

Contribution from the Departments of Chemistry, Tulane University, New Orleans, Louisiana 70118, and Louisiana State University, Baton Rouge, Louisiana 70803

Axial Ligand Replacement Reactions in Tetrakis(μ -phosphato)diplatinum(III) Complexes: Coordination of Amine, Thioether, and Thiolate Functionalities

Ramadan El-Mehdawi,^{1a} Frank R. Fronczek,^{1b} and D. Max Roundhill*^{1a}

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The labile water molecules in the diplatinum(III) complex $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ are sequentially replaced by halide, amine, thioether, and thiolate ligands. The products can be identified by chromophore shifts in the intense $d\sigma \rightarrow d\sigma^*$ transitions. These binuclear complexes $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$ and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}_2^{4-}$ (L = uncharged ligand, X = anionic ligand) show a pseudoquintet (1:8:18:8:1) pattern in the ^{31}P NMR spectrum. The X-ray structure of $(\text{Ph}_4\text{As})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2] \cdot 2\text{H}_3\text{PO}_4$ shows the crystals to be triclinic with space group $P\bar{1}$ and $Z = 1$. The unit cell dimensions are as follows: $a = 10.584$ (1) Å; $b = 11.373$ (1) Å; $c = 15.138$ (2) Å; $\alpha = 77.23$ (1)°; $\beta = 70.72$ (1)°; $\gamma = 75.23$ (1)°; $V = 1644.4$ (4) Å³. The Pt-Pt distance is 2.525 (1) Å, and the Pt-S distances are 2.462 (1) Å. All the nonlinear angles about platinum are close to 90°.

The coordination chemistry of platinum with phosphate ligands has become a topic of recent interest because of the chemotherapeutic use of platinum complexes.² Although there is considerable evidence that these complexes act by inducing cross-linking between adjacent guanine base pairs in the DNA chain, little information is available as to the mode of interaction of these complexes with the cell surface. The prevalence of phospholipids at the cell surface³ and the finding that platinum complexes will catalyze the hydrolysis of pyrophosphate and triphosphate ions⁴ make it useful to search for a new chemistry of (phosphato)-platinum complexes that may help us better understand both the binding and transport of platinum complexes within cell surfaces and membranes.⁵

The chemistry of platinum is dominated by kinetically inert monomeric complexes in a divalent or a tetravalent oxidation state.⁶ Trivalent complexes have been implicated as reactive intermediates in a variety of reactions, but with one exception, monomeric complexes of platinum(III) are not isolable.⁷ For bimetallics, stable complexes of platinum(III) are common, and several recent papers have been published on the structural and redox properties of such compounds.⁸ The first well-documented

examples of diplatinum(III) complexes are the "lantern" type tetrakis(μ -O,O-phosphato-O,O) or (μ -O,O-sulfato-O,O) complexes with neutral or anionic ligands in the axial positions. These complexes have a short Pt-Pt bond in the range 2.48–2.52 Å⁸ and show unusual reactivity for platinum complexes in having labile axial ligands. This lability is selectively axial, and we have suggested that the intermetallic bond exerts a significant influence on the chemical reactivity of the axial ligands.⁹ In order to investigate the stereoselectivity and binding constants of ligating groups to these diplatinum(III) complexes, we have qualitatively, and in some cases quantitatively, investigated the complexation of O-, N-, and S-donor ligands into the axial coordination sites.

Experimental Section

Synthesis of Complexes. The complex $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2]$ was prepared by the literature procedure from $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ and phosphoric acid.⁸ A mixture of *cis*- or *trans*- $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ (0.2 g) and H_3PO_4 (2 mL of an 85% solution) was heated at 110 °C until the brown fumes of nitrogen dioxide ceased to be liberated. The resulting solution was allowed to cool, and NaH_2PO_4 (0.1 g) dissolved in water (6 mL) was added. After it was stirred for 20 min, the solution was filtered, and the complex precipitated as a solid by addition of ethanol. The solid was washed several times with ethanol, and after a final washing with diethyl ether the complex was air-dried.⁸ Aqueous solutions containing the anions $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$ (L = ammonia, pyridine, 1,4-pyrazine, guanine, cytosine, thiourea, thioacetamide, tetrahydrothiophene, thiodiethanol, thioglycolic acid, methionine, methylcysteine) were prepared by adding an excess of the reagent L to $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$, except for the case of L = NH_3 , when the reagent was added as ammonium fluoride. For the complexes where L is an N-bonded ligand, the compounds can be isolated as yellow solids by the addition of ethanol, except for the case of L = guanine (G), where $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{G})_2]$ has only limited solubility in water. For the complexes where L is an S-bonded ligand, the compounds can be isolated as yellow solids by addition of methanol. The sodium salts of the complexes are insoluble in organic solvents.

If solubility in an organic solvent is desired, the complexes can be prepared as their bis(diphenylphosphine)nitrogen(1+) (PPN⁺) salts. These PPN⁺ salts, which are soluble in CH_3CN , $(\text{CH}_3)_2\text{CO}$, CH_2Cl_2 , and EtOH solvents, are prepared by addition of (PPN)F to an aqueous solution of the corresponding sodium salt.¹⁰ The complexes precipitate and can be isolated by filtration, followed by washing with water.

All complexes show strong infrared bands ($\nu(\text{PO})$) for the bridging phosphato moiety at 1150 (broad), 1050, 980, and 920 (sh) cm^{-1} . The complexes show an intense band in the UV spectrum in the range 224–446 nm, with molar absorptivity coefficients in the region of 20 000 $\text{M}^{-1} \text{cm}^{-1}$. This absorption is primarily due to a $d\sigma \rightarrow d\sigma^*$ transition in the diplatinum(III) bond. Additional confirmation of the binuclear structure is obtained from the ^{31}P NMR spectrum, which shows a resonance centered in the δ 19–30 region (downfield positive shift relative to 85% H_3PO_4) with a 1:8:18:8:1 pseudoquintet isotopomer splitting pattern due to coupling with two equivalent ^{195}Pt nuclei.¹¹

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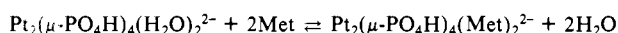
Table I. Electronic Absorption Spectra of the Complexes $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$, $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}_2^{4-}$, $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$, and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}(\text{H}_2\text{O})_3^{3-}$

$\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$		
L	λ_{max} , nm ^a	ϵ_{max} , M ⁻¹ cm ⁻¹ ^b
H ₂ O	224	16 160
S-methyl-L-cysteine	340	23 770
methionine	344	24 200
thiodiethanol	348	24 650
thiodipropionic acid	344	24 820
thiourea	366	
thioacetamide	366	
tetrahydrothiophene	344 ^c	
ammonia	248	17 090
pyridine	294	
1,4-pyrazine	286	
guanine	298 ^d	
cytosine	294	
$\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}_2^{4-}$		
X	λ_{max} , nm	ϵ_{max} , M ⁻¹ cm ⁻¹
OH ⁻	266	
Cl ⁻	296	21 480
Br ⁻	342	22 470
I ⁻	410	
homocysteine ^e	446	
mercaptopyropionic acid ^e	446	
$\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$		
L	λ_{max} , nm	ϵ_{max} , M ⁻¹ cm ⁻¹
S-methyl-L-cysteine	304	22 170
thiodiethanol	308	18 550
thiodipropionic acid	306	21 380
$\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}(\text{H}_2\text{O})_3^{3-}$		
X	λ_{max} , nm	ϵ_{max} , M ⁻¹ cm ⁻¹
Cl ⁻	266	20 000
Br ⁻	292	21 000

^a Measured in aqueous solution except where noted. ^b Accurate extinction coefficients could not be measured in some cases because of overlapping with ligand (L or X) bands. ^c Measured as PPN⁺ salt in acetonitrile solvent. ^d Sodium hydroxide added. ^e Complexed as the thiolato anion.

The complexes are all air- and water-stable in the presence of excess ligand L or X⁻. No significant hydrolytic substitution of the $\mu\text{-PO}_4\text{H}_2^{2-}$ ligands occurs. With a large excess of iodide ion we observe the progressive formation of PtI_6^{2-} .¹² When thiolate ligands are used, the insolubility of the complexes $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}_2^{4-}$ (X = thiolate) likely precludes subsequent bridge-substitution reactions.

Equilibrium Measurements. The equilibrium constants K_1 and K_2 reported in this article have been calculated from the respective concentrations of $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$, $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$, $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$, and L. In order to calculate these individual equilibrium constants, it was necessary to first measure the extinction coefficients (ϵ) for $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$. Furthermore, it was also necessary to correct for peak overlapping before accurate concentrations could be evaluated for the three platinum complexes $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$, $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$, and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$. For added methionine (Met) we find no separate absorption band due to $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{Met})(\text{H}_2\text{O})_2^{2-}$; hence, we can only evaluate K_1K_2 for the overall two-step reaction:



In order to measure K_1 and K_2 for the complexes with overlapping peaks, we have carried out an analysis similar to that used in our previous paper on these (μ -phosphato)diplatinum(III) complexes.⁹ We have evaluated the ϵ_{max} values of $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$ (ϵ_B) from eq 1, where

$$C_{\text{total}} = C_A + C_B + C_C = A_A/\epsilon_A + A_B/\epsilon_B + A_C/\epsilon_C \quad (1)$$

this parameter is the only unknown quantity. The abbreviations A, B, and C refer to $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$, $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}(\text{H}_2\text{O})_2^{2-}$, and

Table II. ³¹P Nuclear Magnetic Resonance Data for the Complexes $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$ and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{X}_2^{4-}$

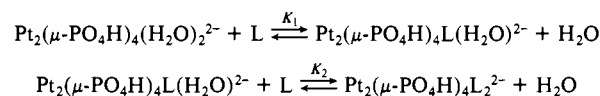
L or X	δ^a	$^2J(\text{PtP})$, Hz
S-methyl-L-cysteine	22.2	64.0
methionine	22.8	63.5
thiodiethanol	26.5 ^b	67.5
thiodipropionic acid	22.9	71.5
thiourea	24.1	65.0
thioacetamide	26.0	63.0
tetrahydrothiophene	23.0 ^b	72.0
ammonia	19.0	62.0
pyridine	20.4	68.0
1,4-pyrazine	20.0	68.0
guanine	20.7 ^c	42.8
cytosine	21.6	67.0
Cl ⁻	23.4	72.0
Br ⁻	26.8	65.0
I ⁻	29.8	57.5

^a Measured in D₂O solvent, except where noted, and referenced to 85% H₃PO₄. ^b Measured as PPN⁺ salt in acetonitrile solvent. ^c Measured in D₂O with added NaOH.

Table III. Equilibrium Measurements for the Replacement of Axially Substituted Water Molecules in $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ by Thioether Ligands^a

added ligand ^b	K_1 , M ⁻¹	K_2 , M ⁻¹	K_1K_2 , M ⁻²
S-methyl-L-cysteine	1300 (50)	1400 (50)	1.8×10^6
methionine			10^7
thiodiethanol	1900 (100)	680 (50)	1.3×10^6
thiodipropionic acid	1150 (50)	1100 (50)	1.3×10^6

^a For the equilibria



^b Aqueous solutions are 1.308×10^{-4} M in $\text{Na}_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2]$ and 5×10^{-4} M in added ligand. The solutions are at constant ionic strength ($\mu = 0.1$ M) and pH 3 in a phosphate buffer solution at 25 °C.

$\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$, respectively (L is an uncharged ligand). The respective concentrations C_A , C_B , and C_C can then be evaluated with use of eq 2–4. Values of ϵ_Y^α and ϵ_Y^β (X = A, B, C) are the extinction

$$C_A = (A_A - (\epsilon_A^\alpha A_B + \epsilon_A^\beta A_C)) / \epsilon_A \quad (2)$$

$$C_B = (A_B - (\epsilon_B^\alpha A_A + \epsilon_B^\beta A_C)) / \epsilon_B \quad (3)$$

$$C_C = (A_C - (\epsilon_C^\alpha A_B)) / \epsilon_C \quad (4)$$

coefficients at the wavelength Y of species that do not have ϵ_{max} at this position. The ϵ_X values are the ϵ_{max} values for the individual complexes A, B, and C. The superscripts α and β denote two of the three (A, B, or C) species that are being subtracted in the calculation of the concentration of the third. These parameters have been evaluated for each of the three cases with X being S-methyl-L-cysteine, thiodiethanol, and thiodipropionic acid. In all cases the data for calculation of C_A , C_B , and C_C have been obtained after equilibrium has been reached. This condition is verified by showing that the concentrations of the different compounds remain unchanged for a time that is approximately 4 half-lives longer than is required for equilibrium to be established.

All solution measurements have been made in solutions of 0.1 M constant ionic strength and buffered to pH 3 with phosphate buffer. The solution temperature was 25 °C. In Tables I–III we give the electronic spectral data, the ³¹P NMR data, and the equilibrium constant values for these complexes.

Equipment. UV-vis spectra were measured on a Hewlett-Packard Model 8451A diode array spectrometer using 1 cm path length quartz cells. ³¹P NMR spectra were measured at ambient temperature on a JEOL FX60 spectrometer operating at 24.15 MHz. IR spectra were measured on a Perkin-Elmer Model 683 infrared spectrophotometer.

Structure Solution. A crystal of $(\text{Ph}_4\text{As})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2] \cdot 2\text{H}_3\text{PO}_4$ was grown by dissolving the compound in methanol and allowing the solvent to slowly evaporate in air at ambient temperature. Yellow-orange crystals were formed in the tube as the solvent was completely lost by evaporation. A crystal fragment of dimensions 0.20 × 0.28 × 0.32 mm was cut from a parallelepiped crystal. Intensity data

(12) The absence of a stoichiometric quantity of PtI_4^{2-} being formed in this reaction implies that aerial oxidation of transient platinum(III) complexes occurs during this reaction.

Table IV. Crystallographic Data

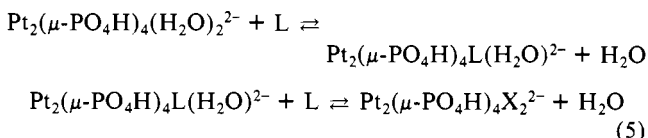
formula	Pt ₂ As ₂ S ₂ P ₆ C ₅₆ H ₆₆ O ₂₄
fw	1913.1
space group	P1
a, Å	10.584 (1)
b, Å	11.373 (1)
c, Å	15.138 (2)
α , deg	77.23 (1)
β , deg	70.72 (1)
γ , deg	75.23 (1)
V, Å ³	1644.4 (4)
Z	1
d_{calc} , g cm ⁻³	1.932
λ , Å (graphite monochromated)	0.71073
μ (Mo K α), cm ⁻¹	55.7
T, °C	19
data collection instrument	Enraf-Nonius CAD4
radiation	Mo K α
scan method	$\omega/2\theta$
data collection range, deg	1–25 (θ)
no. of unique data	5778
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	4839
no. of parameters refined	415
R^a	0.024
R_w^b	0.029
residual density, e Å ⁻³	0.95 (<1° from Pt)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|).$$

were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo K α radiation and a graphite monochromator by $\omega/2\theta$ scans of variable rate designed to yield $\sigma(I) = 0.02I$ for all observable data. A maximum time of 120 s was placed on the scan time for weak reflections. A half-sphere of data was collected and corrected for Lp, background, and absorption effects. The absorption correction was made with use of ψ scans. Data having $I > 3\sigma(I)$ were used in the refinement. The structure was solved by the heavy-atom method. The anion lies on a center (0, $1/2$, $1/2$) with the cation and a phosphoric acid molecule in general positions. Refinement was by full-matrix least squares with weights $w = \sigma^{-2}(F_o)$. Nearly all the H atoms were visible on difference maps. For refinement, difference maps were used to place the hydrogens in HPO₄²⁻ and H₃PO₄, but calculated positions were used for Ph₄As⁺ and S(CH₂)₄. In the calculation we used the values of 0.95 Å for the C–H distance and 5.0 Å² for B . Scattering factor and anomalous coefficients, and computer programs used for the structure solution, are part of a local package.¹³ Final residuals are given in Table IV.

Results and Discussion

Ligand Binding to the Axial Site of Pt₂(μ -PO₄H)₄(H₂O)₂²⁻. The complex Pt₂(μ -PO₄H)₄(H₂O)₂²⁻ has two labile axially substituted water molecules which can be readily substituted by an anionic ligand X⁻ or a neutral ligand L. The reactions are reversible, and with the added anions X⁻ (X = Cl, Br) we have previously shown that it is possible to observe sequential substitution of the axial water ligands to give Pt₂(μ -PO₄H)₄X(H₂O)₃³⁻ and then Pt₂(μ -PO₄H)₄X₂⁴⁻ by UV-vis spectroscopy.⁹ The respective rate constants for X⁻ = Cl⁻ and Br⁻ are in the region of 0.9 M⁻¹ s⁻¹ and 0.3 M⁻¹ s⁻¹ for each forward step. We now find that the substitution reactions with neutral ligands L are also readily reversible (eq 5), and indeed the complexes Pt₂(μ -PO₄H)₄L(H₂O)₂²⁻ and

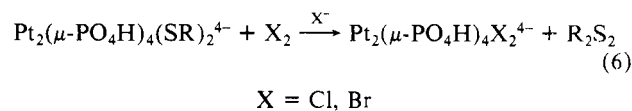


Pt₂(μ -PO₄H)₄L₂²⁻ cannot be obtained in the solid or solution state in the absence of excess ligand L. In the majority of cases for the ligands L, addition of small quantities allows the intermediate complex Pt₂(μ -PO₄H)₄L(H₂O)₂²⁻ to be identified, but in a few cases

where the situation exists with $K_2 \gg K_1$ or with K_1 and K_2 both being large, we cannot spectroscopically observe the intermediate monosubstituted complex Pt₂(μ -PO₄H)₄L(H₂O)₂²⁻.

Ligand binding to platinum(II) centers has been studied in considerable detail. From this work an extensive "nucleophilicity scale" for ligand coordination has been compiled,¹⁴ and the concept of "hard and soft" acids and bases has been developed. We have investigated the equilibrium binding to the axial sites of Pt₂(μ -PO₄H)₄(H₂O)₂²⁻ with a series of ligands L having S-, N-, and O-ligating atoms. The ligands chosen are ones of biological significance. These compounds have a high solubility in aqueous media, and structurally they usually have more than one potential ligating site for complexation to platinum. Two questions can be addressed from our results. The first one is whether the heteroatom binding order S > N > O found for monomeric divalent platinum complexes is also found for trivalent platinum complexes, especially when the axial ligand bond distance is significantly lengthened by the strong intermetallic bond. The second question, which is more speculative, is whether we can detect any significant increases in the stability constants (K_1 , K_2) for ligand binding to the axial site by a synergistic hydrogen bonding between the free oxygen or hydroxyl groups on the equatorial bridging phosphate ligand and the analogous complementary functionalities on the ligand L.

The complex ion Pt₂(μ -PO₄H)₄(H₂O)₂²⁻ in aqueous solution shows an absorption band at 224 nm ($\epsilon = 16160 \text{ M}^{-1} \text{ cm}^{-1}$). Addition of S- or N-donor ligands to the solution causes *selective* sequential substitution of the aquo ligands. These changes can, in most cases, be followed by changes in the $d\sigma \rightarrow d\sigma^*$ transitions in the electronic absorption (UV) spectrum. In those cases where the monosubstituted intermediate cannot be observed, we do see major changes in this absorption range due to the formation of the axially disubstituted complex in the presence of excess ligand. Further confirmation of axial ligand substitution is found in changes in the ³¹P NMR spectra of the complexes. Replacement of the axially substituted water molecules causes changes in the chemical shift (δ) and coupling constant (²J(PtP) Hz) values, and significantly, the pseudoquintet (1:8:18:8:1) splitting pattern diagnostic of a symmetrically bridged bimetallic complex remains. As final confirmation of selectivity in axial substitution, we have verified that an aqueous solution of each complex can be converted to Pt₂(μ -PO₄H)₄X₂⁴⁻ (X = Cl, $\lambda_{\text{max}} = 296 \text{ nm}$; X = Br, $\lambda_{\text{max}} = 342 \text{ nm}$) by the addition of an excess of the appropriate halide ion. The UV and ³¹P NMR spectral data for the complexes in aqueous solution are collected in Tables I and II. For neutral ligands L we find that S donors show λ_{max} in the range 340–366 nm and that N donors are in the range 286–298 nm. For the anionic thiolato ligands we find λ_{max} at 466 nm, which represents a large bathochromic shift from the 224-nm chromophore of the diaquo complex. These bathochromic shifts for the three sets of complexes follow the expected ligand donor abilities S⁻ > S > N, since the ligand-to-metal charge-transfer (LMCT) transition from the axial ligands is into the $d\sigma^*$ (A_{1g}^*) orbital on the diplatinum(III) core. The extinction coefficients are large ($\sim 20000 \text{ M}^{-1} \text{ cm}^{-1}$) because the LMCT and $d\sigma \rightarrow d\sigma^*$ transitions are symmetry-allowed. The homocysteinyll complex is insoluble in water but the mercaptopropionyl complex is soluble, and neither converts to Pt₂(μ -PO₄H)₄X₂⁴⁻ (X = Cl, Br) in the presence of excess halide ion. The conversion of the thiolate complexes into the halides can, however, be carried out quantitatively if a small quantity of the appropriate halogen (X₂) is added to the reaction mixture (eq 6).



For the neutral S-bonded ligands we find that the ³¹P NMR chemical shift range is δ 22.2–26.5, and the range for the N-

(13) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1. Computer programs: Frenz, B. A.; Okaya, Y. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1980.

(14) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; p 399.

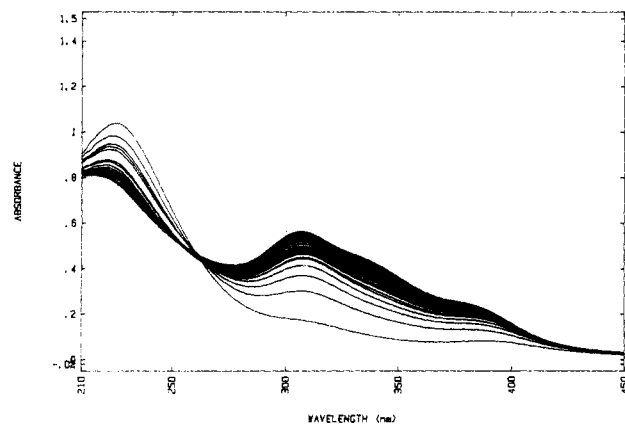
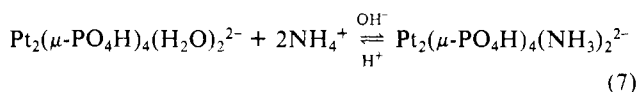


Figure 1. Overlay of the changes in the electronic spectrum upon addition of *S*-methyl-L-cysteine to $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ ($\lambda_{\text{max}} = 224 \text{ nm}$) as it is converted to an equilibrium mixture with $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S-Me-L-Cys})(\text{H}_2\text{O})_2^{2-}$ ($\lambda_{\text{max}} = 304 \text{ nm}$) and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S-Me-L-Cys})_2$ ($\lambda_{\text{max}} = 340 \text{ nm}$).

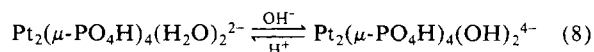
bonded axial ligands is $\delta 19.0\text{--}21.6$. The values for $^2J(\text{PtP})$ are all similar and fall within the range $62.0\text{--}72.0 \text{ Hz}$, except for the case of the iodide complex, where $^2J(\text{PtP}) = 57.5 \text{ Hz}$. The lability of the axial ligands dictates that excess ligand must be added to $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ in order to observe acceptably narrow ^{31}P NMR spectra.

For methionine and *S*-methyl-L-cysteine it is feasible for binding to occur via the S, N, or O functionalities of the ligand. From UV-vis spectral data ($\lambda_{\text{max}} = 344$ and 340 nm , respectively, Table I) and other considerations it is apparent that coordination is via the S-donor ligand. First we can eliminate the possibility of binding via oxygen because we find that simple carboxylate ligands such as acetate do not displace water from $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$. This failure to complex is verified by the absence of any spectral changes in the 224-nm band upon addition of acetate ion. The other two possibilities are S(thioether) or N(amine) complexation. The 344- and 340-nm absorption bands are not in the region for amine complexation ($286\text{--}298 \text{ nm}$), and furthermore, we have separately determined that amines do not complex to $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ under strongly acidic conditions (eq 7). Since



complexation of *S*-methyl-L-cysteine and methionine is unaffected by increasing the acidity of the medium, we can confirm that the two ligands bind via the methyl thioether moiety.

Other than water, the only other O-bonded ligand we have found that will coordinate to the axial ligation sites is the hydroxyl group. Conversion between $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{OH})_2^{4-}$ is accompanied by a shift in the UV spectral band between 224 and 266 nm , and interconversion can be accomplished by changing the solution pH (eq 8). This reaction may be either a substitution or a proton-transfer reaction.



Equilibrium Constants. Our equilibrium measurements have been made by using UV spectroscopy at 25°C in solutions of constant ionic strength ($\mu = 0.1 \text{ M}$), buffered to pH 3 with a phosphate buffer solution. The data for *S*-methyl-L-cysteine (*S*-Me-L-Cys), methionine, thiodiethanol, and thiodipropionic acid show large values of K_1 and K_2 for the replacement of axial waters by sulfur donor ligands (eq 9). In Figure 1 we show the spectral

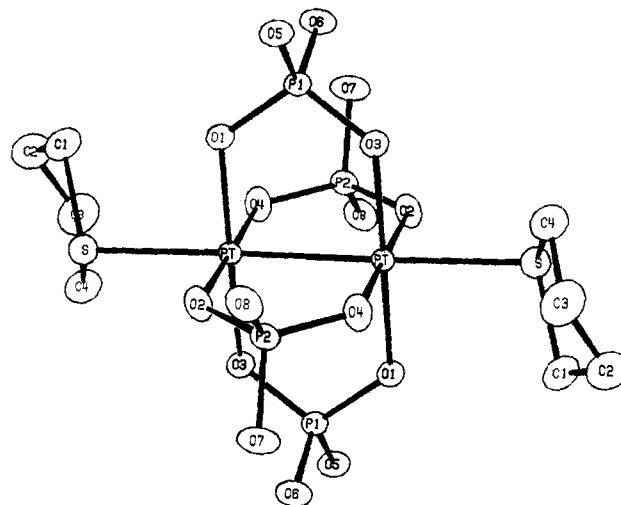
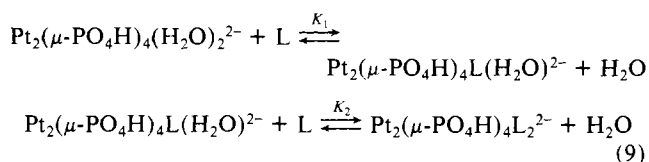


Figure 2. ORTEP view of the anion $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2^{2-}$.

changes as $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{H}_2\text{O})_2^{2-}$ ($\lambda_{\text{max}} = 224 \text{ nm}$) is converted to an equilibrium mixture with $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S-Me-L-Cys})(\text{H}_2\text{O})_2^{2-}$ ($\lambda_{\text{max}} = 304 \text{ nm}$) and $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S-Me-L-Cys})_2$ ($\lambda_{\text{max}} = 340 \text{ nm}$). For the case where L is *S*-methyl-L-cysteine or thiodipropionic acid, we find that $K_1 \approx K_2 \approx 10^3 \text{ M}^{-1}$, but for methionine we only observe the formation of $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{Met})_2^{2-}$, with no intermediate monosubstituted complex. This implies that $K_2 > K_1$. For thiodiethanol the reverse situation exists where $K_1 \approx 3K_2$. However, the overall equilibrium constants K_1K_2 are closely similar and only differ by a factor of 8 over the group of ligands. It appears, therefore, that if the distal hydroxyl groups on the axial ligands are involved in hydrogen bonding with the bridging hydrogen phosphato moieties, there is little selectivity to the carboxyl groups of *S*-methyl-L-cysteine and thiodipropionic acid, or the alcohol groups of thiodiethanol. The difference in the binding constants of *S*-methyl-L-cysteine and methionine is not clear.

Structure of $(\text{Ph}_4\text{As})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2] \cdot 2\text{H}_3\text{PO}_4$. Although there have been recent structural determinations of complexes of μ -hydrogen phosphato and μ -sulfato complexes of diplatinum(III) with water or pyridine ligands coordinated to the axial positions, there have been no structures solved for S-donor ligands bonded to platinum(III) centers.⁸ As confirmation of our structural assignments we have solved the structure of $(\text{Ph}_4\text{As})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2] \cdot 2\text{H}_3\text{PO}_4$ using X-ray crystallography.

The structure of the diplatinum(III) anion shows long $2.462(1) \text{ \AA}$ Pt-S distances, and a short Pt-Pt internuclear separation of $2.525(1) \text{ \AA}$. The anion has the oxygen groups bonded in the equatorial planes and the tetrahydrothiophene ligand complexes in the axial positions. The anion lies at the center at a position $(0, \frac{1}{2}, \frac{1}{2})$, and the Ph_4As^+ and H_3PO_4 molecules are in general positions. The μ -hydrogen phosphato ligands show the alternating bond lengths for P=O and P-OH (P1-O5 = $1.523(3) \text{ \AA}$, P2-O8 = $1.496(3) \text{ \AA}$ and P1-O6 = $1.538(3) \text{ \AA}$, P2-O7 = $1.574(3) \text{ \AA}$). The angles O1-P1-O3 = $109.8(2)^\circ$ and O2-P2-O4 = $111.3(2)^\circ$ are close to the tetrahedral angle. The P-O distances in the bridge are all similar (P1-O1 = $1.543(3) \text{ \AA}$, P1-O3 = $1.541(3) \text{ \AA}$, P2-O2 = $1.537(3) \text{ \AA}$, P2-O4 = $1.541(3) \text{ \AA}$). The C-C and C-S distances in the tetrahydrothiophene ring are all normal for a symmetrical heterocyclic ring. The molecule of phosphoric acid shows one short and three long P-O bond lengths. The bridging bite angle of the HPO_4^{2-} ligand allows the structure to adopt a planar arrangement for the equatorial coordination position about the platinum. The tetrahydrothiophene ligands bond to the axial position, and the angle Pt-Pt-S is $178.74(3)^\circ$. Each H_3PO_4 molecule bridges two anions with a hydrogen bond. This causes the short approximate O-O separations for O6-O9 = 2.520 \AA , O5-O12 = 2.606 \AA , O5-O10 = 2.521 \AA , and O8-O11 = 2.510 \AA to P3. As a consequence the HPO_4^{2-} group containing P2 appears ordered, with a proton localized on O7, but the HPO_4^{2-}

Table V. Fractional Coordinates for Non-Hydrogen Atoms in $(\text{Ph}_4\text{As})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2]\cdot 2\text{H}_3\text{PO}_4$

atom	x	y	z	atom	x	y	z
Pt	0.12270 (2)	0.45236 (1)	0.46233 (1)	C6	0.2942 (6)	0.6818 (5)	0.8723 (4)
As	0.37121 (5)	0.80251 (4)	0.98636 (3)	C7	0.2326 (6)	0.5981 (5)	0.8563 (4)
S	0.3606 (1)	0.3591 (1)	0.38580 (9)	C8	0.1745 (6)	0.5148 (5)	0.9277 (5)
P1	0.0882 (1)	0.6988 (1)	0.53443 (8)	C9	0.1749 (6)	0.5135 (5)	1.0181 (5)
P2	-0.0311 (1)	0.6140 (1)	0.31794 (8)	C10	0.2339 (5)	0.5964 (5)	1.0388 (4)
P3	0.1010 (1)	-0.0145 (1)	0.65153 (9)	C11	0.5240 (5)	0.8256 (4)	0.8774 (3)
O1	0.1837 (3)	0.5974 (3)	0.4768 (2)	C12	0.6225 (5)	0.7220 (5)	0.8505 (4)
O2	0.1033 (3)	0.5372 (3)	0.3351 (2)	C13	0.7337 (5)	0.7357 (5)	0.7730 (4)
O3	-0.0617 (3)	0.6956 (3)	0.5478 (2)	C14	0.7470 (6)	0.8503 (5)	0.7224 (4)
O4	-0.1441 (3)	0.6305 (3)	0.4120 (2)	C15	0.6484 (6)	0.9520 (5)	0.7483 (4)
O5	0.1178 (3)	0.8243 (3)	0.4828 (2)	C16	0.5367 (5)	0.9397 (5)	0.8266 (4)
O6	0.1139 (3)	0.6778 (3)	0.6315 (2)	C17	0.4310 (5)	0.7537 (4)	1.0972 (3)
O7	-0.0778 (4)	0.5407 (3)	0.2614 (2)	C18	0.5657 (5)	0.7527 (5)	1.0897 (3)
O8	-0.0122 (4)	0.7352 (3)	0.2576 (2)	C19	0.6074 (5)	0.7237 (5)	1.1710 (4)
O9	0.1136 (4)	-0.1437 (3)	0.7049 (2)	C20	0.5171 (6)	0.6956 (5)	1.2573 (4)
O10	-0.0502 (3)	0.0430 (3)	0.6578 (3)	C21	0.3847 (6)	0.6967 (5)	1.2649 (4)
O11	0.1564 (4)	0.0636 (3)	0.6949 (3)	C22	0.3388 (5)	0.7271 (5)	1.1857 (4)
O12	0.1863 (4)	-0.0133 (3)	0.5463 (3)	C23	0.2415 (4)	0.9537 (4)	0.9977 (3)
C1	0.4636 (5)	0.4001 (5)	0.4444 (4)	C24	0.2067 (5)	1.0081 (5)	1.0779 (3)
C2	0.5452 (6)	0.2800 (6)	0.4788 (4)	C25	0.1158 (5)	1.1196 (5)	1.0840 (4)
C3	0.4549 (7)	0.1865 (7)	0.5159 (5)	C26	0.0649 (5)	1.1760 (5)	1.0100 (4)
C4	0.3830 (6)	0.1962 (5)	0.4436 (5)	C27	0.0974 (5)	1.1219 (5)	0.9308 (4)
C5	0.2942 (5)	0.6805 (4)	0.9650 (4)	C28	0.1868 (5)	1.0100 (5)	0.9235 (3)

Table VI. Selected Bond Distances and Angles for the Anion and Phosphoric Acid Molecules in $(\text{Ph}_4\text{As})_2[\text{Pt}_2(\mu\text{-PO}_4\text{H})_4(\text{S}(\text{CH}_2)_4)_2]\cdot 2\text{H}_3\text{PO}_4$

Anion Bond Distances (Å)			
Pt-Pt	2.525 (1)	Pt-O3	2.001 (3)
Pt-O1	1.996 (3)	Pt-O4	1.985 (3)
Pt-O2	2.003 (3)	Pt-S	2.462 (1)
P1-O1	1.543 (3)	P2-O2	1.537 (3)
P1-O3	1.541 (3)	P2-O4	1.541 (3)
P1-O5	1.523 (3)	P2-O7	1.574 (3)
P1-O6	1.538 (3)	P2-O8	1.496 (3)
Anion Bond Angles (deg)			
Pt-Pt-S	178.74 (3)	S-Pt-O	90.11 (8)
Pt-Pt-O1	90.34 (8)	O1-Pt-O	89.6 (1)
Pt-Pt-O2	89.52 (8)	O1-Pt-O	89.7 (1)
Pt-Pt-O3	89.53 (8)	O2-Pt-O	92.3 (1)
Pt-Pt-O4	90.93 (8)	O3-Pt-O	88.4 (1)
S-Pt-O1	90.36 (8)	O1-Pt-O	178.1 (1)
S-Pt-O2	89.44 (8)	O2-Pt-O	179.2 (1)
S-Pt-O3	89.80 (8)	O2-P2-O4	111.3 (2)
O1-P1-O3	109.8 (2)	C1-S-C4	93.5
Phosphoric Acid Bond Distances (Å)			
P3-O9	1.509 (3)	P3-O11	1.531 (3)
P3-O10	1.546 (3)	P3-O12	1.549 (3)

group containing P1 appears disordered, with a proton on O5 and O6 with 50% population. As a result the difference between the P2-O7 and P2-O8 distances is much greater than is the difference between P1-O5 and P1-O6. The hydrogen atoms in H_3PO_4 are

disordered over the four oxygen atoms. In most cases the hydrogen atoms have been observed on difference maps. The fractional coordinates for non-hydrogen atoms and selected bond distances and angles are shown in Tables V and VI, and an ORTEP representation of the anion is shown in Figure 2.

The finding of a Pt-Pt distance of 2.525 (1) Å merits comment. This separation is one of the longest observed in binuclear platinum(III) complexes with bridging sulfato and phosphato ligands.⁸ If the nucleophilicity order to platinum(III) correlates with that to platinum(II), we have the order $\text{S}(\text{CH}_2)_4 > \text{py} > \text{H}_2\text{O}$. The Pt-Pt distances in the complexes $\text{Pt}_2(\mu\text{-PO}_4\text{H})_4\text{L}_2^{2-}$ are 2.525 (1), 2.494 (1), and 2.486 (2) Å for L being $\text{S}(\text{CH}_2)_4$, py, and H_2O , respectively. This ordering roughly correlates with the proposal that the stronger donor ligands transfer more electron density into the LUMO ($d\sigma^*$) of the intermetallic bond.

The Pt-S bond distance of 2.462 (1) Å is long. This finding correlates with earlier structural data which indicate that the Pt^{III} bond exerts a high trans influence on the axial ligands.⁸

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Supplementary Material Available: Tables of final atomic coordinates, anisotropic temperature factors, bond distances, and bond angles and a labeled ORTEP view of the Ph_4As^+ cation (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (25 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.