radical anion of bpy. The overall effect is to lower the lowest unoccupied molecular orbital (LUMO) so as to allow the tris complex to be slightly easier to reduce than the bis complex.

**Acknowledgment.** The support of the University of North Dakota Research Committee is acknowledged with gratitude. We wish to especially thank Professor Kenneth J. Klabunde, who provided the metal-vaporization equipment and expertise necessary for the metal atom synthesis of Ni(bpy)$_2$. We also wish to thank Tom Groshens for obtaining the spectral data on the characterization of Ni(bpy)$_2$.

**Registry No.** Ni(bpy)$_2^{3+}$, 88130-85-2; Ni(bpy)$_2^{2+}$, 31042-27-0; Ni(bpy)$_2$, 15186-68-2; Ni(bpy)$_2^-$, 71592-66-0; Ni(bpy)$_2^{2-}$, 88130-86-3; Ni(bpy)$_3^{3+}$, 64592-13-8; Ni(bpy)$_3$(ClO$_4$)$_2$, 16166-37-3; Ni(bpy)$_3$, 88130-87-4; Ni(bpy)$_3^-$, 88130-88-5; Ni(bpy)$_3^{2-}$, 88130-89-6.

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# Synthesis of Some Alkyl Phosphite Complexes of Platinum and Their Structural and Spectral Characterization

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In order to explain why Pt(II) products were frequently observed, the synthetic procedure for Pt(0) alkyl phosphite complexes has been reexamined. According to the procedure the Pt(0) complexes [Pt(P(OEt)$_3$)$_4$], [Pt(P(OMe)$_3$)$_4$], and [Pt(ETPB)$_4$] (ETPB = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) are formed initially by ligand reduction of PtCl$_4^{2-}$ accompanied by Cl$^-$ displacement. Subsequently, the Pt(0) complexes are found to undergo a reoxidation to Pt(II) if O$_2$ is not excluded from the reaction mixture. The oxidation is accelerated by H$^+$, but the nature of the Pt(II) product depends on the counterion. When [Pt(P(OEt)$_3$)$_4$] in alcoholic solution is treated with HClO$_4$ and the solution saturated with air, [Pt(P(OEt)$_3$)$_4$](ClO$_4$)$_2$ can be isolated. In the presence of HCl, [Pt(P(OR)$_3$)$_4$] is converted to [Pt(P(OH)(OR)$_2$)$_2$(P(O)(OR)$_2$)$_2$] for R = Et or Me. These latter complexes contain four equivalent P atoms by $^{31}$P NMR and exhibit a low-field proton resonance ($\delta$ 16.5 (Me$_4$Si) for Me and $\delta$ 16.6 (Me$_4$Si) for Et) assigned to bridging hydrogens linking the (RO)$_2$POH and (RO)$_2$PO$^-$ ligands together in the complex. The structure of [Pt(P(OH)(OMe)$_2$)$_2$(P(O)(OMe)$_2$)$_2$] has been determined by X-ray diffraction techniques. It crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a$ = 7.147 (1) Å, $b$ = 15.204 (2) Å, $c$ = 10.680 (4) Å, $\beta$ = 116.53 (2)°, and $D_{\text{calcd}}$ = 2.02 g cm$^{-3}$ for $Z$ = 2. The Pt atom resides on a crystallographic center of inversion and is bonded in a square-planar geometry to the four P atoms. The two unique P ligands are equivalent, bridged by a symmetric O···H···O hydrogen bond.

## Introduction

When a literature procedure[1,2] for the preparation of [Pt(P(OEt)$_3$)$_4$] was followed, several times a white solid was isolated that gave an elemental analysis and $^{31}$P NMR spectrum that was quite different from that expected for the Pt(0) product. Similar difficulty with the synthetic procedure was reported by Pregosin and Sze,[3] who obtained a white product with an analysis and $^{31}$P NMR spectrum nearly identical with that of ours. These workers formulated the product as the Pt(II) complex [Pt(P(OH)(OEt)$_2$)$_2$(P(O)(OEt)$_2$)$_2$], which is a known compound[4] and which had been characterized by $^{31}$P NMR earlier.[5,6] They also modified the synthesis of the Pt(0) complex slightly by changing the starting material from K$_2$PtCl$_4$ to the more soluble Na$_2$PtCl$_4$. In spite of this change, the procedure in our hands still frequently produced the Pt(II) product and similar results were obtained with the ligands P(OMe)$_3$ and P((OCH$_2$)$_3$CEt), 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPB).

The synthetic procedure has been investigated carefully, and conditions that lead reproducibly to a Pt(0) product are described herein. The relationship between the Pt(II) product and the Pt(0) complex has been formulated, and a method is described for the preparation of [Pt(P(OEt)$_3$)$_4$](ClO$_4$)$_2$ from Pt(P(OEt)$_3$)$_4$. Further, the interesting [Pt(P(OH)(OR)$_2$)$_2$(P(O)(OR)$_2$)$_2$], R = Me or Et, complexes are believed to contain bridging hydrogens linking the (RO)$_2$POH and (RO)$_2$PO$^-$ ligands together.[7-13] In order to characterize the bridge-hydrogen bonding in the Pt(II) complexes, we have determined the structure of [Pt(P(OH)(OMe)$_2$)$_2$(P(O)(OMe)$_2$)$_2$] by X-ray diffraction.

## Experimental Section

**Preparation of Compounds.** The starting material for all of the Pt complexes was K$_2$PtCl$_4$. The ligands were used as purchased (Strem Chemicals, Inc.); their purity was checked by C–H analysis and IR and NMR spectroscopy.

**Tetrakis(trimethyl phosphite)platinum(0), [Pt(P(OMe)$_3$)$_4$], Tetrakis(triethyl phosphite)platinum(0), [Pt(P(OEt)$_3$)$_4$], and Tetrakis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)platinum(0), [Pt(ETPB)$_4$].** The preparation of these compounds represents a modification of two previously reported syntheses.[1-3] Potassium

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tetrachloroplatinate(II) (1.24 g, 3 mmol) was dissolved in 15 mL of $H_2O$, and the solution was purged with $N_2$ for 20 min. This solution was then added dropwise with vigorous stirring to a 10-mL $O_2$-free solution of KOH (0.40 g, 7.0 mmol) and 15 mmol of the appropriate ligand at 70 °C (ETPB, 2.44 g; $P(OEt)_3$, 2.50 g; $P(OMe)_3$, 1.86 g). This latter solution was also purged continuously with $N_2$ during the addition of the $PtCl_4^{2-}$ solution. The pH of the resulting mixture was maintained at 7 or above. As the reaction proceeded, the red color of each additional drop of $PtCl_4^{2-}$ solution remained for increasing periods of time. Addition was stopped when the color persisted for more than 1 min. The solution was then maintained at 70–80 °C for several minutes until it turned colorless again. At this point, the mixture was doubled in volume with cold oxygen-free $H_2O$ and allowed to cool sealed under $N_2$ in a freezer overnight. A white precipitate was formed and was collected by filtration under $N_2$. It was washed with a 50% ethanol/water mixture, dried under vacuum, and stored under $N_2$ in the freezer. The compounds stored at −15 °C, under $N_2$, appear to be stable indefinitely, but they are air sensitive, darken, and decompose within several hours at room temperature on exposure to air.

The $P(OEt)_3$ and ETPB complexes gave good elemental analyses, but the $P(OMe)_3$ complex was too unstable to analyze properly. The small amount of product collected had an ultraviolet spectrum consistent with that of a Pt(0) complex (see below). Upon addition of HCl to an alcohol solution containing the product, it reacted to give a product having a spectrum identical with that of $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ prepared below. In this respect the product behaved in an analogous manner to that of the ethyl complex described below.

**Bis(dimethyl hydrogen phosphite-*P*)bis(dimethyl phosphito-*P*)platinum(II), $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ and Bis(diethyl hydrogen phosphite-*P*)bis(diethyl phosphito-*P*)platinum(II), $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$.** Potassium tetrachloroplatinate(II) (1.24 g, 3.0 mmol) in 15 mL of $H_2O$ was added dropwise with continuous stirring to a 10-mL solution of KOH (0.40 g, 7.0 mmol) and 15 mmol of the appropriate ligand at 75 °C ($P(OMe)_3$, 1.9 g; $P(OEt)_3$, 2.5 g). The addition of the $PtCl_4^{2-}$ was continued until the red color of the solution persisted for more than 1 min. Then, the solution temperature was maintained at 75 °C for several minutes longer until it became clear again. After the solution was allowed to cool overnight in air under a hood so that the volume was reduced through evaporation, a white crystalline material precipitated. This was filtered, washed with a 50% ethanol/water mixture, and dried under vacuum. Both compounds gave good elemental analyses. The ethyl complex melts without decomposition at 93–94 °C, but the methyl complex begins to decompose above 110 °C before it melts.

**Preparation of $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ from $[Pt(P(OEt)_3)_4]$.** The Pt(0) starting material (0.579 g, 0.0673 mmol) was dissolved in 15 mL of ethanol. To this solution was added 1.35 mL of 1 M HCl (1.35 mmol) while the solution was stirred. The resulting mixture was maintained at 70 °C for 20 min. To the hot solution was added about 1 mL of $P(OEt)_3$; then, 10 mL of $H_2O$ was added and the solution was allowed to cool overnight in air under a hood so that the volume was reduced through evaporation. A white precipitate was formed, filtered cold, washed with a 50% ethanol/water mixture, and then dried under vacuum. The compound gave good elemental analyses.

**Tetrakis(triethyl phosphite)platinum(II) Perchlorate, $[Pt(P(OEt)_3)_4](ClO_4)_2$.** Tetrakis(triethyl phosphite)platinum(0) (0.579 g, 0.673 mmol) was dissolved in 15 mL of ethanol. To this solution was added 1.35 mL of 1 M $HClO_4$ (1.35 mmol) while the solution was stirred. The resulting mixture was heated to 60 °C on a hot plate for 20 min after which the solvent was evaporated at room temperature under vacuum to about 5 mL. *Warning! Do not evaporate to dryness by heating because the mixture will explode violently.* Solid $[Pt(P(OEt)_3)_4](ClO_4)_2$ was precipitated by the slow addition of about 3 mL of $H_2O$. The white granular product was filtered, washed with a 30:70 ethanol/water mixture, and dried under vacuum. The compound gave good elemental analyses.

**Spectral Measurements.** Proton NMR spectra ($CDCl_3$ solutions, $Me_4Si$ internal reference) were obtained by using a Varian A60A spectrometer, while $^{31}P$ NMR spectra ($CDCl_3$ solutions, 85% $H_3PO_4$ external reference) were obtained at 29.30 MHz by using a JEOL PFT100 spectrometer. Electronic absorption spectra in the UV were obtained for 95% ethanol solutions by using a Cary 1501 spectrophotometer. All spectra were obtained at room temperature.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

| | $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ | $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ |
|---|---|---|
| mol wt | 631.3 | 743.5 |
| space group | $P2_1/c$ | $P2_1/c$ |
| cell constants (23 ± 1 °C) | | |
| *a*, Å | 7.147 (1) | 11.179 (2) |
| *b*, Å | 15.204 (2) | 15.870 (4) |
| *c*, Å | 10.680 (4) | 9.107 (2) |
| *β*, deg | 116.53 (2) | 106.03 (2) |
| *V*, Å | 1038.3 | 1552.9 |
| *Z* | 2 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 2.02 | 1.59 |
| $\mu_{calcd}$, cm$^{-1}$ | 74.70 | 50.07 |
| max/min transmission factors | 0.86/0.71 | |
| radiation | Mo Kα (λ = 0.710 73 Å) graphite monochromator | |
| max cryst dimens, mm | 0.20 × 0.28 × 0.45 | |
| scan width | 0.80 + 0.20 tan θ | |
| scan rate, deg min$^{-1}$ | variable, 0.4–20.0 | |
| std reflcns | (0,12,0), (006), (400) | |
| decay of stds, % | ±2 | |
| reflcns measd | 1370 | |
| 2θ range, deg | ≤42 | |
| reflcns obsd | 793 | |
| no. of parameters varied | 115 | |
| GOF | 2.23 | |
| *R* | 0.022 | |
| $R_w$ | 0.028 | |

**X-ray Data Collection and Structure Determination and Refinement.** Single crystals of $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$, colorless parallelepipeds, were sealed under $N_2$ in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 reflections ($\theta > 16°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined as $P2_1/c$ from the systematic absences.

One quadrant of data ($\pm h,+k,+l$) was collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta$–$2\theta$ scan technique. The method has been previously described.[14] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects and for absorption.

Calculations were carried out with the SHELX system of computer programs.[15] Neutral-atom scattering factors for Pt, P, O, and C were taken from Cromer and Waber,[16] and the scattering for platinum was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[17]

The position of the platinum atom on a center of inversion was revealed by the inspection of a Patterson map. A difference Fourier map phase on the platinum atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.083$. The hydrogen atoms could not be located. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.022$ and $R_w = 0.028$. A final difference Fourier showed no feature greater than 0.4 e/Å$^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.[18]

X-ray data was collected on $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ in a manner similar to that above. Lattice parameters for this compound are given in Table I. Unfortunately, high thermal motion and unresolvable disorder of the ethyl groups precluded a complete

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**Table II.** Final Fractional Coordinates for $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Pt | 1.0000 | 0.5000 | 0.5000 |
| P(1) | 0.8333 (4) | 0.5885 (2) | 0.3049 (3) |
| P(2) | 0.7552 (4) | 0.3910 (2) | 0.3918 (3) |
| O(1) | 0.874 (1) | 0.6868 (5) | 0.3330 (9) |
| O(2) | 0.906 (1) | 0.5577 (6) | 0.1927 (8) |
| O(3) | 0.587 (1) | 0.5785 (5) | 0.2183 (8) |
| O(4) | 0.827 (1) | 0.2983 (5) | 0.4471 (8) |
| O(5) | 0.660 (1) | 0.3834 (5) | 0.2258 (7) |
| O(6) | 0.556 (1) | 0.4178 (6) | 0.4082 (8) |
| C(1) | 0.824 (2) | 0.599 (1) | 0.054 (1) |
| C(2) | 0.451 (2) | 0.620 (1) | 0.267 (1) |
| C(3) | 0.773 (2) | 0.341 (1) | 0.159 (1) |
| C(4) | 0.357 (2) | 0.369 (1) | 0.345 (2) |

**Table III.** Electronic Absorption Spectra in 95% Ethanol Solution

| compd | $\nu$, $\mu m^{-1}$ ($\epsilon$, $M^{-1}$ $cm^{-1}$) |
|---|---|
| $[Pt(P(OEt)_3)_4]$ | 4.8–4.9[a,b] (30 000) |
| $[Pt(P(OMe)_3)_4]$ | [c] |
| $[Pt(ETPB)_4]$ | 4.8–4.9[a,b] (30 000) |
| $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ | 3.24 (570), 3.73 (8500), 4.12 (3140) |
| $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ | 3.26 (540), 3.75 (7800), 4.17 (2950), 4.70 (13 900)[a] |
| $[Pt(P(OEt)_3)_4](ClO_4)_2$ | 3.23 (730), 3.72 (9900), 4.25 (3400), 4.77 (15 100) |
| $[Au(ETPB)_4]ClO_4$[d] | 4.15 (2000),[a] 4.25 (3000), 4.9 (18 000) |

[a] Shoulder. [b] Broad. [c] Compound unstable. Only qualitative spectra could be obtained, which showed rising absorbance above 4.6 $\mu m^{-1}$. [d] Reference 22; data in 95% ethanol determined here.

structural investigation from the room-temperature data. Nonetheless, the Pt atom was found to reside on a center of inversion, and the P and O atoms were located resulting in an *R* value of 0.012.

## Results and Discussion

**Synthesis and Reactions.** The Pt(0) complexes are formed by a reduction of $PtCl_4^{2-}$ by the phosphite ligand, as has been suggested[2] (eq 1). However, the reaction is complicated, and

$$PtCl_4^{2-} + 5P(OR)_3 + 2OH^- \rightarrow [Pt(P(OR)_3)_4] + 4Cl^- + OP(OR)_3 + H_2O \quad (1)$$

if $O_2$ is not excluded, a subsequent oxidation of the Pt(0) product to give a Pt(II) complex also takes place. That the Pt(0) complex is an intermediate in the formation of the Pt(II) products is demonstrated by the preparation of the Pt(II) compounds from Pt(0) starting material. Further, since the electronic spectra of the Pt(0) and Pt(II) complexes (Table III) are quite different, the reaction could be followed by repetitive scans at time intervals. For example, repetitive scans for $[Pt(P(OEt)_3)_4]$ in dilute alcoholic HCl solution with air showed an isosbestic point at 3.90 $\mu m^{-1}$ between $[Pt(P(OEt)_3)_4]$ and $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$. The oxidation reaction for each of the ligands investigated is accelerated by $H^+$, being relatively slow above pH 7. Therefore if the Pt(0) complex is desired, the pH of the reaction should be carefully controlled to 7 or above and $O_2$ excluded.

When $[Pt(P(OEt)_3)_4]$ is used as a starting material, the Pt(II) product differed depending on whether HCl or $HClO_4$ was used as the acid to promote the oxidation. In the former case, $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ resulted while, in the latter case where the reaction mixture was $Cl^-$ free, $Pt(P(OEt)_3)_4^{2+}$ was formed. It is likely that the $Cl^-$ ion serves as a nucleophile that is capable of alkyl displacement from the phosphite ligand. Such displacement has been observed for organic reactions of alkyl phosphites.[19] The presence of $Cl^-$ as a reaction product in eq 1 thus can account for the formation of $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$, R = Et or Me, in the subsequent oxidation.

**Table IV.** $^{31}P$ NMR Data

| compd | $\delta^a$ ($^1J(Pt,P)$, Hz) |
|---|---|
| $P(OCH_3)_3$ | 141 |
| $P(OC_2H_5)_3$ | 138 |
| ETPB | 93 |
| $[Pt(P(OC_2H_5)_3)_4]$ | 128 (5383), 127.5[b] (5386) |
| $[Pt(ETPB)_4]$ | 92 (5857), 92.1[b] (5836) |
| $[Pt(P(OH)(OCH_3)_2)_2(P(O)(OCH_3)_2)_2]$ | 90 (3455), 88.7[c] (3456) |
| $[Pt(P(OH)(OC_2H_5)_2)_2(P(O)(OC_2H_5)_2)_2]$ | 88 (3452), 86.4[c] (3447) |
| $[Pt(P(OC_2H_5)_3)_4][ClO_4]_2$ | 114 (4256)<br>113 (4165) |
| $[Au(ETPB)_4][ClO_4]$[d] | 104 |

[a] Relative to external $H_3PO_4$ in $CDCl_3$ solutions. [b] Data from ref 3. [c] Data from ref 6. [d] Reference 22.

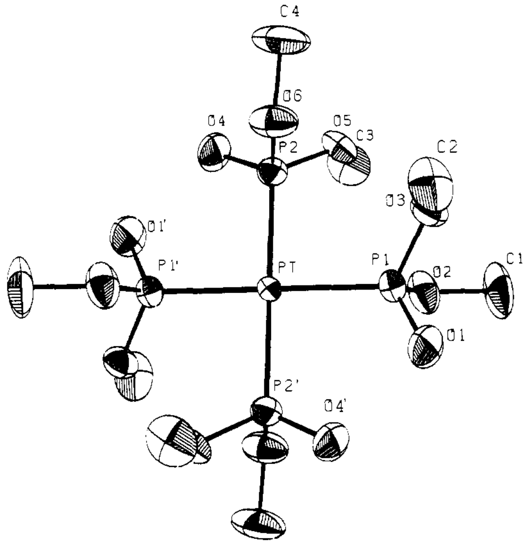

**Figure 1.** Molecular structure and atom-labeling scheme for $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ with the atoms represented by their 50% probability ellipsoids for thermal motion.

In the case of the ETPB ligand, after $[Pt(ETPB)_4]$ was allowed to stand in alcoholic HCl saturated with air, the UV spectrum clearly showed the presence of a Pt(II) complex, but its formulation is not known. All attempts to isolate a solid for analysis were unsuccessful. Evaporation of reaction mixtures or attempted precipitation with $H_2O$ resulted in oily substances.

**Electronic and NMR Spectra.** As a means of characterizing the Pt phosphite complexes prepared here, electronic absorption and NMR spectral data were gathered. Electronic absorption data are given in Table III while $^{31}P$ NMR data are collected in Table IV.

As noted above, the electronic spectra of the Pt(0) and Pt(II) phosphite complexes are quite different. The pattern of bands observed for the planar Pt(II) complexes is quite similar and resembles that for other Pt(II) complexes containing $\pi$-acceptor ligands.[20] Accordingly, the spectra are interpreted as metal to ligand charge transfer (MLCT) involving transitions from the filled 5d orbitals of Pt to empty 3d orbitals of $\pi$ symmetry on the P-donor ligands. Detailed assignments of the absorption spectra of these complexes are

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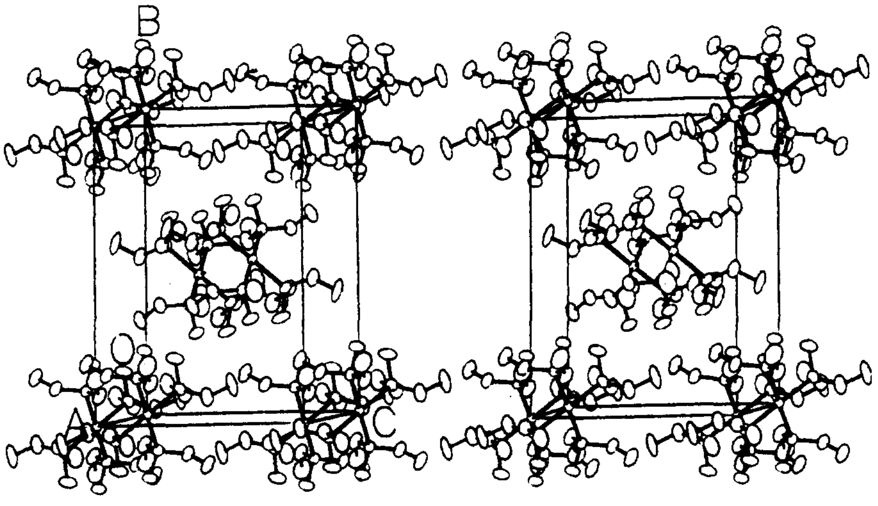

**Figure 2.** Stereoscopic view of the unit cell for $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$.

presented elsewhere, together with an interpretation of some magnetic circular dichroism (MCD) spectra for these complexes.[21]

In contrast to the Pt(II) spectra, the electronic spectra of the Pt(0) complexes exhibit only a broad shoulder about 4.8–4.9 $\mu m^{-1}$. This absorption is blue shifted compared to that of Pt(II) complexes. This shift may seem surprising at first since MLCT should red shift as the metal oxidation state is reduced and the filled 5d orbitals become less stable. However the blue shift observed here is likely a consequence of the structural difference between the Pt(II) and Pt(0) complexes. The low-energy empty ligand orbitals that are weakly $\pi$ bonding in the planar Pt(II) complexes become strongly $\sigma$ and $\pi$ antibonding in the tetrahedral Pt(0) complexes. Thus, the change of symmetry is expected to destabilize the ligand-based acceptor orbitals resulting in a blue shift of MLCT. The spectrum of $[Pt(ETPB)_4]$ can also be compared with that of isoelectronic $[Au(ETPB)_4]ClO_4$,[22] which shows a prominent band at 4.9 $\mu m^{-1}$. The assignment[22] of this band for the Au(I) complex as MLCT may be questioned since a corresponding band in the Pt(0) complex should be found at lower energy.

The $^{31}P$ NMR data, Table IV, show a single P resonance split by $^{195}Pt$ ($I = {}^1/_2$, 33.7%) for each Pt complex except $Pt(P(OEt)_3)_4^{2+}$, where two slightly separated, but Pt-coupled, resonance signals were observed. The single resonance in the former cases is consistent with equivalent P atoms within each complex, but two different types of P both bound to the Pt are indicated in the latter case. The origin of this splitting is not known but may be due to the formation of an unsymmetrical ion pair between the cationic $Pt(P(OEt)_3)_4^{2+}$ complex and the $ClO_4^-$ counterion in the low-dielectric $CDCl_3$ solvent.

The proton NMR of the $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$ complexes showed a low-field resonance ($\delta$ 16.5 for R = Me and $\delta$ 16.6 for R = Et) that is assigned to the bridging hydrogen, P–O···H···O–P, linking the $(RO)_2POH$ and $(RO)_2PO^-$ ligands. This resonance disappeared on deuteration and showed a systematic shift to higher field as the complexes were titrated with trifluoroacetic acid. A marked change in slope of $\delta$ vs. mmol of titrant was observed at a 2:1 ratio of acid to Pt(II) complex for both the ethyl and methyl compounds. This behavior is consistent with the formation of cationic complexes of the type $Pt(P(OH)(OR)_2)_4^{2+}$. It was shown earlier that $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ could be titrated with NaOMe and was found to contain two acidic protons.[9] Removal of these protons presumably gives anions of the type $Pt(P(O)(OR)_2)_4^{2-}$. Thus, the $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$ complexes are amphiprotic and can donate or accept up to 2 mol of $H^+$/mol of complex.

**Table V.** Bond Distances (Å) and Angles (deg) for $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$

| | | | |
|---|---|---|---|
| | Distances | | |
| Pt-P(1) | 2.314 (3) | Pt-P(2) | 2.310 (3) |
| P(1)-O(1) | 1.527 (9) | P(1)-O(2) | 1.574 (8) |
| P(1)-O(3) | 1.591 (8) | P(2)-O(4) | 1.525 (8) |
| P(2)-O(5) | 1.594 (7) | P(2)-O(6) | 1.564 (8) |
| O(2)-C(1) | 1.47 (1) | O(3)-C(2) | 1.43 (1) |
| O(5)-C(3) | 1.45 (1) | O(6)-C(4) | 1.48 (1) |
| | Angles[a] | | |
| P(1)-Pt-P(2) | 89.8 (1) | P(1)-Pt-P(1)′ | 180.000 |
| P(2)-Pt-P(2)′ | 180.000 | Pt-P(1)-O(1) | 114.6 (3) |
| Pt-P(1)-O(2) | 107.5 (3) | O(1)-P(1)-O(2) | 110.0 (5) |
| Pt-P(1)-O(3) | 117.3 (3) | O(1)-P(1)-O(3) | 105.8 (5) |
| O(2)-P(1)-O(3) | 100.7 (4) | Pt-P(2)-O(4) | 114.9 (3) |
| Pt-P(2)-O(5) | 117.4 (3) | O(4)-P(2)-O(5) | 105.4 (5) |
| Pt-P(2)-O(6) | 106.3 (3) | O(4)-P(2)-O(6) | 111.2 (5) |
| O(5)-P(2)-O(6) | 100.7 (4) | P(1)-O(2)-C(1) | 121.3 (8) |
| P(1)-O(3)-C(2) | 120.1 (8) | P(2)-O(5)-C(3) | 121.6 (7) |
| P(2)-O(6)-C(4) | 123.7 (9) | | |

[a] Primed atoms related by $2 - x$, $1 - y$, $1 - z$.

**Structure Determination of $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$.** The molecular structure and atom-labeling scheme for $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ is presented in Figure 1. The Pt atom resides on a crystallographic center of inversion and is coordinated to four P atoms in a square-planar geometry. The square-planar geometry is undistorted, the P–Pt–P angles not fixed by symmetry are 89.8 (1)° (Table V), and the maximum deviation from the plane of the Pt and P atoms is less than 0.001 Å.

The two unique phosphorus ligands are bridged via a symmetric O···H···O hydrogen bond. The O(1)···O(4)′ separation of 2.381 (1) Å is well under the 2.5 Å that is usually indicative of a symmetric hydrogen bond.[23] A symmetric hydrogen bridge between these ligands has been previously observed in two square-planar palladium complexes, $[Pd(S_2PMe_2)(PPh_2OH)(PPh_2O)]$[12] (O···O = 2.41 (2) Å; P–O = 1.54 (1) Å; Pd–P = 2.264 (4) Å) and $[Pd_2(SCN)_2(PPh_2OH)_2(PPh_2O)_2]$[11] (O···O = 2.421 (7) Å; P–O = 1.549 (6), 1.536 (6) Å). It is interesting to note that in $[RuCl_2(NO)[(EtO)_2PO]_2H]_2$[13], even though a short O···O separation was noted (2.432 (5) Å), the O···H···O linkage was not symmetric as seen in the P–O distances of 1.526 (2) and 1.508 (2) Å and

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the O–H lengths of 1.00 (5) and 1.45 (5) Å. In $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ the similarity in Pt–P (2.314 (3), 2.310 (3) Å) and P–O (1.527 (9), 1.525 (8) Å) distances was taken as further evidence of a symmetric O···H···O interaction. A stereoview of the unit cell contents is presented in Figure 2.

In $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ the low melting point appears to manifest itself in very high thermal motion (see Experimental Section). There is, however, strong indication from the gross details of the structure that this compound also contains a symmetric O···H···O hydrogen bond.[24]

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**Registry No.** $Pt(ETPB)_4$, 63372-08-7; $Pt(P(OMe)_3)_4$, 41431-04-3; $Pt(P(OEt)_3)_4$, 23066-15-1; $Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2$, 30053-63-5; $Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2$, 32324-65-5; $[Pt(P(OEt)_3)_4](ClO_4)_2$, 88212-05-9; potassium tetrachloroplatinate(II), 10025-99-7.

**Supplementary Material Available:** Tables of thermal parameters, best planes results, and observed and calculated structure factors for $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$ (7 pages). Ordering information is given on any current masthead page.

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[24] Further details on the structure of $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$ are available from the authors.

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# Notes

Contribution from the Service de Chimie Organique,
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## Synthesis and Spectroscopic and Electrochemical Properties of a New Ruthenium Complex: The Tris(1,4,5,8-tetraazaphenanthrene)ruthenium(II) Dication

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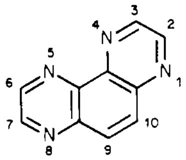
The $Ru(bpy)_3^{2+}$ complex ion has been extensively studied as a photosensitizer for the water-splitting reaction, with the hope of producing elemental hydrogen for use as a fuel.[2-5] The MLCT excited state of this complex is able, at least thermodynamically, to reduce and to oxidize water, leading to its decomposition into $H_2$ and $O_2$. Recently, Crutchley and Lever[6,7] have shown that $Ru(bpz)_3^{2+}$, where bpz is bipyrazine, is a strong oxidizing reagent in its MLCT excited state with an oxidizing potential close to +1.3 V (vs. SCE); $Ru(bpz)_3^{2+}$ should thus be thermodynamically able to oxidize water to $O_2$.

It seems of interest, in connection with this last result, to consider the potentialities of a still little explored ligand: 1,4,5,8-tetraazaphenanthrene, TAP (I),[8] which should show properties similar to those of bipyrazine and can be made with various substitution patterns. We report here the synthesis of $Ru(TAP)_3^{2+}$ (II) and its spectroscopic and electrochemical properties.



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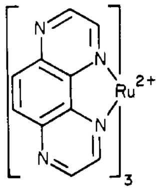

II

### Synthesis

Hunziker and Ludi[9] synthesized $Ru(bipym)_3^{2+}$, where bipym is 2,2′-bipyrimidine, by refluxing $RuCl_3·3H_2O$ and a fivefold excess ligand in ethanol–water. This procedure gives only a 5% yield in $Ru(TAP)_3Cl_2$ when the TAP ligand is used instead of the bipyrimidine. On the other hand, the synthesis of this salt was easily achieved by using $Ru(Me_2SO)_4Cl_2$ as starting material, according to the method described by Crutchley and Lever.[6,7] Refluxing this ruthenium complex with 6 equiv of TAP in ethanol–water (1:1) for 20 h yielded 71% of orange-red crystals recrystallizable from ethanol. The new complex was identified by X-ray diffraction analysis[10] and NMR spectroscopy.

### $^1H$ NMR Spectrum

When dissolved in $D_2O$, $Ru(TAP)_3Cl_2$ shows a singlet at 8.82 ppm (reference SDSS) with a relative intensity 2 and an AB system ($J$ = 2.8 Hz) at 8.57 and 9.19 ppm, each doublet having also a relative intensity of 2 (Figure 1a).

The resonances of the heterocyclic protons were assigned unambiguously by using regioselectively monodeuterated TAP.[11] The spectra of $Ru(TAP\text{-}3\text{-}d)_3^{2+}$ (Figure 1b) and $Ru(TAP\text{-}2\text{-}d)_3^{2+}$ (Figure 1c) clearly show that the 8.82 ppm line corresponds to H(9) and H(10), the 8.57 ppm doublet to H(3) and H(6), and the 9.19 ppm signal to H(2) and H(7). Such a high-field shift of the protons adjacent to the complexation site has already been mentioned in the literature for the corresponding bipyridine,[12] bipyrazine,[6,7] and phenanthroline complexes[13] of ruthenium(II) and has been attributed to the ring current of one aromatic ligand exerting a shielding effect on the 3- and 6-protons of another ligand molecule. The X-ray diffraction analysis of a $Ru(TAP)_3Cl_2.2H_2O$ monocrystal[10] shows indeed that the three TAP ligands are arranged quasi-octahedrally around the metal atom and that the 3- and 6-protons of one TAP ligand are located above the pyrazine

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