(1)-C(3) | 109.8(4)  |
| O(2)-Pt-S(2)   | 174.8(2)  | Pt-S(1)-C(4)   | 109.4(3)  |
| S(1)-Pt-S(2)   | 90.9(1)   | O(5)-S(1)-C(4) | 109.4(4)  |
| Pt-O(1)-C(1)   | 113.6(5)  | C(3)-S(1)-C(4) | 102.6(5)  |
| Pt-O(2)-C(2)   | 113.8(5)  | Pt-S(2)-O(6)   | 114.6(3)  |
| O(1)-C(1)-C(2) | 114.7(7)  | Pt-S(2)-C(5)   | 109.7(3)  |
| O(1)-C(1)-O(3) | 124.8(8)  | O(6)-S(2)-C(5) | 109.3(4)  |
| C(2)-C(1)-O(3) | 120.4(7)  | Pt-S(2)-C(6)   | 111.0(3)  |
| O(2)-C(2)-C(1) | 115.3(7)  | O(6)-S(2)-C(6) | 109.1(4)  |
| O(2)-C(2)-O(4) | 125.1(8)  | C(5)-S(2)-C(6) | 102.5(5)  |

**Table 15.** Anisotropic displacement coefficients ( $\times 10^3$ ) for **18a**.

| Atom | $U_{xx}$ | $U_{yy}$ | $U_{zz}$ | $U_{xy}$ | $U_{xz}$ | $U_{yz}$ |
|------|----------|----------|----------|----------|----------|----------|
| Pt   | 32(1)    | 26(1)    | 19(1)    | 1(1)     | 5(1)     | 0(1)     |
| O(1) | 61(8)    | 21(5)    | 20(5)    | 14(6)    | 6(5)     | 2(4)     |
| O(2) | 33(6)    | 23(6)    | 35(6)    | -11(5)   | 2(5)     | -4(5)    |
| C(1) | 34(10)   | 33(10)   | 26(8)    | -2(7)    | 8(7)     | -2(6)    |
| C(2) | 31(9)    | 26(9)    | 28(7)    | 7(7)     | 15(7)    | 3(7)     |
| O(3) | 61(8)    | 41(8)    | 26(5)    | 0(7)     | 3(6)     | 2(5)     |
| O(4) | 49(7)    | 32(6)    | 39(5)    | 10(7)    | 8(5)     | 6(6)     |
| S(1) | 41(3)    | 31(2)    | 24(2)    | -3(2)    | 8(2)     | -2(2)    |
| O(5) | 69(9)    | 48(8)    | 31(6)    | -17(7)   | 15(6)    | 1(5)     |
| C(3) | 53(11)   | 45(11)   | 33(8)    | 5(11)    | 8(8)     | -8(9)    |
| C(4) | 48(12)   | 32(9)    | 50(11)   | 3(9)     | -1(9)    | -6(9)    |
| S(2) | 37(2)    | 27(2)    | 27(2)    | 3(2)     | 5(2)     | 3(2)     |
| O(6) | 32(7)    | 47(7)    | 41(6)    | 18(6)    | 0(5)     | 7(6)     |
| C(5) | 78(14)   | 19(8)    | 46(10)   | 1(9)     | 17(10)   | -6(8)    |
| C(6) | 47(11)   | 42(11)   | 43(9)    | -1(9)    | 15(9)    | 11(9)    |
| O(7) | 49(8)    | 55(8)    | 51(7)    | -15(7)   | -13(6)   | -1(7)    |

**Table 16.** H-atom coordinates ( $\times 10^4$ ) and isotropic displacement coefficients ( $\times 10^2$ ) for **18a**.

| Atom  | x/a  | y/b  | z/c  | $U_{eq}$ |
|-------|------|------|------|----------|
| H(3A) | 520  | -949 | 2501 | 66(18)   |
| H(3B) | 2648 | -951 | 2058 | 66(18)   |
| H(3C) | 504  | -986 | 1209 | 66(18)   |

**Table 16 (cont.)**

|       |       |      |      |        |
|-------|-------|------|------|--------|
| H(4A) | -2236 | 343  | 2027 | 66(18) |
| H(4B) | -2043 | 227  | 769  | 66(18) |
| H(4C) | -1757 | 1118 | 1321 | 66(18) |
| H(5A) | 4622  | 2643 | 4456 | 66(18) |
| H(5B) | 2269  | 2907 | 4397 | 66(18) |
| H(5C) | 3664  | 3380 | 3669 | 66(18) |
| H(6A) | 6013  | 1970 | 2690 | 66(18) |
| H(6B) | 5009  | 2742 | 1987 | 66(18) |
| H(6C) | 4511  | 1829 | 1535 | 66(18) |

**Table 17.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\times 10^3$ ) for **18b**.

| Atom | x/a      | y/b      | z/c      | $U_{eq}$ |
|------|----------|----------|----------|----------|
| Pt   | 8088(1)  | 9173(1)  | 5549(1)  | 20(1)    |
| O(1) | 7218(7)  | 8811(3)  | 3552(6)  | 29(2)    |
| O(2) | 7064(7)  | 10300(3) | 4967(6)  | 28(2)    |
| C(1) | 6343(10) | 9399(5)  | 2893(9)  | 26(2)    |
| C(2) | 6288(9)  | 10275(5) | 3716(9)  | 24(2)    |
| O(3) | 5544(8)  | 9284(4)  | 1780(6)  | 38(2)    |
| O(4) | 5583(7)  | 10880(4) | 3146(6)  | 38(2)    |
| S(1) | 8933(3)  | 9665(1)  | 7735(2)  | 25(1)    |
| O(5) | 10540(7) | 9398(4)  | 8227(7)  | 37(2)    |
| C(3) | 8807(12) | 10786(6) | 7725(10) | 39(3)    |
| C(4) | 7577(11) | 9379(6)  | 9067(9)  | 40(3)    |
| S(2) | 9033(2)  | 7874(1)  | 6084(2)  | 24(1)    |

Table 17 (cont.)

|      |           |          |          |       |
|------|-----------|----------|----------|-------|
| O(6) | 8517(7)   | 7522(4)  | 7493(6)  | 35(2) |
| C(5) | 8507(11)  | 7150(6)  | 4647(9)  | 36(3) |
| C(6) | 11124(10) | 7864(6)  | 6068(11) | 38(3) |
| O(7) | 10183(8)  | 12500(5) | 9520(7)  | 47(2) |

**Table 18.** Bond lengths for *cis*-bis(dimethylsulfoxide)oxalatoplatinum(II) hydrate (**18b**).

| Bond      | Length (Å) | Bond      | Length (Å) |
|-----------|------------|-----------|------------|
| Pt-O(1)   | 2.020(5)   | C(2)-O(4) | 1.223(10)  |
| Pt-O(2)   | 2.023(6)   | S(1)-O(5) | 1.477(6)   |
| Pt-S(1)   | 2.230(2)   | S(1)-C(3) | 1.751(9)   |
| Pt-S(2)   | 2.228(2)   | S(1)-C(4) | 1.753(9)   |
| O(1)-C(1) | 1.312(10)  | S(2)-O(6) | 1.474(6)   |
| O(2)-C(2) | 1.297(10)  | S(2)-C(5) | 1.775(9)   |
| C(1)-C(2) | 1.560(12)  | S(2)-C(6) | 1.768(8)   |
| C(1)-O(3) | 1.214(10)  |           |            |

**Table 19.** Bond angles ( $^{\circ}$ ) and standard deviations for *cis*-bis(dimethylsulfoxide)oxalatoplatinum(II) hydrate (**18b**).

| Bonds        | Angle    | Bonds          | Angle    |
|--------------|----------|----------------|----------|
| O(1)-Pt-O(2) | 82.4(2)  | C(1)-C(2)-O(4) | 119.6(7) |
| O(1)-Pt-S(1) | 175.5(2) | Pt-S(1)-O(5)   | 116.1(3) |
| O(2)-Pt-S(1) | 93.3(2)  | Pt-S(1)-C(3)   | 108.8(3) |
| O(1)-Pt-S(2) | 93.4(2)  | O(5)-S(1)-C(3) | 109.8(4) |

**Table 19** (cont.)

|                |          |                |          |
|----------------|----------|----------------|----------|
| O(2)-Pt-S(2)   | 174.8(2) | Pt-S(1)-C(4)   | 109.4(3) |
| S(1)-Pt-S(2)   | 90.9(1)  | O(5)-S(1)-C(4) | 109.4(4) |
| Pt-O(1)-C(1)   | 113.6(5) | C(3)-S(1)-C(4) | 102.6(5) |
| Pt-O(2)-C(2)   | 113.8(5) | Pt-S(2)-O(6)   | 114.6(3) |
| O(1)-C(1)-C(2) | 114.7(7) | Pt-S(2)-C(5)   | 109.7(3) |
| O(1)-C(1)-O(3) | 124.8(8) | O(6)-S(2)-C(5) | 109.3(4) |
| C(2)-C(1)-O(3) | 120.4(7) | Pt-S(2)-C(6)   | 111.0(3) |
| O(2)-C(2)-C(1) | 115.3(7) | O(6)-S(2)-C(6) | 109.1(4) |
| O(2)-C(2)-O(4) | 125.1(8) | C(5)-S(2)-C(6) | 102.5(5) |

**Table 20.** H-atom coordinates ( $\times 10^4$ ) and isotropic displacement coefficients for **18b**.

| Atom  | x/a   | y/b   | z/c  | $U_{eq}$ |
|-------|-------|-------|------|----------|
| H(3A) | 7761  | 10956 | 7404 | 77(11)   |
| H(3B) | 9565  | 11015 | 7067 | 77(11)   |
| H(3C) | 9026  | 11000 | 8698 | 77(11)   |
| H(4A) | 6532  | 9552  | 8747 | 77(11)   |
| H(4B) | 7857  | 9658  | 9978 | 77(11)   |
| H(4C) | 7600  | 8769  | 9205 | 77(11)   |
| H(5A) | 8842  | 7378  | 3728 | 77(11)   |
| H(5B) | 7379  | 7072  | 4608 | 77(11)   |
| H(5C) | 9014  | 6608  | 4828 | 77(11)   |
| H(6A) | 11467 | 8092  | 5152 | 77(11)   |
| H(6B) | 11498 | 7286  | 6179 | 77(11)   |
| H(6C) | 11541 | 8208  | 6863 | 77(11)   |

**Table 21:** Anisotropic displacement coefficients ( $\times 10^3$ ) for **18b**.

| Atom | $U_{xx}$ | $U_{yy}$ | $U_{zz}$ | $U_{xy}$ | $U_{xz}$ | $U_{yz}$ |
|------|----------|----------|----------|----------|----------|----------|
| Pt   | 22(1)    | 20(1)    | 19(1)    | 2(1)     | -3(1)    | 1(1)     |
| O(1) | 39(4)    | 21(3)    | 27(3)    | 12(3)    | -10(3)   | -6(2)    |
| O(2) | 34(3)    | 22(3)    | 28(3)    | 5(3)     | -12(3)   | 0(2)     |
| C(1) | 22(4)    | 32(5)    | 26(4)    | -10(4)   | 12(3)    | -2(3)    |
| C(2) | 19(4)    | 23(4)    | 30(4)    | 4(3)     | 1(3)     | 4(3)     |
| O(3) | 52(4)    | 34(4)    | 26(3)    | 0(3)     | -12(3)   | -8(3)    |
| O(4) | 44(4)    | 27(3)    | 41(3)    | 8(4)     | -15(3)   | 4(3)     |
| S(1) | 24(1)    | 28(1)    | 21(1)    | 1(1)     | -5(1)    | -2(1)    |
| O(5) | 25(3)    | 50(4)    | 36(3)    | 12(3)    | -5(3)    | -4(3)    |
| C(3) | 46(6)    | 32(5)    | 39(5)    | 1(5)     | -3(4)    | -9(5)    |
| C(4) | 44(5)    | 51(7)    | 25(4)    | -7(5)    | 3(4)     | 4(4)     |
| S(2) | 24(1)    | 21(1)    | 27(1)    | 1(1)     | -1(1)    | 3(1)     |
| O(6) | 39(4)    | 29(3)    | 36(3)    | 0(3)     | 0(3)     | 4(3)     |
| C(5) | 50(6)    | 24(4)    | 35(5)    | 4(4)     | -9(4)    | -8(4)    |
| C(6) | 22(5)    | 34(5)    | 58(6)    | 7(4)     | -11(4)   | 9(5)     |
| O(7) | 50(4)    | 43(4)    | 49(4)    | -2(4)    | 4(3)     | 1(4)     |

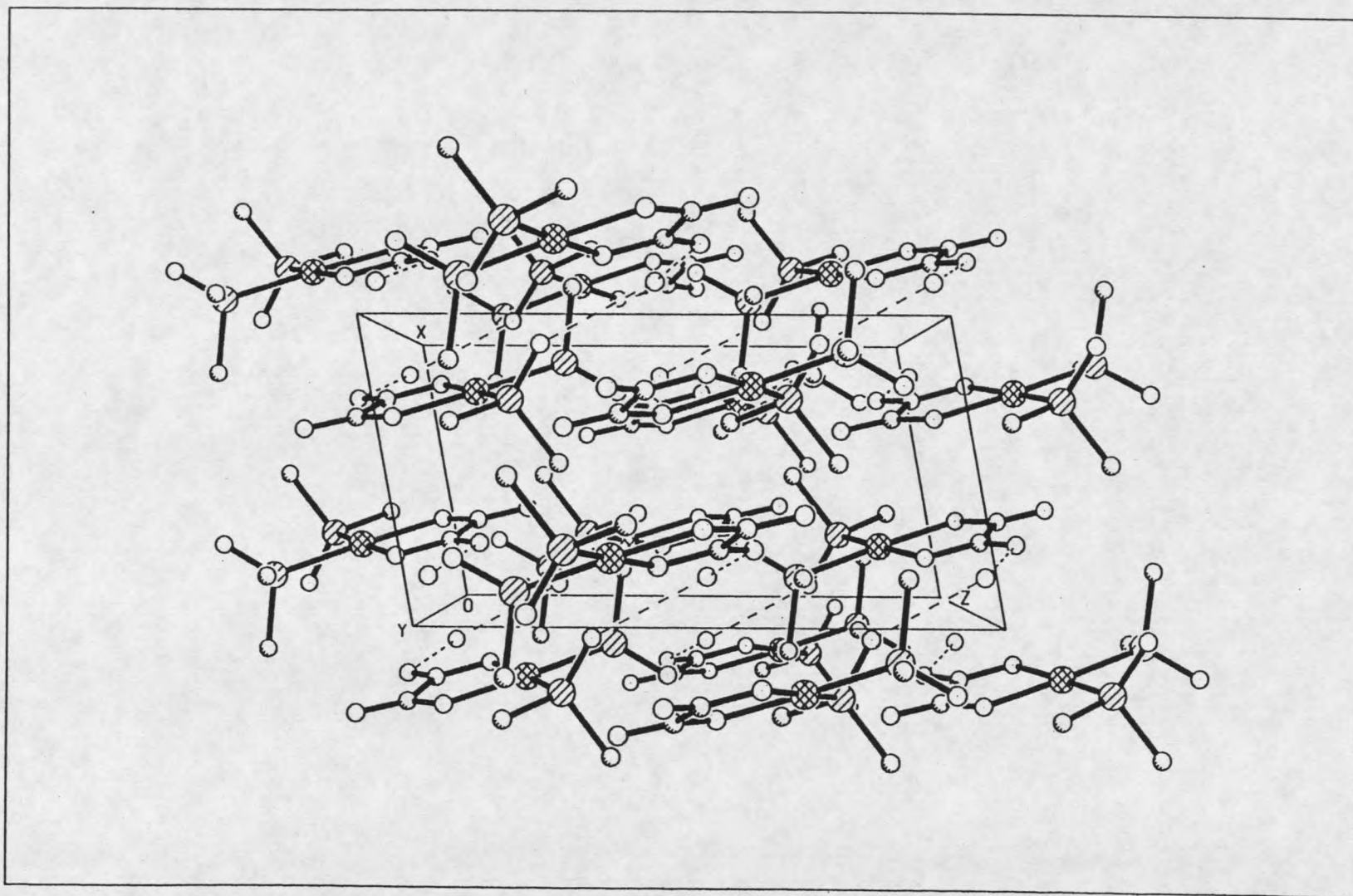
Table 22 summarizes the  $^{195}\text{Pt}$  NMR data for the oxalate and ethylenediamine complexes employed in this study.

**Table 22.**  $^{195}\text{Pt}$  NMR data for oxalate and ethylenediamine complexes.

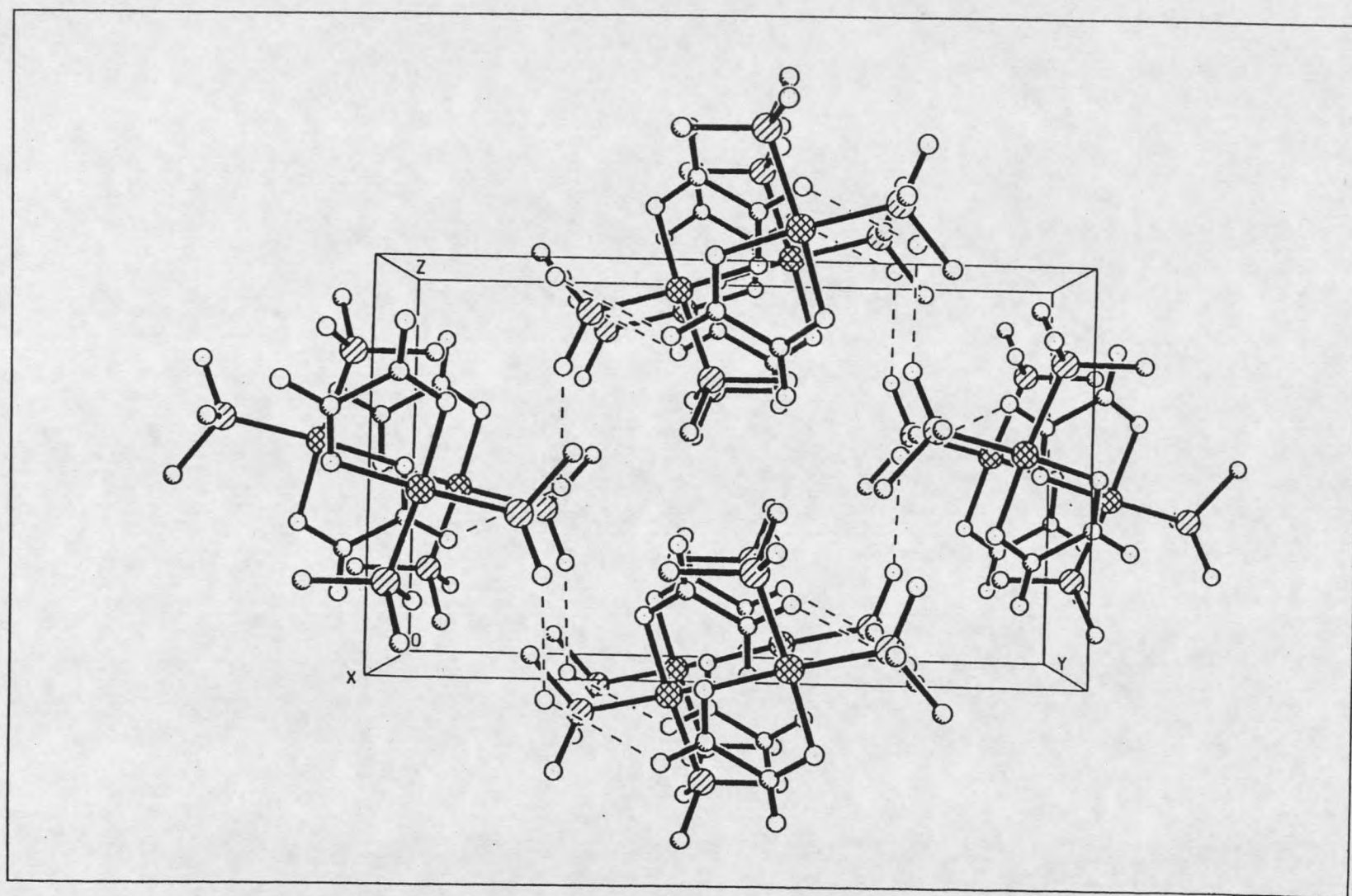
| #  | Complex                                                                | $\delta^{195}\text{Pt}$                  | Ref.      |
|----|------------------------------------------------------------------------|------------------------------------------|-----------|
| 15 | $[\text{Pt}(\text{en})(\text{OH}_2)_2]^{2+}$                           |                                          | This work |
| 16 | $[(\text{en})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{DMSO})_2]^{2+}$ | -2775 <sup>a</sup><br>-1775 <sup>b</sup> | This work |
| 17 | $[\text{Pt}(\text{en})(\text{DMSO})_2]^{2+}$                           | -3000                                    | This work |
| 18 | $\text{Pt}(\text{Ox})(\text{DMSO})_2$                                  | -3276                                    | This work |
| 19 | $[\text{Pt}(\text{Ox})\text{Cl}_2]^{2-}$                               | -1005                                    | 32        |
| 20 | $[\text{Pt}(\text{Ox})(\text{OxH-O})\text{Cl}]^{2-}$                   | -620                                     | 32        |
| 21 | $\text{Pt}(\text{Ox})(\text{OH}_2)_2$                                  | -338                                     | 32        |

a)  $\text{Pt}(\text{DMSO})_2$  fragment; main resonance flanked by satellites.

b)  $\text{Pt}(\text{en})$  fragment; very broad resonance obscuring satellites.



**Figure 46.** Packing diagram for 18a.



**Figure 47.** Packing diagram for 18b.

Monomeric Pt(II) and Pd(II) Complexes  
Containing Bidentate Sulfoxide Ligands

When it was discovered that DMSO was being released in dilute solutions of the equilibrium mixtures of the monomer and dimer, a bidentate sulfoxide ligand was sought which would be expected to show similar behavior similar chemical behavior to the DMSO system yet be more thermodynamically stable due to the chelate effect. The logical choice appeared to be the 1,2-bis-methylsulfinyl ligand described earlier.

The preparation of dichloro- $\alpha$ -1,2-bis(methylsulfinyl)ethaneplatinum(II) (**22**) has been described in the Experimental Section. Maddan and Hull (76) have also prepared this complex but characterized it only by elemental analysis and IR spectroscopy. We have now verified the chelating nature of the MSE ligand in this complex by  $^{13}\text{C}$  NMR spectroscopy. Figure 48 shows the  $^{13}\text{C}$  NMR spectrum of **22**. The characteristic 1:4:1 splitting pattern can be seen for both the methyl and methylene resonances at 54 and 42 ppm respectively. Both of these resonances are shifted several ppm upfield relative to the free ligand. The presence of only two  $^{13}\text{C}$  peaks is definitive proof of a chelating mode for the ligand. Monodentate coordination to Pt would result in four magnetically non-equivalent carbon atoms and four distinct  $^{13}\text{C}$  resonances.

The  $^{13}\text{C}$  NMR spectrum clearly demonstrates the bidentate nature of the ligand as well as providing strong supporting evidence for being exclusively sulfur bonded in aqueous solution. This sulfur coordination is maintained in the solid state as

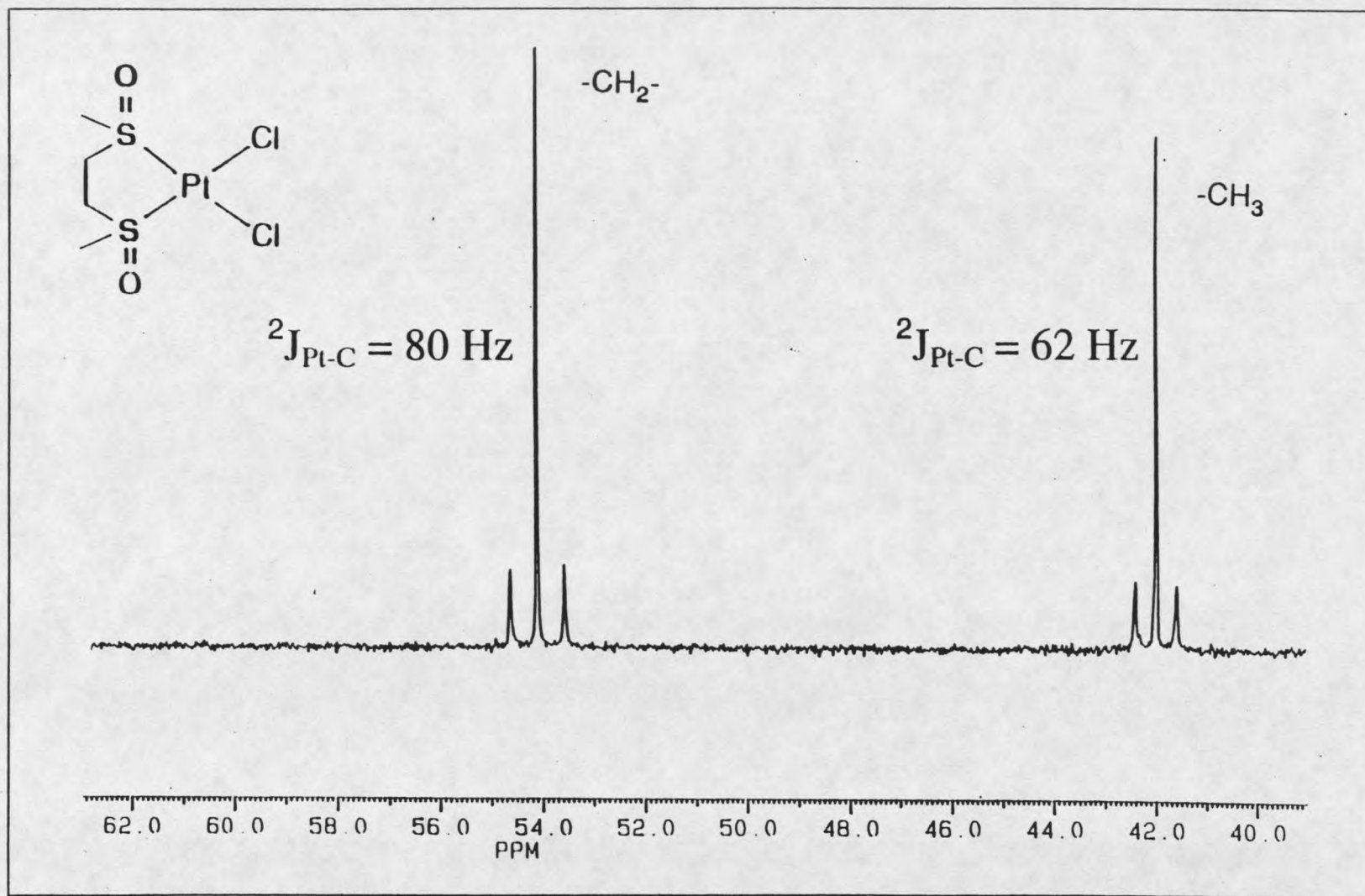


Figure 48.  $^{13}\text{C}$  NMR spectrum of  $\text{PtCl}_2(\text{meso-MSE})$  (22) in DMF.

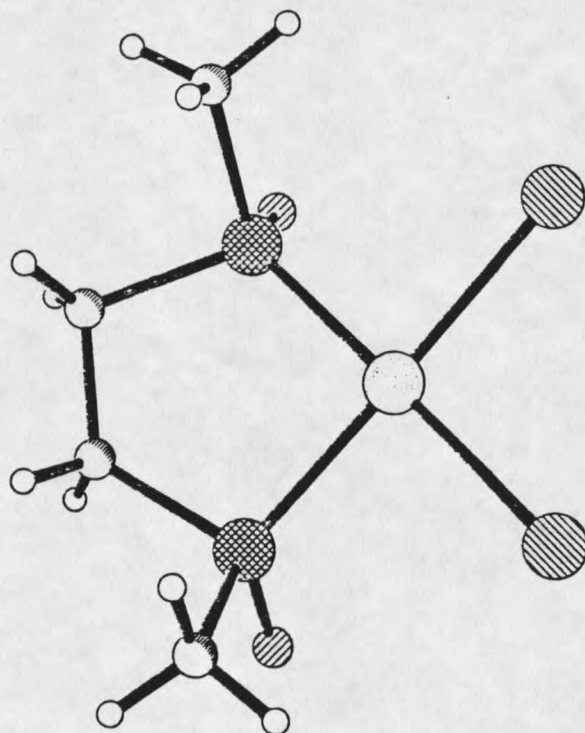
demonstrated by IR and X-ray analysis. Particularly interesting is the significant variation in coupling constant between the methyl and methylene carbons. This difference may be rationalized in several different ways:

1) Coupling constants between adjacent nuclei may be either positive or negative. By definition, a positive sign implies that the coupling interaction stabilizes anti-parallel nuclear spins and a negative sign implies the stabilization of parallel spins (107). Although relative signs of coupling constants can be determined by double resonance techniques or by spectral analysis in favorable cases, absolute signs are more difficult to obtain experimentally. Due to the additive nature of coupling constants, it is generally observed that for a given pair of nuclei,  $^1J \gg ^3J > ^2J$  (108). Inspection of the  $\text{PtCl}_2(\text{meso-MSE})$  complex shown in Figure 49 shows only a single two bond coupling pathway between Pt and the methyl carbons. For the methylene carbons however, there are two pathways available for coupling to Pt;  $^2J_{\text{C-Pt}}$  and a  $^3J_{\text{C-Pt}}$ . Depending on the relative magnitude and sign of these coupling constants, the sum of  $^2J_{\text{C-Pt}}$  and  $^3J_{\text{C-Pt}}$  may account for the larger value for the methylene carbons.

2) Inspection of the crystal structure of the free *meso*-MSE ligand reveals an unusually short bond distance between the methylene carbons (80). The authors explained this observation as being caused by a change in the hybridization of the sulfur atom to accommodate the presence of an electronegative oxygen atom. This general phenomenon has been rationalized by an empirical set of rules proposed by Bent (109) which state that: "More electronegative substituents prefer hybrid orbitals having less s

character and more electronegative substituents prefer hybrid orbitals having more *s* character". Molecular orbital calculations for other molecules have substantiated these observations (110).

It is well known that *J* coupled systems transmit the coupling interaction through the *s* electrons due to the non-zero probability of finding these electrons at the nucleus. It is therefore likely that this rehybridization is responsible for the larger coupling constant seen in the methylene region.



**Figure 49.** Ball and stick model of  $\text{PtCl}_2(\text{meso-MSE})$  (**22**).

Unfortunately, the crystal was found to be highly disordered, precluding the refinement of accurate bond distances to determine whether the short C-C bond distance persists

upon coordination to Pt. Even for the refined structures shown below containing the chelating MSE ligand, the presence of a heavy atom in the molecule normally does not allow for a precise comparison of ligand bond distances and angles. Similar bis-sulfoxide and sulfone molecules with a variety of terminal R groups also show the same general shortening of this bond (111, 112). The dibromo and di-iodo derivatives of  $\text{Pt}(\text{meso-MSE})\text{X}_2$  as well as some mixed halide complexes and a were also prepared by adding an excess of KBr or KI to the initial reaction mixture. Table 23 summarizes the  $^{195}\text{Pt}$  NMR and IR data for these complexes.

**Table 23.** NMR and IR data for monomeric  $\text{M}(\text{meso-MSE})$  halide complexes ( $\text{M}=\text{Pt}$  or  $\text{Pd}$ ).

| #  | Complex                                 | $\delta^{195}\text{Pt}$ (ppm) | $\nu \text{S}=\text{O}$ ( $\text{cm}^{-1}$ ) |
|----|-----------------------------------------|-------------------------------|----------------------------------------------|
| 22 | $\text{Pt}(\text{meso-MSE})\text{Cl}_2$ | -3890                         | 1132, 1155                                   |
| 23 | $\text{Pt}(\text{meso-MSE})\text{ClBr}$ | -4030                         | a                                            |
| 24 | $\text{Pt}(\text{meso-MSE})\text{Br}_2$ | -4187                         | 1130, 1153                                   |
| 25 | $\text{Pt}(\text{meso-MSE})\text{I}_2$  | -4844                         | 1126, 1150                                   |
| 26 | $\text{Pd}(\text{meso-MSE})\text{Cl}_2$ | -----                         | 1149, 1127                                   |

a) Mixed halide complexes were not isolated.

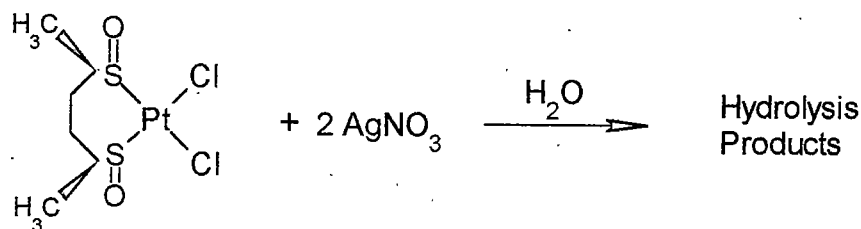
#### Hydrolysis Reactions of $\text{Pt}(\text{meso-MSE})\text{Cl}_2$ (22)

Although the reaction of meso MSE with  $\text{K}_2\text{PtCl}_4$  proceeds smoothly to form the desired *cis*-dichloro complex (22), subsequent attempts to form the diaqua

monomer or dihydroxo bridged dimer revealed a major difference between the chemistry of MSE as compared with DMSO. In particular, the molar solubility of *meso*-Pt(MSE)Cl<sub>2</sub> is considerably less than that of Pt(DMSO)<sub>2</sub>Cl<sub>2</sub> in H<sub>2</sub>O at room temperature, making it much more difficult to carry out the hydrolysis reaction.

Several methods were employed in an attempt to form the dihydroxo bridged MSE dimer. These are described below.

Ag(I) Assisted Hydrolysis of *meso*-PtCl<sub>2</sub>MSE (22).



**Figure 50.** Reaction scheme for the silver assisted hydrolysis of **22**.

Even though the dichloro complex was fairly insoluble, it was felt that dissolution would occur as the hydrolysis reaction proceeded due to the formation of a cationic complex. Initial results using this method however revealed very little AgCl being formed even after prolonged stirring of the reaction mixture. Because both reactants and products, including AgCl, are white in color, and because the hydrolysis product tended to form an insoluble precipitate even at low to moderate concentrations, it was very difficult to determine the extent of reaction by visual

inspection. After filtering off the solid material, the  $^{195}\text{Pt}$  NMR spectrum showed a weak group of peaks around -3520 ppm (Figure 51). The number of scans required to give the observed signal-to-noise indicated a very low concentration of Pt in solution. The chemical shift of these peaks is consistent with a Pt atom coordinated by two sulfur and two oxygen ligands, although the number and distribution of peaks suggests species other than or in addition to the simple diaqua or hydroxo bridged complexes seen in the analogous monodentate sulfoxide cases. Within forty-eight hours, the solution slowly deposited a noncrystalline white precipitate on the sides of the NMR tube and reaction vessel. This precipitate was insoluble in virtually all of the common organic and inorganic solvents, suggesting a polymeric structure.

Although heating the solution to  $\sim 60^\circ\text{C}$  during the initial hydrolysis reaction did increase the solubility of the dichloro species, it also appeared to increase the rate at which the solution became darkly colored, presumably due to degradation of the complex. NMR spectra of these solutions were, in general, not reproducible. The  $^{195}\text{Pt}$  NMR spectrum of a solution from one of the attempts to use this method did however show an extremely interesting result (Figure 52). A detailed analysis of this spectrum reveals two sets of coupled peaks with coupling constants of 1926 Hz and 1967 Hz. It is normally considered a good sign of direct Pt-Pt bonding when coupling constants over two kilohertz are seen, although there are several notable exceptions (37). In the absence of other evidence and with the irreproducibility of these results, this spectrum has, so far, not been fully interpreted.

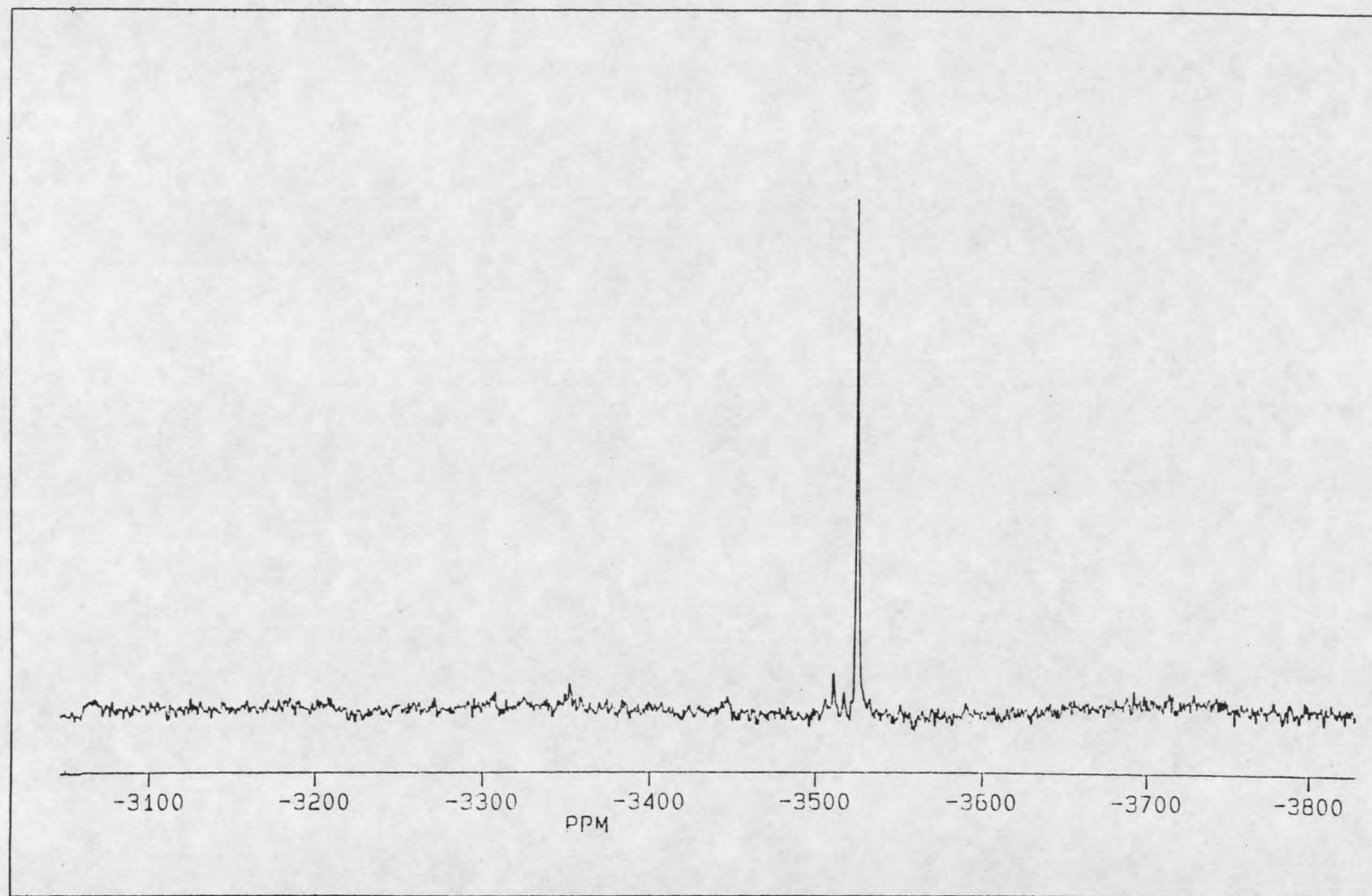
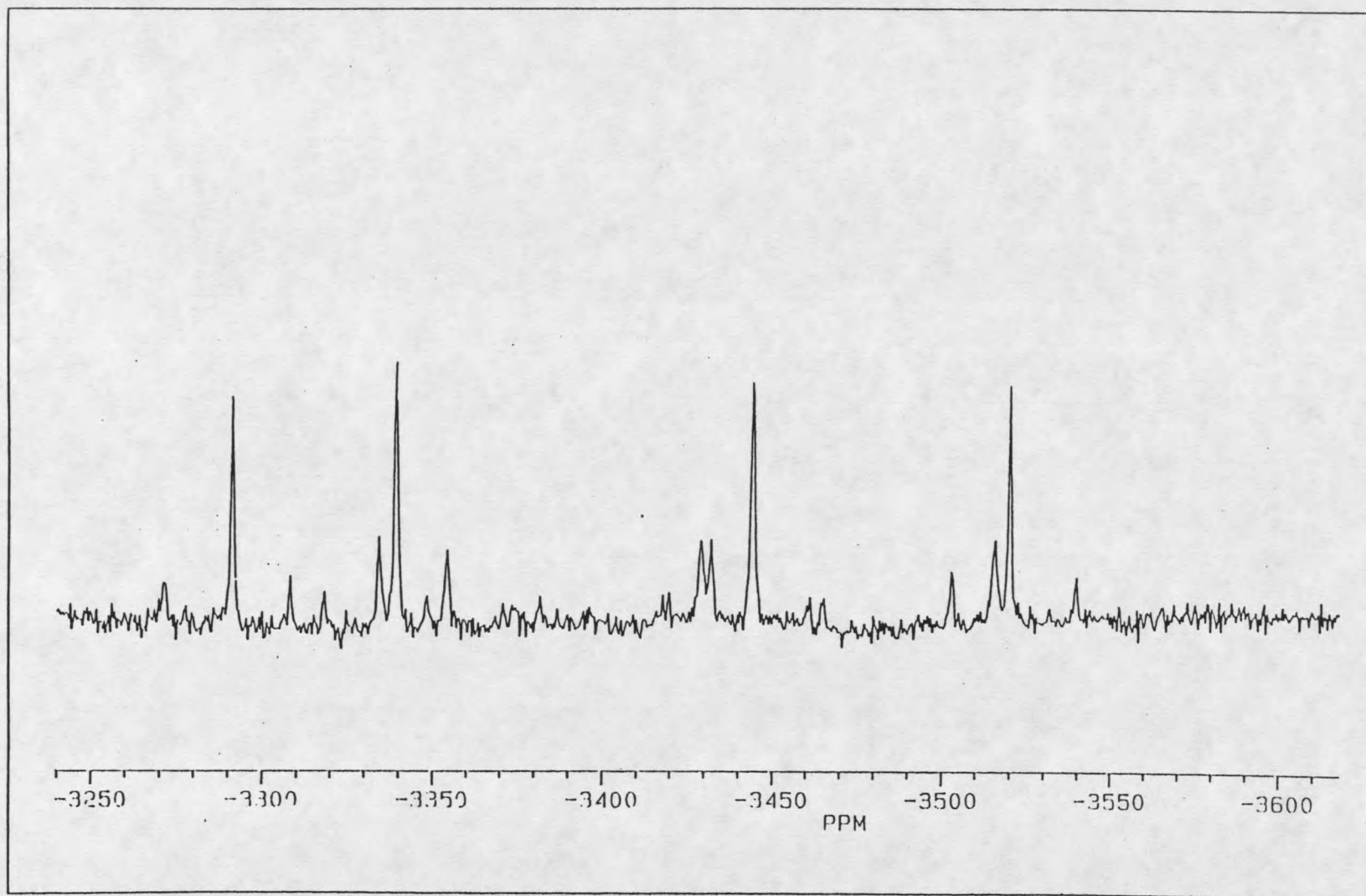


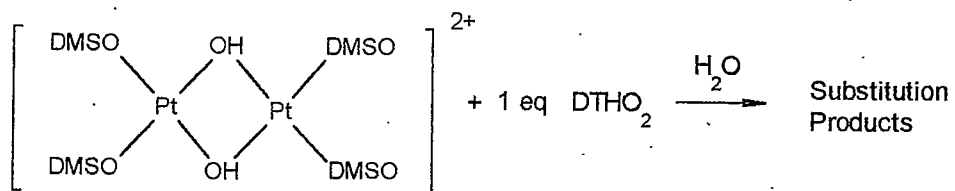
Figure 51.  $^{195}\text{Pt}$  NMR spectrum for the reaction of  $\text{PtCl}_2(\text{meso-MSE})$  (**22**) with  $\text{AgNO}_3$ .



**Figure 52.**  $^{195}\text{Pt}$  NMR spectrum of the reaction of **22** and  $\text{AgCF}_3\text{SO}_3$  at  $60^\circ\text{C}$ .

As with all other hydrolyzed solutions containing this ligand, a dark brown color eventually developed and no crystalline products were formed.

Replacement of DMSO by MSE in the dihydroxo bridged homodimer (2)

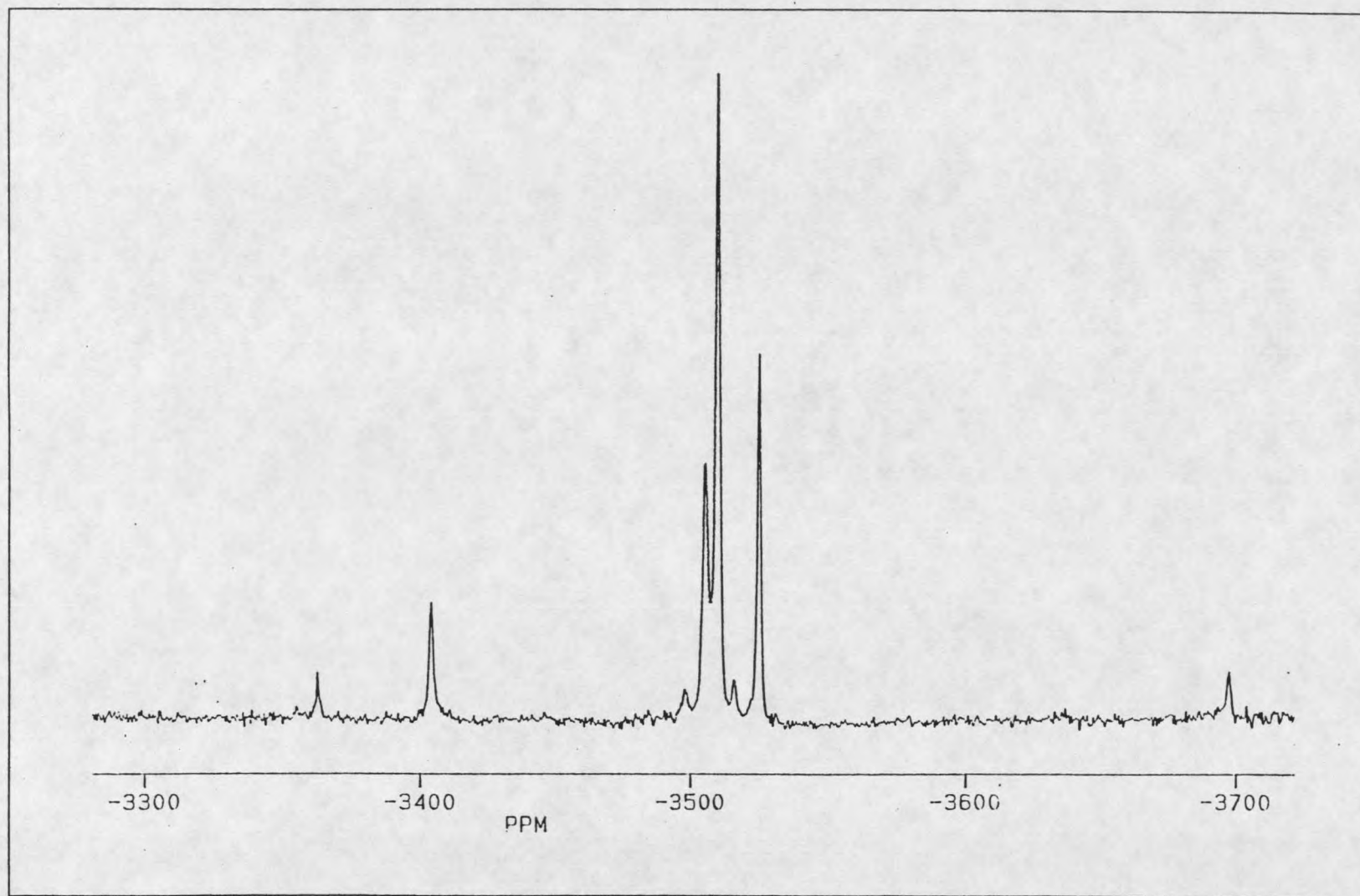


Because the  $\text{PtCl}_2\text{MSE}$  complex is so insoluble in water, it was felt that a more feasible route to the synthesis of the  $\text{PtMSE}$  bridged species would be to react the DMSO homodimer directly with the MSE ligand and rely on the increased thermodynamic stability conferred by the chelate effect to bring about ligand exchange as shown above. Both the dimer and free ligand are extremely soluble in water so getting the reactants into solution was not a problem with this method.

By adding only one equivalent of MSE, a mixed ligand dimer is expected to form as in the DMSO case, resulting in a heterodimeric structure with magnetically non-equivalent Pt atoms. Formation of this species would be revealed by the presence of the characteristic coupling pattern discussed above. The decrease in intensity of the

peak due to **2** and the concomitant appearance of a group of peaks around -3025 ppm, clearly indicates that the MSE ligand is reacting with the complex, but no sign of a resonance corresponding to the mixed ligand dimer is observed. Figure 53 shows the  $^{195}\text{Pt}$  NMR spectrum of the reaction of *meso*-MSE with **2**. Comparing figures 51 and 53, it can be seen that the product is essentially the same for both methods. A white precipitate followed by darkening of the solution is eventually observed in both cases.

As seen in the figure, a set of closely spaced peaks within 20 ppm of each other dominates the spectrum. Considering the previously described sensitivity of the  $^{195}\text{Pt}$  nucleus to its environment, this result suggests that the complex(es) responsible for these peaks are very similar, certainly containing the same primary coordination sphere of ligands. Confirmation of this similarity comes from the  $^{13}\text{C}$  NMR spectrum which shows only two peaks with broadened, yet clearly discernible  $^{195}\text{Pt}$  satellites. Also seen is a large peak due to free DMSO which had been replaced by MSE during the reaction. The other two peaks in the spectrum represent the  $-\text{CH}_3$  (41.6 ppm) and the  $-\text{CH}_2-$  (49.7 ppm) groups of excess MSE. What makes this spectrum so striking in comparison to that of  $^{195}\text{Pt}$  is that only a single Pt complex with chelating MSE ligands is revealed. As suggested above, the complex must be composed of fragments with only very slight differences in conformation. In order to confirm that a hetero-dimeric structure was not being formed, an experiment was run adding fractional equivalents of MSE to a monodentate sulfoxide dimer.



**Figure 53.**  $^{195}\text{Pt}$  NMR spectrum for the reaction of **2** with 1 equivalent of *meso*-MSE.

A series of  $^{195}\text{Pt}$  spectra were also taken following the addition of 0.25, 0.50, 0.75, and 1.00 equivalents of the ligand. In this case, the region around the  $[\text{Pt}(\text{DMSO})_2(\text{OH})_2]_2^{2+}$  peak at -2870 ppm was monitored for the appearance of the anticipated heterodimeric complex. No such peak was observed in any of the spectra.

Reaction of  $[\text{Pt}(\text{OH}_2)_4]^{2+}$  with one equivalent of *meso*-MSE.



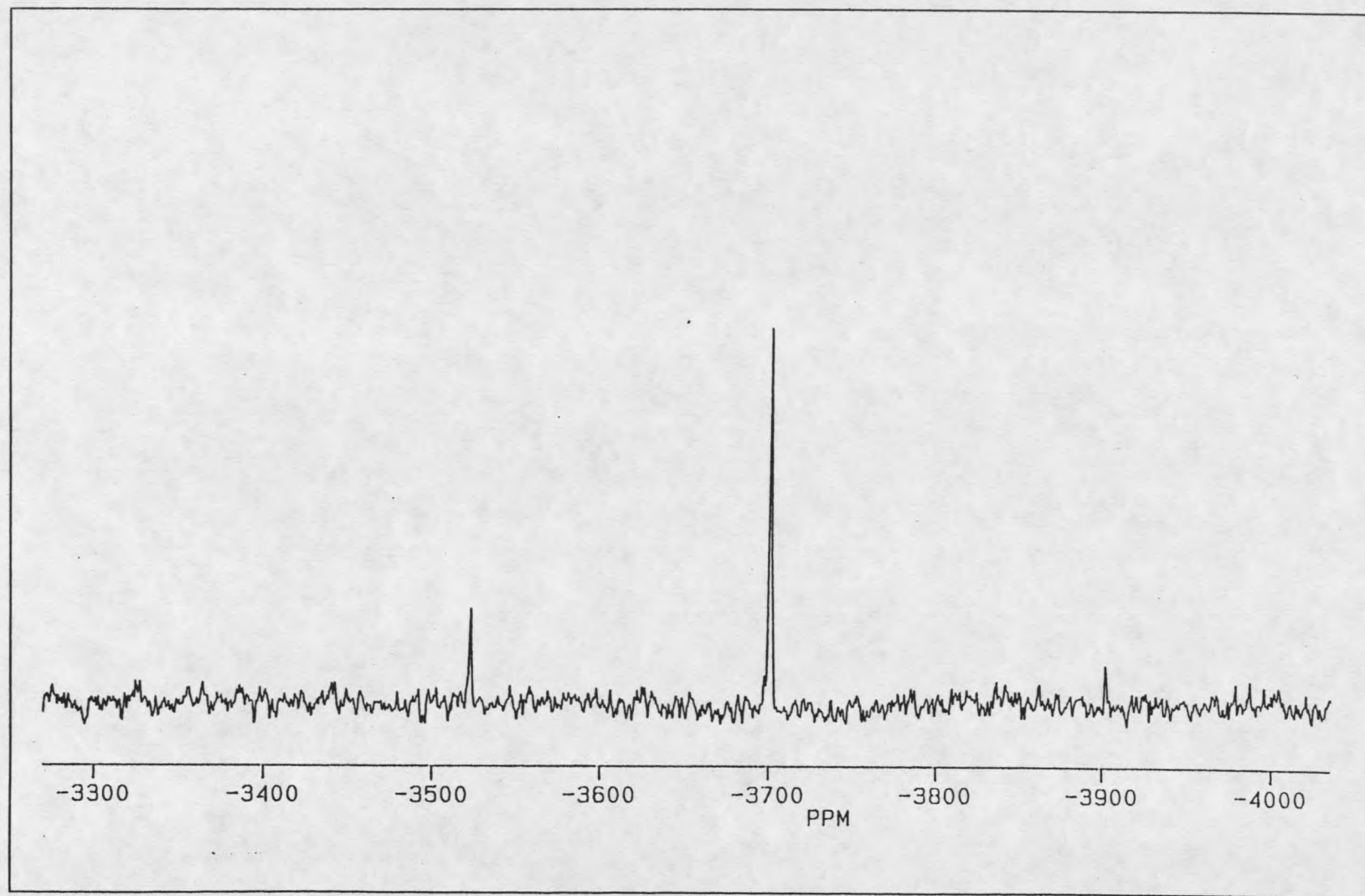
**Figure 54.** Reaction of tetraaquaplatinate(II) with *meso*-MSE.

In order to rule out the presence of chloride as a ligand in the products formed in methods 1 and 2, a solution of *meso*-MSE in 1 M trifluoromethanesulfonic acid was used to dissolve freshly precipitated  $\text{Pt}(\text{OH})_2$ . This complex is obtained by raising the pH of an acidic solution of tetraaquaplatinum(II),  $[\text{Pt}(\text{OH}_2)_4]^{2+}$  (27) to  $\sim 4$  followed by filtration of the white precipitate.  $[\text{Pt}(\text{OH}_2)_4]^{2+}$  was first prepared by Elding (113) and has found considerable use as a versatile starting material for the synthesis of a wide variety of Pt complexes due to the labile nature of the  $\text{H}_2\text{O}$  ligands in acidic solution. Although the  $K_a$ 's of the coordinated waters have not been determined, evidence

suggests that these values are below  $\sim 2$ . Interestingly, the formation of dimeric or higher polymeric tetraaqua complexes has not been reported.

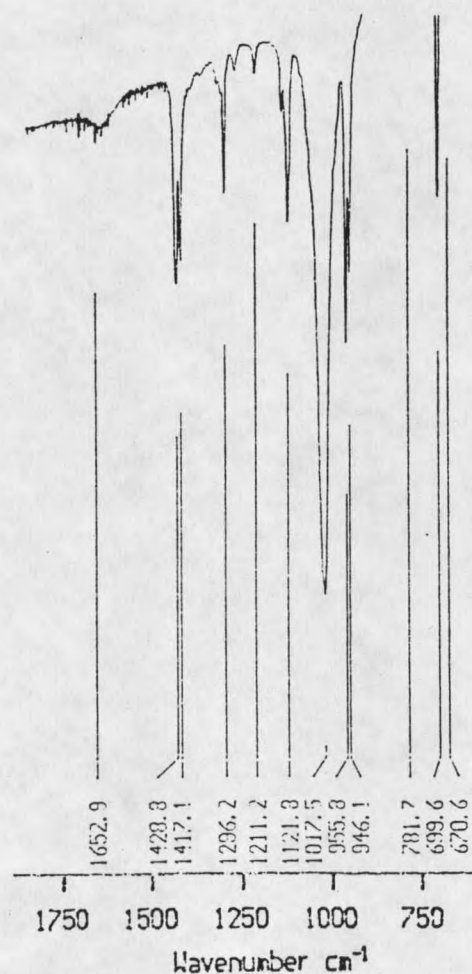
As can be seen in Figure 54, the product of this reaction produces a  $^{195}\text{Pt}$  spectrum similar to that of methods 1 and 2. As seen with the monodentate sulfoxides the formation of a heterodimeric bridged structure results in a very characteristic splitting pattern as the two Pt centers become magnetically (and chemically) non-equivalent. This pattern is not observed in any spectra of reactions involving *meso*-MSE as a ligand. The chemical behavior of the  $\beta$ -form of MSE was essentially the same as for the  $\alpha$ -form. With this isomer however, the solution turned dark brown much more quickly.

The available spectroscopic evidence points to the formation of a polymeric structure when either the  $\alpha$ -form or the  $\beta$ -form of MSE are coordinated to Pt and the chloride ligands are replaced by water. This hypothesis is consistent with the results of Madan et al. when they attempted to prepare the *bis*-MSE complexes of Pt(II) and Pd(II) (76). Although they were also not able to fully characterize the resulting complexes, IR data of the  $[\text{Pt}(\beta\text{-MSE})_2](\text{ClO}_4)_2$  complex led them to propose a polymeric structure with MSE bridging two Pt atoms, with coordination of the ligands through both *S* and *O*. IR spectroscopy is extremely useful for characterizing metal sulfoxide complexes of this type. It has been demonstrated that the sulfinyl stretching frequency is directly related to the mode of coordination of an ambidentate sulfoxide ligand (114).



**Figure 55.**  $^{195}\text{Pt}$  NMR for the reaction of  $[\text{Pt}(\text{OH}_2)]^{2+}$  with *meso*-MSE.

Coordination through sulfur increases the double bond character of the  $S=O$  bond resulting in an increase in the stretching frequency over that of the free ligand. Conversely, coordination through oxygen tends to decrease the double bond character and leads to a decrease in stretching frequency (see Figure 23). This observation has been confirmed in studies examining the IR stretch of the sulfinyl group for a series of hard ( $O$  donor) and soft ( $S$  donor) metal complexes. Figure 56 shows a portion of the IR spectrum of *meso*-MSE.



**Figure 56.** Infrared spectrum of *meso*-MSE in the  $S=O$  stretch region.

The dominant absorbance around  $1017\text{ cm}^{-1}$  has previously been assigned to the  $S=O$  stretch of the sulfinyl groups of the free ligand. The IR spectrum of  $\text{Pt}(\text{meso-MSE})\text{Cl}_2$  in the same general region shows two intense absorbances at  $1131$  and  $1153\text{ cm}^{-1}$  which have also been assigned to the  $S=O$  stretch of  $S$  bound MSE, based on the  $\sim 120\text{ cm}^{-1}$  increase in wavenumber. Comparing this with the IR spectrum of the product of the reaction of  $\text{Pt}(\text{meso-MSE})\text{Cl}_2$  with  $\text{AgNO}_3$  (Figure 57), a similar set of two peaks can be seen at  $1131$  and  $1154\text{ cm}^{-1}$ .

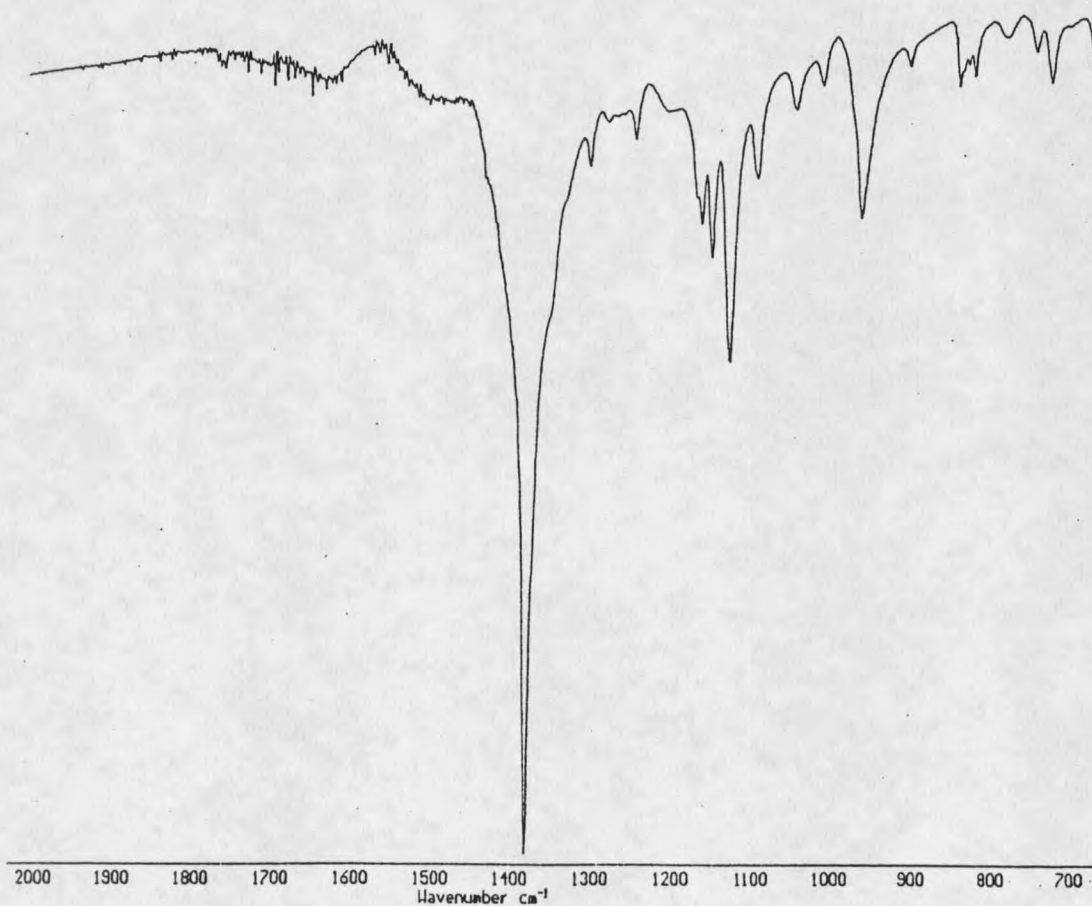


Figure 57.

The intense absorbance at  $1398\text{ cm}^{-1}$  is due to ionic nitrate (115). As in the dichloride, the  $S=O$  stretch is to higher wavenumber, indicating coordination through sulfur. No absorbance assignable to  $O$  bound ligand is seen around  $\sim 900\text{ cm}^{-1}$ . Based on this evidence, it may be concluded that the MSE ligand remains exclusively  $S$  bound in the polymeric material.

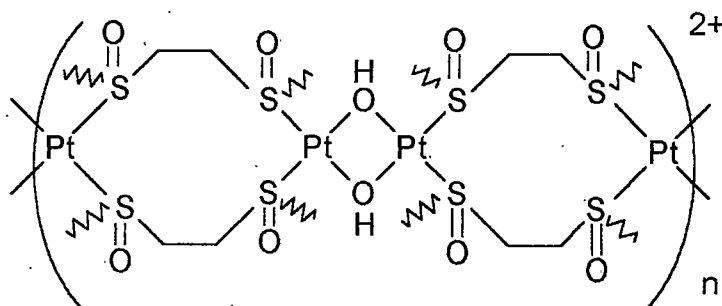
The following points need to be considered in any formulation of a hypothetical structure for the product of these reactions:

- 1) The dichloro MSE complex is a distinct, stable, monomeric species, as demonstrated by  $^1\text{H}$ ,  $^{13}\text{H}$ , and  $^{195}\text{Pt}$  NMR and IR spectroscopy.
- 2) Substitution of halogen with water apparently leads to a polymeric species with very similar ligand geometry around each Pt.
- 3) The pH dependence of the number of peaks observed in the  $^{195}\text{Pt}$  NMR spectrum of this complex suggests that some form of hydroxo bridging is present.

Although bridging chloride dimers are not uncommon for  $\text{Pt(II)}$ , we have seen no evidence for their formation in these systems. The strong absorbance of ionic nitrate in the IR spectra indicate that the chlorides were indeed removed by complexation with silver and that  $\text{NO}_3^-$  is now serving to balance the charge of a cationic Pt complex. As has been shown for other sulfoxide complexes, once the chloride ligands have been hydrolyzed, hydroxo bridge formation readily occurs as a function of pH. It is therefore reasonable to conclude that the same general type of reaction is occurring in

this case. Because chloride is much higher in the trans effect series than water, it seems unlikely that chelating MSE would remain bidentate in the dichloride complex, then revert to a monodentate or bridging mode following hydrolysis. As the "simplest" interpretation of the data then, we propose that the multitude of peaks seen in the  $^{195}\text{Pt}$  NMR spectra represents a distribution of monomeric and dimeric or possibly even trimeric hydroxo bridged structures. The closely spaced peaks could simply be a non-statistical sampling of the chelate ring conformations. The apparent polymeric nature of the product and the failure to form heterodimers remains unexplained.

A second interpretation is that the MSE ligand adapts a bridging role in at least part of the complex. Again considering the "simplest" case, a structure such as that shown in Figure 58 is proposed. This structure is consistent with the  $^{13}\text{C}$  NMR data which shows only a single  $J_{\text{C-Pt}}$  coupling constant to each of the  $-\text{CH}_3$  and  $-\text{CH}_2-$  carbon atoms.



**Figure 58.** Proposed structure for the hydrolysis product of **22**.

### Bidentate Thioether Complexes of Pt(II)

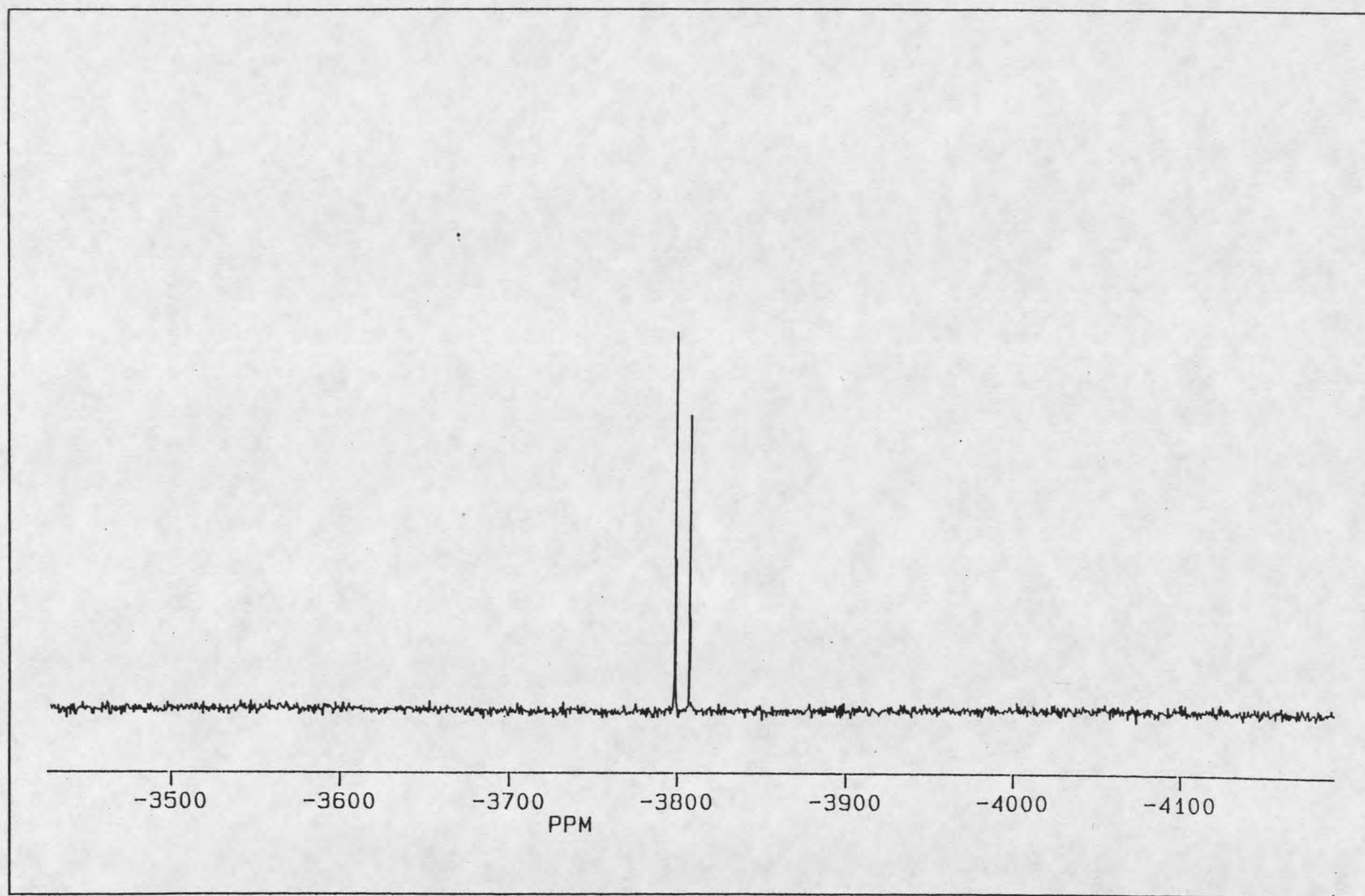
In order to obtain a better understanding of what was happening in the MSE system just discussed, and specifically to determine the role, if any, of the sulfinyl groups in determining product outcome, an analogous series of Pt(II) complexes were synthesized employing the chelating thioether ligand 1,2-methylthioethane. This is one of a class of thioethers having the general structure  $\mathbf{R-S-(CH)_n-S-R'}$  where  $\mathbf{R}$  and  $\mathbf{R'}$  are methyl or phenyl groups and  $\mathbf{n}$  ranges from two to twelve.

The dihalogen complexes of general formula  $\mathbf{M(L)X_2}$  ( $\mathbf{M} = \text{Pt, Pd}$ ;  $\mathbf{L} =$  thioether) have been investigated and trends in reaction products noted with changes in  $\mathbf{R}$  and  $\mathbf{R'}$  and as  $\mathbf{n}$  is varied (116). These authors reported that for  $\mathbf{M} = \text{Pd}$ ,  $\mathbf{R} = \text{phenyl}$  and  $\mathbf{n} = 6$  or  $8$ , the products of reaction of these ligands with the tetrachloro metal complexes were polymeric  $[\text{PdLX}_2]_n$  species and for  $\mathbf{M} = \text{Pd or Pt}$   $\mathbf{n} = 12$ , the products were the *trans* chelates. Because these ligands have a non-bonded lone pair of electrons on sulfur, in the metal complexes, they can exist as *meso* and *dl* forms. The rate of inversion of coordinated sulfur has been found to depend on the metal ( $\text{Pt} < \text{Pd}$ ), the *trans* halogen ligand ( $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ) and the nature of the ligand "backbone" ( $-\text{CH}_2\text{CH}_2- < \text{O}-\text{C}_6\text{H}_4 < \text{cis}-\text{CH}=\text{CH}- < -\text{CH}_2\text{CH}_2\text{CH}_2-$ ).

The metal dependence of these complexes follows from the observed rate of substitution ( $\text{Pd} \gg \text{Pt}$ ) and the halogen dependence follows the relative ordering of the *trans* effect and *trans* influence series. Inversion can be monitored by observing the

temperature at which the  $^1\text{H}$  NMR signals coalesce into a single peak. Coalescence of NMR signals occurs when the rate of inversion or chemical exchange becomes fast on the NMR time scale (104). The  $^{195}\text{Pt}$  NMR spectrum of  $\text{Pt}(\text{DTH})\text{Cl}_2$  (**28**) shown in Figure 59 clearly shows two resolved peaks due to the two invertomers indicating that inversion at  $S$  is not taking place in this complex at room temperature. That these peaks are separated by  $\sim 27$  ppm further attests to the sensitivity of platinum to the conformation of the primary coordination sphere. The presence of resolved invertomer peaks was invaluable in proving the formation of both homo- and hetero dimeric complexes following hydrolysis of the chloride ligands. These reactions are discussed below.

Figure 60 shows the  $^{195}\text{Pt}$  NMR spectrum of the product of the silver assisted hydrolysis reaction  $\text{Pt}(\text{DTH})\text{Cl}_2$ . The group of peaks between -2950 and -3050 ppm are readily assigned to the expected statistical distribution of invertomers shown in Figure 61. The  $^2J_{\text{Pt-Pt}}$  of the non-equivalent Pt centers clearly indicate the presence of dimeric species, and the coupling constants are consistent with those observed for other di- $\mu$ -hydroxo bridged complexes. The upfield shift of 250-300 ppm is consistent with the change in coordination mode of the bis-sulfide ligand from bidentate to monodentate. The group of peaks centered around -3300 ppm is reminiscent of the pattern seen for the corresponding MSE case and serves to strengthen the hypothesis of polymer formation for that ligand, with each MSE ligand now bridging two Pt atoms.



**Figure 59.**  $^{195}\text{Pt}$  NMR spectrum of  $\text{Pt}(\text{DTH})\text{Cl}_2$  (**28**) in DMF.

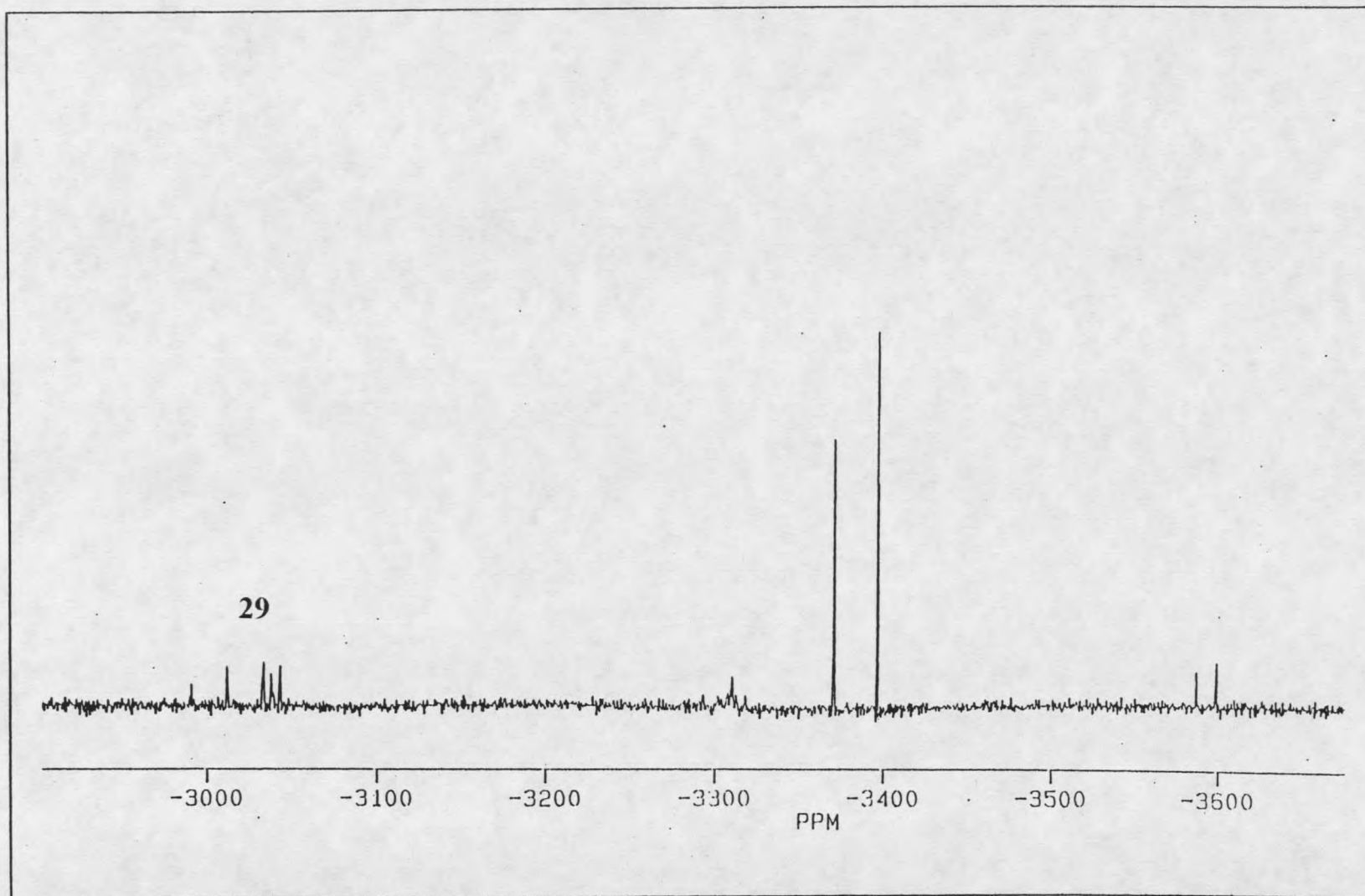
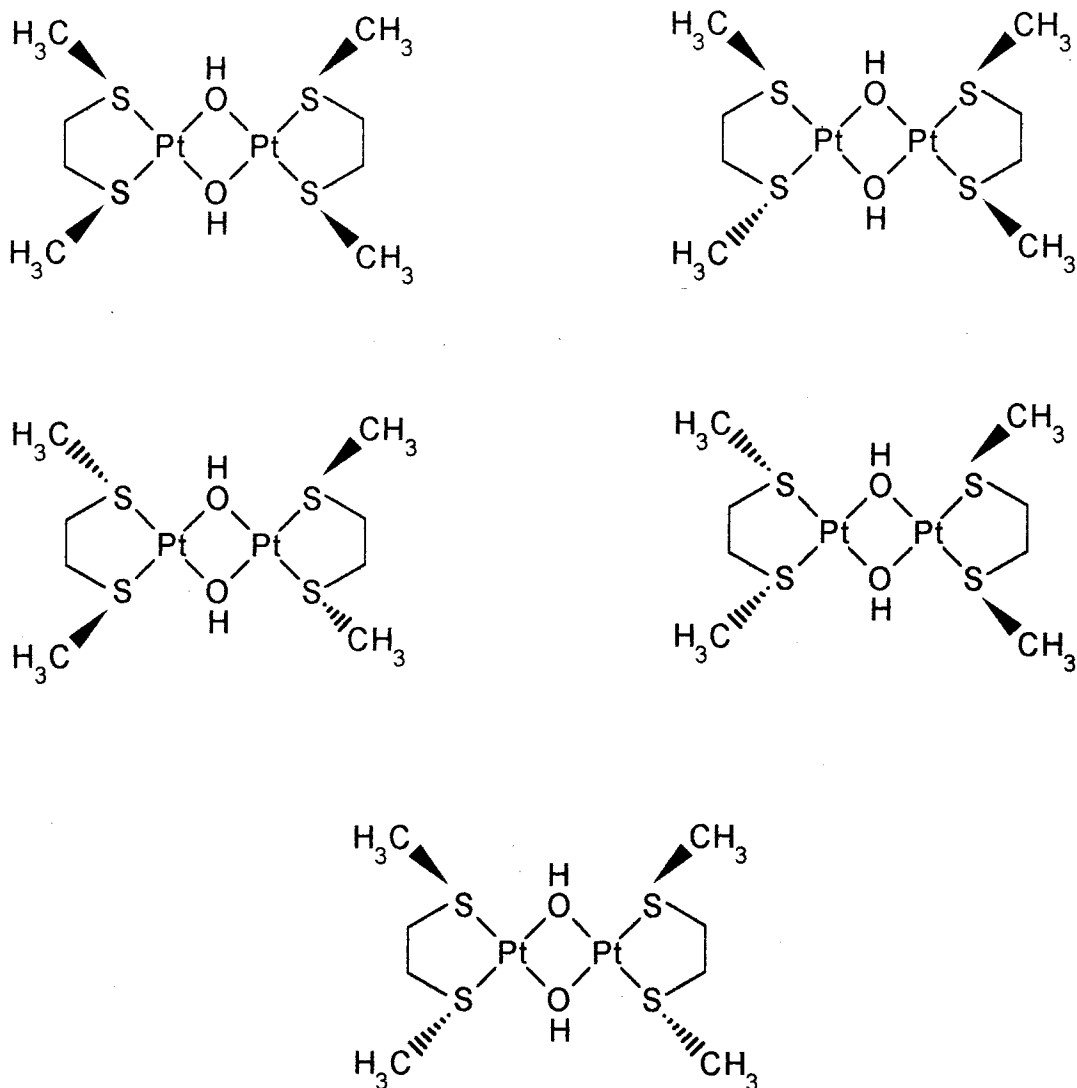


Figure 60.  $^{195}\text{Pt}$  NMR spectrum of the hydrolysis product of 28.



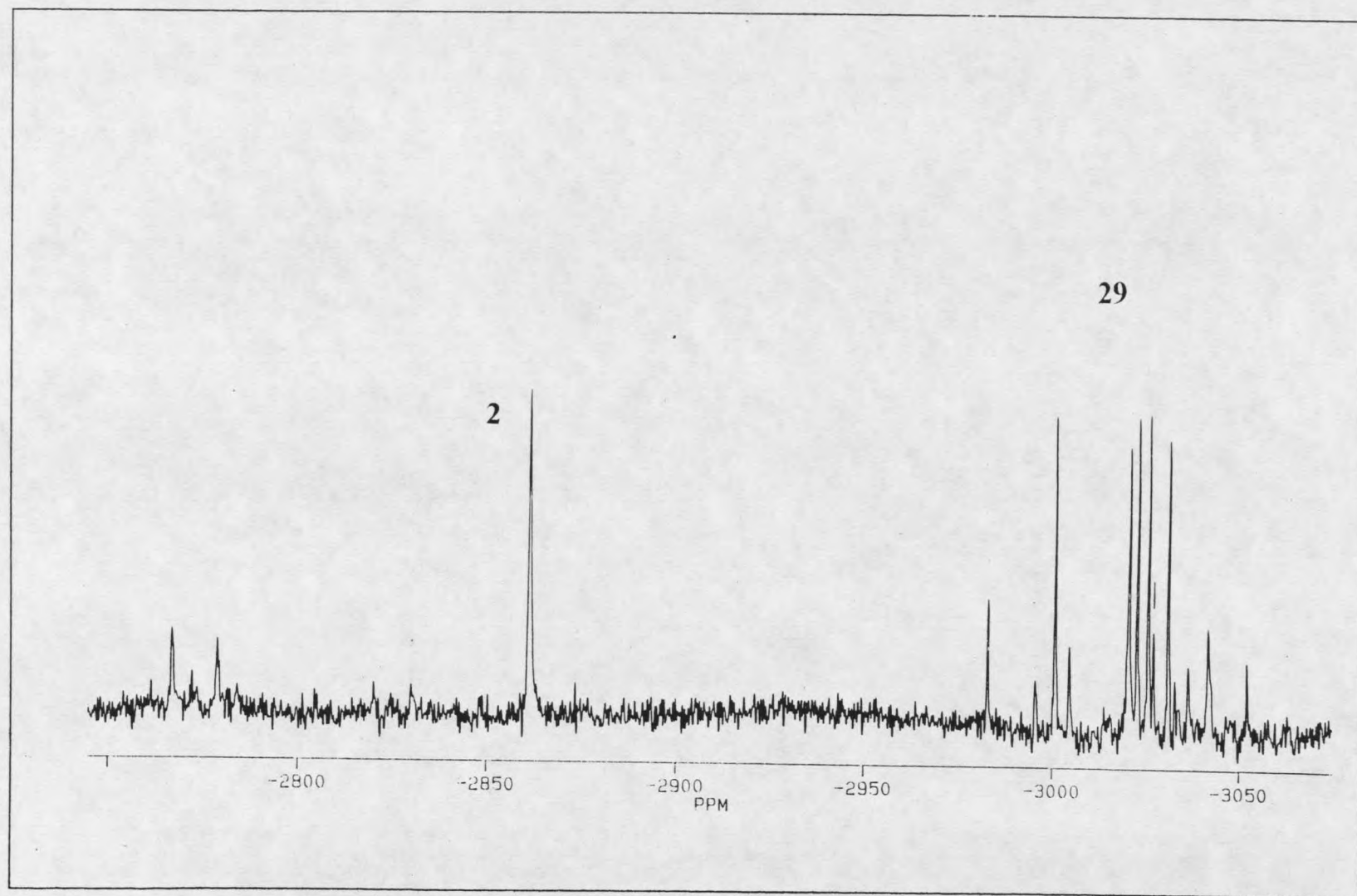
**Figure 61.** The five invertomers of  $[\text{Pt}(\text{DTH})(\mu\text{-OH})]_2^{2+}$  (**29**).

This mode of coordination relieves the ring strain imposed by bidentate coordination resulting in an upfield shift. Comparing the DTH system to the MSE system, the absence of a set of peaks assignable to an MSE dimer downfield from the group of

peaks around -3525 ppm suggests that for MSE, dimer formation is unstable with respect to polymer formation.

After it had been determined that a DTH homodimer could be formed, a series of reactions was run in an attempt to form a heterodimer containing the DTH ligand. Figure 62 shows the  $^{195}\text{Pt}$  NMR spectrum of the distribution of species formed when an equimolar amount of the DTH homodimer (29) and the DMSO homodimer (2) are reacted. The intense singlet around -2870 ppm has previously been shown to be the DMSO homodimer and the upfield group of peaks around -3025 ppm, with the exception of the furthest upfield set of peaks at -3042 ppm is seen to be identical with the DTH homodimer of Figure 59. The new peak at -3042 ppm has a set of flanking Pt satellites with  $^2J_{\text{Pt-Pt}} = \text{Hz}$ . Another set of peaks around -2775 ppm also appears during the course of the reaction which appear to be coupled to the peak at -3042 ppm. Presumably, these peaks represent the Pt fragment of the dimer coordinated by two DMSO ligands, consistent with the fairly small ( $\sim 100$  ppm) downfield shift for the DMSO homodimer resonance.

This spectrum presents an interesting example of the chemical shifts for the heterodimeric complexes shifting away from the spectral region between the homodimer peaks. This is the opposite of what is observed in the case of monodentate mixed ligand sulfoxide dimers and presents an interesting challenge in the context of the Ramsey equation for predicting chemical shifts.



**Figure 62.**  $^{195}\text{Pt}$  NMR for an equilibrium mixture of **2** and **29**.

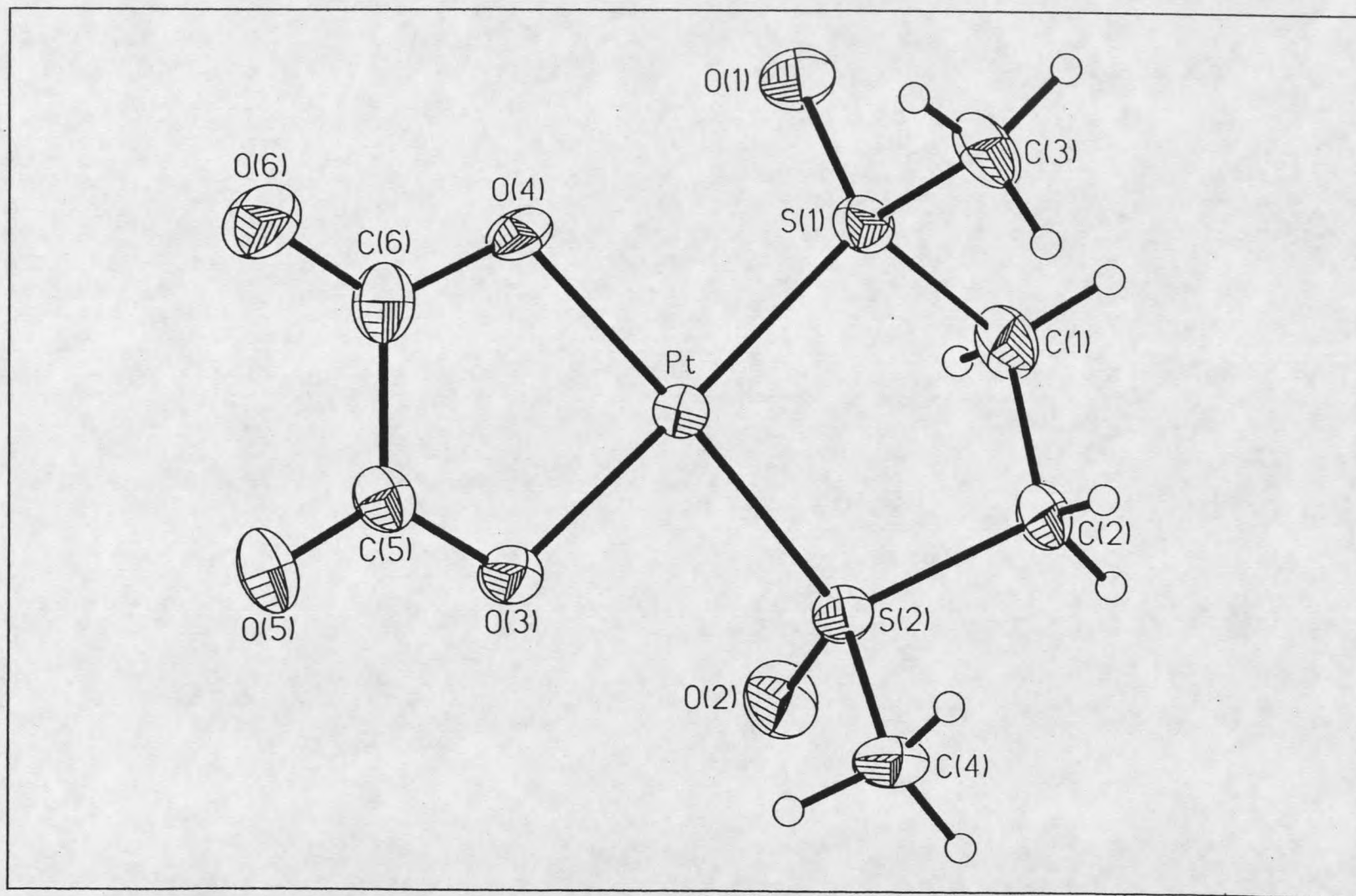
These observations implicate the sulfinyl oxygen atoms of the MSE system as the controlling factor in dimer stability, either through an inductive effect or more likely through a steric effect. It seems less likely that the sulfinyl oxygens are becoming involved in coordination to Pt, although the chemical shift remains consistent with Pt coordinated by two sulfurs and two oxygens. Bridging ligands of this general type are another indication that ionic ligands are necessary to stabilize a Pt(II) center coordinated by an MSE ligand. It may be postulated that the electron withdrawing inductive effect of the sulfinyl oxygen destabilizes the Pt(II) center in the absence of anionic ligands in the trans positions.

#### Reaction of *Cis* and *Trans* Pt(Ox)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub> (30)

As mentioned briefly in the Introduction, oxidation of platinum complexes from Pt(II) to Pt(IV) would provide a means of "locking" ligands in place due to the inertness of the d<sup>6</sup> Pt(IV) ion. Although these higher oxidation state complexes were not the main emphasis of this investigation, several experiments were done to test the feasibility of ligand substitution directly on to Pt(IV). The alternative method, that of carrying out the oxidation after substitution, was also tested and is discussed more fully below.

Although Pt(IV) complexes are normally considered to be substitutionally inert, water exchange is known to be fairly rapid for certain complexes at low pH (31).

In order to further investigate the reactivity of the coordinated waters on *cis*-Pt(Ox)<sub>2</sub>(OH)<sub>2</sub>, and to attempt to form a Pt(IV) complex with the MSE ligand, one equivalent of *meso*-MSE was added to a mixture of *cis* and *trans* **30**. *Cis*-Pt(Ox)<sub>2</sub>(OH)<sub>2</sub> was formed by the hydrogen peroxide oxidation of [Pt(Ox)<sub>2</sub>]<sup>2-</sup> as described in the experimental section. After 24 hrs. at 48 °C and 48 hrs. at 80 °C, <sup>195</sup>Pt NMR showed roughly equal quantities of *cis* and *trans* Pt(Ox)<sub>2</sub>(OH)<sub>2</sub>. This method has been shown to effect virtually quantitative yield of the higher oxidation state product (**31**). The pH of the solution was lowered to ~ 1.6 with triflic acid to ensure that the hydroxide ligands were fully protonated. No evidence was seen, as determined by NMR, of the desired Pt(IV)(MSE) substitution product. The resulting solution was left in the reaction vial and set aside in the hopes of producing crystals. Although crystals did form, they turned out to be the neutral Pt(II) complex Pt(Ox)(*meso*-MSE) (**31**) rather than the desired Pt(IV) substitution product. Presumably, the sulfoxide ligand acted as the reductant in this case, resulting in the formation of a sulfone and Pt(II). It is not known whether substitution on Pt took place before or after the redox reaction. This series of reactions was not pursued beyond this point. Figure 63 shows the ORTEP diagram of *meso*-1,2-bis(methylsulfinyl)ethaneoxalotoplatinum(II) (**31**). It is of interest to compare the bond angles and distances in this complex, which has a chelating sulfoxide ligand, to those in the monodentate bis-sulfoxide structures also coordinated by oxalate (**18a** and **18b**).



**Figure 63.** ORTEP plot of *meso*-1,2-bis(methylsulfinyl)ethaneoxalotoplatinum(II) (31).

The *S*-*Pt*-*S* angles are slightly less (88.8° compared with 90.9° in **18a**) and the *O*-*Pt*-*O* angle is correspondingly greater (83.1° compared with 82.4°). The *Pt*-*O* and *Pt*-*S* bond lengths are virtually identical for **31** and **18a** and **18b**. The Pt(Ox)(MSE) molecules arranged with the oxalate ligands aligned along the **a** axis as in **18a**. Crystallographic data for **31** is presented below.

**Table 24.** Crystallographic data for *meso*-1,2-bis(methylsulfinyl)ethaneoxalotoplatinum(II) (**31**).

|                                  |                                                                 |                           |               |
|----------------------------------|-----------------------------------------------------------------|---------------------------|---------------|
| Formula                          | C <sub>6</sub> H <sub>10</sub> O <sub>6</sub> S <sub>2</sub> Pt | Formula weight            | 437.34        |
| a (Å)                            | 7.688(1)                                                        | Space group               | Pbca          |
| b (Å)                            | 16.241(1)                                                       | Temperature °C            | 27            |
| c (Å)                            | 17.029(3)                                                       | λ (Å)                     | 0.7107        |
| α (°)                            | 90                                                              | ρ calculated              |               |
| β (°)                            | 90                                                              | μ (mm <sup>-1</sup> )     | 13.60         |
| γ (°)                            | 90                                                              | Transmission factor range | 0.018 - 0.388 |
| Cell Volume (Å <sup>3</sup> )    | 2126.25( )                                                      | F (000)                   | 1632          |
| Z                                | 8                                                               | Unique reflections        | 5592          |
| R <sub>w</sub> (F <sub>o</sub> ) | 0.0349                                                          | Observed reflections      | 2116          |
| R (F <sub>o</sub> )              | 0.0399                                                          | Number of parameters      | 138           |
| Scan mode                        | θ / 2θ                                                          | Goodness of fit           | 1.106         |

**Table 25.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients for **31**.

| Atom | x/a      | y/b     | z/c      | $U_{eq}$ |
|------|----------|---------|----------|----------|
| Pt   | 1099(1)  | 1268(1) | 125(1)   | 21(1)    |
| S(1) | 2540(3)  | 414(1)  | 888(2)   | 25(1)    |
| S(2) | 37(3)    | 1862(1) | 1186(2)  | 22(1)    |
| O(1) | 2478(9)  | -461(4) | 704(4)   | 37(2)    |
| O(2) | -1781(9) | 1686(4) | 1367(4)  | 37(2)    |
| C(1) | 1748(14) | 605(5)  | 1851(5)  | 32(3)    |
| C(2) | 1430(13) | 1543(5) | 1975(5)  | 27(3)    |
| C(3) | 4722(12) | 740(6)  | 922(7)   | 41(4)    |
| C(4) | 406(14)  | 2932(5) | 1160(6)  | 34(3)    |
| O(3) | -105(9)  | 2054(3) | -624(4)  | 30(2)    |
| O(4) | 1938(9)  | 736(4)  | -883(4)  | 31(2)    |
| C(5) | 159(12)  | 1872(6) | -1352(6) | 25(3)    |
| C(6) | 1270(13) | 1093(6) | -1510(6) | 32(3)    |
| O(5) | -418(9)  | 2260(4) | -1905(4) | 37(2)    |
| O(6) | 1443(10) | 826(4)  | -2169(4) | 45(3)    |

**Table 26.** Bond lengths for **31**.

| Bond    | Length (Å) | Bond      | Length (Å) |
|---------|------------|-----------|------------|
| Pt-S(1) | 2.200(2)   | S(2)-C(2) | 1.795(10)  |
| Pt-S(2) | 2.204(2)   | S(2)-C(4) | 1.762(9)   |
| Pt-O(3) | 2.028(6)   | C(1)-C(2) | 1.558(12)  |
| Pt-O(4) | 2.028(7)   | O(3)-C(5) | 1.290(12)  |

**Table 26** (cont.)

|           |           |           |           |
|-----------|-----------|-----------|-----------|
| S(1)-O(1) | 1.457(6)  | O(4)-C(6) | 1.319(12) |
| S(1)-C(1) | 1.776(10) | C(5)-C(6) | 1.550(13) |
| S(1)-C(3) | 1.760(10) | C(5)-O(5) | 1.216(12) |
| S(2)-O(2) | 1.460(7)  | C(6)-O(6) | 1.210(12) |

**Table 27.** Bond angles for **31**.

| Bonds          | Angle (°) | Bond           | Angle (°) |
|----------------|-----------|----------------|-----------|
| S(1)-Pt-S(2)   | 88.8(1)   | O(2)-S(2)-C(2) | 110.9(4)  |
| S(1)-Pt-O(3)   | 176.5(2)  | Pt-S(2)-C(4)   | 110.6(4)  |
| S(2)-Pt-O(3)   | 94.1(2)   | O(2)-S(2)-C(4) | 110.6(5)  |
| S(1)-Pt-O(4)   | 94.1(2)   | C(2)-S(2)-C(4) | 102.0(5)  |
| S(2)-Pt-O(4)   | 176.6(2)  | S(1)-C(1)-C(2) | 110.5(6)  |
| O(3)-Pt-O(4)   | 83.1(3)   | S(2)-C(2)-C(1) | 105.9(6)  |
| Pt-S(1)-O(1)   | 118.1(3)  | Pt-O(3)-C(5)   | 112.9(6)  |
| Pt-S(1)-C(1)   | 105.2(3)  | Pt-O(4)-C(6)   | 112.0(6)  |
| O(1)-S(1)-C(1) | 111.0(4)  | O(3)-C(5)-C(6) | 116.1(8)  |
| Pt-S(1)-C(3)   | 108.0(4)  | O(3)-C(5)-O(5) | 124.5(9)  |
| O(1)-S(1)-C(3) | 109.4(5)  | C(6)-C(5)-O(5) | 119.3(9)  |
| C(1)-S(1)-C(3) | 104.2(5)  | O(4)-C(6)-C(5) | 115.6(8)  |
| Pt-S(2)-O(2)   | 116.3(3)  | O(4)-C(6)-O(6) | 123.4(9)  |
| Pt-S(2)-C(2)   | 105.4(3)  | C(5)-C(6)-O(6) | 120.9(9)  |

**Table 28.** Anisotropic displacement coefficients ( $\times 10^4$ ) for **31**.

| Atom | $U_{xx}$ | $U_{yy}$ | $U_{zz}$ | $U_{xy}$ | $U_{xz}$ | $U_{yz}$ |
|------|----------|----------|----------|----------|----------|----------|
| Pt   | 20(1)    | 20(1)    | 21(1)    | 2(1)     | -1(1)    | -1(1)    |
| S(1) | 25(1)    | 19(1)    | 30(1)    | 2(1)     | -5(1)    | 0(1)     |
| S(2) | 21(1)    | 24(1)    | 23(1)    | 0(1)     | 3(1)     | 0(1)     |
| O(1) | 50(5)    | 17(3)    | 44(5)    | 6(3)     | -8(4)    | -4(3)    |
| O(2) | 22(3)    | 49(4)    | 41(5)    | -3(3)    | 1(3)     | -3(4)    |
| C(1) | 42(6)    | 30(5)    | 24(5)    | 4(5)     | -7(5)    | 11(4)    |
| C(2) | 33(6)    | 28(4)    | 20(5)    | 4(4)     | -6(4)    | 5(4)     |
| C(3) | 22(5)    | 50(6)    | 52(7)    | 6(5)     | -17(5)   | -5(6)    |
| C(4) | 38(6)    | 23(4)    | 39(6)    | 12(5)    | 0(5)     | -3(4)    |
| O(3) | 37(4)    | 26(3)    | 26(4)    | 8(3)     | -2(3)    | -1(3)    |
| O(4) | 38(4)    | 35(3)    | 19(3)    | 16(4)    | 5(3)     | -8(3)    |
| C(5) | 19(4)    | 31(5)    | 27(6)    | -2(4)    | 1(4)     | 2(4)     |
| C(6) | 33(5)    | 38(5)    | 24(5)    | -7(5)    | -1(5)    | 3(4)     |
| O(5) | 39(4)    | 45(4)    | 27(4)    | 0(4)     | -10(4)   | 10(3)    |
| O(6) | 63(6)    | 47(4)    | 25(4)    | 15(4)    | 4(4)     | -4(3)    |

**Table 29.** H-atom coordinates ( $\times 10^4$ ) and isotropic displacement coefficients ( $\times 10^3$ ) for **31**.

| Atom  | x/a  | y/b  | z/c  | $U_{eq}$ |
|-------|------|------|------|----------|
| H(1A) | 2576 | 406  | 2228 | 80       |
| H(1B) | 677  | 311  | 1925 | 80       |
| H(2A) | 883  | 1644 | 2473 | 80       |

Table 29 (cont.)

|       |      |      |      |        |
|-------|------|------|------|--------|
| H(2B) | 2512 | 1837 | 1958 | 80     |
| H(3A) | 5375 | 375  | 1253 | 44(13) |
| H(3B) | 5197 | 729  | 400  | 44(13) |
| H(3C) | 4786 | 1290 | 1126 | 44(13) |
| H(4A) | -64  | 3182 | 1625 | 44(13) |
| H(4B) | 1633 | 3037 | 1133 | 44(13) |
| H(4C) | -153 | 3161 | 705  | 44(13) |

Although these platinum oxalate reactions did yield a novel complex containing the chelating MSE ligand, the reduction of Pt(IV) to Pt(II) proved to be both unexpected and somewhat disappointing. The *cis* and *trans* Pt(Ox)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub> complex was employed a second time however in an attempt to form a mixed valence dimer containing one Pt(IV) and one Pt(II) metal center. The results of that experiment are presented following the next section which represents a brief departure from platinum chemistry in order to further investigate the chelating and bridging properties of the MSE ligand.

### Ruthenium Complexes Containing Monodentate Sulfur Ligands

Ruthenium complexes have found widespread applications in synthetic transition metal chemistry as well as showing great promise as second and third generation anti tumor drugs (117). Several of these have previously been mentioned in the context of structure directed synthesis and biologically active complexes above. Because of its well known propensity for coordinating "soft" donor atoms, Ru was chosen as a suitable substrate for studies involving sulfoxide ligands (118).

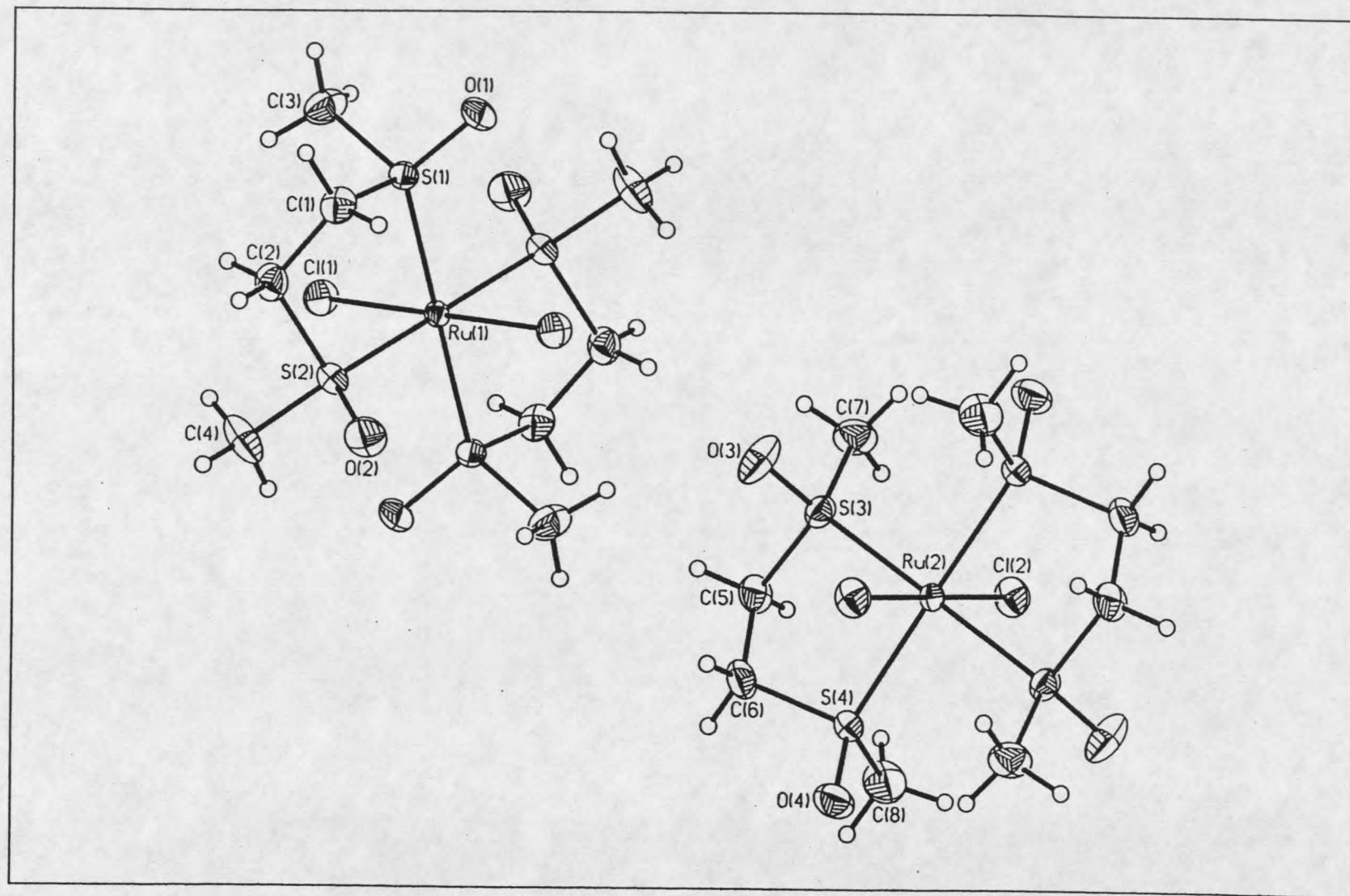
The neutral complex  $\text{RuCl}_2(\text{DMSO})_4$  has previously been characterized (119) and it was felt that, just as in the case of the various platinum complexes, substitution of chelating MSE for DMSO would be a practical method for the synthesis of  $\text{Ru}(\text{MSE})$  species. When  $\text{Ru}(\text{DMSO})_4\text{Cl}_2$  was first synthesized by prolonged heating of " $\text{RuCl}_3 \cdot 3 \text{H}_2\text{O}$ " under hydrogen, it was assigned the *trans* configuration although it was suggested, based on far IR evidence, that after recrystallization there may be a mixture of *cis* and *trans* isomers with mixed oxygen and sulfur coordination to Ru (120). In our hands, recrystallization by slow cooling of a hot concentrated DMSO solution initially formed very thin, elongated hexagonal plates similar to those described by Evans et al. but very different from those described by Mercer (119) who structured the *cis* complex after recrystallization from methanol. Based on preliminary rotation photographs, the unit cell of this crystal was found to be identical with that of *trans*-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) (32) previously reported by Alessio et

al. (117). These authors demonstrated that the *cis* isomer could be photoisomerized to the *trans* by irradiation with visible light.

When two equivalents of *meso*-MSE were combined with an aqueous solution of **32** and allowed to stand, pale yellow crystals slowly formed. X-ray analysis subsequently showed these to be the desired substitution product *trans*-RuCl<sub>2</sub>(*meso*-MSE) (**33**). Since no measures were taken to exclude light as the **33** crystallized, it is not clear whether *cis/trans* isomerization of **32** occurred before ligand substitution, or whether it occurred in the resulting *bis*-MSE product. Figure 64 shows the ORTEP diagram of *trans*-dichlorobis-*meso*-1,2-bis(methylsulfinyl)ethaneruthenium(II) (**33**) and Table 30 presents the crystallographic data.

**Table 30.** Crystallographic data for *trans*-RuCl<sub>2</sub>(*meso*-MSE)<sub>2</sub> (**33**).

|                                  |                                                                                 |                           |               |
|----------------------------------|---------------------------------------------------------------------------------|---------------------------|---------------|
| Formula                          | C <sub>8</sub> H <sub>22</sub> O <sub>5</sub> S <sub>4</sub> Cl <sub>2</sub> Ru | Formula weight            | 498.48        |
| a (Å)                            | 7.5505(5)                                                                       | Space group               | P-1           |
| b (Å)                            | 8.8598(5)                                                                       | Temperature °C            | 27            |
| c (Å)                            | 14.461(1)                                                                       | λ (Å)                     | 0.7107        |
| α (°)                            | 77.230(5)                                                                       | ρ calculated              | 1.866         |
| β (°)                            | 76.632(6)                                                                       | μ (mm <sup>-1</sup> )     | 1.73          |
| γ (°)                            | 66.697(5)                                                                       | Transmission factor range | 0.703 - 0.844 |
| Cell Volume (Å <sup>3</sup> )    | 855.26(12)                                                                      | F (000)                   | 504           |
| Z                                | 2                                                                               | Unique reflections        | 8870          |
| R <sub>w</sub> (F <sub>o</sub> ) | 0.0283                                                                          | Observed reflections      | 5701          |
| R (F <sub>o</sub> )              | 0.0313                                                                          | Number of parameters      | 186           |
| Scan mode                        | θ / 2θ                                                                          | Goodness of fit           | 1.1967        |



**Figure 64.** ORTEP diagram of *trans*-dichlorobis-*meso*-1,2-bis(methylsulfinyl)ethaneruthenium(II) (33).

**Table 31.** Atomic Coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\times 10^3$ ) for *trans*-RuCl<sub>2</sub>(*meso*-MSE)<sub>2</sub> (**33**).

| Atom  | x/a      | y/b      | z/c      | U <sub>eq</sub> |
|-------|----------|----------|----------|-----------------|
| Ru(1) | 0        | 0        | 0        | 15(1)           |
| Cl(1) | -1428(1) | -274(1)  | -1247(1) | 28(1)           |
| S(1)  | 2489(1)  | -2561(1) | -85(1)   | 20(1)           |
| S(2)  | 2058(1)  | 1092(1)  | -1133(1) | 21(1)           |
| O(1)  | 3054(3)  | -3670(2) | 810(1)   | 31(1)           |
| O(2)  | 2911(3)  | 2114(2)  | -845(1)  | 36(1)           |
| C(1)  | 4587(3)  | -2091(3) | -753(2)  | 28(1)           |
| C(2)  | 3997(4)  | -701(3)  | -1586(2) | 29(1)           |
| C(3)  | 2220(4)  | -3802(3) | -820(2)  | 35(1)           |
| C(4)  | 1103(4)  | 2190(4)  | -2196(2) | 40(1)           |
| Ru(2) | 5000     | 5000     | 5000     | 17(1)           |
| Cl(2) | 1788(1)  | 5090(1)  | 5760(1)  | 31(1)           |
| S(3)  | 4977(1)  | 3443(1)  | 3913(1)  | 24(1)           |
| S(4)  | 3794(1)  | 7295(1)  | 3888(1)  | 23(1)           |
| O(3)  | 6858(3)  | 2460(3)  | 3384(2)  | 46(1)           |
| O(4)  | 4655(3)  | 8593(2)  | 3649(1)  | 37(1)           |
| C(5)  | 3509(4)  | 4955(3)  | 3059(2)  | 31(1)           |
| C(6)  | 4092(4)  | 6465(3)  | 2811(2)  | 30(1)           |
| C(7)  | 3572(4)  | 2159(3)  | 4346(2)  | 38(1)           |
| C(8)  | 1213(4)  | 8352(3)  | 4119(2)  | 44(1)           |
| O(5)  | 1167(4)  | 2997(4)  | 2476(2)  | 86(2)           |

**Table 32.** Bond lengths for *trans*-RuCl<sub>2</sub>(*meso*-MSE)<sub>2</sub>.

| Bond         | Length (Å) | Bond         | Length (Å) |
|--------------|------------|--------------|------------|
| Ru(1)-Cl(1)  | 2.403(1)   | Ru(2)-Cl(2)  | 2.398(1)   |
| Ru(1)-S(1)   | 2.311(1)   | Ru(2)-S(3)   | 2.316(1)   |
| Ru(1)-S(2)   | 2.312(1)   | Ru(2)-S(4)   | 2.306(1)   |
| Ru(1)-Cl(1A) | 2.403(1)   | Ru(2)-Cl(2A) | 2.398(1)   |
| Ru(1)-S(1A)  | 2.311(1)   | Ru(2)-S(3A)  | 2.316(1)   |
| Ru(1)-S(2A)  | 2.312(1)   | Ru(2)-S(4A)  | 2.306(1)   |
| S(1)-O(1)    | 1.477(2)   | S(3)-O(3)    | 1.474(2)   |
| S(1)-C(1)    | 1.804(3)   | S(3)-C(5)    | 1.81(2)    |
| S(1)-C(3)    | 1.783(3)   | S(3)-C(7)    | 1.774(3)   |
| S(2)-O(2)    | 1.479(3)   | S(4)-O(4)    | 1.475(2)   |
| S(2)-C(2)    | 1.809(2)   | S(4)-C(6)    | 1.799(3)   |
| S(2)-C(4)    | 1.768(3)   | S(4)-C(8)    | 1.784(3)   |
| C(1)-C(2)    | 1.525(3)   | C(5)-C(6)    | 1.514(4)   |

**Table 33.** Bond angles for *trans*-RuCl<sub>2</sub>(*meso*-MSE)<sub>2</sub>.

| Atoms              | Angle (°) | Atoms              | Angle (°) |
|--------------------|-----------|--------------------|-----------|
| Cl(1)-Ru(1)-S(1)   | 93.2(1)   | Cl(2)-Ru(2)-S(3)   | 89.6(1)   |
| Cl(1)-Ru(1)-S(2)   | 90.6(1)   | Cl(2)-Ru(2)-S(4)   | 92.5(1)   |
| S(1)-Ru(1)-S(2)    | 86.9(1)   | S(3)-Ru(2)-S(4)    | 86.3(1)   |
| Cl(1)-Ru(1)-Cl(1A) | 180.0(1)  | Cl(2)-Ru(2)-Cl(2A) | 180.0(1)  |
| S(1)-Ru(1)-Cl(1A)  | 86.8(1)   | S(3)-Ru(2)-Cl(2A)  | 90.4(1)   |
| S(2)-Ru(1)-Cl(1A)  | 89.4(1)   | S(4)-Ru(2)-Cl(2A)  | 87.5(1)   |
| Cl(1)-Ru(1)-S(1A)  | 86.8(1)   | Cl(2)-Ru(2)-S(3A)  | 90.4(1)   |
| S(1)-Ru(1)-S(1A)   | 180.0(1)  | S(3)-Ru(2)-S(3A)   | 180.0(1)  |

Table 33 (cont.)

|                    |          |                    |          |
|--------------------|----------|--------------------|----------|
| S(2)-Ru(1)-S(1A)   | 93.1(1)  | S(4)-Ru(2)-S(3A)   | 93.7(1)  |
| Cl(1A)-Ru(1)-S(1A) | 93.2(1)  | Cl(2A)-Ru(2)-S(3A) | 89.6(1)  |
| Cl(1)-Ru(1)-S(2A)  | 89.4(1)  | Cl(2)-Ru(2)-S(4A)  | 87.5(1)  |
| S(1)-Ru(1)-S(2A)   | 93.1(1)  | S(3)-Ru(2)-S(4A)   | 93.7(1)  |
| S(2)-Ru(1)-S(2A)   | 180.0(1) | S(4)-Ru(2)-S(4A)   | 180.0(1) |
| Cl(1A)-Ru(1)-S(2A) | 90.6(1)  | Cl(2A)-Ru(2)-S(4A) | 92.5(1)  |
| S(1A)-Ru(1)-S(2A)  | 86.9(1)  | S(3A)-Ru(2)-S(4A)  | 86.3(1)  |
| Ru(1)-S(1)-O(1)    | 119.6(1) | Ru(2)-S(3)-O(3)    | 118.6(1) |
| Ru(1)-S(1)-C(1)    | 104.5(1) | Ru(2)-S(3)-C(5)    | 104.2(1) |
| O(1)-S(1)-C(1)     | 108.0(1) | O(3)-S(3)-C(5)     | 108.8(1) |
| Ru(1)-S(1)-C(3)    | 114.6(1) | Ru(2)-S(3)-C(7)    | 115.6(1) |
| O(1)-S(1)-C(3)     | 106.3(1) | O(3)-S(3)-C(7)     | 107.9(1) |
| C(1)-S(1)-C(3)     | 102.2(1) | C(5)-S(3)-C(7)     | 99.8(1)  |
| Ru(1)-S(2)-O(2)    | 119.4(1) | Ru(2)-S(4)-O(4)    | 119.6(1) |
| Ru(1)-S(2)-C(2)    | 104.4(1) | Ru(2)-S(4)-C(6)    | 104.7(1) |
| O(2)-S(2)-C(2)     | 109.4(1) | O(4)-S(4)-C(6)     | 108.5(1) |
| Ru(1)-S(2)-C(4)    | 114.6(1) | Ru(2)-S(4)-C(8)    | 114.6(1) |
| O(2)-S(2)-C(4)     | 106.7(1) | O(4)-S(4)-C(8)     | 106.2(1) |
| C(2)-S(2)-C(4)     | 100.6(1) | C(6)-S(4)-C(8)     | 101.8(1) |
| S(1)-C(1)-C(2)     | 110.3(2) | S(3)-C(5)-C(6)     | 108.9(2) |
| S(2)-C(2)-C(1)     | 109.5(2) | S(4)-C(6)-C(5)     | 109.6(2) |

**Table 34.** Anisotropic displacement coefficients ( $\times 10^3$ ) for  
*trans*-RuCl<sub>2</sub>(*meso*-MSE)<sub>2</sub>.

| Atom  | U <sub>xx</sub> | U <sub>yy</sub> | U <sub>zz</sub> | U <sub>xy</sub> | U <sub>xz</sub> | U <sub>yz</sub> |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ru(1) | 15(1)           | 16(1)           | 14(1)           | -4(1)           | -4(1)           | -1(1)           |
| Cl(1) | 32(1)           | 29(1)           | 27(1)           | -9(1)           | -15(1)          | -4(1)           |
| S(1)  | 19(1)           | 17(1)           | 20(1)           | -2(1)           | -5(1)           | -2(1)           |
| S(2)  | 20(1)           | 22(1)           | 21(1)           | -8(1)           | -4(1)           | 2(1)            |
| O(1)  | 36(1)           | 24(1)           | 24(1)           | -1(1)           | -11(1)          | 4(1)            |
| O(2)  | 43(1)           | 36(1)           | 40(1)           | -25(1)          | -7(1)           | -4(1)           |
| C(1)  | 19(1)           | 30(1)           | 31(1)           | -3(1)           | -3(1)           | -7(1)           |
| C(2)  | 25(1)           | 32(1)           | 24(1)           | -8(1)           | 2(1)            | -4(1)           |
| C(3)  | 38(1)           | 28(1)           | 43(1)           | -8(1)           | -14(1)          | -12(1)          |
| C(4)  | 32(1)           | 51(2)           | 27(1)           | -15(1)          | -9(1)           | 15(1)           |
| Ru(2) | 20(1)           | 17(1)           | 15(1)           | -6(1)           | -4(1)           | -2(1)           |
| Cl(2) | 25(1)           | 36(1)           | 30(1)           | -12(1)          | 0(1)            | -4(1)           |
| S(3)  | 29(1)           | 23(1)           | 23(1)           | -7(1)           | -7(1)           | -7(1)           |
| S(4)  | 29(1)           | 20(1)           | 19(1)           | -7(1)           | -7(1)           | 0(1)            |
| O(3)  | 36(1)           | 50(1)           | 49(1)           | -3(1)           | -2(1)           | -32(1)          |
| O(4)  | 53(1)           | 27(1)           | 35(1)           | -21(1)          | -13(1)          | 3(1)            |
| C(5)  | 42(1)           | 34(1)           | 24(1)           | -16(1)          | -16(1)          | -2(1)           |
| C(6)  | 40(1)           | 33(1)           | 18(1)           | -15(1)          | -8(1)           | -1(1)           |
| C(7)  | 54(2)           | 28(1)           | 43(2)           | -22(1)          | -16(1)          | -2(1)           |
| C(8)  | 32(1)           | 39(2)           | 43(2)           | 5(1)            | -7(1)           | -1(1)           |
| O(5)  | 58(2)           | 123(2)          | 105(2)          | -34(2)          | 2(2)            | -82(2)          |

**Table 35.** H-atom coordinates ( $\times 10^4$ ) and isotropic displacement coefficients ( $\times 10^2$ ) for *trans*-RuCl<sub>2</sub>(*meso*-MSE)<sub>2</sub>.

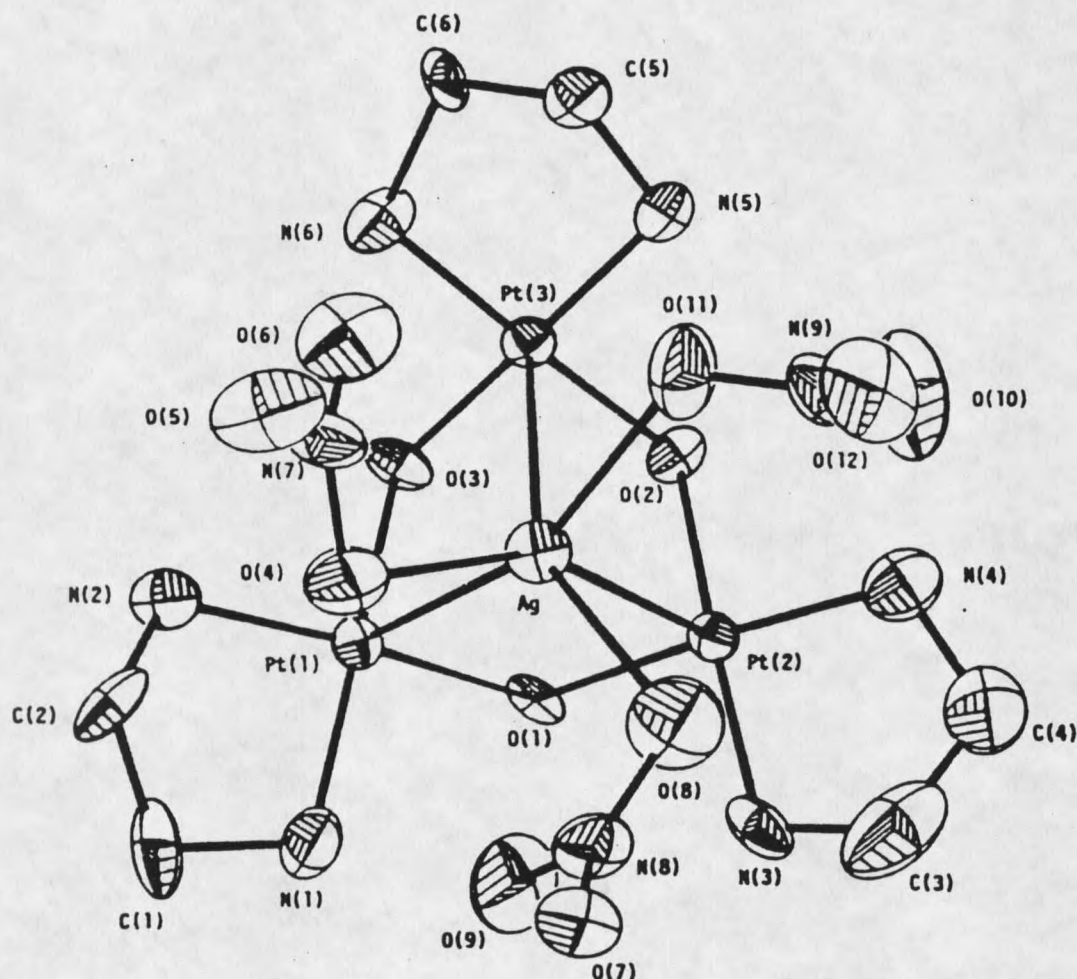
| Atom   | x/a  | y/b   | z/c   | U <sub>eq</sub> |
|--------|------|-------|-------|-----------------|
| H(1A)  | 5563 | -3067 | -993  | 44(3)           |
| H(1B)  | 5139 | -1748 | -338  | 44(3)           |
| H(2A)  | 5099 | -408  | -1919 | 44(3)           |
| H(2B)  | 3550 | -1076 | -2031 | 44(3)           |
| H(3A)  | 3306 | -4841 | -819  | 63(3)           |
| H(3B)  | 1028 | -4007 | -575  | 63(3)           |
| H(3C)  | 2180 | -3226 | -1466 | 63(3)           |
| H(4A)  | 2039 | 2602  | -2627 | 63(3)           |
| H(4B)  | 834  | 1458  | -2496 | 63(3)           |
| H(4C)  | -82  | 3104  | -2040 | 63(3)           |
| H(5A)  | 2150 | 5277  | 3334  | 44(3)           |
| H(5B)  | 3703 | 4482  | 2490  | 44(3)           |
| H(6A)  | 5433 | 6149  | 2506  | 44(3)           |
| H(6B)  | 3303 | 7296  | 2372  | 44(3)           |
| H(7A)  | 3648 | 1564  | 3849  | 63(3)           |
| H(7B)  | 4068 | 1382  | 4888  | 63(3)           |
| H(7C)  | 2235 | 2838  | 4539  | 63(3)           |
| H(8A)  | 826  | 9288  | 3628  | 63(3)           |
| H(8B)  | 577  | 7604  | 4119  | 63(3)           |
| H(8C)  | 844  | 8729  | 4734  | 63(3)           |
| H(5C)  | 475  | 2772  | 2178  | 97              |
| H(5D)  | 438  | 2895  | 3012  | 97              |
| H(5D') | 395  | 3614  | 2886  | 97              |

### A Brief Digression on Silver Chemistry

Silver is well known for its unique ability among transition metals to form extended linear chain and network structures in the solid state (29). This ability is explained in part by the hybridization of *d* and *s* atomic orbitals forming two bonding orbitals directed 180° apart, leading to linear chain structures (121).

Virtually all of the syntheses described above, utilizing the silver assisted hydrolysis of halide complexes as well as most literature preparations, use slightly less than the stoichiometric amount of silver salt. Even so, we have found that excess silver ion often remains in solution. In some cases, this excess has been involved in undesirable redox reactions resulting in deposition of a metallic silver mirror on the walls of the reaction vessel. In other cases, the excess silver crystallizes out of solution along with potential platinum ligands and in some cases, as a mixed metal platinum-silver complex. An example of this last result is seen in the crystal structure of a cyclic trihydroxo- bridged Pt(II) ethylenediamine compound with a silver atom bound in the center of the ring (122). The coordination around the silver atom defines a distorted trigonal antiprism with three of the coordination sites occupied by platinum atoms at distances (2.838 Å, 2.890 Å, 2.893 Å) which suggest the presence of *Pt-Ag* bonds. The other three coordination sites are occupied by nitrate oxygen atoms. The fact that there are no bridging ligands coordinated to the Ag atom, serving to hold it in place,

supports the claim for a significant bonding interaction between Ag and Pt. An ORTEP diagram of this structure is shown in Figure 65.



**Figure 65.** ORTEP plot of  $\{[\text{Pt}(\text{en})(\mu\text{-OH})]_3\text{Ag}(\text{NO}_3)_3\}^+$  which crystallized from a solution of  $\text{Pt}(\text{en})\text{Cl}_2$  following Ag (I) assisted hydrolysis of  $\text{Cl}^-$  (122).

We have also obtained this compound, as determined by X-ray analysis, during a series of experiments aimed at synthesizing the mixed ligand dimer containing the MSE and ethylenediamine ligands previously described.

In addition to that mixed metal structure, we have also obtained a novel network silver structure formed in one of the attempts to prepare the  $\text{Pt}(\text{meso-MSE})(\mu\text{-OH})_2 \text{CF}_3\text{SO}_3$  dimer. Crystals were obtained in which silver (I) atoms were coordinated by a framework of MSE ligands and trifluoromethanesulfonate ions. In contrast to the cyclic structure just described, platinum was totally absent from this complex. Subsequent investigations into this system showed that the  $\text{Pt}(\text{II})$  present in the original reaction mixture was not required for formation of this complex and that it can easily be obtained by simply combining the *meso* form of MSE with silver trifluoromethanesulfonate in aqueous solution and allowing the solvent to slowly evaporate at room temperature. Figure 66 shows an ORTEP plot of silver(I)*meso*-1,2-bis(methylsulfinyl)ethane-trifluoromethanesulfonate (**34**) and crystallographic data is given in table 36. Each unit cell contains four unique silver atoms, three of which (Ag1, Ag2, Ag3) show six bonding interactions, to the oxygens in the  $\text{CF}_3\text{SO}_3$  ion and to a sulfur atom in the MSE ligand, in a distorted octahedral coordination sphere and one of which (Ag4) is five coordinate in a distorted trigonal bipyramidal geometry. This coordination is more easily seen in the polyhedron diagram in Figure 67. As can also be seen, the network structure is made up of linear chains of these polyhedra running parallel to the **b** crystallographic axis. These chains in turn form parallel sheets which are cross-linked by MSE molecules as shown in the packing diagram in Figure 68.

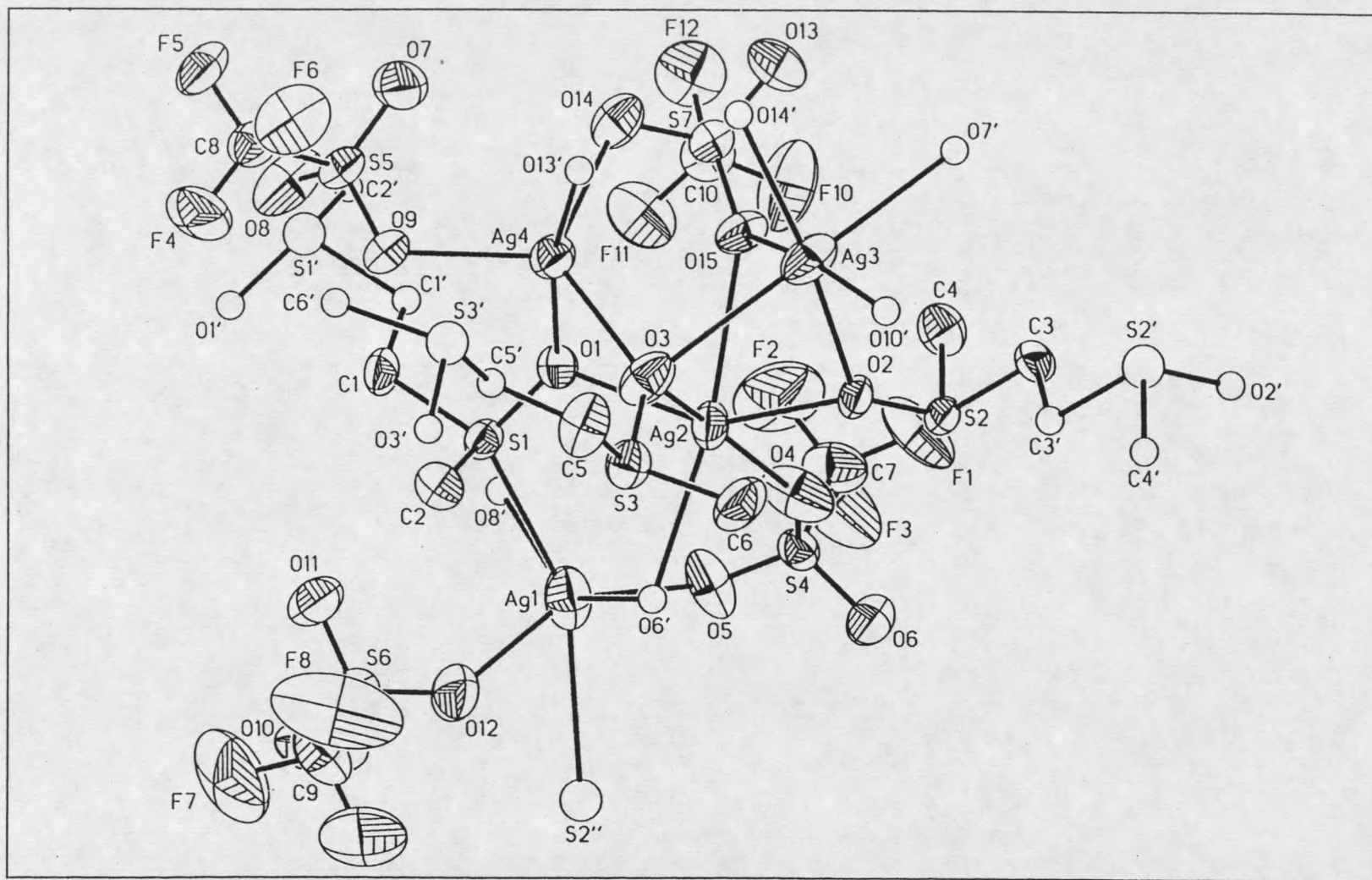


Figure 66. ORTEP plot for silver(I)*meso*-1,2-bis(methylsulfinyl)ethane-trifluoromethanesulfonate (34)

**Table 36.** Crystallographic data for silver(I)*meso*-1,2-bis(methylsulfinyl)ethane-trifluoromethanesulfonate (**34**).

|                                  |                                                                                                  |                           |               |
|----------------------------------|--------------------------------------------------------------------------------------------------|---------------------------|---------------|
| Formula                          | C <sub>10</sub> H <sub>26</sub> O <sub>15</sub> F <sub>12</sub> S <sub>3.5</sub> Ag <sub>2</sub> | Formula weight            | 942.26        |
| a (Å)                            | 11.003(1)                                                                                        | Space group               | P-1           |
| b (Å)                            | 12.388(2)                                                                                        | Temperature °C            | 27            |
| c (Å)                            | 13.046(1)                                                                                        | λ (Å)                     | 0.7107        |
| α (°)                            | 105.11(1)                                                                                        | ρ calculated              | 2.219         |
| β (°)                            | 99.98(1)                                                                                         | μ (mm <sup>-1</sup> )     | 1.58          |
| γ (°)                            | 105.55(1)                                                                                        | Transmission factor range | 0.688 - 0.869 |
| Cell Volume (Å <sup>3</sup> )    | 1596.34(34)                                                                                      | F (000)                   | 928           |
| Z                                | 2                                                                                                | Unique reflections        | 11105         |
| R <sub>w</sub> (F <sub>o</sub> ) | 0.0510                                                                                           | Observed reflections      | 4082          |
| R (F <sub>o</sub> )              | 0.0515                                                                                           | Number of parameters      | 434           |
| Scan mode                        | θ / 2θ                                                                                           | Goodness of fit           | 1.59          |

**Table 37.** Atomic Coordinates (x 10<sup>4</sup>) and equivalent isotropic displacement coefficients (Å<sup>2</sup> x 10<sup>3</sup>) for **34**.

| Atom  | x/a     | y/b      | z/c     | U     |
|-------|---------|----------|---------|-------|
| Ag(1) | 255(1)  | -1315(1) | 1531(1) | 67(1) |
| Ag(2) | 436(1)  | 2100(1)  | 2149(1) | 47(1) |
| Ag(3) | 819(1)  | 5225(1)  | 3074(1) | 58(1) |
| Ag(4) | 1298(1) | 3469(1)  | 5029(1) | 45(1) |
| S(1)  | 983(2)  | 474(2)   | 3772(2) | 35(1) |
| O(1)  | 464(6)  | 1482(5)  | 3741(4) | 41(3) |
| C(1)  | 728(8)  | 143(8)   | 5000(7) | 39(4) |
| C(2)  | 2712(8) | 1119(8)  | 4217(7) | 45(4) |

Table 37 (cont.)

|        |           |           |          |        |
|--------|-----------|-----------|----------|--------|
| S(2)   | -588(2)   | 3302(2)   | 294(2)   | 37(1)  |
| O(2)   | 399(6)    | 3656(5)   | 1385(4)  | 39(2)  |
| C(3)   | -668(9)   | 4670(8)   | 101(7)   | 45(4)  |
| C(4)   | -2158(9)  | 2860(8)   | 560(8)   | 52(5)  |
| S(3)   | 3680(3)   | 3883(2)   | 3408(2)  | 46(1)  |
| S (3') | 3391(6)   | 4919(6)   | 3589(6)  | 46(1)  |
| O(3)   | 2366(4)   | 3847(6)   | 3622(5)  | 58(3)  |
| C(5)   | 4943(7)   | 5108(6)   | 4471(6)  | 63(5)  |
| C(6)   | 3779(11)  | 4475(8)   | 2307(6)  | 66(5)  |
| S(4)   | -1832(2)  | -642(2)   | -306(2)  | 38(1)  |
| O(4)   | -1233(7)  | 545(6)    | 391(7)   | 77(4)  |
| O(5)   | -1524(6)  | -1527(6)  | 96(6)    | 69(4)  |
| O(6)   | -1783(7)  | -797(7)   | -1425(6) | 76(4)  |
| C(7)   | -3569(10) | -943(11)  | -375(11) | 67(6)  |
| S(5)   | 1905(2)   | 3247(2)   | 7490(2)  | 43(1)  |
| O(7)   | 1108(7)   | 3984(7)   | 7570(5)  | 79(4)  |
| O(8)   | 1335(8)   | 2087(6)   | 7547(6)  | 84(4)  |
| O(9)   | 2569(7)   | 3246(6)   | 6632(5)  | 55(3)  |
| C(8)   | 3219(10)  | 3944(10)  | 8741(8)  | 55(5)  |
| S(6)   | 2614(2)   | -2132(2)  | 2907(2)  | 45(1)  |
| O(10)  | 2297(9)   | -3372(6)  | 2543(8)  | 104(5) |
| O(11)  | 2366(8)   | -1620(6)  | 3929(5)  | 73(4)  |
| O(12)  | 2183(8)   | -1678(8)  | 2066(6)  | 93(5)  |
| C(9)   | 4362(12)  | -1587(12) | 3126(12) | 77(7)  |
| S(7)   | -1631(2)  | 3537(2)   | 4034(2)  | 37(1)  |
| O(13)  | -2293(6)  | 4390(5)   | 4055(6)  | 60(3)  |

**Table 37** (cont.)

|       |           |           |          |        |
|-------|-----------|-----------|----------|--------|
| O(14) | -936(6)   | 3587(6)   | 5092(5)  | 57(3)  |
| O(15) | -854(6)   | 3438(5)   | 3249(5)  | 49(3)  |
| C(10) | -2972(10) | 2129(9)   | 3507(9)  | 53(5)  |
| F(1)  | -3999(6)  | -210(6)   | -784(7)  | 103(4) |
| F(2)  | -3717(8)  | -741(10)  | 603(8)   | 147(6) |
| F(3)  | -4248(6)  | -1990(6)  | -943(8)  | 124(5) |
| F(4)  | 4122(7)   | 3492(8)   | 8776(6)  | 115(5) |
| F(5)  | 2751(6)   | 3956(6)   | 9615(4)  | 71(3)  |
| F(6)  | 3783(7)   | 5090(6)   | 8863(6)  | 92(4)  |
| F(7)  | 4887(9)   | -2140(10) | 3726(8)  | 166(7) |
| F(8)  | 4843(8)   | -500(8)   | 3573(10) | 181(7) |
| F(9)  | 4682(8)   | -1916(9)  | 2193(8)  | 132(6) |
| F(10) | -3545(7)  | 1940(6)   | 2491(5)  | 108(4) |
| F(11) | -2528(6)  | 1251(5)   | 3567(6)  | 83(3)  |
| F(12) | -3831(6)  | 2140(6)   | 4085(6)  | 83(3)  |

**Table 38:** Bond Distances ( Å ) for **34**.

| Bond        | Distance  | Bond        | Distance  |
|-------------|-----------|-------------|-----------|
| Ag(1)-O(5)  | 2.367(7)  | S(4)-O(4)   | 1.414(6)  |
| Ag(1)-O(12) | 2.313(10) | S(4)-O(5)   | 1.425(9)  |
| Ag(1)-O(8A) | 2.419(9)  | S(4)-O(6)   | 1.434(8)  |
| Ag(2)-O(1)  | 2.391(6)  | S(4)-C(7)   | 1.827(12) |
| Ag(2)-O(2)  | 2.396(6)  | O(6)-Ag(2A) | 2.583(9)  |
| Ag(2)-O(4)  | 2.585(6)  | C(7)-F(1)   | 1.316(18) |
| Ag(2)-O(6A) | 2.583(9)  | C(7)-F(2)   | 1.282(18) |

**Table 38** (cont.)

|              |           |              |           |
|--------------|-----------|--------------|-----------|
| Ag(3)-O(2)   | 2.404(5)  | C(7)-F(3)    | 1.255(13) |
| Ag(3)-S(3')  | 2.942(7)  | S(5)-O(7)    | 1.423(10) |
| Ag(3)-O(15)  | 2.562(6)  | S(5)-O(8)    | 1.433(8)  |
| Ag(3)-O(10A) | 2.377(10) | S(5)-O(9)    | 1.439(8)  |
| Ag(3)-O(14A) | 2.421(6)  | S(5)-C(8)    | 1.811(9)  |
| Ag(4)-O(1)   | 2.413(5)  | O(8)-Ag(1A)  | 2.419(9)  |
| Ag(4)-O(3)   | 2.422(6)  | C(8)-F(4)    | 1.264(16) |
| Ag(4)-O(9)   | 2.429(7)  | C(8)-F(5)    | 1.328(13) |
| Ag(4)-O(14)  | 2.515(7)  | C(8)-F(6)    | 1.342(13) |
| Ag(4)-O(13A) | 2.449(6)  | S(6)-O(10)   | 1.408(8)  |
| S(1)-O(1)    | 1.512(7)  | S(6)-O(11)   | 1.426(8)  |
| S(1)-C(1)    | 1.803(10) | S(6)-O(12)   | 1.424(10) |
| S(1)-C(2)    | 1.777(8)  | S(6)-C(9)    | 1.803(13) |
| C(1)-C(1A)   | 1.544(18) | O(10)-Ag(3A) | 2.377(10) |
| S(2)-O(2)    | 1.511(5)  | C(9)-F(7)    | 1.323(21) |
| S(2)-C(3)    | 1.799(11) | C(9)-F(8)    | 1.238(15) |
| S(2)-C(4)    | 1.790(10) | C(9)-F(9)    | 1.319(19) |
| C(3)-C(3A)   | 1.582(19) | S(7)-O(13)   | 1.432(8)  |
| S(3)-S(3')   | 1.375(9)  | S(7)-O(14)   | 1.434(7)  |
| S(3)-O(3)    | 1.511(6)  | S(7)-O(15)   | 1.446(7)  |
| S(3)-C(5)    | 1.806(6)  | S(7)-C(10)   | 1.827(9)  |
| S(3)-C(6)    | 1.781(10) | O(13)-Ag(4A) | 2.449(6)  |
| S(3')-O(3)   | 1.510(9)  | O(14)-Ag(3B) | 2.421(6)  |
| S(3')-C(5)   | 1.805(10) | C(10)-F(10)  | 1.296(13) |
| S(3')-C(6)   | 1.781(11) | C(10)-F(11)  | 1.320(14) |
| C(5)-C(5A)   | 1.465(16) | C(10)-F(12)  | 1.307(14) |

**Table 39.** Bond angles for **34**.

| Atoms               | Angle (°) | Atoms            | Angle (°) |
|---------------------|-----------|------------------|-----------|
| O(5)-Ag(1)-O(12)    | 148.6(3)  | S(3)-C(5)-C(5A)  | 110.3(6)  |
| O(5)-Ag(1)-O(8A)    | 87.4(3)   | S(3')-C(5)-C(5A) | 122.4(8)  |
| O(12)-Ag(1)-O(8A)   | 111.2(3)  | S(3)-C(6)-S(3')  | 45.4(4)   |
| O(1)-Ag(2)-O(2)     | 146.8(2)  | O(4)-S(4)-O(5)   | 116.7(5)  |
| O(1)-Ag(2)-O(4)     | 113.3(2)  | O(4)-S(4)-O(6)   | 113.2(5)  |
| O(2)-Ag(2)-O(4)     | 91.0(2)   | O(5)-S(4)-O(6)   | 113.5(5)  |
| O(1)-Ag(2)-O(6A)    | 91.9(2)   | O(4)-S(4)-C(7)   | 104.3(5)  |
| O(2)-Ag(2)-O(6A)    | 116.0(2)  | O(5)-S(4)-C(7)   | 103.5(6)  |
| O(4)-Ag(2)-O(6A)    | 78.1(2)   | O(6)-S(4)-C(7)   | 103.7(5)  |
| O(2)-Ag(3)-S(3')    | 84.8(2)   | Ag(2)-O(4)-S(4)  | 150.4(5)  |
| O(2)-Ag(3)-O(15)    | 75.2(2)   | Ag(1)-O(5)-S(4)  | 129.0(3)  |
| S(3')-Ag(3)-O(15)   | 107.1(2)  | S(4)-O(6)-Ag(2A) | 115.4(5)  |
| O(2)-Ag(3)-O(10A)   | 93.3(3)   | S(4)-C(7)-F(1)   | 109.9(9)  |
| S(3')-Ag(3)-O(10A)  | 72.5(3)   | S(4)-C(7)-F(2)   | 109.0(8)  |
| O(15)-Ag(3)-O(10A)  | 168.4(2)  | F(1)-C(7)-F(2)   | 106.6(12) |
| O(2)-Ag(3)-O(14A)   | 165.9(2)  | S(4)-C(7)-F(3)   | 112.6(10) |
| S(3')-Ag(3)-O(14A)  | 97.3(2)   | F(1)-C(7)-F(3)   | 109.3(10) |
| O(15)-Ag(3)-O(14A)  | 90.9(2)   | F(2)-C(7)-F(3)   | 109.3(12) |
| O(10A)-Ag(3)-O(14A) | 100.7(3)  | O(7)-S(5)-O(8)   | 116.0(5)  |
| O(1)-Ag(4)-O(3)     | 81.9(2)   | O(7)-S(5)-O(9)   | 114.7(5)  |
| O(1)-Ag(4)-O(9)     | 102.8(2)  | O(8)-S(5)-O(9)   | 113.1(5)  |
| O(3)-Ag(4)-O(9)     | 118.2(2)  | O(7)-S(5)-C(8)   | 104.6(5)  |
| O(1)-Ag(4)-O(14)    | 93.9(2)   | O(8)-S(5)-C(8)   | 102.7(5)  |
| O(3)-Ag(4)-O(14)    | 124.5(2)  | O(9)-S(5)-C(8)   | 103.7(5)  |
| O(9)-Ag(4)-O(14)    | 116.7(2)  | S(5)-O(8)-Ag(1A) | 132.7(5)  |
| O(1)-Ag(4)-O(13A)   | 165.8(2)  | Ag(4)-O(9)-S(5)  | 112.5(4)  |

Table 39 (cont.)

|                    |          |                   |           |
|--------------------|----------|-------------------|-----------|
| O(3)-Ag(4)-O(13A)  | 84.3(2)  | S(5)-C(8)-F(4)    | 114.5(7)  |
| O(9)-Ag(4)-O(13A)  | 86.7(2)  | S(5)-C(8)-F(5)    | 110.5(7)  |
| O(14)-Ag(4)-O(13A) | 91.0(2)  | F(4)-C(8)-F(5)    | 110.1(10) |
| O(1)-S(1)-C(1)     | 106.1(4) | S(5)-C(8)-F(6)    | 110.0(8)  |
| O(1)-S(1)-C(2)     | 105.9(4) | F(4)-C(8)-F(6)    | 106.5(9)  |
| C(1)-S(1)-C(2)     | 97.8(4)  | F(5)-C(8)-F(6)    | 104.8(8)  |
| Ag(2)-O(1)-Ag(4)   | 94.6(2)  | O(10)-S(6)-O(11)  | 116.5(6)  |
| Ag(2)-O(1)-S(1)    | 117.4(3) | O(10)-S(6)-O(12)  | 113.4(5)  |
| Ag(4)-O(1)-S(1)    | 127.2(3) | O(11)-S(6)-O(12)  | 113.5(6)  |
| S(1)-C(1)-C(1A)    | 110.7(9) | O(10)-S(6)-C(9)   | 104.0(6)  |
| O(2)-S(2)-C(3)     | 105.5(3) | O(11)-S(6)-C(9)   | 105.9(6)  |
| O(2)-S(2)-C(4)     | 105.8(4) | O(12)-S(6)-C(9)   | 101.4(7)  |
| C(3)-S(2)-C(4)     | 96.3(5)  | S(6)-O(10)-Ag(3A) | 127.7(6)  |
| Ag(2)-O(2)-Ag(3)   | 98.1(2)  | Ag(1)-O(12)-S(6)  | 131.2(5)  |
| Ag(2)-O(2)-S(2)    | 115.9(3) | S(6)-C(9)-F(7)    | 108.2(10) |
| Ag(3)-O(2)-S(2)    | 130.7(4) | S(6)-C(9)-F(8)    | 113.3(11) |
| S(2)-C(3)-C(3A)    | 108.5(9) | F(7)-C(9)-F(8)    | 110.5(11) |
| S(3')-S(3)-O(3)    | 62.9(4)  | S(6)-C(9)-F(9)    | 110.5(8)  |
| S(3')-S(3)-C(5)    | 67.6(4)  | F(7)-C(9)-F(9)    | 103.3(13) |
| O(3)-S(3)-C(5)     | 109.2(4) | F(8)-C(9)-F(9)    | 110.6(14) |
| S(3')-S(3)-C(6)    | 67.3(5)  | O(13)-S(7)-O(14)  | 115.0(4)  |
| O(3)-S(3)-C(6)     | 106.0(5) | O(13)-S(7)-O(15)  | 115.7(5)  |
| C(5)-S(3)-C(6)     | 97.6(4)  | O(14)-S(7)-O(15)  | 111.6(4)  |
| Ag(3)-S(3')-S(3)   | 128.4(3) | O(13)-S(7)-C(10)  | 102.9(5)  |
| Ag(3)-S(3')-O(3)   | 71.4(3)  | O(14)-S(7)-C(10)  | 105.9(5)  |
| S(3)-S(3')-O(3)    | 63.0(4)  | O(15)-S(7)-C(10)  | 104.0(4)  |

**Table 39** (cont.)

|                  |          |                    |           |
|------------------|----------|--------------------|-----------|
| Ag(3)-S(3')-C(5) | 155.2(4) | S(7)-O(13)-Ag(4A)  | 125.6(3)  |
| S(3)-S(3')-C(5)  | 67.7(4)  | Ag(4)-O(14)-S(7)   | 109.8(4)  |
| O(3)-S(3')-C(5)  | 109.3(6) | Ag(4)-O(14)-Ag(3B) | 108.7(2)  |
| Ag(3)-S(3')-C(6) | 106.1(5) | S(7)-O(14)-Ag(3B)  | 130.8(5)  |
| S(3)-S(3')-C(6)  | 67.3(5)  | Ag(3)-O(15)-S(7)   | 123.3(3)  |
| O(3)-S(3')-C(6)  | 106.0(5) | S(7)-C(10)-F(10)   | 109.8(8)  |
| C(5)-S(3')-C(6)  | 97.6(6)  | S(7)-C(10)-F(11)   | 110.3(7)  |
| Ag(4)-O(3)-S(3)  | 135.5(4) | F(10)-C(10)-F(11)  | 109.1(8)  |
| Ag(4)-O(3)-S(3') | 132.6(4) | S(7)-C(10)-F(12)   | 110.6(6)  |
| S(3)-O(3)-S(3')  | 54.1(4)  | F(10)-C(10)-F(12)  | 108.9(9)  |
| S(3)-C(5)-S(3')  | 44.7(3)  | F(11)-C(10)-F(12)  | 108.0(10) |

**Table 40.** Anisotropic displacement coefficients for **34**.

| Atom  | $U_{xx}$ | $U_{yy}$ | $U_{zz}$ | $U_{xy}$ | $U_{xz}$ | $U_{yz}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 51(1)    | 85(1)    | 76(1)    | 22(1)    | 13(1)    | 47(1)    |
| Ag(2) | 69(1)    | 43(1)    | 35(1)    | 26(1)    | 9(1)     | 18(1)    |
| Ag(3) | 79(1)    | 45(1)    | 39(1)    | 7(1)     | 20(1)    | 5(1)     |
| Ag(4) | 54(1)    | 43(1)    | 38(1)    | 17(1)    | 13(1)    | 12(1)    |
| S(1)  | 44(1)    | 32(1)    | 30(1)    | 12(1)    | 13(1)    | 12(1)    |
| O(1)  | 49(4)    | 41(3)    | 42(3)    | 20(3)    | 17(3)    | 20(3)    |
| C(1)  | 45(5)    | 45(5)    | 36(5)    | 17(5)    | 13(4)    | 25(4)    |
| C(2)  | 36(5)    | 42(5)    | 53(6)    | 10(4)    | 9(5)     | 13(5)    |
| S(2)  | 55(1)    | 37(1)    | 26(1)    | 23(1)    | 12(1)    | 11(1)    |
| O(2)  | 57(4)    | 38(3)    | 24(3)    | 20(3)    | 6(3)     | 11(3)    |
| C(3)  | 60(6)    | 47(6)    | 54(6)    | 35(5)    | 30(5)    | 31(5)    |

Table 40 (cont.)

|       |        |        |         |        |       |       |
|-------|--------|--------|---------|--------|-------|-------|
| C(4)  | 42(6)  | 54(6)  | 60(6)   | 16(5)  | 10(5) | 20(5) |
| S(3)  | 43(2)  | 47(2)  | 46(2)   | 10(1)  | 12(1) | 19(1) |
| O(3)  | 43(4)  | 80(5)  | 43(4)   | 5(4)   | 16(3) | 17(4) |
| C(5)  | 50(6)  | 71(7)  | 55(6)   | 1(6)   | 5(5)  | 26(6) |
| C(6)  | 69(8)  | 93(8)  | 50(6)   | 25(7)  | 31(6) | 34(6) |
| S(4)  | 31(1)  | 42(1)  | 44(1)   | 16(1)  | 11(1) | 16(1) |
| O(4)  | 44(4)  | 57(5)  | 101(6)  | 15(4)  | 0(4)  | -8(4) |
| O(5)  | 45(4)  | 66(5)  | 110(6)  | 20(4)  | 11(4) | 53(5) |
| O(6)  | 80(6)  | 122(7) | 49(4)   | 57(5)  | 25(4) | 36(4) |
| C(7)  | 39(7)  | 77(9)  | 79(9)   | 19(7)  | 18(6) | 12(7) |
| S(5)  | 48(1)  | 48(1)  | 28(1)   | 13(1)  | 12(1) | 7(1)  |
| O(7)  | 74(5)  | 120(7) | 46(4)   | 63(5)  | 5(4)  | 10(4) |
| O(8)  | 114(7) | 55(5)  | 55(5)   | -11(5) | 30(5) | 8(4)  |
| O(9)  | 72(5)  | 70(5)  | 37(4)   | 35(4)  | 25(3) | 23(3) |
| C(8)  | 55(7)  | 67(7)  | 35(6)   | 25(6)  | 6(5)  | 5(5)  |
| S(6)  | 48(2)  | 38(1)  | 44(1)   | 9(1)   | 12(1) | 10(1) |
| O(10) | 103(7) | 40(4)  | 166(9)  | 11(5)  | 76(7) | 12(5) |
| O(11) | 111(6) | 74(5)  | 49(4)   | 42(5)  | 37(4) | 22(4) |
| O(12) | 89(6)  | 168(9) | 59(5)   | 81(6)  | 25(5) | 54(6) |
| C(9)  | 62(8)  | 78(9)  | 109(11) | 38(8)  | 24(8) | 42(8) |
| S(7)  | 38(1)  | 32(1)  | 36(1)   | 5(1)   | 11(1) | 8(1)  |
| O(13) | 58(4)  | 40(4)  | 86(5)   | 22(3)  | 21(4) | 18(4) |
| O(14) | 53(4)  | 61(4)  | 37(4)   | 2(4)   | 3(3)  | 6(3)  |
| O(15) | 58(4)  | 48(4)  | 44(4)   | 13(3)  | 27(3) | 14(3) |
| C(10) | 42(6)  | 46(6)  | 58(7)   | 1(5)   | 11(5) | 13(5) |
| F(1)  | 54(4)  | 92(5)  | 165(8)  | 43(4)  | 9(5)  | 37(5) |

**Table 40** (cont.)

|       |        |         |         |        |        |        |
|-------|--------|---------|---------|--------|--------|--------|
| F(2)  | 81(6)  | 240(11) | 140(8)  | 57(7)  | 71(6)  | 62(8)  |
| F(3)  | 45(4)  | 62(5)   | 217(10) | -1(4)  | -10(5) | 19(6)  |
| F(4)  | 95(6)  | 187(8)  | 80(5)   | 107(6) | 6(4)   | 18(5)  |
| F(5)  | 85(4)  | 102(5)  | 32(3)   | 38(4)  | 20(3)  | 19(3)  |
| F(6)  | 81(5)  | 74(5)   | 87(5)   | -9(4)  | 19(4)  | 9(4)   |
| F(7)  | 108(7) | 203(10) | 170(10) | 87(7)  | -36(6) | 44(8)  |
| F(8)  | 89(7)  | 71(6)   | 303(15) | -21(5) | 69(8)  | -31(7) |
| F(9)  | 92(6)  | 185(9)  | 160(8)  | 67(6)  | 87(6)  | 67(7)  |
| F(10) | 101(6) | 105(6)  | 59(4)   | -16(5) | -33(4) | 18(4)  |
| F(11) | 76(5)  | 42(4)   | 117(6)  | 11(3)  | 16(4)  | 19(4)  |
| F(12) | 55(4)  | 83(5)   | 111(6)  | 6(4)   | 36(4)  | 37(4)  |

**Table 41.** H-atom coordinates ( $\times 10^4$ ) and isotropic displacement coefficients for **34**.

| Atom  | x/a   | y/b  | z/c  | $U_{eq}$ |
|-------|-------|------|------|----------|
| H(1A) | 21    | 514  | 4251 | 140(14)  |
| H(1B) | 1399  | 1702 | 4932 | 140(14)  |
| H(2A) | 3095  | 1490 | 3706 | 140(14)  |
| H(2B) | 2959  | 5012 | -372 | 140(14)  |
| H(2C) | 3018  | 4997 | 231  | 140(14)  |
| H(3A) | -231  | 2623 | -111 | 140(14)  |
| H(3B) | -1347 | 3511 | 1093 | 140(14)  |
| H(4A) | -2827 | 2206 | 838  | 140(14)  |
| H(4B) | -2251 | 5811 | 4550 | 140(14)  |
| H(4C) | -2237 | 5232 | 4261 | 140(14)  |
| H(5A) | 4708  | 3969 | 1747 | 140(14)  |

**Table 41 (cont.)**

|       |      |         |      |         |
|-------|------|---------|------|---------|
| H(5B) | 5747 | 5251    | 2579 | 140(14) |
| H(6A) | 4026 | 4526    | 2002 | 140(14) |
| H(6B) | 4423 | 140(14) |      | 140(14) |
| H(6C) | 2945 |         |      |         |

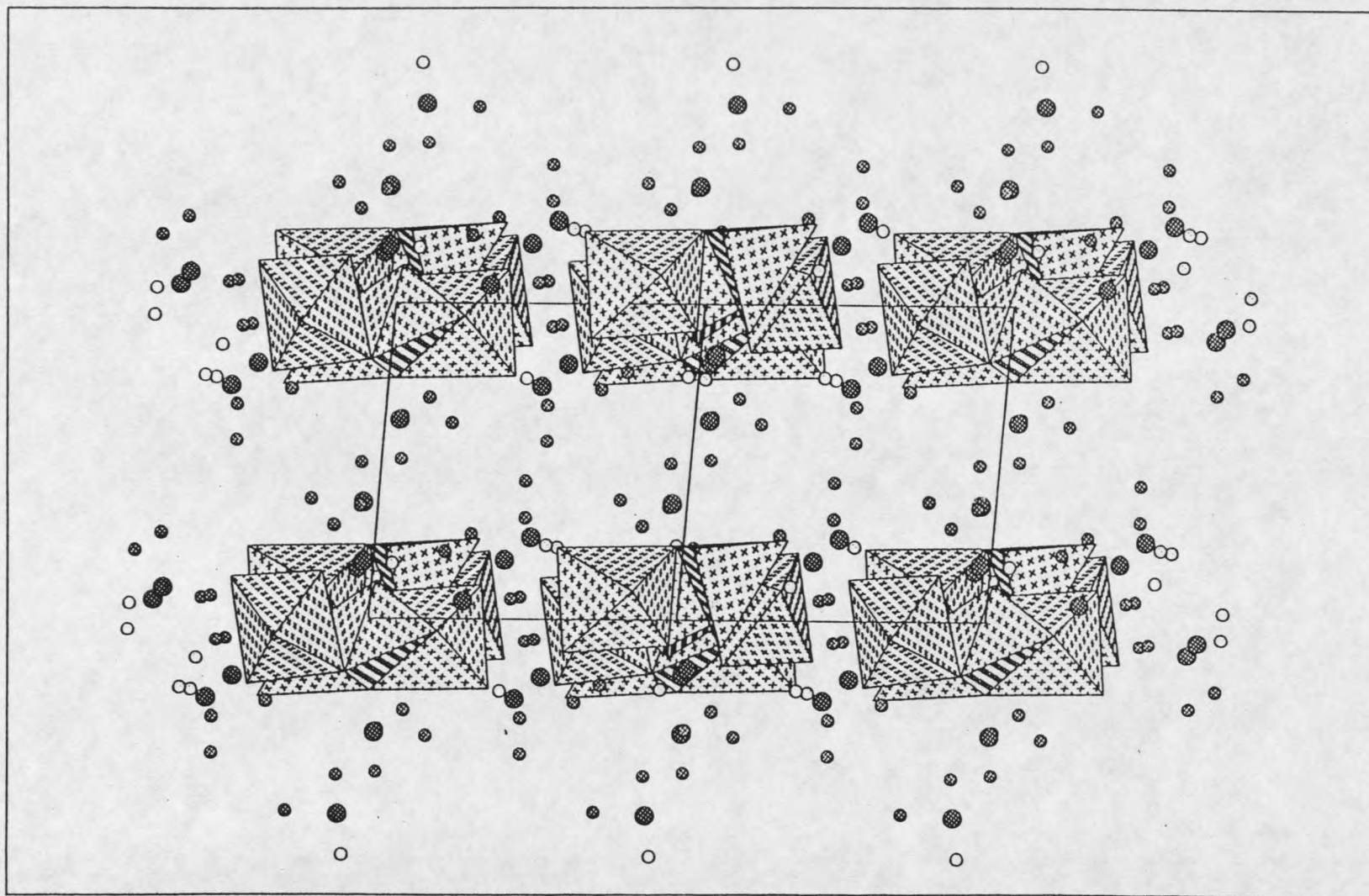


Figure 67. Polyhedron diagram for 34.

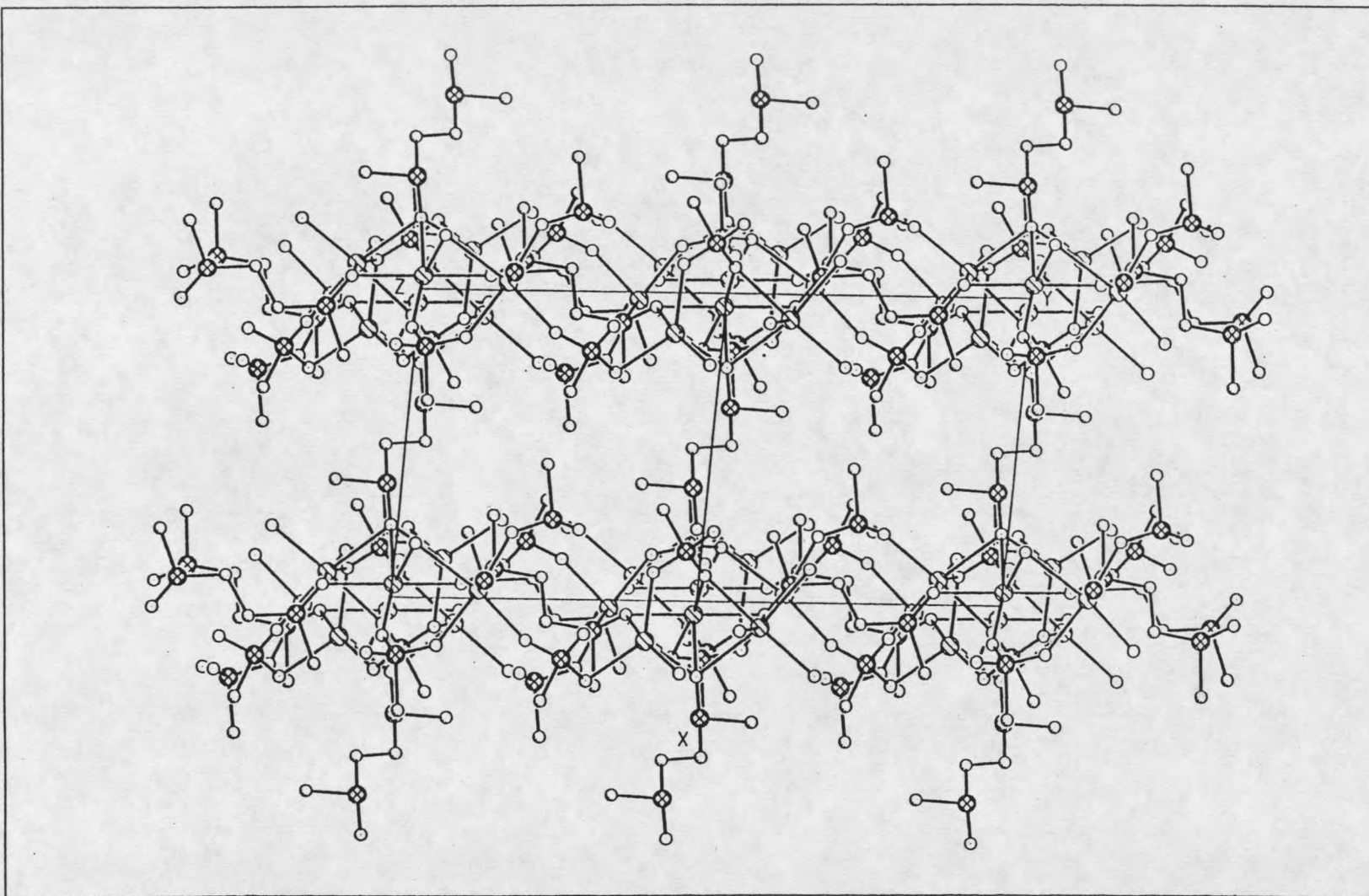


Figure 68. Packing diagram for 34.

### Oxidation of Sulfoxide Complexes

Preliminary experiments involving oxidation of Pt(sulfoxide) monomer and dimer complexes proved rather disappointing. In general, oxidation of the di- $\mu$ -hydroxo bridged complexes produced a mixture of products, most likely including various Pt(II) halide substitution products when  $\text{Cl}_2$  or  $\text{Br}_2$  were used as oxidants. When two equivalents of  $\text{Br}_2$  is added to an aqueous solution of **2** as the tetrafluoroborate salt, a large quantity of orange-brown precipitate forms almost immediately. When this solution is filtered,  $^{195}\text{Pt}$  NMR of the filtrate reveals no fewer than nine peaks of varying intensity, ranging from +779 ppm to -2556 ppm. The two peaks downfield of 0 ppm are almost certainly Pt(IV) species but were not positively identified. The fact that most of the upfield peaks occur  $\sim 325$  ppm down field of **2** suggests that the DMSO ligands are no longer coordinated to platinum, at least not through the sulfur atom, and that a variety of Br and  $\text{H}_2\text{O}$  substitution products have been formed. These filtrate solutions slowly deposited more of the orange-brown precipitate on standing. This precipitate proved to be insoluble in water, suggesting some sort of polymeric material. When  $\text{Br}_2$  is stirred with a suspension of **22** in  $\text{CCl}_4$  at room temperature and the solid filtered off and dissolved in DMF,  $^{195}\text{Pt}$  NMR reveals only the unreacted dichloro complex (**22**) and the Br substitution product (**24**). These assignments are confirmed by the previously determined chemical shifts for these

complexes prepared by direct methods (Table 23). This line of experimentation was not actively pursued beyond these initial results.

### Mixed Valence Dimers

As stated in the introduction, formation of bridged dimeric structures containing both Pt(II) and Pt(IV) oxidation states is important for a couple of reasons. By having one substitutionally inert (Pt(IV)) and one substitutionally labile (Pt(II)) fragment in the same complex, it may be possible to selectively react the labile end with another bridge-forming complex to form a linear trimer or tetramer. More importantly however, is the possibility that a one electron transfer may occur between the Pt(II) and Pt(IV) centers, resulting in the formation of a Pt(III) metal-metal bonded dimer.

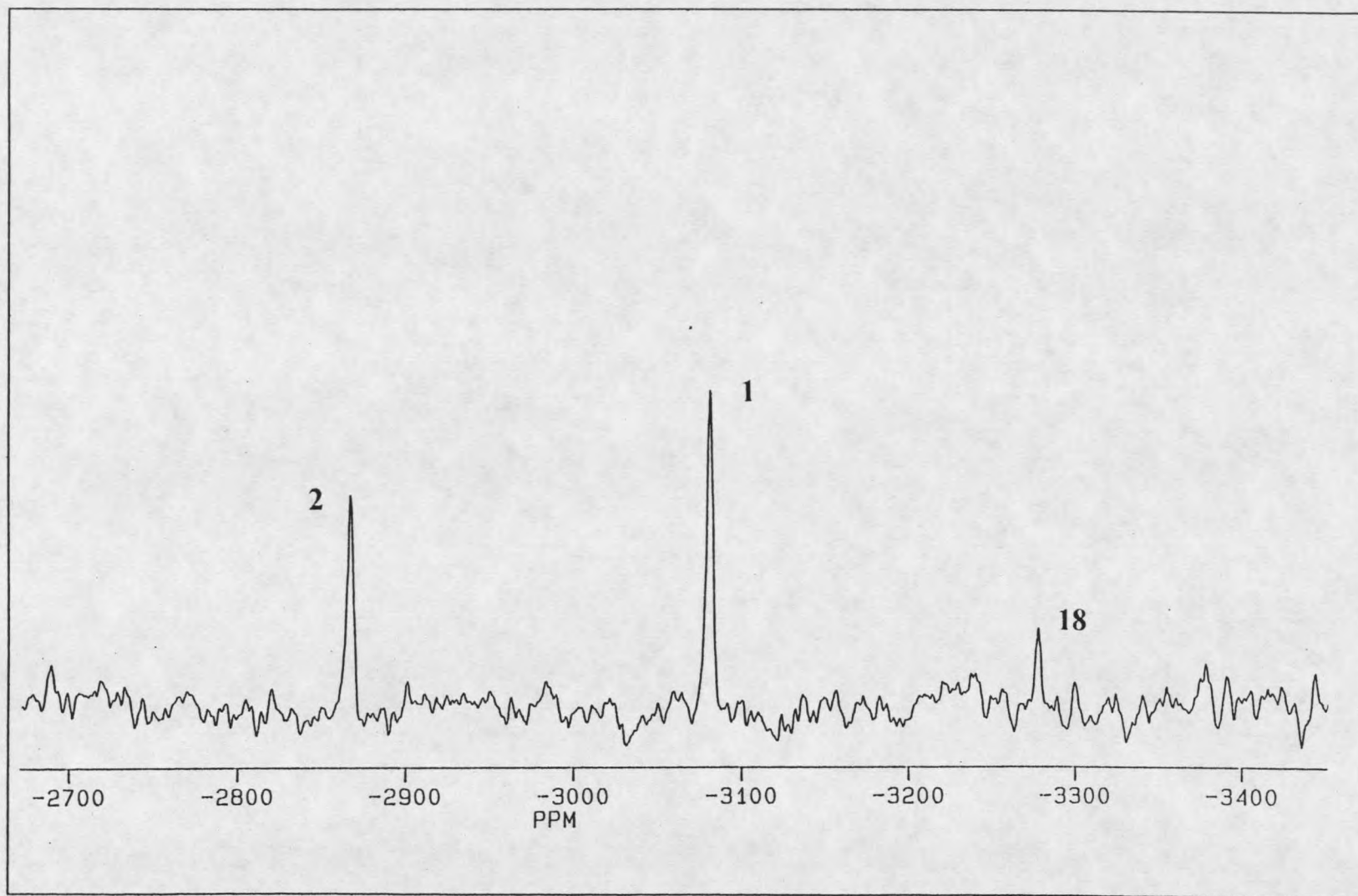
Formation of these mixed valence complexes can conceivably be accomplished in one of two ways; by the selective two electron oxidation of one of the Pt(II) fragments in a mixed ligand dimer or by direct bridge formation between Pt(II) and Pt(IV) complexes. For the direct bridge formation approach, *cis*-Pt(Ox)<sub>2</sub>(OH)<sub>2</sub> (**30**) was again chosen as the Pt(IV) fragment because the fairly rapid water exchange rate, mentioned earlier, at low pH. For the Pt(II) fragment, [Pt(DMSO)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (**1**) was chosen because of the apparently low value for K<sub>a1</sub>. It was hoped that H<sub>2</sub>O substitution would occur as shown in Figure 69. The resulting neutral complex should selectively crystallize, leaving the ionic starting material in solution.



**Figure 69.** Proposed method for formation of mixed valence platinum dimers.

$cis\text{-Pt}(\text{Ox})_2(\text{OH}_2)_2$  was prepared by the thermal isomerization of  $trans\text{-Pt}(\text{Ox})_2(\text{OH}_2)_2$  as described in the Experimental section. A roughly 1:1 mixture of *cis* and *trans* isomers was used for this reaction in order to observe the selective reaction of only the *cis* isomer with the  $\text{Pt}(\text{DMSO})_2$  complex. The *trans* isomer is not able to form a dibridged complex so should remain in solution. Figure 70 shows the  $^{195}\text{Pt}$  NMR spectrum of the reaction mixture. Once again, the  $\text{Pt}(\text{DMSO})_2$  region was monitored for the appearance of peaks which show the characteristic 1:4:1 splitting pattern indicative of mixed ligand dimer formation. The spectrum in Figure 70 shows only the peaks at -3081 and -2873 ppm, previously assigned to **1** and **2** respectively, plus an additional peak at -3277 ppm which had been tentatively assigned to  $\text{Pt}(\text{Ox})(\text{DMSO})_2$  (**18**). No sign of the desired mixed ligand dimer is seen. Upon slow evaporation of the solvent, crystals did form but after X-ray analysis were found to be the complex ion pair of  $[\text{Pt}(\text{Ox})_2(\text{OH})_2]^{2-} [\text{Pt}(\text{DMSO})_2(\mu\text{-OH})_2]^{2+} \cdot 3 \text{H}_2\text{O}$  (**35**). Figure

71 shows the ORTEP plot for this structure. This structure represents one of only a few containing both Pt(II) and Pt(IV) oxidation states. These complex ions exhibit virtually identical bond distances and angles with the previously determined structures of the individual complexes (12, 31). Crystallographic data are presented in Table 42.



**Figure 70.**  $^{195}\text{Pt}$  NMR for the reaction of **1** and *trans* **30**.

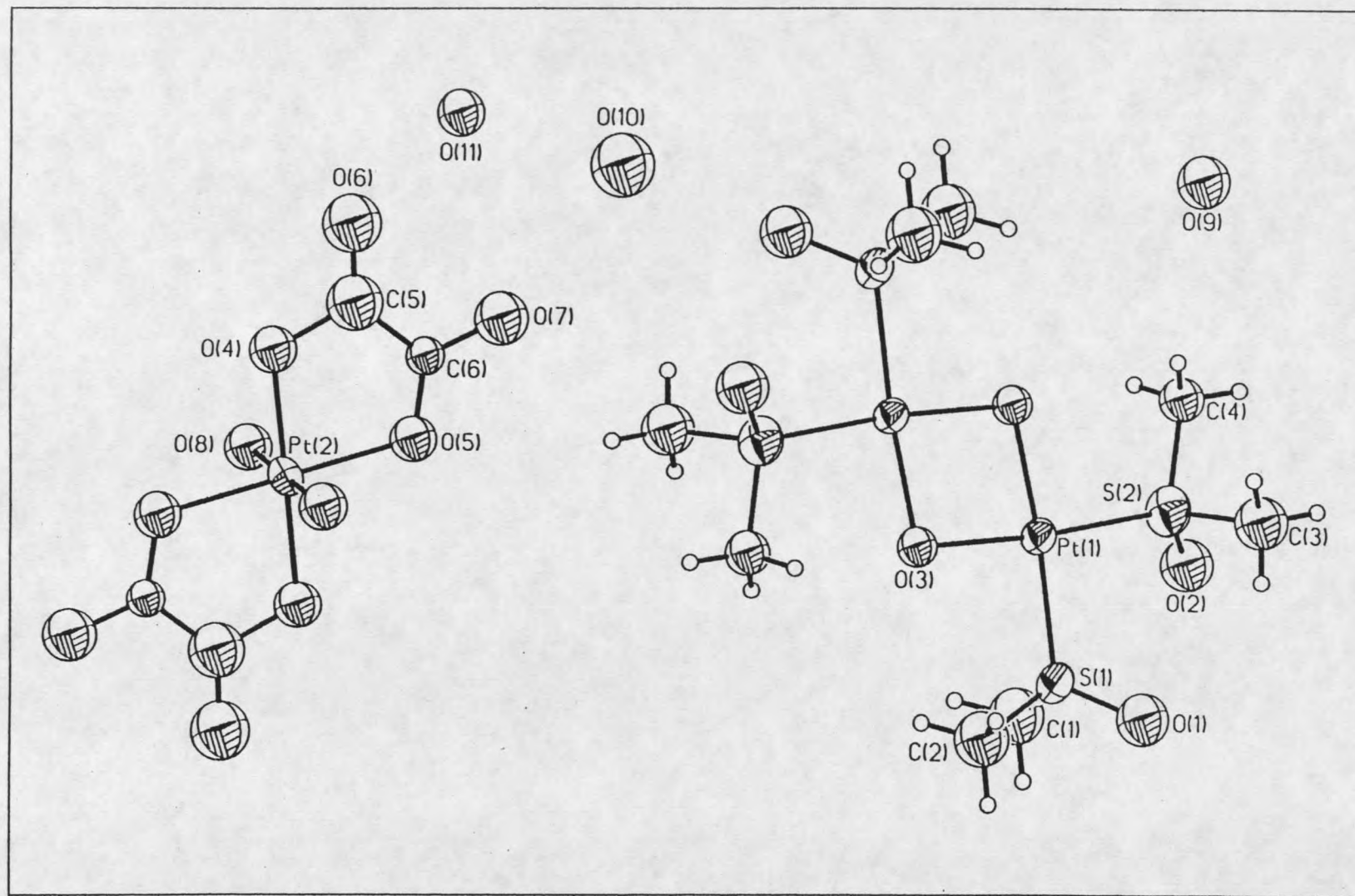


Figure 71. ORTEP plot of  $[\text{Pt}(\text{Ox})_2(\text{OH})_2]^{2-} [\text{Pt}(\text{DMSO})_2(\mu\text{-OH})]_2^{2+} \cdot 3 \text{H}_2\text{O}$ .

**Table 42.** Crystallographic data for **35**.

|                                  |                                                                  |                           |               |
|----------------------------------|------------------------------------------------------------------|---------------------------|---------------|
| Formula                          | C <sub>6</sub> H <sub>14</sub> O <sub>11</sub> S <sub>2</sub> Pt | Formula weight            | 521.37        |
| a (Å)                            | 9.168(2)                                                         | Space group               | Pbca          |
| b (Å)                            | 18.497(3)                                                        | Temperature °C            | 27            |
| c (Å)                            | 19.597(3)                                                        | $\lambda$ (Å)             | 0.7107        |
| $\alpha$ (°)                     | 90                                                               | $\rho$ calculated         | 1.937         |
| $\beta$ (°)                      | 90                                                               | $\mu$ (mm <sup>-1</sup> ) | 8.74          |
| $\gamma$ (°)                     | 90                                                               | Transmission factor range | 0.487 - 0.772 |
| Cell Volume (Å <sup>3</sup> )    | 3327.4(64)                                                       | F (000)                   | 1984          |
| Z                                | 8                                                                | Unique reflections        | 2915          |
| R <sub>w</sub> (F <sub>o</sub> ) | 0.0434                                                           | Observed reflections      | 819           |
| R (F <sub>o</sub> )              | 0.0479                                                           | Number of parameters      | 103           |
| Scan mode                        | $\theta / 2\theta$                                               | Goodness of fit           | 1.2451        |

**Table 43.** Atomic coordinates and equivalent isotropic displacement coefficients (x 10<sup>3</sup>) for **35**.

| Atom  | x/a       | y/b      | z/c      | U <sub>eq</sub> |
|-------|-----------|----------|----------|-----------------|
| Pt(1) | -13(5)    | 4383(1)  | 5544(1)  | 32(1)           |
| S(1)  | -794(13)  | 4305(6)  | 6614(5)  | 46(4)           |
| O(1)  | 81(50)    | 3905(12) | 7090(11) | 62(7)           |
| C(1)  | -2572(47) | 3945(21) | 6611(20) | 72(15)          |
| C(2)  | -1072(49) | 5170(20) | 6945(19) | 69(15)          |
| S(2)  | 743(13)   | 3250(5)  | 5561(6)  | 50(4)           |
| O(2)  | -240(41)  | 2734(12) | 5877(10) | 64(9)           |
| C(3)  | 2478(44)  | 3159(21) | 5961(19) | 64(13)          |
| C(4)  | 1141(45)  | 2923(19) | 4744(16) | 47(11)          |

**Table 43** (cont.)

|       |          |          |          |        |
|-------|----------|----------|----------|--------|
| O(3)  | -675(26) | 5425(11) | 5428(11) | 37(7)  |
| Pt(2) | 5000     | 5000     | 5000     | 39(1)  |
| O(4)  | 5985(33) | 5191(13) | 4105(12) | 51(8)  |
| O(5)  | 6218(30) | 4094(13) | 4975(13) | 50(8)  |
| C(5)  | 6950(56) | 4634(25) | 3940(24) | 72(15) |
| C(6)  | 6957(43) | 4051(21) | 4423(19) | 34(10) |
| O(6)  | 7564(38) | 4705(15) | 3397(15) | 78(10) |
| O(7)  | 7803(33) | 3520(15) | 4310(13) | 66(10) |
| O(8)  | 3376(31) | 4476(14) | 4523(14) | 52(8)  |
| O(9)  | 4435(28) | 3625(13) | 3488(12) | 63(9)  |
| O(10) | 4584(36) | 7516(14) | 7806(13) | 93(11) |
| O(11) | 2166(29) | 6727(12) | 7319(11) | 51(9)  |

**Table 44.** Bond lengths for **35**.

| Bond         | Length ( Å ) | Bond        | Length ( Å ) |
|--------------|--------------|-------------|--------------|
| Pt(1)-S(1)   | 2.220(10)    | Pt(2)-O(4)  | 2.004(25)    |
| Pt(1)-S(2)   | 2.207(10)    | Pt(2)-O(5)  | 2.014(25)    |
| Pt(1)-O(3)   | 2.033(21)    | Pt(2)-O(8)  | 2.008(28)    |
| Pt(1)-Pt(1A) | 3.123(2)     | Pt(2)-O(4A) | 2.004(25)    |
| Pt(1)-O(3A)  | 2.038(21)    | Pt(2)-O(5A) | 2.014(25)    |
| S(1)-O(1)    | 1.435(32)    | Pt(2)-O(8A) | 2.008(28)    |
| S(1)-C(1)    | 1.761(44)    | O(4)-C(5)   | 1.396(55)    |
| S(1)-C(2)    | 1.745(38)    | O(5)-C(6)   | 1.279(46)    |
| S(2)-O(2)    | 1.451(31)    | C(5)-C(6)   | 1.435(60)    |

**Table 44** (cont.)

|             |           |           |           |
|-------------|-----------|-----------|-----------|
| S(2)-C(3)   | 1.781(42) | C(5)-O(6) | 1.211(58) |
| S(2)-C(4)   | 1.751(34) | C(6)-O(7) | 1.272(48) |
| O(3)-Pt(1A) | 2.038(21) |           |           |

**Table 45.** Bond Angles for **35**.

| Atoms              | Angle (°) | Atoms             | Angle (°) |
|--------------------|-----------|-------------------|-----------|
| S(1)-Pt(1)-S(2)    | 91.4(4)   | O(4)-Pt(2)-O(5)   | 82.8(10)  |
| S(1)-Pt(1)-O(3)    | 94.1(7)   | O(4)-Pt(2)-O(8)   | 90.7(11)  |
| S(2)-Pt(1)-O(3)    | 174.4(7)  | O(5)-Pt(2)-O(8)   | 89.9(11)  |
| S(1)-Pt(1)-Pt(1A)  | 134.0(3)  | O(4)-Pt(2)-O(4A)  | 180.0(1)  |
| S(2)-Pt(1)-Pt(1A)  | 134.6(3)  | O(5)-Pt(2)-O(4A)  | 97.2(10)  |
| O(3)-Pt(1)-Pt(1A)  | 40.0(6)   | O(8)-Pt(2)-O(4A)  | 89.3(11)  |
| S(1)-Pt(1)-O(3A)   | 173.7(7)  | O(4)-Pt(2)-O(5A)  | 97.2(10)  |
| S(2)-Pt(1)-O(3A)   | 94.7(7)   | O(5)-Pt(2)-O(5A)  | 180.0(1)  |
| O(3)-Pt(1)-O(3A)   | 79.8(9)   | O(8)-Pt(2)-O(5A)  | 90.1(11)  |
| Pt(1A)-Pt(1)-O(3A) | 39.9(6)   | O(4A)-Pt(2)-O(5A) | 82.8(10)  |
| Pt(1)-S(1)-O(1)    | 117.9(15) | O(4)-Pt(2)-O(8A)  | 89.3(11)  |
| Pt(1)-S(1)-C(1)    | 108.6(13) | O(5)-Pt(2)-O(8A)  | 90.1(11)  |
| O(1)-S(1)-C(1)     | 109.0(21) | O(8)-Pt(2)-O(8A)  | 180.0(1)  |
| Pt(1)-S(1)-C(2)    | 109.8(14) | O(4A)-Pt(2)-O(8A) | 90.7(11)  |
| O(1)-S(1)-C(2)     | 108.2(17) | O(5A)-Pt(2)-O(8A) | 89.9(11)  |
| C(1)-S(1)-C(2)     | 102.3(20) | Pt(2)-O(4)-C(5)   | 111.0(24) |
| Pt(1)-S(2)-O(2)    | 115.8(13) | Pt(2)-O(5)-C(6)   | 111.5(23) |
| Pt(1)-S(2)-C(3)    | 112.1(14) | O(4)-C(5)-C(6)    | 113.9(38) |

**Table 45** (cont.)

|                   |           |                |           |
|-------------------|-----------|----------------|-----------|
| O(2)-S(2)-C(3)    | 107.8(18) | O(4)-C(5)-O(6) | 114.7(38) |
| Pt(1)-S(2)-C(4)   | 112.3(12) | C(6)-C(5)-O(6) | 131.2(43) |
| O(2)-S(2)-C(4)    | 107.0(16) | O(5)-C(6)-C(5) | 120.6(36) |
| C(3)-S(2)-C(4)    | 100.5(19) | O(5)-C(6)-O(7) | 121.3(34) |
| Pt(1)-O(3)-Pt(1A) | 100.2(9)  | C(5)-C(6)-O(7) | 117.9(36) |

**Table 46.** H-atom coordinates ( $\times 10^4$ ) and isotropic displacement coefficients ( $\times 10^2$ ) for **35**.

|       |       |      |      |        |
|-------|-------|------|------|--------|
| H(1A) | -2933 | 3906 | 7069 | 80(36) |
| H(1B) | -3211 | 4248 | 6349 | 80(36) |
| H(1C) | -2529 | 3473 | 6407 | 80(36) |
| H(2A) | -1415 | 5144 | 7408 | 80(36) |
| H(2B) | -156  | 5420 | 6933 | 80(36) |
| H(2C) | -1772 | 5424 | 6671 | 80(36) |
| H(3A) | 2783  | 2663 | 5963 | 80(36) |
| H(3B) | 3171  | 3444 | 5711 | 80(36) |
| H(3C) | 2418  | 3333 | 6421 | 80(36) |
| H(4A) | 1472  | 2431 | 4767 | 80(36) |
| H(4B) | 273   | 2948 | 4471 | 80(36) |
| H(4C) | 1887  | 3218 | 4542 | 80(36) |

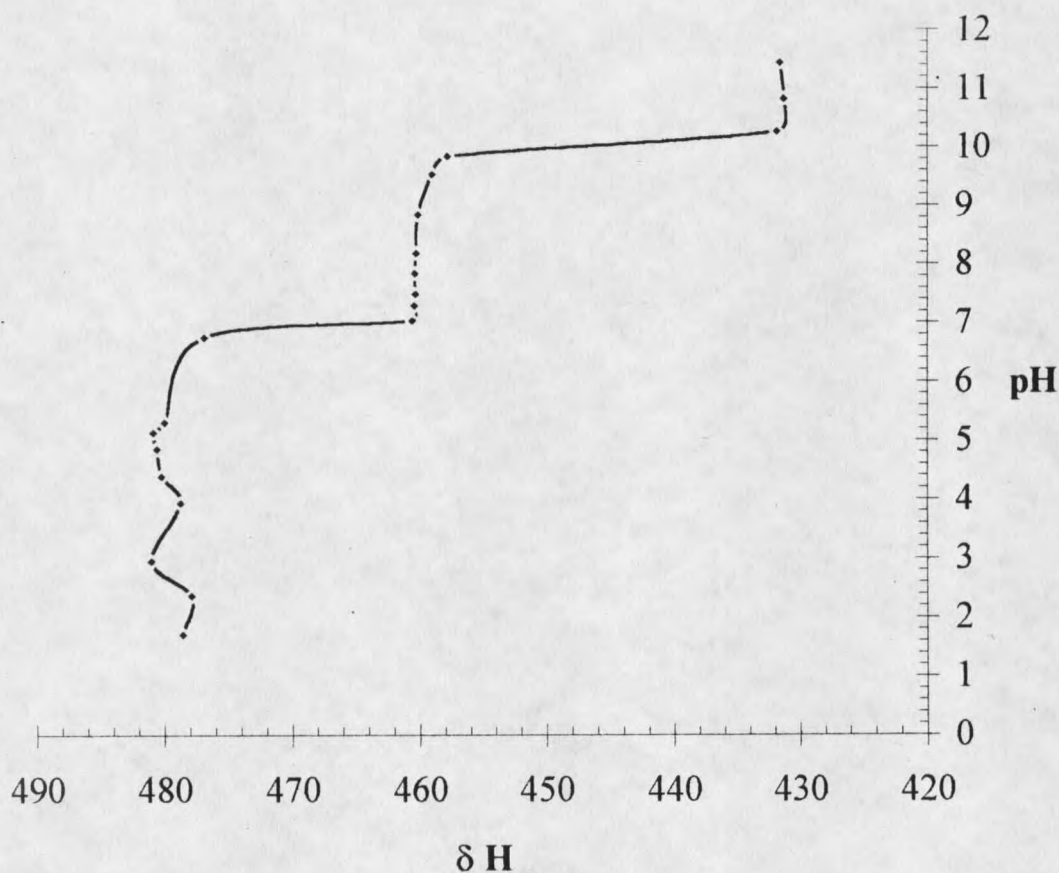
### Platinum (II) Complexes With Phosphane Ligands

The next series of experiments represents a major departure from the previous course of investigation, specifically in the choice of ancillary ligands coordinated to platinum. Due to the labile nature of the *cis*-bis sulfoxide complexes and the formation of insoluble polymeric species using bidentate sulfoxides, we turned our attention to a new class of water soluble trialkyl phosphane complexes. These phosphane complexes turned out to have several advantages over the sulfoxide systems described above, not the least of which was the presence of the spin 1/2 NMR active  $^{31}\text{P}$  nucleus. The presence of  $^{31}\text{P}$  coupled directly to platinum provided an additional probe of structure and allowed species to be characterized on the basis of their phosphorus NMR spectrum. This resulted in an enormous increase in sensitivity and allowed for a much broader range of solution concentrations to be used.

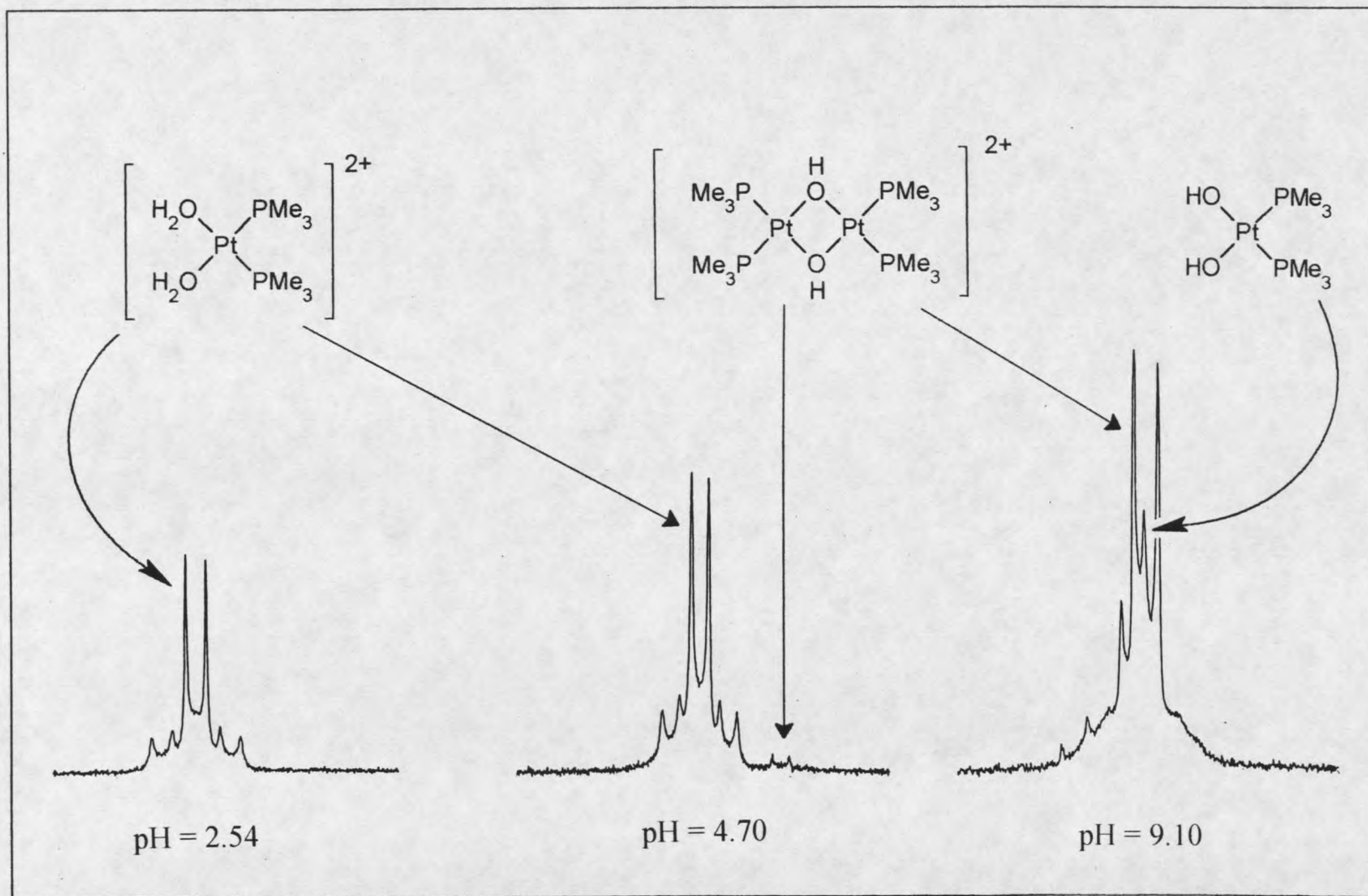
Water soluble metal-phosphane complexes have only very recently been investigated (90, 123, 124). Following a method developed for a new preparation of diammine platinum complexes, using anion-exchange resins to quantitatively form the *cis*-bis dihydroxo species, a series of bis phosphane complexes which show behavior similar with the *S* and *N* donor complexes discussed above have been synthesized (123). In particular, di- $\mu$ -hydroxo bridged dimeric species are formed upon hydrolysis of the dichloro species (125). These dimers exhibit the same pH dependent behavior as the analogous sulfoxide species and appear to have the same propensity to polymerize

in acidic solution. At this time, no values have been reported for the  $K_a$ 's of the coordinated waters in the diaqua species, either by potentiometric or spectroscopic methods. The same complications which cast doubts on the reliability of potentiometric data in the sulfoxide and ammine cases are also expected to be present with the phosphane system although initial investigations into extremely dilute solutions have so far revealed no tendency for ligand dissociation. NMR titrations were therefore performed on the monomeric di-aqua complexes in an attempt to determine one or both  $K_a$ 's. Figure 72 shows a plot of  $^1\text{H}$  chemical shift vs pH for  $[\text{Pt}(\text{PMe}_3)_2(\text{OH}_2)_2]^{2+}$  (36). Of the three NMR active nuclei in these complexes, the signal from the methyl protons on phosphorus proved to be the most sensitive to changes in pH even though these protons are four bonds removed from the oxygen atoms undergoing protonation or deprotonation. Figure 73 shows three of the  $^1\text{H}$  NMR spectra used to generate the titration curve shown in Figure 72. These solutions were prepared by dilution, with  $\text{D}_2\text{O}$ , of a stock solution containing an equilibrium mixture of the monomer (36) and dimer (37). In any equilibrium of this type, dilution always results in a shift toward increased monomer concentration. Dilution was continued until it was possible to observe the monomer resonance over the entire pH range of the titration. The total platinum concentration of the resulting solution was  $\sim 4.6 \times 10^{-4}$  M. This solution was then divided into twenty separate aliquots and the pH of each adjusted with microliter quantities of  $\text{CF}_3\text{SO}_3\text{D}$  (low pH) or  $\text{NaOD}$  (high pH).  $\sim 0.6$  ml of each aliquot was then transferred to an NMR tube and the proton

spectrum recorded. The pH electrode was kept immersed in the remaining solution during the NMR run and the pH recorded again afterwards (~ 10-15 minutes). In general, the pH changed very little, with the largest change (~ 0.2 units) occurring near the "inflection points" around pH 6.5 and 9.6.



**Figure 72.**  $^1\text{H}$  NMR titration of  $[\text{Pt}(\text{PMe}_3)_2(\text{OH}_2)_2]^{2+}$ .

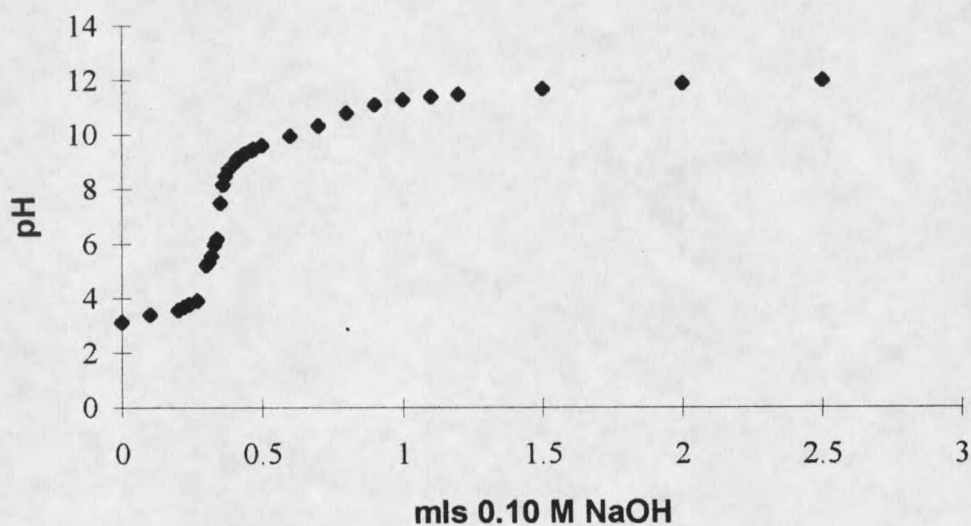


**Figure 73.**  $^1\text{H}$  NMR spectra for the titration of  $[\text{Pt}(\text{PMe}_3)_2(\text{OH}_2)_2]^{2+}$ . (Intensity scaling varies)

Although proton exchange between the diaqua, aqua-hydroxo, and dihydroxo monomers is expected to be fast on the NMR time scale throughout the pH range of the titration, the abrupt changes in chemical shift suggests otherwise. At high pH ( $\sim 9.1$ ), three distinct resonances are visible corresponding to dimer, dihydroxo monomer and presumably to the aqua-hydroxo monomer. The monomer peaks observed in the titration can be identified by the well resolved satellites flanking the central pair of resonances. For the dimer, these are broadened out into shoulders, presumably due to coupling to a second  $^{195}\text{Pt}$  nucleus or to slower tumbling in solution.  $^{31}\text{P}$  NMR confirms the assignments of the diaqua and dihydroxo monomers as well as the dimer based on published values of chemical shift and coupling constants for these species. With increasing pH, the monomer resonance shifts upfield, eventually passing through the dimer peaks and finally emerging upfield as the di-hydroxo monomer.

If the two abrupt changes in chemical shift, at 6.5 and 9.6, correspond to the pH at which the acid and conjugate base are present in roughly equal quantities, then they represent the  $\text{pK}_a$ 's according to the Henderson-Hasselbach approximation. If these  $\text{pK}_a$ 's are compared with those in Table 3 for nitrogen donor complexes, the higher values are consistent with the higher *trans*-influence of phosphorus compared with nitrogen, according to the theory of Appleton et al discussed previously (59). Comparison of the sum of the two  $\text{pK}_a$ 's with the sum of  $\text{pK}_f$  and  $\text{pK}_d$  is discussed in the final section dealing with thermodynamic aspects of dimer formation.

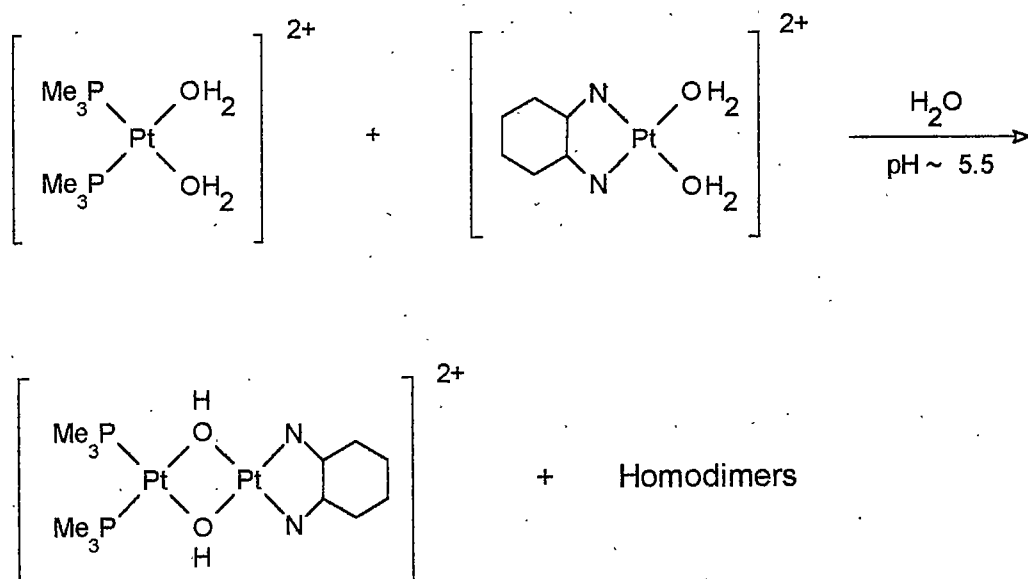
Potentiometric titrations of more concentrated solutions (Figure 74) yielded results qualitatively similar to the sulfoxide system described previously. As in that case, the presence of only one apparent endpoint in these titrations strongly suggests interference due to rapid dimer formation during the course of the titration.



**Figure 74.** Potentiometric titration of  $[\text{Pt}(\text{PMe}_3)_2(\text{OH}_2)_2]^{2+}$ .

# Formation of Pt(II)-Phosphane Mixed Ligand Dimers

Reaction of  $cis\text{-Pt}(\text{PMe}_3)_2(\text{OH}_2)_2$  (36) and  $cis\text{-Pt}(\text{L})_2(\text{OH}_2)_2$ . Mixed ligand dimers were formed with a variety of ligands (L) incorporating the  $\text{Pt}(\text{PMe}_3)_2$  fragment. A typical procedure is given for  $\text{L} = (\pm)\text{-trans-1,2-diaminocyclohexane}$  (*trans-dach*) as shown in Figure 75.



**Figure 75.** Reaction scheme for the formation of  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})\text{Pt}(\text{trans-dach})]^{2+}$  (39).

To a suspension of 0.1000 g (0.239 mmol)  $\text{Pt}(\text{PMe}_3)_2\text{Cl}_2$  (38) in 5 ml  $\text{H}_2\text{O}$  was added 0.0796 g (0.469 mmol)  $\text{AgNO}_3$  as a solid. A white precipitate of  $\text{AgCl}$  began to

form almost immediately. The solution was covered to exclude light and allowed to stir at room temperature for 24 hours. *Cis*-Pt(*trans*-dach)<sub>2</sub>Cl<sub>2</sub> (**38**) (0.0909 g, 0.239 mmol) was added to 10 ml of a solution of H<sub>2</sub>O / EtOH (2:1). AgNO<sub>3</sub> (0.469 mmol) was added as a solid. The initially yellow solution slowly turned white over the course of several hours, but no precipitate other than AgCl was observed to form. This solution was also covered and allowed to stir for 24 hrs. These solutions were then filtered through glass wool and centrifuged to remove precipitated AgCl. The solution of *Cis*-[Pt(*trans*-dach)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (**40**) was rotovaped to ~ 2 ml and 0.5 ml D<sub>2</sub>O added as an NMR lock signal. The pH of the solution was measured (2.14) and the <sup>195</sup>Pt NMR spectrum recorded to verify the presence of the diaqua complex at -1869 ppm. <sup>31</sup>P NMR was used to verify the presence of the *cis*-diaqua phosphane complex (**36**) at -23.3 ppm shown in Figure 76.

The two solutions were then combined and rotovaped to ~ 5 ml. The pH was adjusted with 3 M KOH to ~ 5.5 and the <sup>31</sup>P and <sup>195</sup>Pt NMR spectra run simultaneously. The total time between mixing the solutions and acquiring spectra was about 1 hour. Figure 77 shows the <sup>31</sup>P spectrum of the reaction mixture. Two main resonances are seen, each symmetrically flanked by Pt satellites. The less intense of the two peaks at -26.3 ppm shows a <sup>1</sup>J<sub>P-Pt</sub> of 3407 Hz and is therefore assigned to the Pt(PMe<sub>3</sub>)<sub>2</sub> homodimer (**37**) based on the known coupling constant for this complex (123).

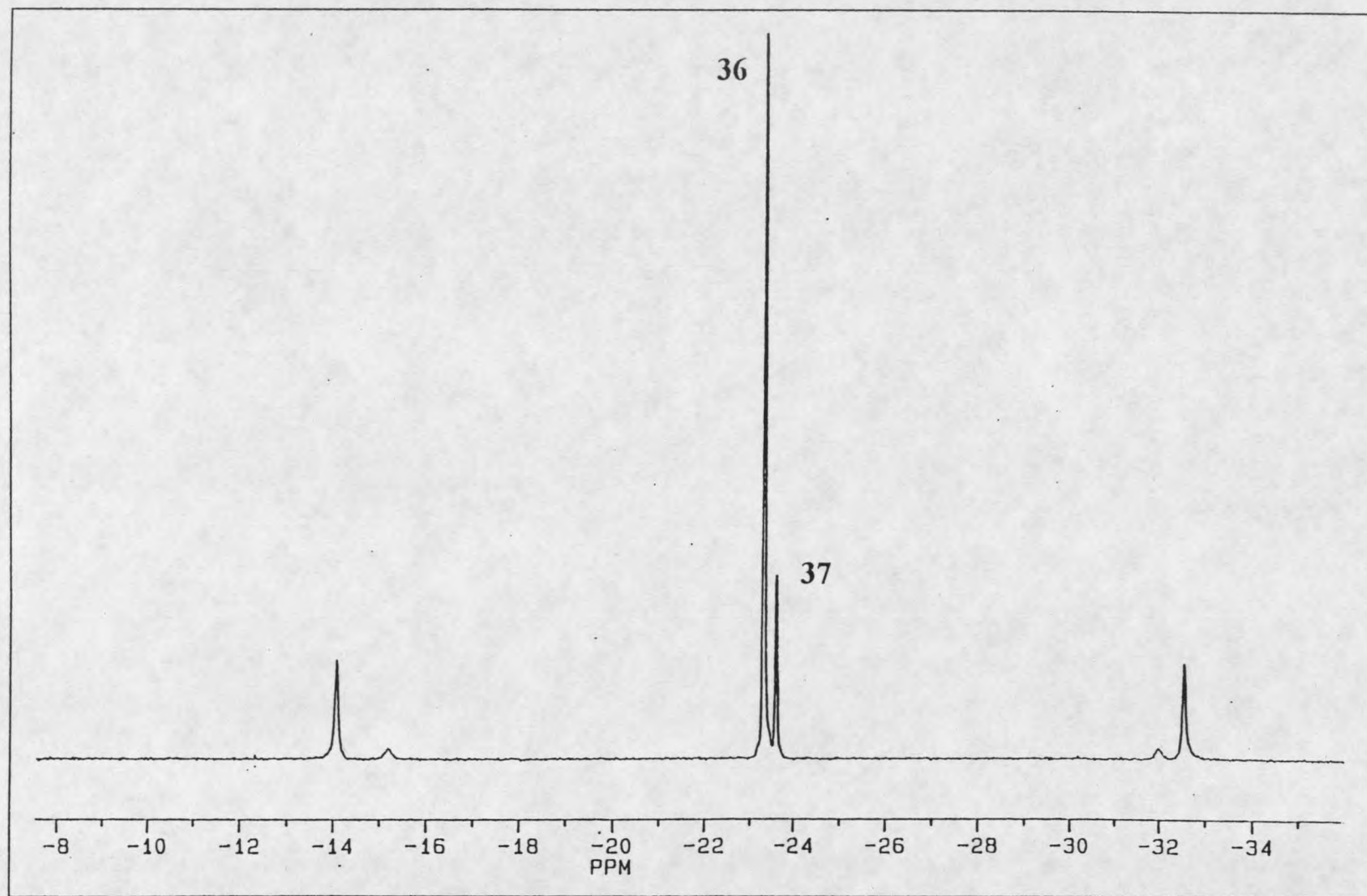


Figure 76.  $^{31}\text{P}$  NMR for the silver assisted hydrolysis of  $\text{Pt}(\text{PMe}_3)_2\text{Cl}_2$ ; pH=1.51.

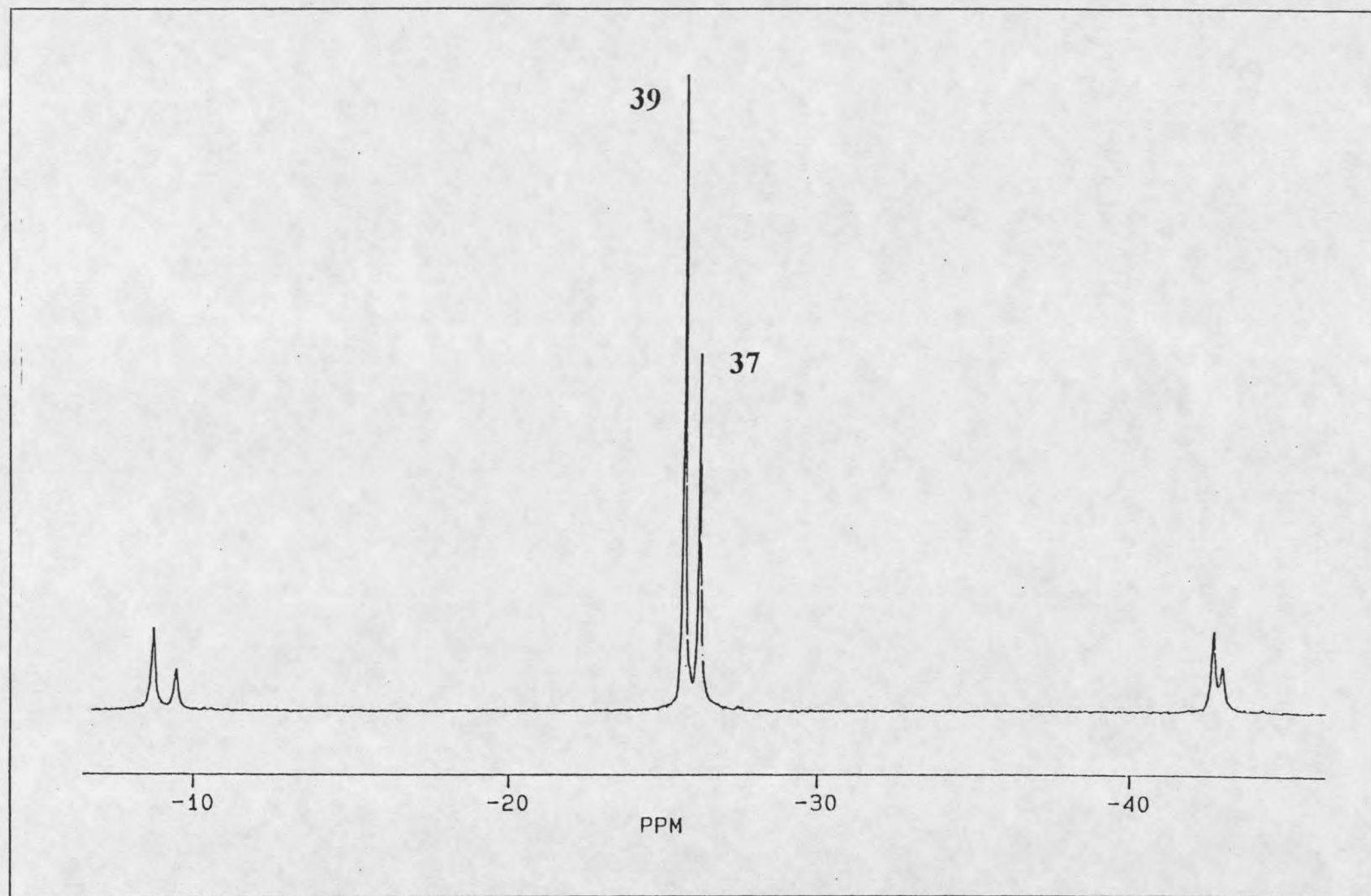


Figure 77.  $^{31}\text{P}$  NMR of the reaction product of **37** and  $[\text{Pt}(\text{trans-dach})(\mu\text{-OH})_2]_2^{2+}$  (**41**); pH=5.5.

The more intense peak at -25.8 ppm shows a  $^1J_{\text{P-Pt}}$  of 3440 Hz, substantially different than either the dimer or monomer yet close enough to both to indicate the same basic connectivity i.e. phosphorus *trans* to oxygen. This peak is therefore assigned to the heterodimeric structure, **39**. Support for this assignment comes from the analysis of the  $^{195}\text{Pt}$  NMR spectrum shown in Figure 78. The peak at -3918 has previously been assigned to the phosphane homodimer (**37**). The value of the platinum-phosphorus coupling constant matches that in the corresponding  $^{31}\text{P}$  spectrum. The new, more intense peak at -3922 ppm shows a  $^1J_{\text{P-Pt}}$  of 3440 Hz and therefore corresponds to the  $\text{Pt}(\text{Me}_3)_2$  fragment of the heterodimeric complex (**39**). Confirmation that this fragment is part of a dimeric structure comes from the presence of platinum satellites on each member of the triplet splitting pattern. Only one of these satellite peaks is visible, the downfield one of each pair being obscured by the resonance from the phosphane homodimer (**37**). The  $^2J_{\text{Pt-Pt}}$  coupling constant of 211 Hz agrees well with that taken from the  $^{31}\text{P}$  spectrum of the phosphane homodimer (Figure 79). Inspection of the  $\text{Pt}(\text{trans-dach})$  fragment region of the  $^{195}\text{Pt}$  spectrum reveals only a group of broad peaks some 2000 ppm downfield which have been previously assigned to the homodimer. This broadening, caused by one bond coupling to  $^{14}\text{N}$ , precludes the observation of Pt satellites in this region. Assuming an equimolar concentration of the two diaqua complexes, a 1:2:1 ratio of homodimer to heterodimer would be expected on purely statistical grounds. The qualitative appearance of the singlet resonances in the  $^{31}\text{P}$  spectrum appears to support this ratio.

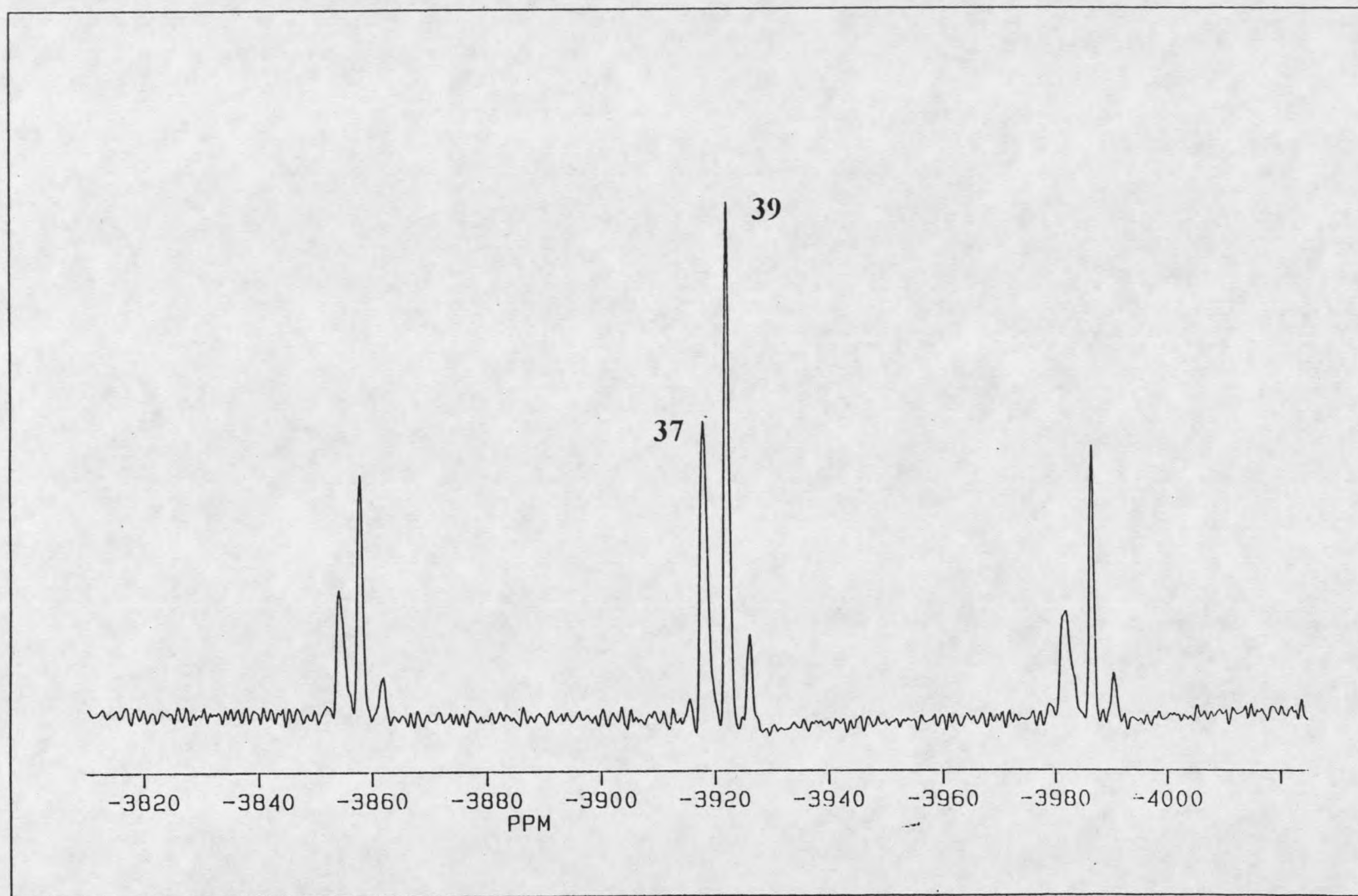
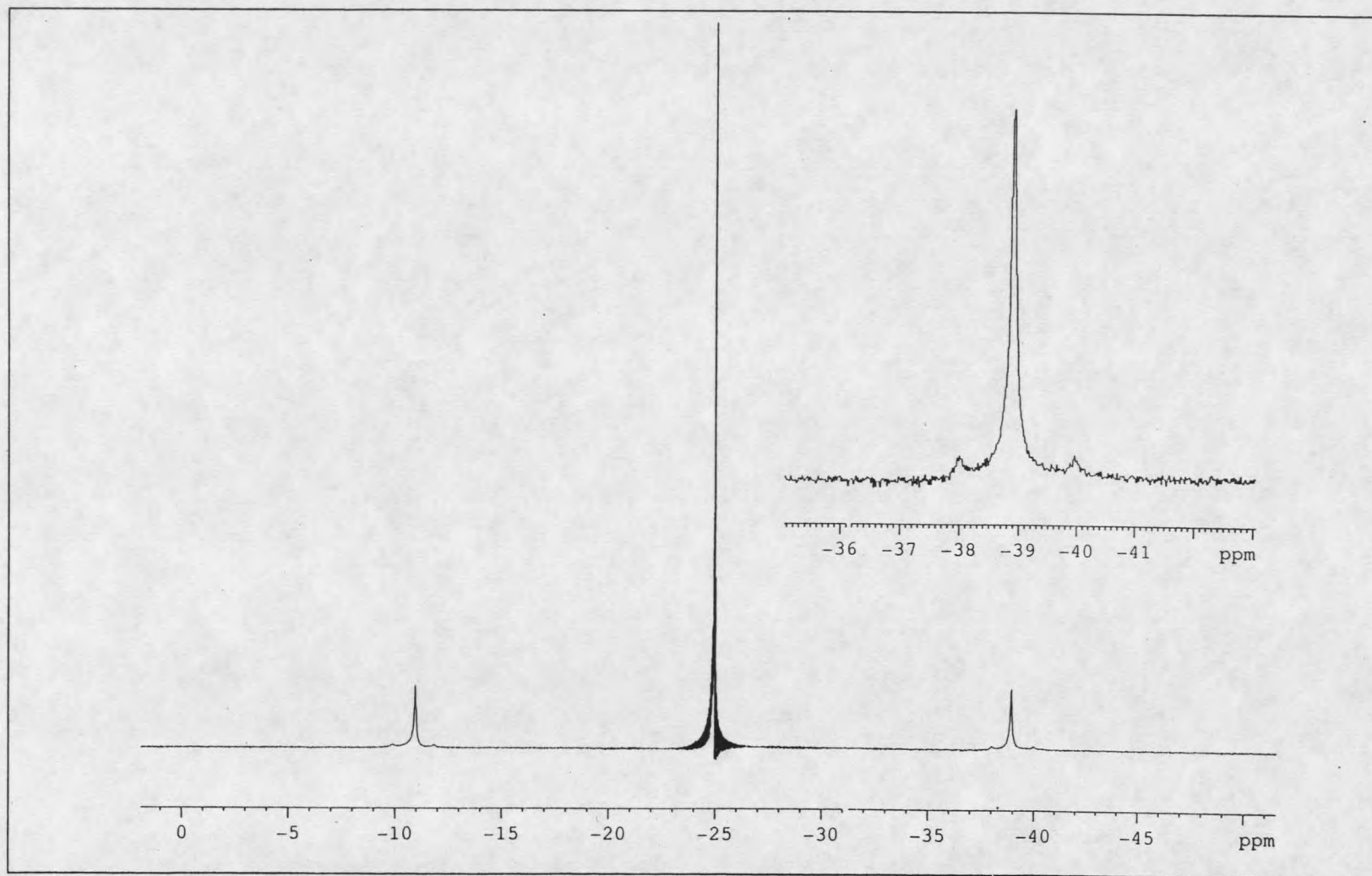


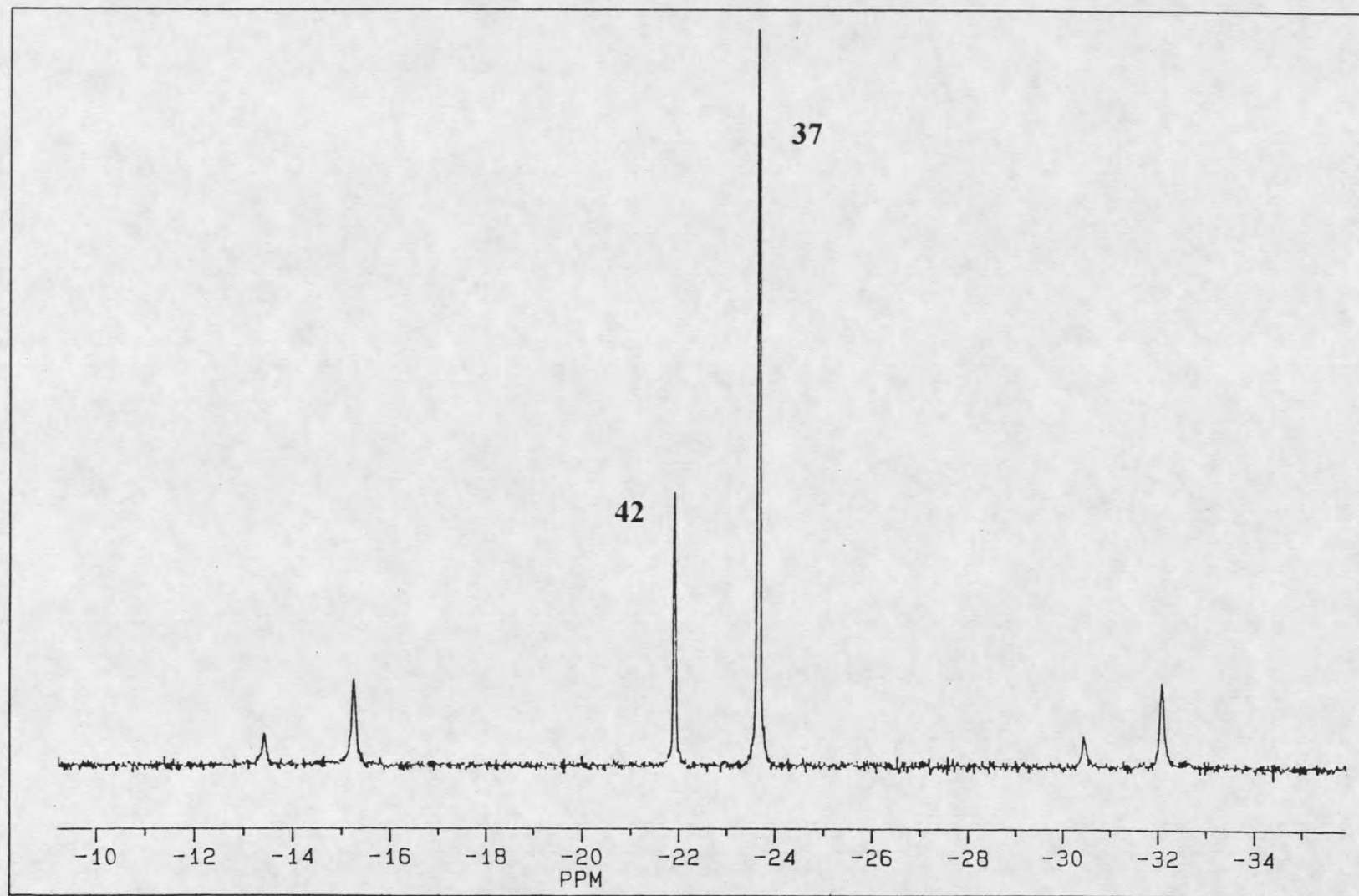
Figure 78.  $^{195}\text{Pt}$  NMR of the reaction product of **37** and  $[\text{Pt}(\text{trans-dach})(\mu\text{-OH})_2]_2^{2+}$  (**41**).



**Figure 79.** 300 MHz  $^{31}\text{P}$  NMR spectrum for  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})]_2^{2+}$  (**37**) demonstrating the presence of magnetically non-equivalent Pt nuclei.

Reaction of 36 With  $[\text{Pt}(\text{bipy})(\text{OH}_2)_2]^{2+}$  For the bipyridyl system, the solutions were reacted at 60 °C to keep the sparingly soluble  $[\text{Pt}(\text{bipy})(\mu\text{-OH})_2]^{2+}$  from precipitating out of solution along with the silver chloride. Figure 80 shows the  $^{31}\text{P}$  NMR spectrum for the reaction of  $[\text{Pt}(\text{PMe}_3)_2(\text{OH}_2)_2]^{2+}$  (36) and  $[\text{Pt}(\text{bipy})(\text{OH}_2)_2]^{2+}$  at pH = 4.61. The more intense resonance at -23.7 ppm is once again assigned to the  $\text{Pt}(\text{PMe}_3)_2$  homodimer (37) based on the characteristic coupling constant to platinum. The  $^1\text{J}_{\text{P-Pt}}$  coupling constant of 3440 Hz for the less intense resonance at -21.9 ppm agrees well with those other heterodimeric complexes containing nitrogen donor ligands (Table 47). It is therefore assigned to the heterodimeric structure  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})_2\text{Pt}(\text{bipy})]^{2+}$  (42). Upon cooling, the solution deposited a non-crystalline yellow-brown precipitate. Attempts to isolate the heterodimer from the reaction mixture has so far been unsuccessful.

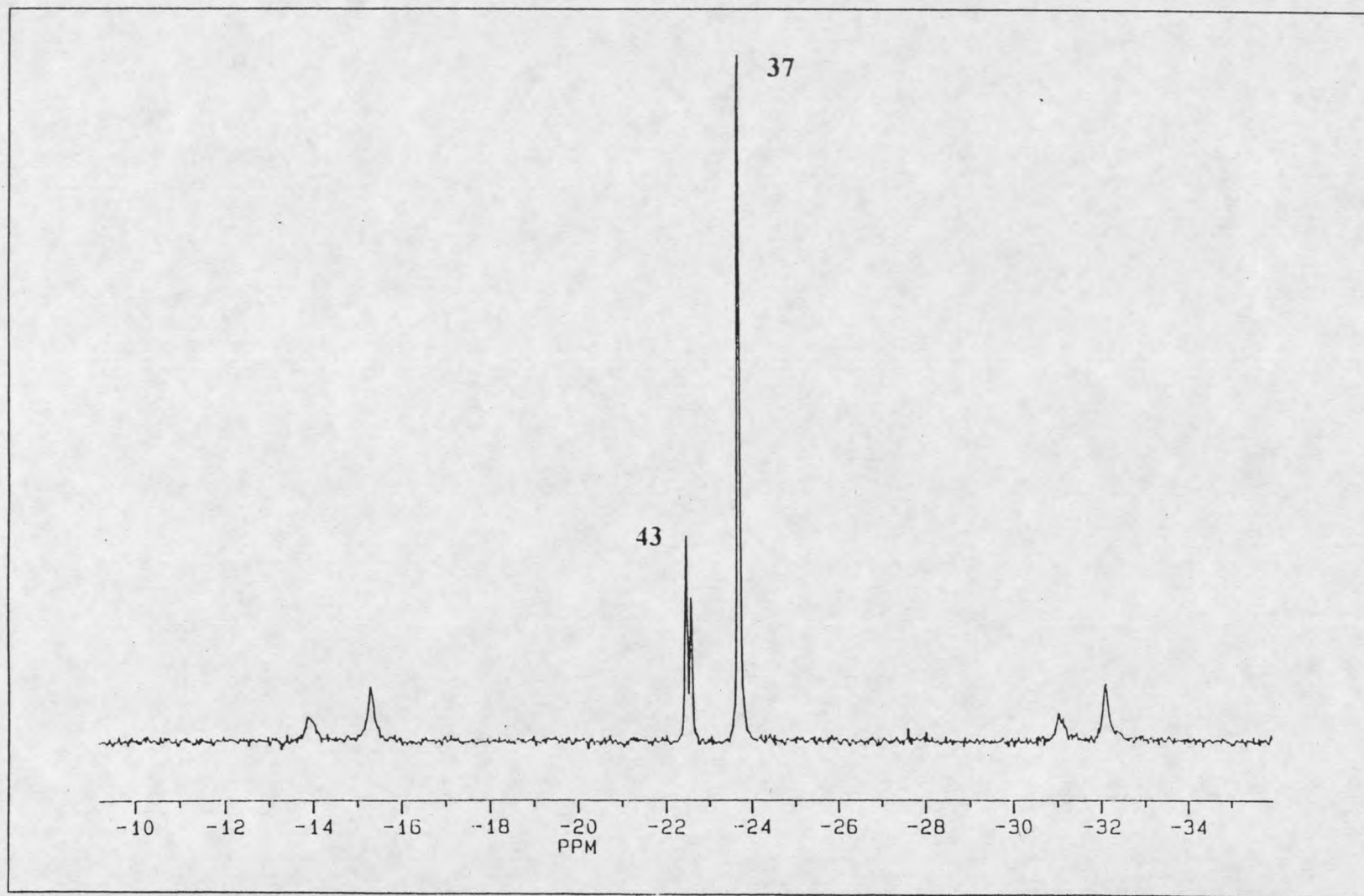
Bushnell et al. have observed that when Pt(II) is coordinated by triphenylphosphane, the di- $\mu$ -hydroxo bridges are extremely stable, resisting bridge cleavage by tertiary phosphane ligands under conditions which would readily cleave analogous chloro bridged species (126). The inertness of these hydroxo bridges seems even more remarkable considering the very high *trans* labelizing effect of coordinated phosphane ligands.



**Figure 80.**  $^{31}\text{P}$  NMR for the reaction of **37** with  $[\text{Pt}(\text{bipy})(\mu\text{-OH})_2]^{2+}$ . pH  $\sim$  4.61

Reaction of 37 With  $[(\text{dth})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{dth})]^{2+}$  The heterodimeric complexes discussed so far were all formed by combining the two *cis*-diaqua fragments followed by raising the pH to promote dimerization. For the Pt(dth) system, the pH of each solution was adjusted individually to promote dimerization, followed by mixing the two solutions. The appearance of the resulting spectra for these two methods seems to be qualitatively the same, indicating that dimers are at least as reactive as monomers in forming these mixed ligand complexes.

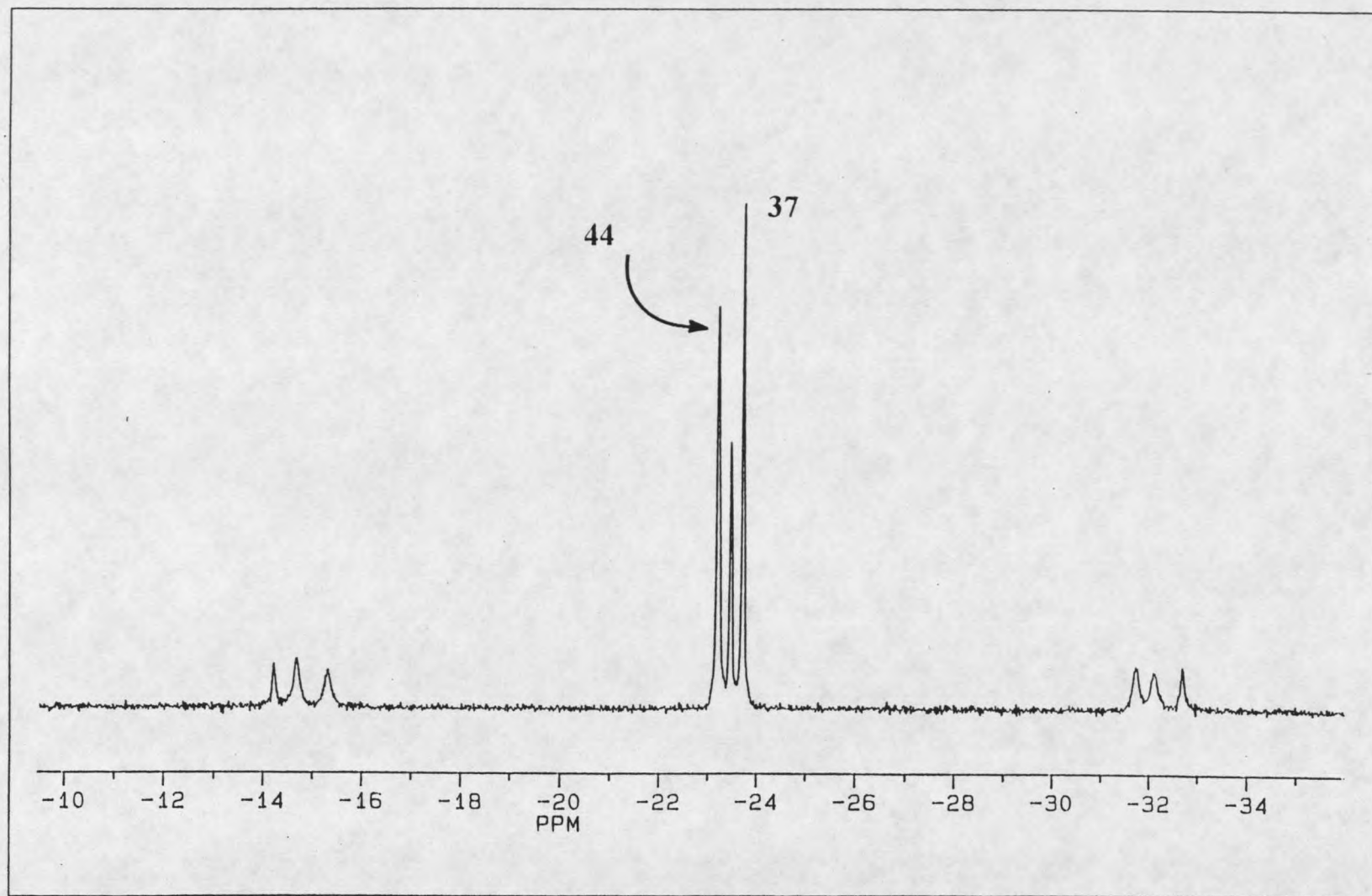
The coordination of a bidentate thioether ligand to Pt(II) results in the formation of diastereomeric products due to the presence of two chiral sulfur donor atoms, as discussed above in connection with the dth homodimer (29). The presence of magnetically non-equivalent Pt centers is also useful for assigning structure to the heterodimers containing phosphane ligands. Figure 81 shows the  $^{31}\text{P}$  NMR spectrum for the reaction of (37) and  $[(\text{dth})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{dth})]^{2+}$ . Once again, the peak at -23.72 ppm is assigned to 37 based on the  $^1J_{\text{P-Pt}}$  of 3392 Hz. The two peaks separated by ~ 23 Hz around -22.5 ppm provide definitive proof for the presence of the dth invertomers in this complex. This resonance is therefore assigned to the heterodimeric complex  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})_2\text{Pt}(\text{dth})]^{2+}$  (43). The broadening of the Pt satellites in this spectrum almost completely obscures the analogous splitting expected in these peaks.



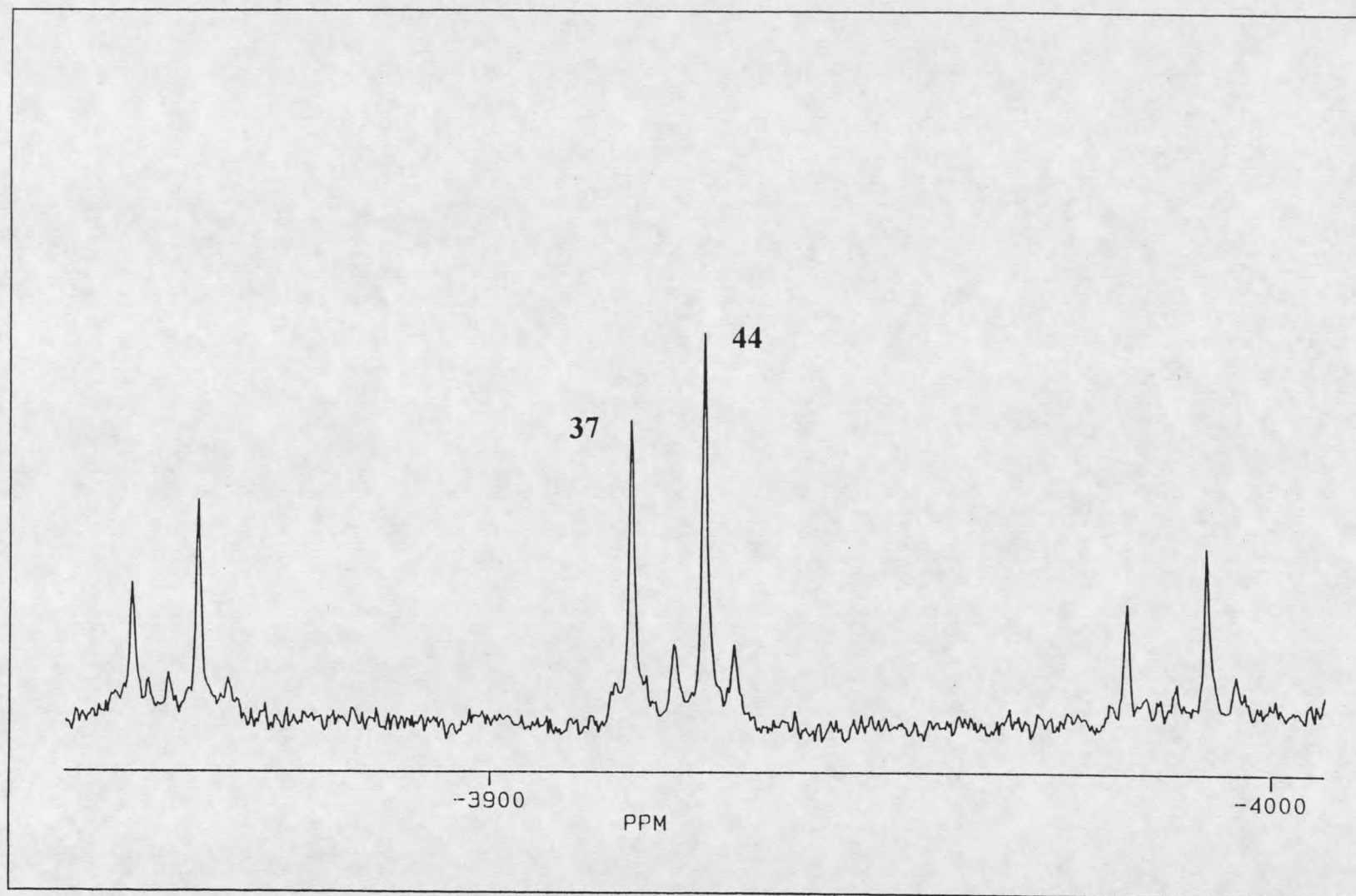
**Figure 81.**  $^{31}\text{P}$  NMR for the reaction of **37** with  $[\text{Pt}(\text{dth})(\mu\text{-OH})_2]^{2+}$  (**29**). pH ~ 4.61

Reaction of 37 With  $[\text{Pt}(\text{en})(\text{OH}_2)_2]^{2+}$  (15) The monomeric diaqua ethylenediamine complex (15) had previously been shown to form a heterodimeric complex with  $\text{Pt}(\text{DMSO})(\text{OH}_2)_2$  (1). It was therefore a good candidate for the formation of a hetero dimer incorporating the  $\text{Pt}(\text{PMe}_3)_2$  fragment. Figure 82 shows the  $^{31}\text{P}$  NMR spectrum for the reaction of 36 and 15 at  $\text{pH} = 2.5$ . The single resonance at -23.5 ppm with its associated satellites is assigned to the monomeric diaqua complex (36), based on the  $^1\text{J}_{\text{P-Pt}}$  coupling constant of 3735 Hz. The resonance just upfield of the monomer at -23.7 ppm can also be assigned to the homodimeric complex, 37. The third resonance just downfield of the monomer is therefore assigned to the heterodimeric complex  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})_2\text{Pt}(\text{en})]^{2+}$  (44). The value of  $^1\text{J}_{\text{P-Pt}}$  is similar to that of the  $\text{Pt}(\text{bipy})$  heterodimer in which one of the platinum atoms is also coordinated by an  $^{14}\text{N}$  donor ligand.

The presence of magnetically non-equivalent Pt centers is easily seen in the  $^{195}\text{Pt}$  NMR spectrum in the region of the  $\text{Pt}(\text{PMe}_3)_2$  fragment (Figure 83). The central peak at -3927 ppm with a pair of flanking satellites is entirely consistent with the heterodimeric complex 44. Of particular interest is the large value of the two bond Pt-Pt coupling constant ( $^2\text{J}_{\text{Pt-Pt}} = 410$  Hz). This is almost twice the value seen for the homodimeric phosphane dimer (37) and is presumably due to the greater *trans* effect of the  $\text{PMe}_3$  ligand as compared with ethylenediamine. When the pH of this solution is raised to  $\sim 9$ , the resonance due to 44 increases in intensity at the expense of 37 (Figure 84).



**Figure 82.**  $^{31}\text{P}$  NMR for the reaction of **36** and  $[\text{Pt}(\text{en})(\text{OH}_2)_2]^{2+}$  (**15**).



**Figure 83.**  $^{195}\text{Pt}$  NMR spectrum in the region of the  $\text{Pt}(\text{PMe}_3)_2$  fragment for the reaction of **36** and **15**.

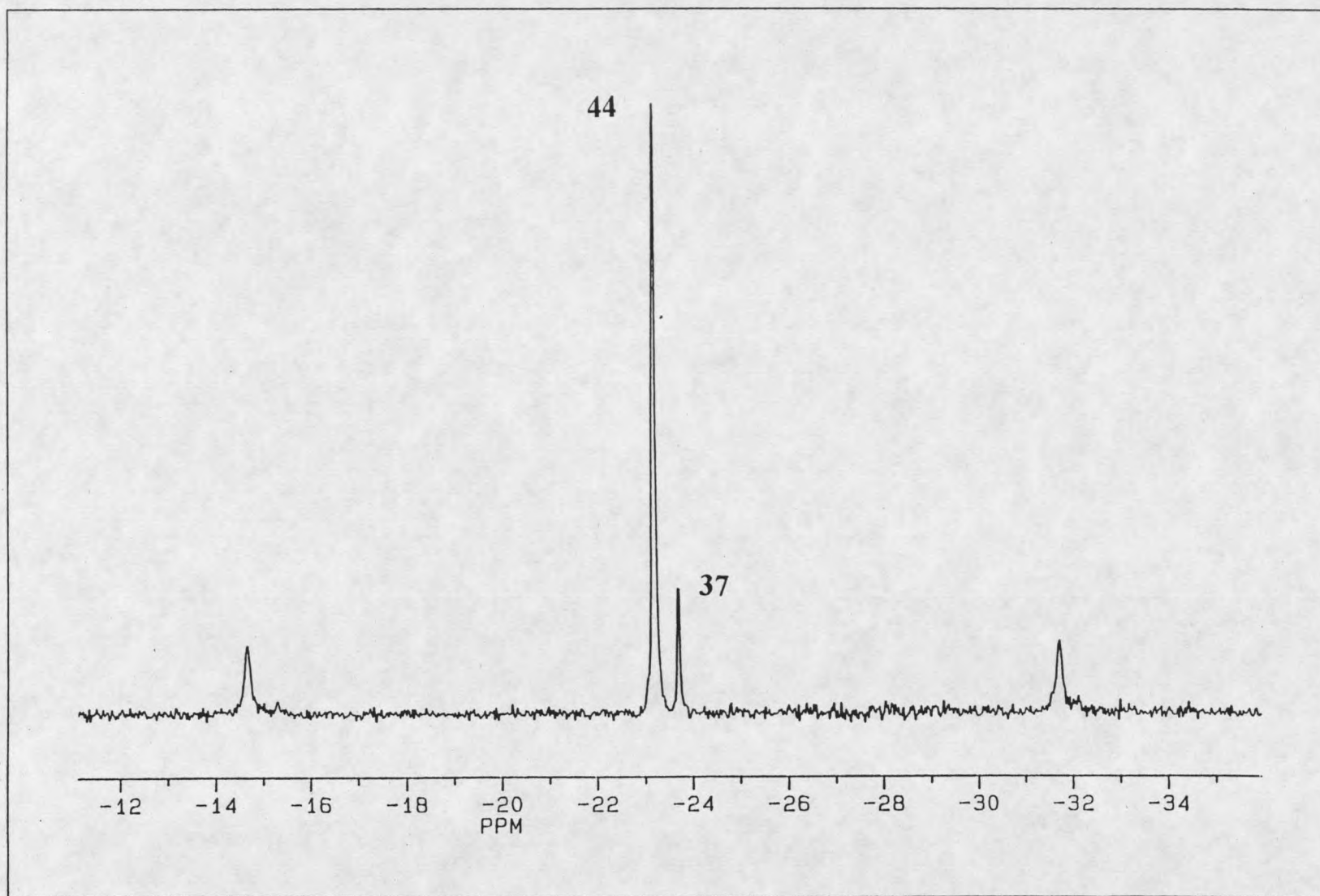


Figure 84.  $^{31}\text{P}$  NMR spectrum for the reaction of 36 and 15; pH= ~ 9.

Several other heterodimeric complexes were also formed under similar reaction conditions. Table 47 summarizes the relevant NMR data and Figures 84 and 85 show the resulting spectra for the reaction of **37** with **2** to form  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})_2\text{Pt}(\text{DMSO})_2]^{2+}$  (**46**) and for the reaction of **37** with  $[\text{Pt}(\text{Et}_2\text{S})_2(\mu\text{-OH})_2]^{2+}$  (**47**) to form  $[\text{Pt}(\text{PMe}_3)_2(\mu\text{-OH})_2\text{Pt}(\text{Et}_2\text{S})_2]^{2+}$  (**48**) respectively.

**Table 47.** NMR data for trimethylphosphane heterodimeric complexes.

| #  | Complex <sup>a, b</sup>                                                                         | $\delta$ <sup>31</sup> P (ppm) | <sup>1</sup> J <sub>P-Pt</sub> (Hz) |
|----|-------------------------------------------------------------------------------------------------|--------------------------------|-------------------------------------|
| 37 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{PMe}_3)_2]^{2+}$             | -25.58 <sup>c</sup>            | 3398                                |
| 37 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{PMe}_3)_2]^{2+}$             | -23.73                         | 3395                                |
| 39 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\textit{trans}\text{-dach})]^{2+}$ | -24.64                         | 3441                                |
| 42 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{bipy})]^{2+}$ <sup>d</sup>   | -21.95                         | 3442                                |
| 43 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{dth})]^{2+}$                 | -22.48 <sup>e</sup><br>-22.59  | 3443                                |
| 44 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{en})]^{2+}$                  | -23.22                         | 3462                                |
| 46 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{DMSO})]^{2+}$                | f                              | 3549                                |
| 48 | $[(\text{Me}_3\text{P})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{Et}_2\text{S})_2]^{2+}$      | -22.70                         | 3461                                |

a) In H<sub>2</sub>O/D<sub>2</sub>O at 300 K unless otherwise indicated

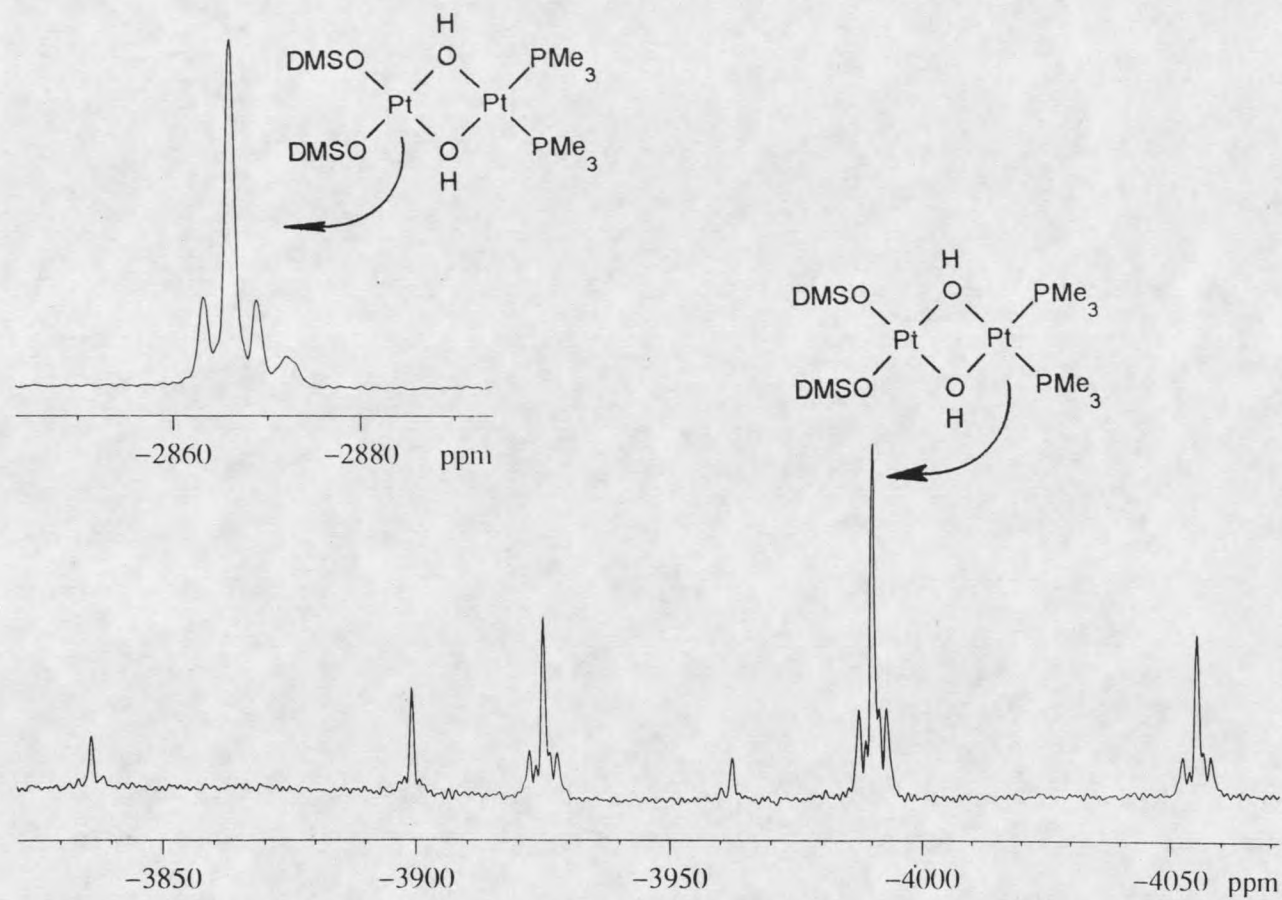
b) All cations have NO<sub>3</sub><sup>-</sup> counterion

c) From ref. 25 in D<sub>2</sub>O.

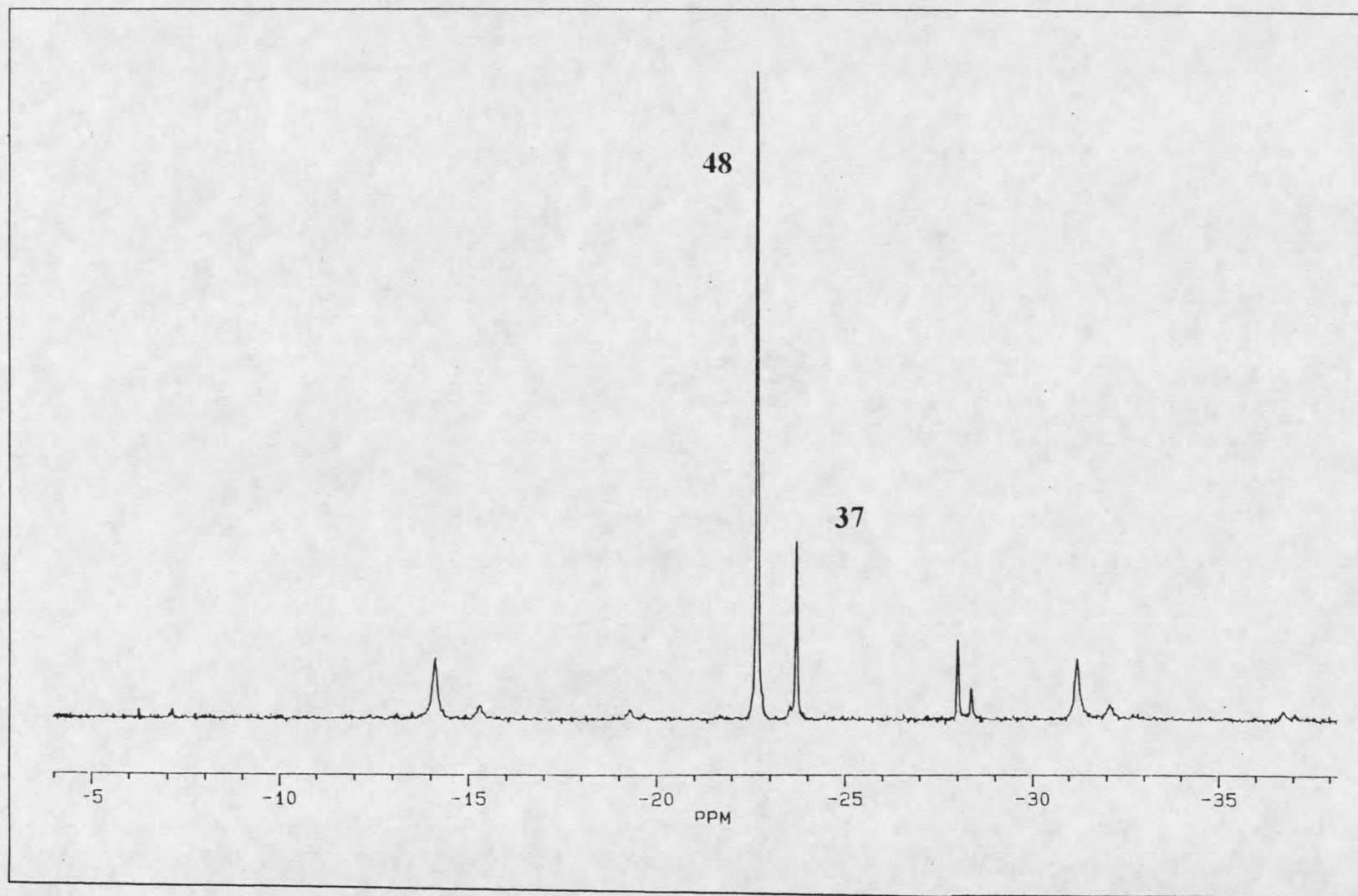
d) 325 K

e) Two shift values for the two invertomers of dth (= 2,5-dithiahexane)

f) Only the <sup>195</sup>Pt spectrum was acquired.



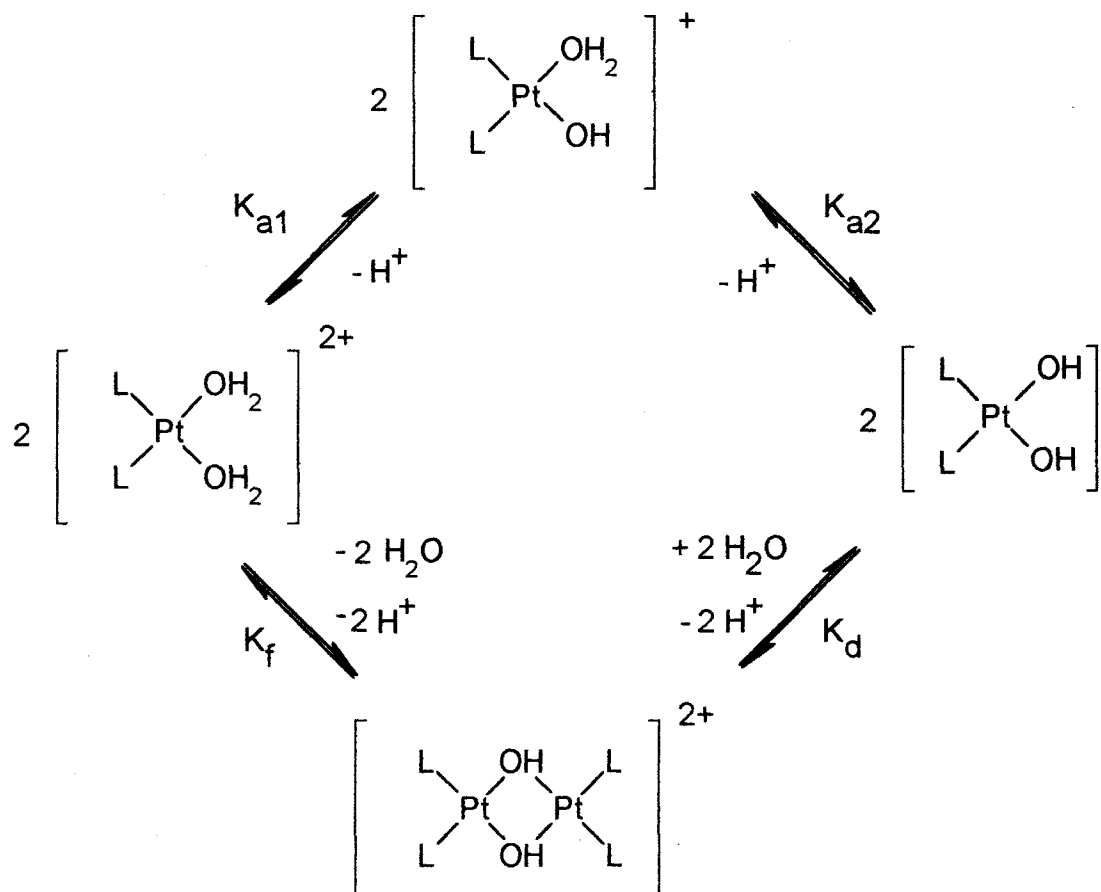
**Figure 85.**  $^{195}\text{Pt}$  NMR spectrum for the reaction of **2** and **37**.



**Figure 86.**  $^{31}\text{P}$  NMR spectrum for the reaction of **37** and  $[\text{Pt}(\text{Et}_2\text{S})_2(\mu\text{-OH})_2]^{2+}$  (**47**).

### Thermodynamic Aspects of Dimer Formation

As can be seen in the reaction scheme of Figure 4, which has been reproduced here for convenience, there are two possible pathways for the formation of the dihydroxo monomer from the diaqua complex.



The first of these pathways simply involves the deprotonation of both coordinated waters, a process which depends inherently on the two dissociation constants,  $K_{a1}$  and  $K_{a2}$ . The second pathway involves the formation of the dimeric complex followed by decomposition to yield the dihydroxo species. This pathway is seen to be a function of the dimer formation constant,  $K_f$  and the dimer dissociation constant,  $K_d$ . Because these two pathways lead to the same product, forming a closed cycle, it was postulated that there must be a quantitative relationship between the four parameters ( $K_{a1}$ ,  $K_{a2}$ ,  $K_f$ ,  $K_d$ ). In order to test this hypothesis, we set out to determine the values of  $K_f$  and  $K_d$  in hopes they might provide some independent verification of the combined sum of  $pK_{a1}$  and  $pK_{a2}$ .

#### Determination of Dimer Formation Constant, $K_f$ and Dissociation Constant, $K_d$

For the determination of  $K_f$ , a pH was chosen which would allow the observation of both the diaqua monomer (36) and the hydroxo bridged dimer (37), at equilibrium, in the  $^{31}\text{P}$  NMR spectrum. The integrated peak areas of these two species were then determined for a series of solutions of varying concentrations. A value of  $K_f$  was then calculated for each solution using the equilibrium constant expression shown in Equation 5.

**Equation 5.** 
$$K_f = \frac{[ \text{Pt(PMe}_3)_2(\mu\text{-OH})_2\text{Pt(PMe}_3)_2 ] [ \text{H}^+ ]^2}{[ \text{Pt(PMe}_3)_2(\text{OH}_2)_2 ]^2}$$

Table 48 lists the data used in these calculations, including the resulting values of  $\text{pK}_f$ . A typical  $^{31}\text{P}$  NMR spectrum for this determination is shown in Figure 87. Because the main resonances for the monomer and dimer have such a small chemical shift separation, a more accurate peak area was achieved by integration of the platinum satellites for each complex. The mean value for  $\text{pK}_f$  was determined to be  $2.701 \pm 0.050$ .

**Table 48.** Data used for calculation of dimer formation constant,  $K_f$ .

| Trial | Relative Peak Area for Monomer | Relative Peak Area for Dimer | Total Pt Concentration (M) | pD <sup>a</sup> | $\text{pK}_f$ |
|-------|--------------------------------|------------------------------|----------------------------|-----------------|---------------|
| 1     | 10.554                         | 1.098                        | 0.07991                    | 1.708           | 2.759         |
| 2     | 1.000                          | 0.168                        | 0.03996                    | 1.934           | 2.678         |
| 3     | 4.233                          | 0.966                        | 0.02664                    | 2.083           | 2.645         |
| 4     | 1.048                          | 0.160                        | 0.05327                    | 1.869           | 2.720         |

a)  $\text{pH} = \text{pD} - 0.4$

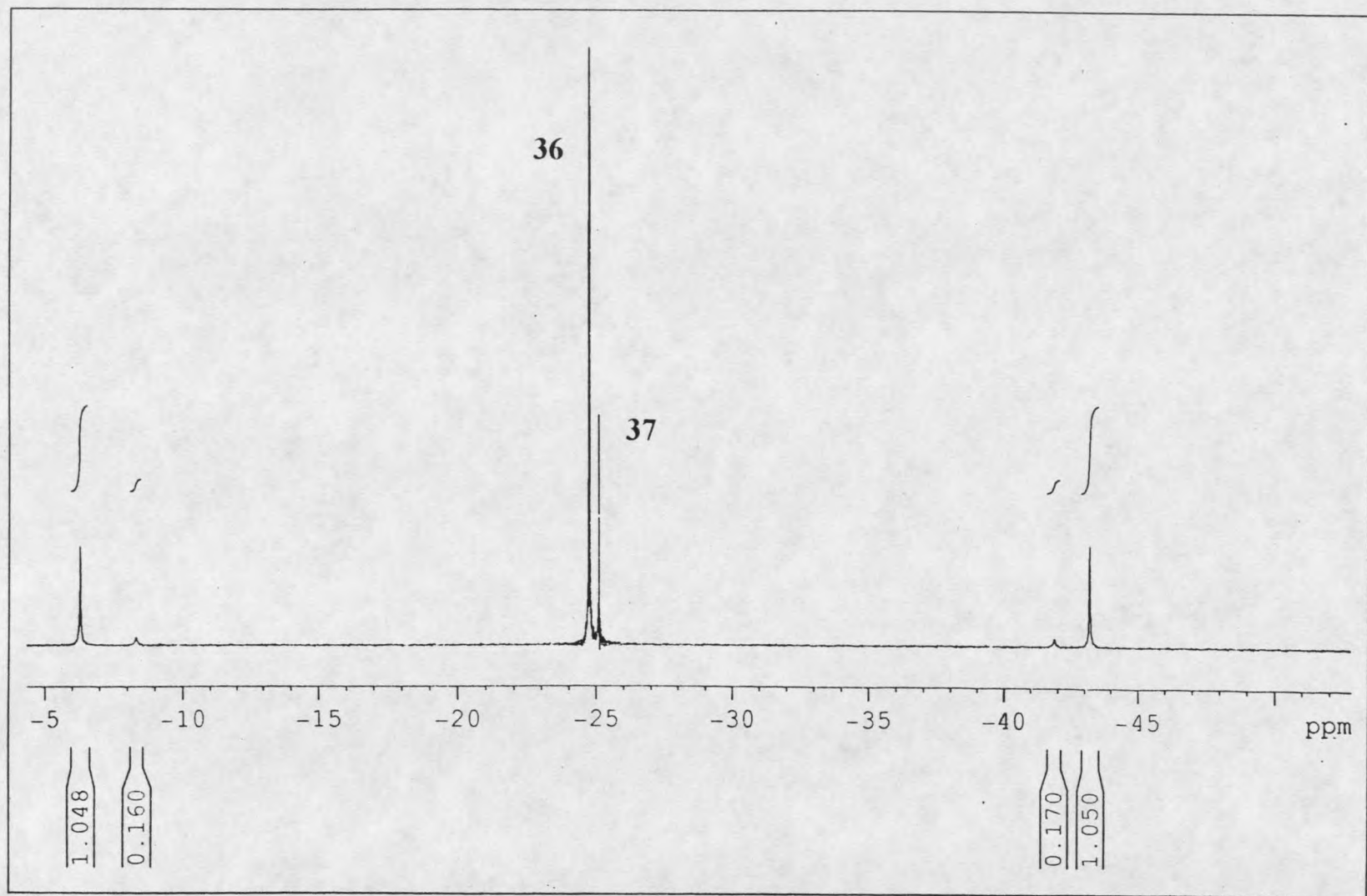


Figure 87.  $^{31}\text{P}$  NMR spectrum showing the integration of Pt satellites used for the determination of  $K_f$ .

A second series of experiments was run using the same solutions after raising the pD with NaOD to a value such that the dimer and dihydroxo monomer could be observed. The equilibrium expression shown in Equation 6 was used for the determination of  $K_d$ , consistent with the reaction scheme shown above.

$$\text{Equation 6. } K_d = \frac{[ \text{Pt(PMe}_3)_2(\text{OH})_2 ]^2 [\text{H}^+]^2}{[ \text{Pt(PMe}_3)_2(\mu\text{-OH})_2\text{Pt(PMe}_3)_2 ]}$$

Table 49 shows the data used in the calculation of the dimer dissociation constant,  $K_d$ .

The mean value was found to be  $22.008 \pm 0.059$ .

**Table 49.** Data used for calculation of dimer dissociation constant,  $K_d$ .

| Trial | Relative Peak Area for Monomer | Relative Peak Area for Dimer | Total Pt Concentration (M) | pD <sup>a</sup> | pK <sub>d</sub> |
|-------|--------------------------------|------------------------------|----------------------------|-----------------|-----------------|
| 1     | 0.142                          | 1.000                        | 0.07991                    | 10.174          | 22.097          |
| 2     | 0.267                          | 1.000                        | 0.03996                    | 10.217          | 21.981          |
| 3     | 0.277                          | 1.000                        | 0.02664                    | 10.161          | 22.017          |
| 4     | 0.189                          | 1.000                        | 0.05327                    | 10.120          | 21.935          |

a) pH = pD - 0.4

The positive value for  $pK_f$  indicates that the diaqua monomer-dimer equilibrium slightly favors the monomer under these conditions whereas the large positive value for  $pK_d$  indicates that the dimer is favored over the dihydroxo monomer. These results are more or less consistent with the apparent stability of the dimer over a wide pH range.

In order to compare the sums of the constants around the cycle, it is necessary to take half of the sum of  $pK_f$  and  $pK_d$  to compensate for the coefficient on the monomers. This gives a value of 12.3 as compared with a sum of 16.1 for the two acid dissociation constants. At this time, we have no explanation for the apparent discrepancy between the two values beyond the compounding of random error involved in integration, pH measurement, dilution etc. It is of interest to compare the value of 12.3 obtained by determining the formation and dissociation constants for the phosphane complex with the sum of  $pK_a$ 's for the nitrogen donor complexes listed in Table 3. The fairly high values for the two acid dissociation constants suggests that for the trimethylphosphane system, the presence of dimers in solution at low pH is due to an inherent stability of the dihydroxo bridged complex rather than to the  $pK_a$ 's of the coordinated waters.

## SUMMARY AND CONCLUSIONS

Platinum(II) complexes coordinated in a *cis* fashion by certain sulfoxide or trimethylphosphane ligands readily undergo hydrolysis in aqueous solution to produce the corresponding di- $\mu$ -hydroxo bridged dimers. These reactions are both concentration and pH dependent but appear to occur at lower pH than the analogous Pt(II) ammine complexes which have been intensively studied as anti cancer agents. Ligand substitution occurs more readily in the sulfoxide systems as evidenced by the formation of all seven possible substitutional dimeric isomers. This rapid scrambling of ligands is presumed to be due to the fairly large *cis* effect of sulfoxides. In dilute aqueous solution, these ligands are displaced by solvent.

Replacement of monodentate sulfoxide ligands with the bidentate sulfoxide *meso*-1,2-bis(methylsulfinylethane), followed by hydrolysis, yielded a complex mixture of products which did not appear to include a hydroxo bridged species. Based on multinuclear NMR and IR evidence, it is proposed that the product(s) are polymeric in nature. Several monomeric Pt(II) complexes containing this ligand as well as a six coordinate, monomeric ruthenium(II) complex, were characterized by x-ray crystallography, confirming the bidentate nature of this ligand in the solid state.

For both the monodentate sulfoxide and phosphane complexes, reaction with a *cis*-diaqua complex coordinated by other neutral ligands eg. ethylenediamine, *trans*-dach, etc. results in the formation of mixed ligand (hetero) dimers, whereas reaction

with a Pt(II) fragment containing the anionic oxalate ligand results in substitution of oxalate into the phosphane complex.

In general, halogen or peroxide oxidation of dimeric sulfoxide and phosphane complexes in aqueous solution yielded a complex mixture of Pt(II) and Pt(IV) products.

Due to the extensive use of silver salts for the removal of chloride ions in the preparation of the diaqua complexes, two structures containing the Ag(I) ion were characterized. Although one of these had been previously been structured, the other turned out to be a novel network silver complex containing the *meso*-MSE ligand and trifluoromethanesulfonate, as well as Ag(I).

An investigation into the thermodynamic stability of the dimeric complex relative to the diaqua and dihydroxo monomers yielded a  $pK_f$  of  $2.701 \pm 0.050$  and a  $pK_d$  of  $22.008 \pm 0.059$ . These results suggest that the strong tendency for dimer formation is due to an inherent stability of the di-bridged complex and not to the values of the acid dissociation constants of coordinated water.

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