

CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY,  
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## Transition Metal Complexes of a Constrained Phosphite Ester.

### I. Compounds of Copper(I), Silver(I), Gold(I), Palladium(II), Platinum(II), and Rhodium(III) with 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

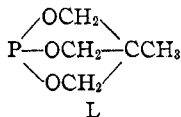
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The preparation and characterization of transition metal complexes of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane,  $P(OCH_2)_3CCH_3$ , have been described. The crystalline perchlorate and nitrate salts of the copper(I) and silver(I) complexes exhibit maximum coordination numbers for the metal ions with only phosphite molecules in the first coordination sphere. Reasons for this phenomenon in terms of ligand-ligand repulsion are discussed. The palladium(II) and platinum(II) chloride complexes have the general formula  $[M\{P(OCH_2)_3CCH_3\}_2Cl_2]$ . A dimeric gold(I) complex having the formula  $[Au\{P(OCH_2)_3CCH_3\}_2Cl]_2$  also has been isolated. Phosphorus and proton n.m.r. spectra of the phosphite and its 1-arsa analog support the bicyclic structure. Evidence that the hybridization of the phosphorus atom has changed on cyclization stems from a comparison of the phosphorus n.m.r. absorption to that in triethyl phosphite.

One of us<sup>2</sup> recently reported the synthesis and properties of the previously unknown phosphite ester 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (L). In this article we will report on some of the unusual coordination compounds formed by this compound with transition metal ions.

This phosphite ester is derived from the triol, 2-hydroxymethyl-2-methyl-1,3-propanediol, and has the structure



Additional support for the postulated<sup>2</sup> bicyclic structure stems from the proton n.m.r. spectrum, which exhibits a methyl singlet at +6.5 p.p.m. and a methylene doublet at +3.3 p.p.m. with respect to chloroform. Structures of lower symmetry would reveal more proton splittings. This was shown in the spectrum of liquid triethyl phosphite, which revealed a methylene pentuplet ( $J_{PH} = 8$  c.p.s.) at +3.8 p.p.m. and a methyl triplet ( $J_{HH} = 8$  c.p.s.) at +6.4 p.p.m. with respect to chloroform in a capillary. That the methylene splitting in L is due to proton interaction through the carbon-oxygen bond with the

phosphorus nucleus ( $J_{PH} = 1$  c.p.s.) is confirmed by the fact that the spectrum of the 1-arsa analog of L exhibits a methylene singlet at the same frequency.

Comparison of the chemical shift of phosphorus in triethyl phosphite<sup>3</sup> (-139 p.p.m.) and L (-92 p.p.m.) with respect to phosphoric acid yields no secure information concerning the relative electron densities around the phosphorus atom, since orbitals higher than s are involved. It is apparent, however, from the chemical shift and the coupling constants for the phosphorus-hydrogen interaction that a change in hybridization has taken place on constraining the molecule into a bicyclic structure.

The bicyclic structure of L is essentially strainless. It is highly symmetric, possessing a three-fold axis of symmetry. It has an unusually high dipole moment (4.15 D.)<sup>4</sup> compared to triethyl phosphite (1.82 D.).<sup>4</sup>

Previous attempts to prepare complexes with trialkyl phosphites have met with only limited success. Trialkyl phosphites form complexes with heavy transition metals such as platinum(II)<sup>5</sup> and a few of the post-transition metals such as

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(4) T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

(5) A. E. Arbuzov and V. Zoroastrova, *Izv. Akad. Nauk SSSR, Old. Khim. Nauk*, 809, 818, 826 (1952); *Chem. Abstr.*, **47**, 9898h (1953); see also "Soviet Research on Complex and Coordination Compounds," Part II, Consultants Bureau, New York, N. Y., pp. 733, 740, 746.

(1) Author to whom correspondence regarding this article should be addressed, at: Department of Chemistry, Iowa State University, Ames, Iowa.

(2) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

mercury(II). However, first series transition metals such as cobalt(II) and nickel(II) invariably yield only intractable oils although some reaction is indicated by color changes.<sup>6,7</sup> A variety of polymeric complexes of copper(I) and silver(I) have been isolated as well as monomeric gold(I) complexes with various trialkyl phosphites.<sup>5,6</sup>

The effect of reducing the steric hindrance to coordination has been studied previously in connection with the comparison of quinuclidine and triethyl amine as bases toward boron trimethyl.<sup>8</sup> In this paper the additional effect of low ligand-ligand repulsion in transition metal complexes is demonstrated for a similar bicyclic base.

### Experimental

**Analysis.**—Carbon, hydrogen, and nitrogen analyses were carried out by the University Microanalytical Laboratory. Chloride analyses were obtained potentiometrically.<sup>9</sup> Silver and copper analyses were carried out by electrolytic deposition<sup>9</sup> and the remaining metals by decomposition of the complex, reduction of the metal, and gravimetric determination as metal.<sup>10</sup>

**Instrumentation.**—Infrared spectra were obtained in Nujol and hexachlorobutadiene mulls using a Perkin-Elmer Model 21 spectrophotometer. Conductivity studies were done at 25° using an Industrial Instruments Incorporated Model RC-16B2 conductivity bridge. Nuclear magnetic resonance spectra of L and its 1-arsa analog were obtained from spinning samples on a Varian Associates Model V 4300-2 n.m.r. spectrometer. Where chloroform was used as a solvent, 30% solutions were employed. External referencing was used in all cases. Proton and phosphorus spectra were obtained at 40 and 13.6 Mc., respectively.

**Tetrakis-L-copper(I) Perchlorate.**—To 0.185 g. (0.0005 mole) of copper(II) perchlorate hexahydrate dissolved in 3 ml. of absolute ethanol was slowly added a solution of 0.592 g. (0.0040 mole) of L in 5 ml. of absolute ethanol. The blue-green solution became colorless as the ligand solution was added and a white precipitate formed immediately. The precipitate was separated by filtration and washed with absolute ethanol and ether. Drying the product in a vacuum desiccator furnished a 93% yield.

The white powder is insoluble in water, benzene, methanol, methylene chloride, and nitrobenzene. It is very slightly soluble in acetone and ethanol from which a microcrystalline colorless solid can be obtained on evaporation.

(6) A. E. Arbuzov and V. Zoroastrova, *Dokl. Akad. Nauk SSSR*, **84**, 503 (1952); *Chem. Abstr.*, **46**, 10038f (1952).

(7) It is noteworthy in this respect that results of preliminary experiments indicate the existence of a variety of stable complexes of cobalt and nickel salts with L (to be published).

(8) H. C. Brown and S. Sujishi, *J. Am. Chem. Soc.*, **70**, 2878 (1948).

(9) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953.

(10) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1948.

*Anal.* Calcd. for  $\text{CuC}_{20}\text{H}_{36}\text{ClO}_{16}\text{P}_4$ : C, 31.82; H, 4.77; Cu, 8.42. Found: C, 32.11; H, 4.76; Cu, 8.38.

Evaporation of the mother liquor and sublimation of the residue yielded a white crystalline solid which was characterized by its melting point and infrared spectrum as the 4-oxide of L.<sup>2</sup>

**Tetrakis-L-copper(I) Nitrate.**—The preparation of this compound was analogous to that of the preceding perchlorate except that copper(II) nitrate trihydrate was used in place of the perchlorate salt. A yield of 74% was obtained.

The white solid is slightly soluble in ethanol, methanol, and methylene chloride and can be recrystallized from the latter. The compound is insoluble in water, acetone, benzene, and nitrobenzene.

*Anal.* Calcd. for  $\text{CuC}_{20}\text{H}_{36}\text{NO}_{15}\text{P}_4$ : C, 33.50; H, 5.02; N, 1.96. Found: C, 33.60; H, 5.07; N, 1.76.

**Tetrakis-L-silver(I) Perchlorate.**—To a solution of 0.0849 g. (0.0005 mole) of silver nitrate and 0.370 g. (0.0025 mole) of L in 500 ml. of absolute ethanol was added 0.0612 g. (0.0005 mole) of anhydrous sodium perchlorate. The relatively large volume of ethanol was necessary to dissolve the slightly soluble silver nitrate. The mixture was shaken until the sodium perchlorate dissolved and the solution allowed to stand for 6 hr. The white precipitate which slowly formed on standing was removed by filtration, washed with water, ethanol, and ether, and dried *in vacuo*. A 50% yield was realized.

The white product is insoluble in water but slightly soluble in ethanol, from which it was recrystallized.

*Anal.* Calcd. for  $\text{AgC}_{20}\text{H}_{36}\text{ClO}_{16}\text{P}_4$ : C, 30.00; H, 4.50. Found: C, 30.04; H, 4.40.

**Tetrakis-L-silver(I) Nitrate.**—The preparation of this compound was carried out analogously to that of the preceding perchlorate salt except that the ethanolic solution of silver nitrate and L was evaporated under reduced pressure to dryness. The white residue was washed with ethanol and dried *in vacuo*. A yield of 93% was obtained.

The compound is insoluble in water but slightly soluble in ethanol, from which it was recrystallized.

*Anal.* Calcd. for  $\text{AgC}_{20}\text{H}_{36}\text{NO}_{15}\text{P}_4$ : C, 31.55; H, 4.73; N, 1.84; Ag, 14.15. Found: C, 31.54; H, 4.68; N, 1.64; Ag, 14.20.

**Chlorobis-L-gold(I) Dimer.**—To a solution of 0.972 g. (0.0025 mole) of chlorauric acid trihydrate in 15 ml. of ether was slowly added a solution of 1.120 g. (0.00756 mole) of L in 30 ml. of ether. The precipitate which immediately formed was allowed to digest overnight. Filtration of the reaction mixture and washing with ether yielded 1.750 g. of a mixture of at least two materials. The complex was isolated by washing the mixture with absolute ethanol followed by repeated extraction with methylene chloride. Upon dissolving the residue in a minimum of boiling acetone and cooling the solution to 0°, colorless crystals of the complex were obtained.

The complex is slightly soluble in ethanol and methylene chloride but moderately soluble in acetone.

*Anal.* Calcd. for  $\text{Au}_2\text{C}_{10}\text{H}_{18}\text{ClO}_6\text{P}_2$ : C, 22.70; H, 3.41; Cl, 6.71; Au, 37.3. Found: C, 24.49; H, 3.86; Cl, 6.97; Au, 36.7. Molecular weight calcd. for  $\text{Au}_2\text{C}_{20}\text{H}_{36}\text{Cl}_2\text{O}_{12}\text{P}_4$ : 1057. Found (isopiestic method in acetone): 962.

Evaporation of the ethanol and methylene chloride

extractions produced a hygroscopic white organic material. Heating this residue under vacuum yielded no 1-oxide of L. Heating the material in water did produce free chloride and an acid solution.

**Dichlorobis-L-palladium(II).**—To a solution of 0.1248 g. (0.0005 mole) of palladium(II) chloride tetrahydrate in 10 ml. of absolute ethanol was added a solution of 0.370 g. (0.0025 mole) of L in 5 ml. of ether. The brown color of the palladium solution disappeared and a white precipitate formed. The reaction mixture was allowed to stand for 5 hr., after which the white complex was separated by filtration, washed with absolute ethanol, and dried *in vacuo*. A 98% yield of complex was obtained.

The complex is nearly insoluble in water, ethanol, acetone, methanol, and nitrobenzene. It is sufficiently soluble in methylene chloride to be recrystallized therefrom.

*Anal.* Calcd. for  $\text{PdC}_{10}\text{H}_{18}\text{Cl}_2\text{O}_6\text{P}_2$ : C, 25.40; H, 3.81; Cl, 14.9; Pd, 22.5. Found: C, 25.48; H, 3.21; Cl, 15.2; Pd, 23.0.

**Dichlorobis-L-platinum(II).**—A standard method<sup>11</sup> was employed to prepare potassium tetrachloroplatinate(II). To a solution of 0.207 g. (0.0005 mole) of potassium tetrachloroplatinate(II) in 2 ml. of water was added 0.185 g. (0.0013 mole) of L dissolved in 4 ml. of ethanol. Upon warming on a steam bath, a white precipitate formed which after 0.5 hr. standing at room temperature was filtered from the colorless solution, washed with water followed by ethanol, and dried *in vacuo*. An 80% yield was obtained.

The complex exhibits the same solubility properties as the analogous palladium compound. Microcrystals can be obtained by cooling a solution of the complex in methylene chloride from the boiling point to 0°.

*Anal.* Calcd. for  $\text{PtC}_{10}\text{H}_{18}\text{Cl}_2\text{O}_6\text{P}_2$ : C, 21.40; H, 3.21; Cl, 12.65; Pt, 34.8. Found: C, 21.53; H, 3.56; Cl, 12.40; Pt, 34.7.

**Dichlorotetrakis-L-rhodium(III) Chloride Dihydrate.**—To 0.1407 g. (0.0005 mole) of rhodium(III) chloride tetrahydrate dissolved in 2 ml. of absolute ethanol was added a solution of 0.5180 g. (0.0035 mole) of L in 3 ml. of ether. The pink precipitate which immediately formed was filtered from the red supernatant liquid, washed with ether, and dried *in vacuo*. The hygroscopic compound formed in 61% yield. Recrystallization could not be accomplished since the solubility of the complex is very high in water. Addition of methanol or ethanol to a concentrated aqueous solution did not precipitate the complex. The compound is insoluble in organic solvents.

*Anal.* Calcd. for  $\text{RhC}_{20}\text{H}_{40}\text{Cl}_2\text{O}_{14}\text{P}_4$ : C, 28.70; H, 4.78; Cl, 12.7; Rh, 12.3. Found: C, 28.57; H, 5.08; Cl, 12.3; Rh, 12.2

**Attempted Preparations.**—Treatment of ethanolic solutions of manganese(II) chloride, iron(II) chloride tetrahydrate, cadmium nitrate tetrahydrate, and the hexahydrated perchlorate salts of zinc(II), iron(II), iron(III), cadmium(II), and manganese(II) with L dissolved in ethanol produced no visible reaction. Evaporation of the reaction mixtures *in vacuo* produced viscous materials from which unreacted L was recovered by sublimation at 0.05 mm. Heating the reaction mixtures on a steam bath also produced no reaction. Treatment in an inert atmos-

phere of a suspension of chromium(II) acetate in ethanol with L resulted in no reaction at room temperature for 24 hr. with shaking. Heating the mixture on a steam bath also was fruitless. Unreacted starting materials were recovered at both temperatures. However, a green oil which has thus far resisted recrystallization efforts was obtained upon heating an alcoholic solution of chromium(III) perchlorate hexahydrate with L. Mercury(II) bromide was found to yield mercury(I) bromide when an ethanolic solution of L was added to an ethanolic solution of mercury(II) bromide.

## Discussion

The compounds synthesized in this work are given in Table I with conductance values and

TABLE I  
CONDUCTIVITY DATA AND PROBABLE CONFIGURATIONS OF COMPLEXES

	$\lambda$	Configuration
$[\text{CuL}_4]\text{ClO}_4^e$		Tetrahedral
$[\text{CuL}_4]\text{NO}_3$	147 <sup>a</sup>	Tetrahedral
$[\text{AgL}_4]\text{NO}_3$	162 <sup>a</sup>	Tetrahedral
$(n\text{-C}_4\text{H}_9)_4\text{NNO}_3$	158 <sup>a</sup>	
$[\text{AgL}_4]\text{ClO}_4$	29 <sup>b</sup>	Tetrahedral
$(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$	31 <sup>b</sup>	
$[\text{AuL}_2\text{Cl}]_2$	5.6 <sup>a</sup> , 3.6 <sup>a</sup>	Tetrahedral
$[\text{PdL}_2\text{Cl}_2]$	2.6 <sup>a</sup>	Sq. planar
$[\text{PtL}_2\text{Cl}_2]$	5.9 <sup>a</sup>	Sq. planar
$(n\text{-C}_4\text{H}_9)_4\text{NBr}^f$	150 <sup>a</sup> , 123 <sup>a</sup>	
$[\text{RhL}_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$	153 <sup>a</sup>	Octahedral
Uni-univalent complex	118–131 <sup>a, g</sup>	

<sup>a</sup> Acetonitrile. <sup>b</sup> Nitrobenzene. <sup>c</sup> Acetone. <sup>d</sup> Water.

<sup>e</sup> Not sufficiently soluble. <sup>f</sup> The difference in ionic conductance between the bromide and chloride (3%) is sufficiently small to justify the use of the more moisture stable bromide as a reference for the gold, platinum, and palladium complexes. <sup>g</sup> Typical range for uni-univalent coordination compounds.<sup>12</sup>

probable configurations. The structures are in full accord with the conductivity data and the well known bonding tendencies of the individual metal atoms. For comparison of molar conductance ( $\lambda$ ) values with expected values of the complexes, reference compounds have been interspersed at appropriate places.

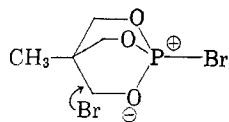
The most remarkable aspect of this series of complexes is that for the perchlorates and nitrates, the maximum coordination number is achieved with only L molecules in the first coordination sphere. This is the strongest experimental evidence for the reduction of ligand–ligand steric repulsion. The high ( $\text{C}_{3v}$ ) symmetry of L undoubtedly also promotes crystallinity in the

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(12) M. Sneed and J. Maynard, "General Inorganic Chemistry," D. Van Nostrand Company, New York, N. Y., 1942, p. 813.

complexes herein described. Recently<sup>13</sup> Cotton and Goodgame have reported the isolation of complexes of triphenylphosphine with various silver(I) and copper(I) salts. In the case of the perchlorates, four triphenyl phosphine molecules were found in the coördination sphere. It is noteworthy that when nitrate is the anion, only two triphenylphosphine molecules enter the copper(I) coördination sphere. It is probable that nitrate ion is in some way coördinated to the copper ion in the triphenyl phosphine complex.<sup>13</sup> It is interesting to compare the behavior of L in this system since four L molecules are coördinated and the nitrate is outside the coördination sphere.

Although two- and three-covalent gold(I) ammine complexes are known,<sup>14</sup> only monomeric two-covalent complexes are found with phosphorus<sup>5,6,15</sup> and arsenic.<sup>15</sup> Furthermore, these complexes contain only one phosphorus- or arsenic-containing ligand while the other coördination position is occupied by a halogen. It is significant, therefore, that the gold(I) complex of L is a dimeric four-covalent system with two L molecules and two chlorides in the coördination sphere. Although the stoichiometry and molecular weight of the compound have been established, the structure has not. It is very probable, however, that the chlorine atoms function as bridges in the tetrahedral structure. That the gold(III) ion has indeed been reduced to the monovalent state is supported by the isolation of an unstable chloro derivative of L. Barnes and Hoffman<sup>16</sup> find that reaction of L with bromine yields a compound having the formulation  $\text{O}=\text{P}(\text{Br})(\text{OCH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{Br}$ . The intermediate in this reaction is postulated to have the structure



and can undergo hydrolysis to the 1-oxide of L.<sup>16</sup> Since water (from the chlorauric acid trihydrate) is present in the gold(III) reduction with L, a similar reaction might be expected to take place. However, no 1-oxide of L could be isolated from the reaction mixture. It is probable, therefore, that cleavage by chlorine occurs before hydrolysis to the 1-oxide can take place. It is significant to

observe, however, that the oxidation product in the formation of the copper(I) complex from the copper(II) ion is the stable 1-oxide of L.

It has not as yet been determined whether the configurations of the palladium and platinum complexes are *cis* or *trans*. The insolubility of the compounds precluded efforts to obtain dipole moment data. It is evident from the solubility and conductance data, however, that these complexes are not appreciably ionized and hence are not double salts (*i.e.*,  $[\text{ML}_4][\text{MCl}_4]$ ).

It is not clear at present what configuration the rhodium complex possesses. The conductivity data in water indicate a relatively slow aquation of both chlorides in the coördination sphere. Extrapolation of the molar conductance to zero time reveals a molar conductance corresponding to a uni-univalent electrolyte ( $\lambda = 153$ , extrapolated).

The C-H, C-CH<sub>3</sub>, and P-O-C infrared absorptions of L lie within the range generally assigned to alkyl phosphites.<sup>17</sup>

Under the conditions employed in this research, complexes of L with manganese(II), iron(II), zinc(II), cadmium(II), mercury(I), and mercury(II) were not observed. It has been proposed<sup>18</sup> that the weakening of phosphine complexes on passing from silver to cadmium is an indication that the strength of the dative  $\pi$ -bonding from the metal atom to the ligand declines sharply at the end of a transition series. It is possible that the same reasoning holds for the isolation of stable complexes of L with copper, silver, and gold and the apparent lack of such complexes with zinc, cadmium, and mercury. The stability of the d<sup>5</sup> configuration in manganese(II) may preclude coördination by L. It is possible that more vigorous reaction conditions are necessary to cause coördination of L with the other metal ions.

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(15) N. V. Sidgwick, *ibid.*, p. 140.

(16) R. A. Barnes and J. A. Hoffman, private communication.

(17) L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., Ed. 2, 1958. A more detailed discussion of this spectrum will be published shortly.

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