

CONTRIBUTION FROM CHEMISTRY HALL,  
IOWA STATE UNIVERSITY, AMES, IOWA

## Transition Metal Complexes of a Constrained Phosphite Ester. IV. Compounds of Cobalt(I), Cobalt(III), Nickel(II), and Nickel(0)<sup>1</sup>

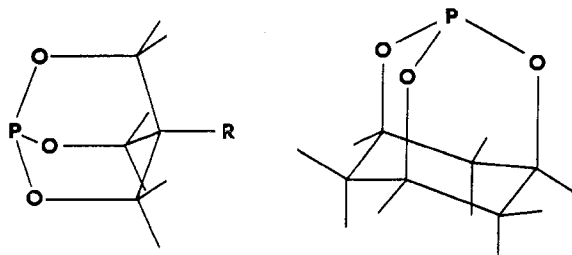
BY T. J. HUTTEMANN, JR., B. M. FOXMAN, C. R. SPERATI, AND J. G. VERKADE

Received January 25, 1965

Cobalt and nickel complexes of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (I), the 4-ethyl analog of I (I'), and 2,8,9-trioxa-1-phosphaadamantane (II) are described. Maximum coordination numbers for the metals are observed for the yellow  $[\text{Co}(\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3)_3]^+$ , colorless  $[\text{Co}(\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3)_3]^{+3}$ , yellow  $[\text{Co}(\text{P}(\text{OCH})_3(\text{CH}_2)_3)_3]^+$ , and colorless  $[\text{Co}(\text{P}(\text{OCH})_3(\text{CH}_2)_3)_3]^{+3}$  ions, all of which are diamagnetic. Calculations of  $Dq$  from ultraviolet spectra of the colorless cobalt complexes show that I' and II provide ligand fields of about the same strength as that of the cyanide ion. The yellow diamagnetic  $[\text{Ni}(\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3)_3]^{+2}$ ,  $[\text{Ni}(\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3)_3]^{+2}$ , and  $[\text{Ni}(\text{P}(\text{OCH})_3(\text{CH}_2)_3)_3]^{+2}$  ions are also described and their possible configurations discussed. The reduction of the  $[\text{NiL}_6]^{+2}$  ions (where L = I, I', or II) to the corresponding  $\text{NiL}_4$  complexes wherein nickel is zerovalent is also reported.

### Introduction

A series of transition metal ion complexes of the polycyclic phosphite designated as I in the group of ligands shown in Figure 1 has been reported.<sup>2,3</sup> More



I, R =  $\text{CH}_3$  ( $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ )  
I', R =  $\text{CH}_2\text{CH}_3$  ( $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ )  
II ( $\text{P}(\text{OCH})_3(\text{CH}_2)_3$ )

Figure 1.—Polycyclic phosphite ligands.

recently, the interaction of I with transition metal carbonyls has been studied.<sup>4</sup> To facilitate our spectral investigations on the nature of phosphorus-metal bonds formed from constrained ligands, it was necessary to obtain more soluble complexes than those formed with I. The results of the present investigation indicate that I' is eminently suited for this purpose since the bridgehead ethyl group on the ligand drastically increases solubilities of the complexes in organic solvents while the stoichiometries of the coordination compounds are the same as those observed for I. Since II is more bulky than I or I' with respect to possible ligand-ligand repulsions, it was of interest to study its ligand properties as well.

### Experimental

**Ligands.**—The phosphite ligands I and II were prepared according to a modification<sup>5</sup> of a method described elsewhere.<sup>6</sup> Ligand I' was prepared in the same manner as that described for

I except that the triol  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$  was used in place of  $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_3$ .

**Pentakis-( $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ )-cobalt(I) Perchlorate and Hexakis-( $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ )-cobalt(III) Perchlorate.**—These compounds were prepared according to an earlier method.<sup>3</sup>

**Pentakis-( $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ )-cobalt(I) Perchlorate and Hexakis-( $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ )-cobalt(III) Perchlorate.**—To a solution of 0.37 g. (1.0 mmole) of cobalt(II) perchlorate hexahydrate in 10 ml. of acetone was added 2.0 g. (13 mmoles) of I'. The yellow solution which formed slowly deposited colorless crystals. Ether was slowly added to the solution until no more white precipitate formed. The colorless complex was recrystallized from boiling absolute ethanol. The supernatant liquid from the reaction mixture yielded a dark yellow oil on evaporation under vacuum which was dissolved in 20 ml. of methylene chloride. The solution was extracted with three 10-ml. portions of water, whereupon the dark yellow color of the methylene chloride layer lightened considerably and a pink coloration characteristic of hydrated cobalt(II) ion developed in the water layer. The methylene chloride layer was separated from the water layer and dried over anhydrous magnesium sulfate. Evaporation of the methylene chloride solution under vacuum yielded a yellow powder which could be recrystallized from a minimal amount of ethanol by adding ether to the cloud point and cooling to ice temperature.

**Pentakis-( $\text{P}(\text{OCH})_3(\text{CH}_2)_3$ )-cobalt(I) Perchlorate and Hexakis-( $\text{P}(\text{OCH})_3(\text{CH}_2)_3$ )-cobalt(III) Perchlorate.**—To a solution of 0.74 g. (2.0 mmoles) of cobalt(II) perchlorate hexahydrate in 15 ml. of acetone was added a solution of 3.5 g. (22 mmoles) of II in 15 ml. of acetone. A mixture of yellow and white solid formed immediately in the supernatant yellow solution. Recrystallization of the mixture from boiling water afforded a 100% yield (1.3 g.) of the colorless complex  $[\text{Co}(\text{P}(\text{OCH})_3(\text{CH}_2)_3)_3](\text{ClO}_4)_3$  based on one-half of the available cobalt. Evaporation of the mother liquor to dryness under vacuum yielded a solid from which excess ligand was sublimed at 80° and 0.02 mm. pressure. The residue was recrystallized from boiling methanol to give an 88% yield (0.84 g.) of  $[\text{Co}(\text{P}(\text{OCH})_3(\text{CH}_2)_3)_3](\text{ClO}_4)_3$  based on cobalt.

**Hexakis-( $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ )-nickel(II) Perchlorate.**—To a solution of 1.5 g. (2.0 mmoles) of hexakis(dimethyl sulfoxato)nickel(II) perchlorate<sup>7</sup> in 10 ml. of acetone was added 1.8 g. (12 mmoles) of I in 5 ml. of acetone. Upon cooling the yellow solution which formed, a 95% yield of the complex based on nickel was recov-

(1) Presented in part at the Eighth International Conference on Coordination Chemistry, Vienna, Austria, Sept. 1964.

(2) J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **1**, 453 (1962). References 2, 3, and 4 constitute parts I, II, and III, respectively, of this series.

(3) J. G. Verkade and T. S. Piper, *ibid.*, **2**, 944 (1963).

(4) J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *ibid.*, **4**, 228 (1965).

(5) J. G. Verkade, T. Huttemann, M. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).

(6) C. W. Heitsch and J. G. Verkade, *ibid.*, **1**, 392 (1962); K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, M. Peterson, E. A. Pier, and J. G. Verkade, *Tetrahedron*, **20**, 323 (1964).

(7) Prepared according to J. Selbin, W. E. Bull, and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **16**, 219 (1961).

ered. The compound was recrystallized from a minimal amount of methylene chloride by adding ether to the cloud point and cooling to ice temperature.

**Hexakis-(P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>)-nickel(II) Perchlorate.**—To a solution of 1.8 g. (5.0 mmoles) of nickel(II) perchlorate hexahydrate in 15 ml. of acetone was added 11 g. (65 mmoles) of I' dissolved in 10 ml. of acetone. Because the yellow solution which formed deposited no crystals upon cooling, it was evaporated to dryness and extracted with five 25-ml. portions of ether to remove unreacted ligand. The residue was dissolved in a minimum of methylene chloride and ether was added to the cloud point. Cooling of the solution in an ice bath produced an 82% yield of the complex based on nickel.

**Hexakis-(P(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)-nickel(II) Perchlorate.**—The hexakis(dimethyl sulfoxato)nickel(II) perchlorate was carefully analyzed by the dimethylglyoxime method such that 2.065 mmoles of nickel ion was present in an acetone solution of the complex. To this solution was added 2.2423 g. (14.000 mmoles) of II dissolved in 15 ml. of acetone, and the reaction mixture was stirred magnetically for 1 hr. After cooling the mixture to 0°, the yellow compound formed was filtered from the colorless supernatant under nitrogen, washed with two 5-ml. portions of ether, and dried under vacuum at room temperature. A total of 2.4976 g. or a 99.50% yield of hexakis-(P(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)-nickel-

The crude tetrakis-L-nickel(0) complexes thus obtained were recrystallized from methylene chloride (55% yield where L = I), boiling ethanol (88% yield where L = I'), and boiling acetonitrile (99% yield where L = II), respectively. Yields are based on the parent nickel(II) complexes.

That the oxidation product in the reduction of the nickel(II) complex of II is the phosphate derivative of II was shown by sublimation of the phosphate from the dried reaction mixture at 150° and 0.02 mm. It was not possible to duplicate this result by similar treatment of the reaction mixtures involving ligands I and I' due to their hydrolysis (see the Discussion).

**Analyses.**—In Table I are reported the analyses of the compounds reported in this work. Methods described previously<sup>3</sup> were used to obtain metal contents. Carbon, hydrogen, and chlorine analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**Magnetic Susceptibilities.**—That all of the compounds herein reported are diamagnetic at room temperature is supported by direct measurement<sup>8</sup> and by the proton n.m.r. spectra.<sup>9</sup>

**Ultraviolet-Visible Spectra.**—Solutions (1–5 mM) were scanned in the ultraviolet, visible, and near-infrared regions on a Cary Model 14 spectrophotometer. Pertinent data are summarized in Table II.

TABLE I  
ANALYSES

Compound	Calculated, %				Found, %			
	Metal	C	H	Cl	Metal	C	H	Cl
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>5</sub> ]ClO <sub>4</sub>	6.08	37.2	5.67	3.67	6.11	37.2	6.38	3.43
[Co(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>5</sub> ]ClO <sub>4</sub>	6.15	37.6	4.74	3.70	6.09	37.6	4.86	3.42
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	4.43	32.4	4.96		4.48	33.0	5.05	
[Co(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	4.47	32.8	4.10	8.08	4.43	32.5	4.20	8.07
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	5.13				5.11			
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	4.77	29.3	5.36		4.65	29.0	6.66	
[Ni(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	4.82	35.4	4.47	5.82	4.91	34.4	4.55	5.74
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub> ] <sup>a</sup>								
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub> ]	8.30	40.8	6.27		7.80	40.4	6.20	
[Ni(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> ]	8.39	41.3	5.20		8.15	40.6	5.14	

<sup>a</sup> N.m.r. and infrared spectrum identical with those of the compound whose analysis is reported in ref. 4.

TABLE II  
ULTRAVIOLET AND VISIBLE SPECTRA

Compound	Solvent	λ, mμ <sup>a</sup>
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>5</sub> ]ClO <sub>4</sub> <sup>b</sup>	H <sub>2</sub> O	230° (1.0 × 10 <sup>4</sup> ), 350 (1.1 × 10 <sup>3</sup> )
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>5</sub> ]ClO <sub>4</sub>	H <sub>2</sub> O	220° (1.3 × 10 <sup>4</sup> ), 350 (1.4 × 10 <sup>3</sup> )
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>5</sub> ]ClO <sub>4</sub>	H <sub>2</sub> O	230° (1.5 × 10 <sup>4</sup> ), 342 (1.4 × 10 <sup>3</sup> )
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub> <sup>d</sup>	H <sub>2</sub> O	224 (3.5 × 10 <sup>4</sup> ), 253 (1.7 × 10 <sup>4</sup> ), 280 (2.0 × 10 <sup>3</sup> ), 325 (340)
[Co(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub> <sup>e</sup>	H <sub>2</sub> O	226 (4.2 × 10 <sup>4</sup> ), 262 (1.6 × 10 <sup>4</sup> ), 287 (4.5 × 10 <sup>3</sup> ), 322 (300)
[Co(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub> <sup>e</sup>	H <sub>2</sub> O	232 (5.0 × 10 <sup>4</sup> ), 265 (1.1 × 10 <sup>4</sup> ), 298 (2.0 × 10 <sup>3</sup> ), 320 (337)
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>f</sup>		
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>f</sup>		
[Ni(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	365 (3.5 × 10 <sup>3</sup> )
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub> ]	CH <sub>2</sub> Cl <sub>2</sub>	290 (1.9 × 10 <sup>4</sup> )
[Ni(P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub> ]	CH <sub>2</sub> Cl <sub>2</sub>	243° (2.4 × 10 <sup>6</sup> )
[Ni(P(OCH) <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> ]	CH <sub>3</sub> CN	222 (2.7 × 10 <sup>4</sup> )

<sup>a</sup> Extinction coefficients based on decadic logarithms in units of l. mole<sup>-1</sup> cm.<sup>-1</sup> appear in parentheses. <sup>b</sup> Although the 350 mμ band was reported earlier,<sup>3</sup> the 230 mμ band was not. <sup>c</sup> Appears as a shoulder on the ultraviolet tail. <sup>d</sup> See ref. 3. <sup>e</sup> The bands reported for these compounds were resolved by gaussian analysis; see ref. 3. <sup>f</sup> These compounds are either insufficiently soluble in a variety of spectral solvents or react with them.

(II) perchlorate based on nickel(II) ion originally present was obtained.

**Tetrakis-(P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>)-nickel(0), Tetrakis-(P(OCH)<sub>3</sub>C-CH<sub>2</sub>CH<sub>3</sub>)-nickel(0), and Tetrakis-(P(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)-nickel(0).**—These complexes were prepared by suspending the parent hexakis-L-nickel(II) perchlorate complexes (where L = I, I', or II) in water and adding 2 moles of sodium hydrogen carbonate per mole of complex. The reaction mixtures evolved carbon dioxide when heated on a steam bath. Continued heating produced white suspensions which were filtered and dried under vacuum.

**Infrared Spectra.**—Nujol-hexachlorobutadiene mulls prepared in a drybox were employed to obtain spectra on a Perkin-Elmer Model 21 spectrophotometer. The spectra obtained were

(8) The authors are grateful to Professor T. S. Piper of the University of Illinois for the magnetic susceptibility measurements carried out on a Faraday balance.

(9) J. G. Verkade, T. J. Huttemann, B. M. Foxman, S. C. Goodman, and R. W. King, to be published.



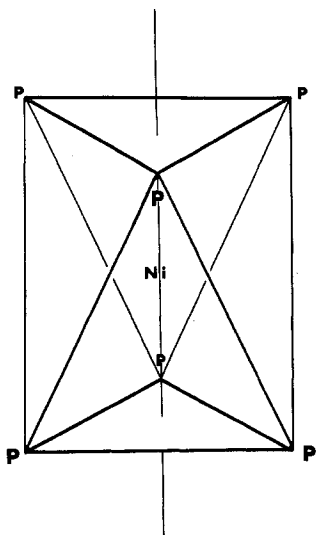
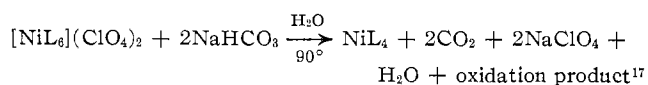


Figure 3.—Possible geometry of the  $[\text{NiL}_6]^{+2}$  species where  $L = \text{I}, \text{I}', \text{or II}$ .

motion of electrons from  $\sigma$  phosphorus orbitals to empty metal orbitals. That the zerovalent nickel complexes are indeed stable is reflected in their very high yields and the relatively mild conditions under which they were formed. In contrast to  $[\text{Ni}(\text{P}(\text{OCH}_3)_3)_4]$  and  $[\text{Ni}(\text{P}(\text{OCH}_2\text{CH}_3)_3)_4]$ ,<sup>15</sup> the analogous complexes with I, I', or II are stable in air and moisture. The reaction shown below differs from that reported by Vinal and Reynolds in that the reduction is carried out on an isolated hexacoordinate nickel(II) complex.<sup>16</sup>



Low ligand–ligand repulsion has been cited previously<sup>2,3</sup> as a determinative factor in the high ligand fields and maximum coordination number exhibited by

(15) D. G. Hendricker, J. G. Verkade, R. E. McCarley, and R. W. King, to be published.

(16) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, **3**, 1062 (1964).

(17) As shown in the Experimental section, the phosphate derivative of II was isolated when L is II. Due to competing hydrolysis of I and I', the oxidation products are undoubtedly phosphoric acid or a partially hydrolyzed phosphate.

transition metal complexes of L. This conclusion was based on scale models of these systems as well as the fruitless efforts to isolate any cobalt or nickel complexes of trialkyl phosphites.<sup>18</sup> Although the constraint of the polycyclic phosphite ligands is undoubtedly a distinct advantage, experiments now in progress indicate that, under proper conditions, cobalt and nickel as well as other transition metals form isolable crystalline complexes with trialkyl phosphites.<sup>19</sup> The relatively high dipole moment of the polycyclic ligands (*ca.* 4 D.)<sup>20</sup> is about twice as large as those of trialkyl phosphites and should therefore exert larger crystal fields. In light of the isolated complexes<sup>19</sup> of trialkyl phosphites, however, the necessary orientation of the alkoxy groups on these ligands due to ligand–ligand repulsion upon approach of the ligand to the metal ion will undoubtedly increase their dipole moments. By use of suitable orbitals on phosphorus higher than the metal  $T_{2g}$  orbital, a significant amount of  $d_{\pi}-d_{\pi}$  back bonding from the metal can account for the large value of  $\Delta$  observed in the octahedral cobalt(III) complexes of L. Such a postulate can also account for the high extinction coefficients assigned to the d–d bands since significant orbital overlap increases the “allowedness” of these transitions and hence also the nephelauxetic effect. It should be noted, however, that these bands occur along with a very strong charge-transfer band probably originating in transitions from  $\sigma$ -bonding orbitals to the metal  $\sigma$ -antibonding orbitals.

**Acknowledgments.**—The authors wish to thank Dr. C. K. Jørgensen for very helpful discussion and results of calculations in advance of publication. They are also grateful to the National Science Foundation for aid in the form of a grant (G.P.-2328) to J. G. V. and Undergraduate Research Participation Fellowships to B. M. F. and C. R. S. T. J. H. thanks the Texaco Company for a Texaco Research Fellowship.

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

(19) T. J. Huttemann and J. G. Verkade, to be published.

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