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New Mixed Metal Chain Complexes of Platinum(II) with Copper(II), Cobalt(II), Nickel(II), Zinc(II), Uranium(VI), and Thorium(IV) Having Substituted Phosphonito Groups as Bridging Ligands^{1,2}

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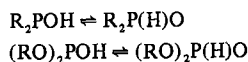
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Complexes $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{L}$ ($\text{L} = \text{PEt}_3, \text{PPh}_3$) are acidic and the proton bonded to oxygen can be removed by titration with sodium methoxide or 1,5-diazabicyclo[4.3.0]non-5-ene. The resulting anionic compound will chelate to copper(II), cobalt(II), dioxouranium(VI), and thorium(IV) through the oxygens to give mixed metal compounds $[\text{PtCl}[\text{OP}(\text{OR})_2]_2\text{L}]_n\text{M}$ ($n = 2, \text{R} = \text{Me}, \text{L} = \text{PEt}_3, \text{M} = \text{Cu}, \text{UO}_2$ and $\text{L} = \text{PPh}_3, \text{M} = \text{Co}; n = 2, \text{R} = \text{Ph}, \text{L} = \text{PEt}_3, \text{M} = \text{Cu}; n = 4, \text{R} = \text{Me}, \text{L} = \text{PPh}_3, \text{M} = \text{Th}$). The complex $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{F}_2\text{BOP}(\text{OMe})_2]\text{PEt}_3$ can be prepared by treating $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PEt}_3$ with $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Mixed metal trimetallic compounds are also obtained by treating the compounds $\text{Pt}[\text{OP}(\text{OMe})_2]_2(\text{L-L})$ with the appropriate metal salt ($\text{L-L} = 1,2$ -bis(diphenylphosphino)ethane (dppe), *o*-phenylenebis(dimethylarsine) (diars)). Complexes $[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2(\text{L-L})_2\text{M}\}(\text{ClO}_4)_2]$ ($\text{M} = \text{Cu}, \text{Zn}, \text{L-L} = \text{dppe}, \text{diars}; \text{M} = \text{Ni}, \text{Co}, \text{L-L} = \text{dppe}$) have been prepared. Electronic spectra of the mixed metal complexes show a square-planar geometry about copper(II) and nickel(II) and a tetrahedral geometry about cobalt(II). The cobalt(II) complexes show unusually low extinction coefficients for the visible and near-infrared bands, although with Racah parameter B values in the 650–700- cm^{-1} range the explanation for the low extinction coefficients is likely distortion rather than highly ionic character about Co(II). Electron paramagnetic resonance spectra of complexes $[\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3]_2\text{Cu}$ and $[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Cu}\}(\text{ClO}_4)_2$ show resolved resonances for g_{\perp} and hyperfine structure for g_{\parallel} . Calculated Δ/δ from these data is 0.676, which is in agreement with a square-planar geometry about copper(II). The complex $[\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3]_2\text{Co}$ shows resolved resonances for g_{\parallel} , g_{\perp} , and g_{\perp}' , which is in agreement with elongation and twist distortion from tetrahedral geometry about Co(II). The complex $[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Cu}\}(\text{ClO}_4)_2$ has a magnetic moment μ_{eff} of 1.89 μ_{B} , and a plot of $1/\chi$ against T shows that the solid follows Curie-Weiss behavior over the range 4.3–31.6 K. This result confirms that there is no interlayer coupling between copper atoms in the molecules. The magnetic moment for $[\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3]_2\text{Co}$ is 4.49 μ_{B} , and again a plot of $1/\chi$ against T shows that Curie-Weiss behavior is very closely obeyed. The compounds $\text{Pt}(\text{OPPh}_2)_2(\text{HOPPh}_2)_2$ and $\text{Pt}[\text{OP}(\text{OMe})_2]_2[\text{HOP}(\text{OMe})_2]_2$ are dibasic acids, and for the latter complex a conductivity curve against added sodium methoxide solution shows separate breaks for K_1 and K_2 .

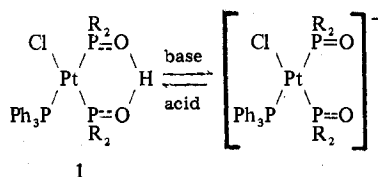
The problem of synthesizing mixed metal chain oligomers with different metal ions in specific ligand sites has challenged coordination chemists for a long period of time. One potential method is to use a solution of a bifunctional ligand in the presence of a mixture of different metal ions and to then separate and purify the mixed metal complexes formed. This inelegant method invariably leads to poor yields of mixed metal product, even after carrying out tedious separation procedures. A more rational approach is to use a bifunctional ligand having widely discrepant coordination stabilities to the separate metals and then to coordinate the second metal to a kinetically inert complex of the first one. This approach has been used by two groups of workers with metallo-2,4-pentanedionato type ligands. Lewis has prepared a number of C-bonded 2,4-pentanedionato complexes of platinum(II) having the ligand in the keto form and has then proceeded to insert the second metal ion into chelating sites between pairs of oxygens of the C-bonded 2,4-pentanedionate.³ A series of complexes of similar type has been prepared in an elegant manner by Lukehart.⁴ These authors used the approach of building a

similar type of chelate ligand, except that now the first metal is part of the ring system bidentate "metallo" 2,4-pentanedionato ligand. This structural moiety is formed by nucleophilic attack on a coordinated carbonyl group, and the second metal ion is subsequently inserted to give the mixed metal complex. Our approach is to use a P-bonded substituted phosphonito ligand as the first complex and then to coordinate the second metal into the chelating oxygen site. In this article we describe our synthetic work leading to the isolation of linear mixed metal chain compounds and present spectroscopic evidence for the geometric arrangements about the metal centers along the chain.

Phosphinous and phosphonic acids, R_2POH and $(\text{RO})_2\text{POH}$, can exist in two tautomeric forms, one with the phosphorus in a formal trivalent state and one in the pentavalent state. When $\text{R} = \text{Me}$ or Ph the predominant tautomeric form is the one with the phosphorus formally pentavalent.⁵ These compounds and their conjugate bases are potentially ambidentate although platinum metal complexes are formed by coordination through phosphorus.



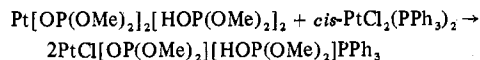
The ligand will bond as an electron pair donor through the lone pair of electrons on the phosphorus of the parent acid, or alternatively the conjugate base R_2PO^- or $(RO)_2PO^-$ can act as a monodentate anionic ligand. For complexes of palladium(II) and platinum(II) both types of phosphorus coordination occur within the same molecule, and it is becoming increasingly apparent that the hydrogen atom is symmetrically bonded between the two oxygens from cisoid phosphinito or phosphonito ligands.⁶⁻⁹ These compounds with an ionizable acidic hydrogen structurally resemble a 2,4-pentanedionate or imidodiphenyl phosphate¹⁰ ion, both of which have been used as chelating ligands to first row transition metal ions. We now find that the complex $PtCl[OP(OMe)_2][HOP(OMe)_2]PPh_3$ (**1**) shows a distinct break in the conductivity curve against added base after the addition of a single equivalent of base, verifying that the complex is a monoprotic acid. Replacement of this proton with a metal ion is therefore a viable synthetic route to mixed metal chain oligomers having the platinum metal coordinated through phosphorus, and the second metal ion, likely one from the actinide or first transition series, chelated to oxygens.



The subject of this paper is a report on our synthetic work on the preparation of such mixed metal chain oligomers with substituted phosphonito ligands and to show how we can use the spectral and magnetic data obtained to make detailed conclusions about the geometry and bonding about the central metal ion.

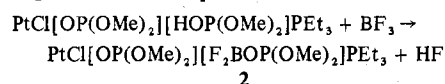
Results and Discussion

Synthesis. When the compound $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$ is treated with a stoichiometric quantity of *cis*- $PtCl_2(PEt_3)_2$ the complex $PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3$ is obtained in good yield.¹¹ We have now used this reaction to prepare the complex $PtCl[OP(OMe)_2][HOP(OMe)_2]PPh_3$ (**1**). The colorless compound shows broad



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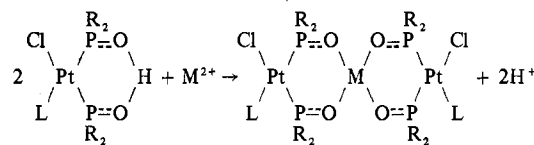
strong bands due to $\nu(C-O-P)$ at 1020 and 1040 cm^{-1} and resonances in the 1H NMR spectrum at δ 3.73 and 3.15 ($J(P-H) = 12$ Hz) for the methoxy groups. Under high resolution the upfield resonance shows small additional coupling to the ^{31}P nucleus of triphenylphosphine, and hence these tertiary phosphines must be mutually trans since *cis* coupling is significantly smaller. Previous workers have shown that the acidic hydrogen in substituted phosphinito and phosphonito complexes of platinum(II) can be replaced by a chelated BF_2 group,¹² and as anticipated, upon treating compound $PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3$ with $BF_3 \cdot Et_2O$, the new compound **2** is obtained. The infrared spectrum



of complex **2** shows a new band at 1150 cm^{-1} which we can assign to $\nu(B-F)$. The 1H NMR spectrum of **2** shows two separate methoxy resonances centered at δ 3.545 and 3.475 ($J(P-H) = 13$ Hz). Trimetallic complexes have been prepared using both $PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3$ and com-

pound **1**. We find that use of compound **1** has the advantage that the complexes obtained are easier to purify since they are less likely to tightly occlude chlorocarbon solvent in the lattice.

Treatment of these substituted phosphonitoplatinum(II) complexes with a stoichiometric amount of the methoxide or 2,4-pentanedionate compound of a second metal ion leads to substitution of the O-bonded acidic hydrogen with the second metal ion and formation of a new multimetallic compound. Since the platinum(II) center is kinetically inert and also shows a strong tendency for P-bonded ligands, no scrambling occurs and the second metal ion coordinates exclusively into the O^2 -chelate coordination site of the platinum complexes. Using this synthetic procedure we have prepared the trimetallic complexes $\{PtCl[OP(OMe)_2]_2L\}_2M$ ($L = PEt_3$ and $M = Cu$ (**3**), UO_2 (**4**); $L = PPh_3$ and $M = Co$ (**5**)). Similarly the diphenylphosphonito-bridged mixed metal complex $\{PtCl[OP(OPh)_2]_2PEt_3\}_2Cu$ (**6**) has been prepared from $PtCl[OP(OPh)_2][HOP(OPh)_2]PEt_3$.¹¹



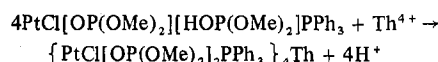
3, R = OMe; L = PEt_3 ; M = Cu

4, R = OMe; L = PEt_3 ; M = UO_2

5, R = OMe; L = PPh_3 ; M = Co

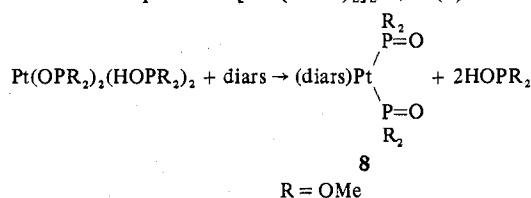
6, R = OPh; L = PEt_3 ; M = Cu

The copper(II) complexes are square planar about both platinum(II) and copper(II), whereas the cobalt(II) complex is tetrahedral about the central metal ion. The uranyl complex is six-coordinate about uranium(VI) with two (dimethylphosphonito)platinum(II) complexes chelated to the linear uranyl ion. Complexes **3**, **5**, and **6** are blue and complex **4** is yellow because of the uranyl ion. An interesting pentametallic compound **7** has been prepared in high yield by treating 4 equiv of compound **1** with tetrakis(2,4-pentanedionato)thorium(IV).



The compound is soluble in benzene and determination of the molecular weight by osmometer in this solvent gives a value of 2700 (theoretical 3075). No structural data have been collected on this compound with four platinum and one thorium atoms; nevertheless by reference to previous octa-coordinate thorium(IV) compounds a square antiprismatic geometrical arrangement about thorium is anticipated. The 1H NMR spectra of complexes **4** and **7** show respective resonances for the methoxy group at δ 3.77 and 3.736 for **4** and δ 3.715 and 3.680 for **7**. In each case coupling to phosphorus ($J(P-H) = 12$ Hz) splits the resonances into doublets.

We have further extended the use of substituted phosphonito ligands to prepare *cationic* trimetallic compounds. Treating the compound $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$ with 1,2-bis(diphenylphosphino)ethane gives $Pt[OP(OMe)_2]_2dpppe$. The corresponding complex with *o*-phenylenebis(dimethylarsine) (*diars*) has not been previously isolated, although we now find that this compound $Pt[OP(OMe)_2]_2diars$ (**8**) can be prepared



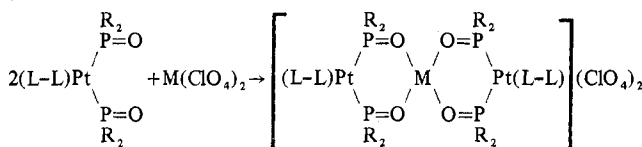
by an analogous procedure. Complex **8** shows resonances in

Table I. Electronic Spectra of Trimetallic Complexes in the Visible Region

Complex	E_{\max} , cm^{-1} ^a
$\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PEt}_3\}_2\text{Cu}$ (3)	14700 (25)
$[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Cu}](\text{ClO}_4)_2$ (9)	13070 (22)
$[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{diars}\}_2\text{Cu}](\text{ClO}_4)_2$ (10)	13070 (18)
$\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Co}$ (5)	7580 (41), 16000 (125), 17250, 18690
$[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Co}](\text{ClO}_4)_2$ (11)	7550 (23), 15750 (86), 17090, 18180
$[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Ni}](\text{ClO}_4)_2$ (13)	23500 (29)

^a Extinction coefficients (ϵ) in parentheses.

the ¹H NMR spectrum at δ 3.095 ($J(\text{P-H}) = 13$ Hz) and δ 1.30 (Me of diars). Cationic trimetallic compounds of general formula $[\{\text{Pt}[\text{OP}(\text{OR})_2]_2(\text{L-L})\}_2\text{M}](\text{ClO}_4)_2$ can be prepared by treating these dppe or diars (dimethylphosphonito)platinum(II) complexes with the appropriate transition metal perchlorate.



The geometries about the central metal ion again are square planar for copper(II) and nickel(II) and tetrahedral for Co(II) and presumably Zn(II).

Electronic Spectra. The monomeric complexes $\text{PtCl}[\text{OP}(\text{OMe})_2]_2[\text{HOP}(\text{OMe})_2]_2\text{L}$ ($\text{L} = \text{PEt}_3, \text{PPh}_3$) with square-planar geometry about platinum(II) are colorless with the lowest energy bands in the electronic spectra being of charge-transfer type above $30\,000\text{ cm}^{-1}$. This consequently means that the electronic transitions in the visible region are ones to be identified with the ligand field geometry about the second metal with no interference from the platinum center. The electronic spectra in the visible region for the colored compounds are shown in Table I.

Complexes **3**, **9**, and **10** show spectra typical of a square-planar environment about copper(II) in a moderately weak ligand field. The spectra are measured in chloroform solution and show broad absorption maxima at $14\,700$, $13\,070$, and $13\,070\text{ cm}^{-1}$, with extinction coefficients of 25, 22, and $18\text{ L mol}^{-1}\text{ cm}^{-1}$ for compounds **3**, **9** and **10**, respectively. The energy of the transition is not affected by changing diars for dppe in the backbone of the platinum; however there is a significant increase in energy between the cationic complexes **9** and **10** and the uncharged complex **3**. This lowering of energy of the visible band in compounds **9** and **10** does not correlate with any corresponding increase in extinction coefficient, and hence a distortion toward a tetrahedral geometry is not a likely explanation for this shift. A more likely reason for this difference is that a chelating uncharged dppe or diars backbone causes both an increase in double bond character of the phosphorus-oxygen bond and a greater rigidity of the bite angle. It appears that a small bite angle may lead to distortion by an elongation from the square plane along the Pt-Cu-Pt axis. The nickel complex **13** is diamagnetic and shows the ν_2 transition at $23\,500\text{ cm}^{-1}$ with an extinction coefficient of $29\text{ L mol}^{-1}\text{ cm}^{-1}$. These observations are in agreement with a square-planar arrangement about nickel(II) and indicate that the compound $\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}$ has a sufficiently high ligand field strength about the oxygen ligands to stabilize a square-planar geometry about nickel(II). If we assume that the highest energy filled orbital in complex **13** is d_{xy} , we can assign the band at $23\,500\text{ cm}^{-1}$ to the $^1\text{A}_{2g} \leftarrow ^1\text{A}_{1g} (b_{2g} \rightarrow b_{1g})$ transition.¹⁴ It follows that we can make a reasonable comparison of the ligand field of $\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}$ to that of thiocyanate ion in the yellow octahedral complex $[\text{Ph}_4\text{As}]_2\text{Ni}(\text{NCS})_4$,¹⁵ which shows an

Table II. g Values and Hyperfine Coupling Constants from EPR Spectra

Complex	g value	Hyperfine coupling const, G
$\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Cu}$	$g_{\perp} = 2.058,$ $g_{\parallel} = 2.365$	$A_{\parallel}({}^{63}\text{Cu}/{}^{65}\text{Cu}) = 141$
$[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Cu}](\text{ClO}_4)_2$	$g_{\perp} = 2.057,$ $g_{\parallel} = 2.336$	$A_{\parallel}({}^{63}\text{Cu}/{}^{65}\text{Cu}) = 156$
$\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Co}$	$g_{\perp} = 2.068,$ $g_{\parallel} = 4.329$	
$[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Co}](\text{ClO}_4)_2$	$g'_{\perp} = 2.049,$ $g'_{\parallel} = 4.336$	

absorption maximum for this transition at $23\,260\text{ cm}^{-1}$.

For the cobalt complexes the electronic absorption bands are in the expected positions for a tetrahedral cobalt(II) compound, but the extinction coefficients are considerably smaller than anticipated. There is some difference, however, between the respective spectra of the uncharged and cationic cobalt(II) complexes and those of the copper(II) case, since the energies of the ν_2 and ν_3 bands for the cationic complex $[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Co}](\text{ClO}_4)_2$ (**11**) are not shifted from those found in the complex $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Co}$ (**5**). It is apparent from Table I that the extinction coefficients of the d-d bands for complexes **5** and **11** are considerably less than predicted for a tetrahedral geometry. Nevertheless previous workers have reported similar low extinction coefficients for tetrahedral cobalt(II) complexes of chelating dipivaloylmethane ligands¹⁶ and a determination of the geometry about cobalt(II) by single-crystal x-ray diffraction showed that the low extinction coefficient was not a consequence of distortion but was due to a high degree of ionic character in the bonding about cobalt(II). This feature of the bonding was reflected in an unusually high value for the Racah parameter B (in the region of 800 cm^{-1}). We have calculated $10Dq$ and B for complexes **5** and **11**, and the respective values of $10Dq$ are 4400 and 4380 cm^{-1} and of B are 692 and 677 cm^{-1} . Since the cobalt(II) complexes of dipivaloylmethane show values for B in the vicinity of 800 cm^{-1} it is apparent that a high degree of ionic character is not a likely explanation for the low extinction coefficients in our case. We believe therefore that the most reasonable explanation for the low extinction coefficients in the cobalt(II) complexes is that there is distortion from the tetrahedral geometry. Comparison of the values of $10Dq$ and B with other tetrahedral cobalt(II) complexes shows that these platinum-containing oxygen-chelate ligands again have a ligand field energy and nephelauxetic effect comparable to those of $-\text{NCS}$. Our success in the synthesis of trimetallic complexes with these ligands has been limited to cases where the ionic radius of the central metal ion is not larger than 0.9 \AA . This implies that there is only limited flexibility in the bite angle of this chelate ligand, and it appears probable that there is an elongation along the Pt-Co-Pt axis with a possible simultaneous twist toward a square-planar geometry. Further evidence for our proposed geometrical arrangements about copper(II) and cobalt(II) in these complexes will be presented in the following section on electron paramagnetic resonance spectroscopy.

Electron Paramagnetic Resonance. Electron paramagnetic resonance spectra have been recorded for the complexes $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Cu}$, $[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Cu}](\text{ClO}_4)_2$ (**9**), $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Co}$ (**5**), and $[\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Co}](\text{ClO}_4)_2$ (**11**). The spectra have been recorded with the samples as powders at 77 K . Values for g_{\perp} and g_{\parallel} are shown in Table II along with parameters for the resolved hyperfine structure. The copper complexes show well-resolved spectra with the parallel and perpendicular resonances quite separated. The resonance assigned to g_{\parallel} shows a quartet splitting pattern due to nuclear hyperfine

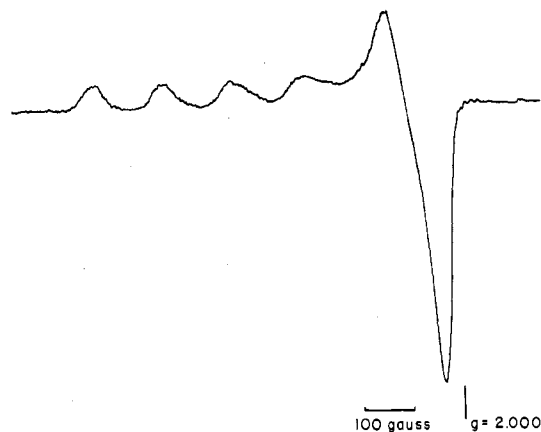


Figure 1. EPR spectrum of $[[\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}]_2\text{Cu}](\text{ClO}_4)_2$.

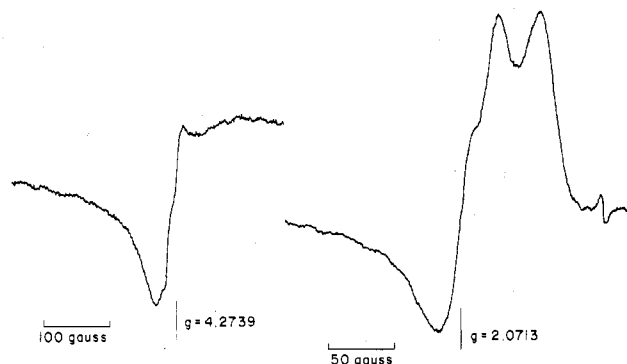


Figure 2. EPR spectrum of $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2(\text{PPh}_3)_2\}\text{Co}$.

coupling with ^{63}Cu and ^{65}Cu (Figure 1). The value for g_{\perp} is at a lower position and shows a slight shoulder due to an additional unresolved g_{\perp}' resonance. This extra g_{\perp}' value is to be anticipated for these square-planar dichelated complexes because of the assignment of a D_{2h} rather than a D_{4h} point group symmetry about copper. Using the relationships $g_{\perp} = 2.00 - 2\lambda/\delta$ and $g_{\parallel} = 2.00 - 8\lambda/\Delta$ with the data from complex 9, we obtain a value of 0.676 for the ratio Δ/δ .¹⁷ This value being less than unity confirms that the tetragonal distortion from octahedral geometry has occurred to such an extent that we have a square-planar geometry about copper(II).

The cobalt EPR spectra, showing resonances with g factors in the range of 2 to 4, are characteristic of a spin $1/2$ powder sample. These are interpreted as $\Delta M_s = \pm 1$ transitions between the $M_s = \pm 1/2$ levels of a distorted tetrahedral CoL_4 moiety. We therefore assign the resonances at low g (greater intensity) value to be due to g_{\perp} and the one at high g (lower intensity) value to g_{\parallel} . For the compound $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Co}$ the spectrum resolves into two separate resonances which can be assigned to g_{\perp} and one resonance which can be assigned to g_{\parallel} (Figure 2). The spectrum indicates the likelihood of both an elongation distortion along the Pt-Co-Pt axis and a slight twist from the tetrahedral geometry giving the two separate resonances assignable to g_{\perp} . With powdered samples we can find no evidence for superhyperfine coupling, although with the compound $\{\text{PtCl}(\text{PEt}_3)(\text{OPPh}_2)_2\}_2\text{VO}$ in dichloromethane unresolved hyperfine coupling from ^{31}P is reported.¹⁸

Magnetic Measurements. Measurements of magnetic moment and molar susceptibility have been made at low temperatures on the complexes $[[\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}]_2\text{Cu}](\text{ClO}_4)_2$ (9) and $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Co}$ (5). For complex 9 susceptibility measurements have been made over the temperature range of 4.3–31.6 K, and the plot of $1/\chi$ against T is shown in Figure 3. The plot is very closely linear, indicating that Curie-Weiss

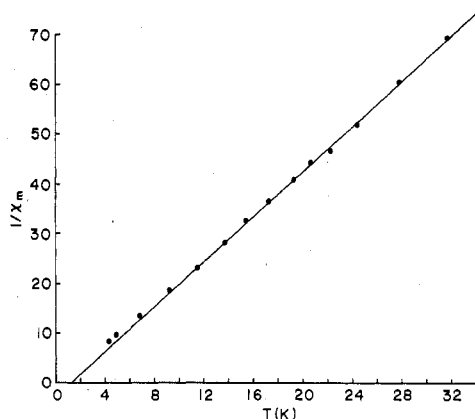


Figure 3. Low-temperature magnetic data for $[[\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}]_2\text{Cu}](\text{ClO}_4)_2$.

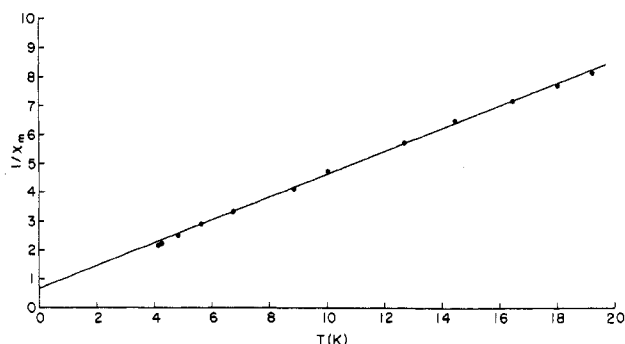


Figure 4. Low-temperature magnetic data for $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2(\text{PPh}_3)_2\}\text{Co}$.

behavior is followed at these low temperatures with negligible ferromagnetic or antiferromagnetic coupling between layers of copper ions. Using a molar diamagnetic susceptibility correction of 973×10^{-6} cgs units,¹⁹ the regression slope of the Curie-Weiss plot gives a value for the Curie constant C of 0.4465, with a Weiss constant θ of +0.9116 K. Calculation of μ_{eff} from these data gives a value of $1.89 \mu_B$. The literature range for copper(II) compounds is 1.8–2.2 μ_B .²⁰ If we calculate an average \bar{g} from these data using the spin-only equation $\bar{g} = (3k/n\beta e^2)^{1/2}[C/S(S+1)]^{1/2}$, we find a value of 2.182. This compares favorably with the value of $\bar{g}_{\text{EPR}} = 1/3(2g_{\perp} + g_{\parallel}) = 2.149$, the difference being 1.5%.

The magnetic susceptibility of complex 5 has been measured over the temperature range of 4.22–19.24 K, and $1/\chi$ has again been plotted against T (Figure 4). The molar diamagnetic susceptibility correction is 751×10^{-6} cgs units, and from linear regression, values of 2.517 and -1.484 K are obtained for the Curie constant C and Weiss constant θ , respectively. The plot is strictly linear with a correlation coefficient of 0.999. From these data we obtained a value for μ_{eff} of $4.49 \mu_B$, which corresponds closely with the range of values 4.2–4.8 μ_B previously found for tetrahedral cobalt(II) complexes.²⁰ It is not entirely correct, however, to refer to this complex as being tetrahedral and to make close comparisons with complexes of T_d symmetry since distortion caused by the coordination of two bidentate chelates eliminates the possibility of T_d symmetry. This is shown by the failure of the equation $\mu_{\text{eff}} = 3.86(1 - 4\lambda/10Dq)$ to give a reasonable value for the spin-orbit coupling constant λ . The calculated value for λ is -176 cm^{-1} , which is too close to the free ion value of -178 cm^{-1} to correspond with the normal value of the Racah parameter B found from the electronic spectrum.¹⁴

Infrared Spectra. The infrared spectra of these multimetallic compounds show few diagnostic features in the infrared region which distinguish them from the monomeric platinum com-

was evaporated to dryness under reduced pressure. The residue was dissolved in a mixture of chloroform (15 mL) and methanol (15 mL). The volume was reduced to 10 mL. The complex precipitated from the cool solution. Further reduction in volume of the solution to 5 mL gave a second crop of product. The colorless compound was filtered, washed with ether, and dried in vacuo at 80 °C for 30 min, mp 163–164 °C. Yield, 0.592 g (63%).

Chlorobis(dimethylphosphonito)-O-difluoroboron(triethylphosphine)platinum(II) ($\text{PtCl}[\text{OP}(\text{OMe})_2][\text{F}_2\text{BOP}(\text{OMe})_2]\text{PEt}_3$) (2). To a solution of $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PEt}_3$ (0.1 g) in dry benzene (20 mL) was added $\text{BF}_3\text{-etherate}$ (0.1 mL). Crude product precipitated. The reaction mixture was stirred for 15 min under an atmosphere of N_2 and the solvent was removed under reduced pressure. Dry benzene (2×10 mL) was added and evaporated to remove volatile impurities. The residue was recrystallized from dichloromethane to give pure colorless product, mp 115–116 °C.

Bis(chlorobis(dimethylphosphonito)(triethylphosphine)platinum(II)-O⁴copper(II)) ($\{\text{PtCl}[\text{OP}(\text{OMe})_2]\text{PEt}_3\}_2\text{Cu}$) (3). A mixture of $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PEt}_3$ (0.708 g) and $\text{Cu}(\text{OMe})_2$ (0.078 g) was refluxed in toluene (10 mL) for 1 h. The mixture was cooled and the deep blue solution was filtered. The solution was concentrated to a volume of 2 mL by a stream of air to give the compound. The pale blue complex was filtered and dried under vacuum at 56 °C for 12 h, mp 148–151 °C. Final purification can be effected by chromatography on Sephadex followed by crystallization from a mixture of dichloromethane and diethyl ether, mp 150–151 °C.

Bis(chlorobis(diphenylphosphonito)(triethylphosphine)platinum(II)-O⁴copper(II)) ($\{\text{PtCl}[\text{OP}(\text{OPh})_2]\text{PEt}_3\}_2\text{Cu}$) (6). Using a similar procedure as for compound 3 using $\text{PtCl}[\text{OP}(\text{OPh})_2][\text{HOP}(\text{OPh})_2]\text{PEt}_3$ (0.187 g) and $\text{Cu}(\text{OMe})_2$ (0.0144 g) the complex was obtained as a pale blue material: mp 148–151 °C; mol wt 1196 (theoretical 1198).

Bis(chlorobis(dimethylphosphonito)(triphenylphosphine)platinum(II)-O⁴cobalt(II)) ($\{\text{PtCl}[\text{OP}(\text{OMe})_2]\text{PPh}_3\}_2\text{Co}$) (5). To a solution of $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PPh}_3$ (0.115 g) in hot toluene was added bis(2,4-pentanedionato)cobalt(II) (0.0207 g). The solvent was removed under vacuum. Subsequent aliquots of toluene (2×10 mL) were added and distilled off under vacuum along with the 2,4-pentanedione. The residue was recrystallized from a mixture of toluene and hexane to give the blue complex, which was dried in vacuo at 56 °C, mp 112–116 °C.

Bis(chlorobis(dimethylphosphonito)(triethylphosphine)platinum(II)-O⁴dioxouranium(VI)) ($\{\text{PtCl}[\text{OP}(\text{OMe})_2]\text{PEt}_3\}_2\text{UO}_2$) (4). To a solution of $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PEt}_3$ (0.326 g) in hot mesitylene (20 mL) was added bis(2,4-pentanedionato)uranyl(VI) (0.135 g). Following a similar procedure to the one above for complex 5, the final residue obtained was recrystallized from a mixture of chloroform and diethyl ether to give the yellow complex, followed by vacuum drying of the product at 138 °C.

Tetrakis(chlorobis(dimethylphosphonito)(triphenylphosphine)platinum(II)-O⁶thorium(IV)) ($\{\text{PtCl}[\text{OP}(\text{OMe})_2]\text{PPh}_3\}_4\text{Th}$) (7). Using a similar procedure to the one used for compound 4 using $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PPh}_3$ (0.512 g) and tetrakis(2,4-pentanedionato)thorium(IV) (0.113 g) in mesitylene, this complex was obtained as a colorless residue. The complex was recrystallized from a mixture of benzene and diethyl ether and dried in vacuo at 80 °C; mp 164–166 °C; mol wt 2735 (theoretical 3077).

Bis(dimethylphosphonito)-o-phenylenebis(dimethylarsine)platinum(II) ($\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{diars}$) (8). To a stirred warm solution of $\text{Pt}[\text{OP}(\text{OMe})_2]_2[\text{HOP}(\text{OMe})_2]_2$ (0.976 g) in benzene (50 mL) was added diars (STREM Chemicals) (0.441 g). Upon cooling and evaporation under reduced pressure the compound precipitated as colorless crystals. The complex was washed with cold benzene (2×5 mL) and then with diethyl ether (2×5 mL), yield 0.748 g (69%). Final purification was by a recrystallization from a mixture of dichloromethane and benzene, followed by in vacuo drying at 80 °C for 1 h, mp 240 °C dec.

Bis[bis(dimethylphosphonito)[1,2-bis(diphenylphosphino)ethane]platinum(II)-O⁴copper(II) perchlorate ($\{\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Cu}\}(\text{ClO}_4)_2$) (9). Stoichiometric quantities of $\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dpe}$ and copper(II) perchlorate were refluxed in ethanol (0.3 g of platinum complex required 10 mL of ethanol) for 15 min. The blue complex was formed on cooling and dried in vacuo, mp > 200 °C dec.

Bis[bis(dimethylphosphonito)[1,2-bis(diphenylphosphino)ethane]platinum(II)-O⁴cobalt(II) perchlorate ($\{\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Co}\}(\text{ClO}_4)_2$) (11). Using a similar procedure gave a blue complex when the pink precipitate initially formed was dried in vacuo, mp > 200 °C dec.

Bis[bis(dimethylphosphonito)[1,2-bis(diphenylphosphino)ethane]platinum(II)-O⁴nickel(II) perchlorate ($\{\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Ni}\}(\text{ClO}_4)_2$) (13). Using a similar procedure gave the complex as a light yellow powder, mp > 200 °C dec.

Bis[bis(dimethylphosphonito)[1,2-bis(diphenylphosphino)ethane]platinum(II)-O⁴zinc(II) perchlorate ($\{\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dppe}\}_2\text{Zn}\}(\text{ClO}_4)_2$) (14). Again using a similar procedure the complex was obtained as a colorless powder, mp > 200 °C dec.

Bis[bis(dimethylphosphonito)[o-phenylenebis(dimethylarsine)]platinum(II)-O⁴copper(II) ($\{\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{diars}\}_2\text{Cu}\}(\text{ClO}_4)_2$) (10). Stoichiometric quantities of $\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{diars}$ and copper(II) perchlorate were refluxed in ethanol (0.1 g of platinum complex required 5 mL of ethanol) for 15 min. The solution was evaporated to dryness under reduced pressure. The blue compound was recrystallized from hot ethanol.

Bis[bis(dimethylphosphonito)[o-phenylenebis(dimethylarsine)]platinum(II)-O⁴zinc(II) perchlorate ($\{\{\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{diars}\}_2\text{Zn}\}(\text{ClO}_4)_2$) (12). This complex was prepared by a similar procedure except that recrystallization was from hot methanol.

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Registry No. 1, 63292-78-4; 2, 63678-34-2; 3, 63280-64-8; 4, 63239-09-8; 5, 63280-66-0; 6, 63280-65-9; 7, 63310-65-6; 8, 63264-39-1; 9, 63280-68-2; 10, 63280-76-2; 11, 63280-70-6; 12, 63678-30-8; 13, 63280-72-8; 14, 63280-74-0; $\{\text{PtCl}[\text{OP}(\text{OMe})_2]_2\text{PPh}_3\}_2\text{Cu}$, 63678-31-9; $\text{Pt}[\text{OP}(\text{OMe})_2]_2[\text{HOP}(\text{OMe})_2]_2$, 21794-30-9; $\text{PtCl}[\text{OP}(\text{OMe})_2][\text{HOP}(\text{OMe})_2]\text{PEt}_3$, 63264-38-0; $\text{PtCl}[\text{OP}(\text{OPh})_2][\text{HOP}(\text{OPh})_2]\text{PEt}_3$, 63292-77-3; $\text{Pt}[\text{OP}(\text{OMe})_2]_2\text{dpe}$, 21657-30-7; *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$, 15604-36-1; $\text{Cu}(\text{OMe})_2$, 1184-54-9; bis(2,4-pentanedionato)cobalt(II), 14024-48-7; bis(2,4-pentanedionato)uranyl(VI), 18039-69-5; tetrakis(2,4-pentanedionato)thorium(IV), 17499-48-8; $\text{BF}_3\text{-etherate}$, 109-63-7.

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