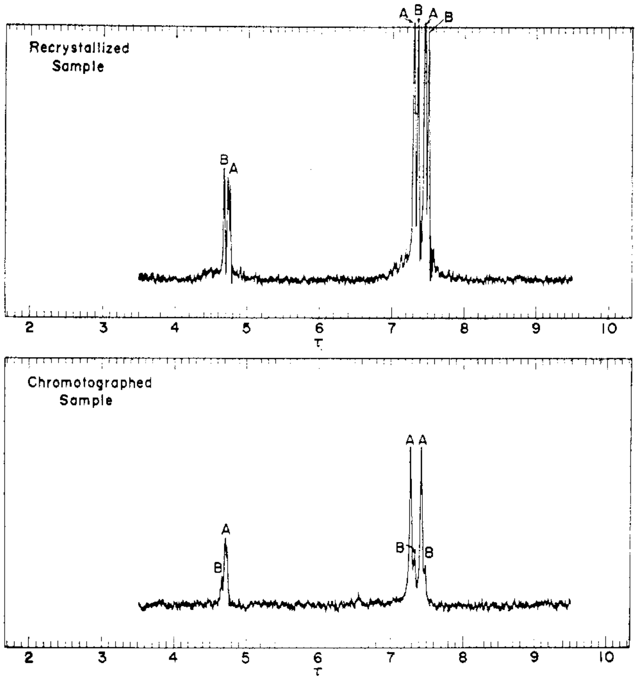
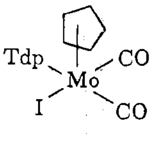


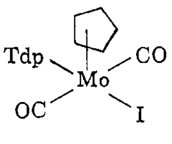
Fig. 2.—Proton n.m.r. spectra of different samples of $C_5H_5Mo(CO)_2(Tdp)I$.

Such isomerism cannot occur in $C_7H_7MoCO(Tdp)I$ (III), which has only three groups besides the seven-membered ring bonded to the metal atom.

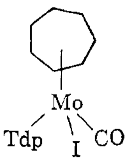
The reaction of the halide derivative $C_3H_5Fe(CO)_3I$[21] with tris-(dimethylamino)-phosphine was entirely different from the reactions described above. In this case the ligand displaced both the allyl group and the iodine atom to form the complex $(Tdp)_2Fe(CO)_3$, which was identical with the product obtained from the reaction of $Fe_3(CO)_{12}$ or $C_8H_8Fe(CO)_3$ with tris-(dimethylamino)-phosphine.



I



II



III

Reactions of tris-(dimethylamino)-phosphine with manganese pentacarbonyl bromide and heptafluoropropyliron tetracarbonyl iodide were investigated. In the former case the yellow-orange crystalline product was not obtained pure; in the latter case a brown viscous liquid was obtained which defied attempts at crystallization. Reaction of tris-(dimethylamino)-phosphine with germanium(II) iodide gave a yellow liquid which could not be crystallized. This product, which was not obtained in the pure state, is presumably the compound $(Tdp)GeI_2$, analogous to other compounds of the type $R_3P \cdot GeI_2$.[1]

**Acknowledgment.**—The author is indebted to Mr. M. Bisnette for experimental assistance; to Dr. F. B. Brown of Union Carbide Olefins Company, South Charleston, West Virginia, for supplying dicobalt octacarbonyl; and to Dr. P. C. Lauterbur for helpful discussions on n.m.r. spectra.

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Contribution from the William Albert Noyes Laboratory of Chemistry,
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# Transition Metal Complexes of a Constrained Phosphite Ester. II. Compounds of Cobalt(I), Cobalt(III), and Nickel(II) with 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

By J. G. Verkade[1] and T. S. Piper

*Received June 17, 1963*

The preparation and characterization of some cobalt and nickel complexes of 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane, $P(OCH_2)_3CCH_3$, are described. Maximum coordination numbers are observed for the yellow diamagnetic $[Co(P(OCH_2)_3CCH_3)_5]ClO_4$ and the colorless diamagnetic $[Co(P(OCH_2)_3CCH_3)_6](ClO_4)_3$ which arise from a disproportionation reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with the ligand. The colorless octahedral complex exhibits bands at 325 mμ (ε 340) and 280 mμ (ε 2000) which are assigned to d → d transitions. The ligand field strength provided by this phosphite is shown to be about the same as that of the cyanide ion. The yellow diamagnetic $[Ni(P(OCH_2)_3CCH_3)_5H_2O](ClO_4)_2$ is also described.

## Introduction

Attempts to synthesize isolable complexes of cobalt and nickel with trialkyl phosphites such as triethyl and trimethyl phosphite have been unsuccessful[2] although some reaction is indicated by color changes. We have been investigating the coordinating properties of the phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane, $P(OCH_2)_3CCH_3$. This polycyclic ligand, hereafter referred to as L, in contrast to trialkyl phosphites has associated with it very low ligand–ligand repulsion due to steric effects and hence can function as a strong coordinating agent. In the first paper of

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[1] Author to whom correspondence regarding this article should be addressed at the Department of Chemistry, Iowa State University, Ames, Iowa.

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

this series[3] we reported the complexes of copper(I), silver(I), gold(I), palladium(II), platinum(II), and rhodium(III) with L. These studies indicated that L can stabilize lower oxidation states as in the case of the tetrahedral $CuL_4^+$ ion which is formed upon reduction of $Cu^{+2}$ ion in the presence of excess L.

In this paper we wish to report the reactions of the hydrated perchlorate and nitrate salts of cobalt(II) and the perchlorate salt of nickel(II) with L. In addition to the effects of low steric hindrance to repulsion and low ligand–ligand repulsion, the ability of L to stabilize the positive one and positive three oxidation states in the case of cobalt will be demonstrated.

## Experimental

**Pentakis-L-cobalt(I) Perchlorate and Hexakis-L-cobalt(III) Perchlorate.**—To 0.915 g. (0.0025 mole) of $Co(ClO_4)_2 \cdot 6H_2O$ in 15 ml. of absolute ethanol was added 4.280 g. of L (0.029 mole) in 15 ml. of absolute ethanol. The mixture was immediately cooled to 0° whereupon fine crystals appeared and continued to form for about 3 hr. During this time, the crystals were filtered every 30 min. A total of 2.50 g. of yellow crystalline material was collected or 93% yield based on cobalt if the product was assumed to have a stoichiometry $Co_2L_{11}(ClO_4)_4$.

*Anal.* Calcd. for $Co_2L_{11}(ClO_4)_4$: C, 30.90; H, 4.63. Found: C, 31.09; H, 5.09.

The supernatant liquid was very light pink in color and upon evaporation yielded an ether-soluble oil whose infrared spectrum revealed a P=O stretching frequency at 1325 $cm.^{-1}$.

Microscopic examination of the yellow solid dried *in vacuo* over concentrated $H_2SO_4$ revealed a mixture of yellow plates which were probably monoclinic or orthorhombic and colorless plates which were classed as hexagonal on the basis of their morphology and optical extinction properties. The two components were separated by extracting the more soluble yellow compound from 0.100 g. of mixture with three 1.5-ml. portions of boiling methanol. The colorless residue weighed 0.051 g. The yellow complex can be recrystallized from hot absolute ethanol and is soluble in methanol and water. The colorless residue can be recrystallized from water and is slightly soluble in methanol. The colorless complex decomposes over a period of hours in hot methanol or water and produces a pink solution. Analysis of the compounds reveals the stoichiometry $CoL_5ClO_4$ and $CoL_6(ClO_4)_3$ for the yellow and colorless complexes, respectively.

*Anal.* Calcd. for $CoP_5C_{25}H_{45}O_{19}Cl$: Co, 6.55; C, 33.40; H, 5.00; Cl, 3.92. Found: Co, 6.44; C, 33.41; H, 4.97; Cl, 4.08.

*Anal.* Calcd. for $CoP_6C_{30}H_{54}O_{30}Cl_3$: Co, 4.73; C, 28.90; H, 4.33; $ClO_4$, 17.4. Found: Co, 4.65; C, 28.26; H, 4.27; $ClO_4$, 17.1.

The molar ratio of Co(I)/Co(III) complex formed in the disproportionation reaction was shown by this separation to be 1.28/1 or about 1/1. The discrepancy in the ratio may be related to the fact that a strong odor of trimethyl phosphite was noted during the extraction with methanol. This odor was also noted on subsequent recrystallizations of the white compound from methanol but not in the case of the yellow Co(I) complex. Partial decomposition of the colorless Co(III) complex may have taken place by an ester interchange process on the ligand L.[4]

An identical preparation as described above was carried out except that the stoichiometric mole ratio of L/Co(II) of 11/2 was used instead of 11.5/1. A yield of only 26% of the mixture was realized.

**Pentakis-L-cobalt(I) Nitrate.**—When the preparation described above involving a mole ratio of 11.5L/1Co was repeated using $Co(NO_3)_2 \cdot 6H_2O$, violet paramagnetic crystals formed which were hygroscopic and decomposed on standing in air. A yellow crystalline material was a persistent contaminant and the two compounds defied satisfactory separation by fractional crystallization to determine relative yields because of the instability of the violet compound and the high solubility of the yellow complex. Dissolution of the mixture in hot ethanol and cooling to 0° produced yellow crystals which were repeatedly crystallized from ethanol. The stoichiometry for the yellow compound as revealed by analysis is $CoL_5NO_3$.

*Anal.* Calcd. for $CoP_5C_{25}H_{45}O_{18}N$: Co, 6.78; C, 34.90; H, 5.23; N, 1.63. Found: Co, 6.63; C, 34.77; H, 5.29; N, 1.68.

The compound is very soluble in water and methanol and decomposes over a period of hours to a pink solution.

**Hexakis-L-cobalt(III) Nitrate.**—A 0.112-g. sample of $CoL_6(ClO_4)_3$ was dissolved in 3.5 ml. of hot water; the solution was quickly passed through a column of 1 g. of Dowex X-10 chloride exchange resin. The column was washed with three 1-ml. portions of water. The eluate was immediately titrated with 0.100 *N* $AgNO_3$ solution. The end point occurred within 2% of the expected stoichiometry, 1 mole of complex/3 moles of chloride. The precipitated AgCl was removed by filtration and the filtrate quickly evaporated to dryness *in vacuo* at room temperature. The white residue was extracted with 10 ml. of absolute ethanol and filtered. The filtrate was evaporated *in vacuo* at room temperature to 1 ml., cooled to 0°, and the colorless needles collected. The analysis is commensurate with the formula $CoL_6(NO_3)_3$.

*Anal.* Calcd. for $CoP_6C_{30}H_{54}O_{27}N_3$: Co, 5.20; C, 31.70; H, 4.77; N, 3.67. Found: Co, 5.12; C, 31.25; H, 5.01; N, 3.54.

The compound is very soluble in water and methanol and in these solutions decomposes over a period of hours to form a pink solution. It also decomposes to a pink sticky mass over a period of days in a desiccator.

**Aquopentakis-L-nickel(II) Perchlorate.**—To a solution of 0.914 g. (0.0025 mole) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 10 ml. of absolute ethanol was added 4.070 g. (0.0275 mole) of L; the resulting L/Ni(II) ratio was 11/1. The green nickel solution immediately turned yellow on addition of the ligand solution and brilliant yellow crystals appeared. The mixture was cooled to 0° overnight. Upon filtration and washing with ether, 2.50 g. of crystals was obtained; analysis suggests the stoichiometry $NiL_5H_2O(ClO_4)_2$. The yield of the complex based on nickel was 98.5%. The supernatant liquid had a very slight greenish tint.

*Anal.* Calcd. for $NiP_5C_{25}H_{47}O_{24}Cl_2$: Ni 5.78; C, 29.6; H, 4.63; P, 15.30. Found: Ni, 5.61; C, 29.52; H, 4.90; P, 15.46.

The complex was only slightly soluble in methanol, water, and ethanol and insoluble in ether. The yellow methanol and water solutions became green on standing overnight. A small amount of complex could be dissolved in methylene chloride from which fine yellow needles were obtained by adding anhydrous ether.

When the above preparation was repeated using a molar ratio of only 5L/1Ni(II), a yield of 55% of the complex based on nickel was obtained. The supernatant liquid was definitely green, revealing a substantial amount of unreacted nickel ion.

**Analyses.**—Cobalt analyses were carried out on 8 to 12 mg. samples. One ml. of concentrated $HNO_3$ was slowly added to the sample dissolved in water and slowly evaporated nearly to dryness on a steam bath. This procedure was repeated with 1 ml. of 70% $HClO_4$ and with 1 ml. of concentrated HCl to convert the cobaltous ion to the chloride. The residue was then analyzed for cobalt spectrophotometrically according to the method of Pepkowitz and Marley.[5] Trisacetylacetonatocobalt(III) was used as a standard.

Nickel analyses were carried out by slowly decomposing 200 to 225 mg. samples suspended in 15 ml. of water with 5 ml. of concentrated $HNO_3$ and evaporating nearly to dryness on a steam bath. The evaporation was repeated with 5 ml. of 70% $HClO_4$ followed by dilution to about 100 ml. with water. The nickel content was then determined by a standard procedure[6] as the dimethylglyoxime complex.

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[3] J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **1**, 453 (1962).

[4] C. W. Heitsch and J. G. Verkade, *ibid.*, **1**, 392 (1962).

[5] L. Pepkowitz and J. Marley, *Anal. Chem.*, **27**, 1330 (1955).

[6] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 138.

Phosphorus analyses were carried out by the Schöniger procedure[7] in which the compound is burned forming $P_2O_5$ and the phosphorus content determined by adding excess base to the precipitated quinolinium phosphomolybdate and back-titrating with acid. Macdonald and Stephen[7] state that digestion of the precipitate is unnecessary before filtration. In our hands, however, digestion overnight was found to be necessary to obtain consistent results.

Perchlorate was analyzed gravimetrically as the tetraphenylarsonium salt.[8]

**Magnetic Susceptibilities.**—A modified Curie–Cheneveau balance[9] was used to measure gram susceptibilities under inert atmosphere at 298, 195, and 77°K. The complexes $CoL_5ClO_4$, $CoL_5NO_3$, $CoL_6(ClO_4)_3$, and $NiL_5H_2O(ClO_4)_2$ were diamagnetic with no detectable temperature-independent paramagnetism.

**$P^{31}$ Nuclear Magnetic Resonance.**—A Varian HR-60 n.m.r. spectrometer equipped with a $P^{31}$ radiofrequency unit and matching probe was used to detect a $P^{31}$ chemical shift of $-137$ p.p.m. for $CoL_5NO_3$ with respect to external 85% $H_3PO_4$. An aqueous solution containing 0.300 g. of solute per 200 $\mu$l. of water was employed. The remaining perchlorate salts were much too insoluble in solvents such as water, dimethyl sulfoxide, and acetonitrile to detect $P^{31}$ resonance. Although $CoL_6(NO_3)_3$ is sufficiently soluble for $P^{31}$ n.m.r. measurements, enough paramagnetic impurity formed by the time a fresh solution was scanned in the spectrometer that no resonance could be detected.

**Ultraviolet–Visible Spectra.**—Solutions were scanned in the ultraviolet, visible, and near-infrared regions in water solutions of 0.001 to 0.005 *M* on Cary Model 14 and Beckman DK-2A spectrophotometers. Spectra of the complexes of cobalt(I) showed no change when obtained in solutions buffered at pH 5.07 and 9.17. Both the $CoL_5NO_3$ and the corresponding perchlorate yielded spectra containing a band at 350 $m\mu$ with an extinction coefficient of 1100. The spectrum of the complex $CoL_6(ClO_4)_3$ showed a band at 224 $m\mu$ ($\epsilon$ 35,000) possessing two shoulders. Gaussian analysis of the band at 224 $m\mu$ indicated a second intense band at 253 $m\mu$ ($\epsilon$ 17,000) and resolved the high-energy shoulder into a band of relatively low intensity ($\epsilon$ 2000) at 280 $m\mu$. The second shoulder, which was too weak to be resolved adequately by gaussian analysis, was estimated visually at 325 $m\mu$ and its extinction coefficient ($\epsilon$ 340) obtained by subtracting the contribution of the ultraviolet tail. The instability in water, methanol, and ethanol of solutions of $NiL_5H_2O(ClO_4)_2$ precluded obtaining spectra.

**Infrared Spectra.**—Nujol–hexachlorobutadiene mulls were employed to obtain spectra on a Perkin-Elmer Model 21 spectrophotometer. No significant changes from the spectrum of the free ligand[10] could be seen except for the appearance of the characteristic absorptions of the nitrate and perchlorate ions.[11] The spectrum of $NiL_5H_2O(ClO_4)_2$ showed a peak in the OH stretching region at 3400 cm.$^{-1}$ which persisted on drying for 1 week *in vacuo* over concentrated $H_2SO_4$.

**Molar Conductivities.**—Conductivity measurements were carried out as described previously.[3] Values for λ (molar conductivity) for the complexes as well as for known similar compounds for comparison are contained in Table I. The nitrates of the cobalt(III) and nickel(II) complexes were insoluble in nitrobenzene and decomposed in water too rapidly to obtain meaningful results.

TABLE I

MOLAR CONDUCTIVITIES

| Compound | λ | Solvent |
|---|---|---|
| $CoL_5ClO_4$ | 88.5 | Water |
| Typical 2-ion compound[a] | 118–131 | Water |
| $CoL_5ClO_4$ | 26.2 | Nitrobenzene |
| $(n\text{-}C_4H_9)_4NClO_4$ | 31.0 | Nitrobenzene |
| $CoL_5NO_3$ | 26.4 | Nitrobenzene |
| $(n\text{-}C_4H_9)_4NNO_3$ | 30.5 | Nitrobenzene |
| $CoL_6(ClO_4)_3$ | 333 | Water |
| Typical 4-ion compound[a] | 408–435 | Water |

[a] M. Sneed and J. Maynard, "General Inorganic Chemistry," D. Van Nostrand Company, New York, N. Y., 1942, p. 813.

## Discussion

It is remarkable that the reaction of L with $Co(ClO_4)_2 \cdot 6H_2O$ seems to involve a quantitative disproportionation to a pentacoordinate cobalt(I) and a hexacoordinate cobalt(III) complex according to the equation

$$2Co(ClO_4)_2 \cdot 6H_2O + 11L \longrightarrow CoL_5ClO_4 + CoL_6(ClO_4)_3 + 6H_2O$$

It is significant that when the analogous reaction was carried out with cobalt(II) nitrate hexahydrate, only $[CoL_5]NO_3$ could be isolated in significant yield. The violet crystalline product has thus far resisted purification and is unstable to moisture. This system is presently being investigated under anhydrous reaction conditions. Possibly the nitrate ion is interfering in the formation of the hexacoordinate cobalt(III) complex by coordinating to the metal ion, thereby causing the reaction to follow a different course. However, it is clear that the ion $CoL_6^{+3}$ is relatively inert since $CoL_6(NO_3)_3$ can be isolated by means of an ion-exchange reaction with the $CoL_6(ClO_4)_3$ complex in which the initial product is probably $CoL_6Cl_3$. The chemistry of the cobalt system involving potentially coordinating halide groups is presently being investigated.

Support for the formulation of these complexes as octahedral tripositive cations stems from their molar conductivities as recorded in Table I as well as the expected diamagnetism for a low-spin $d^6$ configuration which was confirmed for the perchlorate. Although diamagnetic cobalt(I) complexes have been isolated before,[12] $CoL_5ClO_4$ and the corresponding nitrate represent the first examples of stabilization of this unusual oxidation state by a phosphorus compound. On the basis of the conductivity and magnetism measurements the complexes are assigned the formulations $[CoL_5]ClO_4$ and $[CoL_5]NO_3$. The stability as revealed by spectral measurements in acidic and basic solutions of this complex is noteworthy.

Although the $P^{31}$ chemical shift of $[CoL_5]NO_3$ ($-137$ p.p.m.) is further downfield than the uncoordinated ligand ($-91.5$ p.p.m.)[13] it cannot be concluded from these data that a depletion in electron density around the phosphorus atom has occurred upon coordination because of the complicated nature of the ligand–metal interaction and the lack of spherical symmetry of the electrons on phosphorus. It is interesting, however, that the $CoL_5^+$ ion is isoelectronic with $Fe(CO)_5$ and could very well have a trigonal-bipyramidal structure. X-Ray diffraction studies are presently being carried out on this compound. The fact that two chemical

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[7] A. M. G. Macdonald and W. I. Stephen, *J. Chem. Educ.*, **39**, 528 (1962).

[8] F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Company, Inc., New York, N. Y., 1948, p. 326.

[9] J. G. Verkade, Ph.D. Thesis, University of Illinois, 1960.

[10] C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 863 (1962).

[11] F. A. Miller and C. H. Wilkin, *Anal. Chem.*, **24**, 1253 (1952).

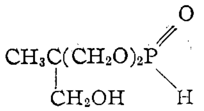
[12] A. Sacco and M. Freni, *Gazz. chim. ital.*, **89**, 1800 (1959).

[13] J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

shifts were not seen for the $P^{31}$ nucleus may be due to rapid exchange of ligands among the various sites. Excess L could not be added to test this hypothesis since L is insoluble in water and hydrolyzes at a moderate rate.

Although conductivity data are lacking for the formulation of the nickel complex as a three-ion compound, the known reluctance of perchlorate to coordinate supports a three-ion structure. The presence of water as confirmed by infrared analysis even under drying conditions seems to indicate that the water molecule is coordinated. A coordinated hydroxyl group causing the nickel atom to have an oxidation state of +3 is ruled out by the diamagnetism of the complex. The complex is therefore tentatively given the formulation $[NiL_5H_2O](ClO_4)_2$. Diamagnetism of a six-coordinate complex is unusual; another example is the $[Ni($*o*-phenylenebis-(dimethylarsine)$)_3]^{+2}$ ion.[14] Within the framework of our present theories, there are two possible explanations. Either a strong tetragonal distortion exists with a pair of electrons in the $d_{z^2}$ orbital or else the field is more nearly octahedral, which probably involves excitation of the electron pair to the $5s^2$ level. The fact that five phosphites coordinate is some evidence for the former idea. X-Ray diffraction studies are planned to determine the ligand–metal bond distances in this complex. Experiments are presently being performed under completely anhydrous conditions to see if a hexacoordinate phosphite complex can be synthesized. Preliminary results indicate that excess L with $Ni(ClO_4)_2 \cdot 6H_2O$ is not sufficient.

Attempted preparations of the nitrate salt of the nickel complex resulted in the formation of a yellow hygroscopic, unstable compound possessing variable quantities of water which has thus far withstood complete characterization. Experiments under anhydrous conditions may yield a more tractable compound. It should be noted that reactions of L with hydrates were best carried out when one mole of L was allowed for each mole of water. Barnes and Hoffman have found that L hydrolyzes to a compound having the postulated structure[15]



$CH_3C(CH_2OH)(CH_2O)_2P(=O)H$

Formation of such a compound could explain the presence of the P=O stretching frequency in the infrared spectrum of the ether-soluble oil in the disproportionation reaction involving cobalt(II) as well as the low yields of complexes when the ligand to metal ratio was merely that for the complex.

The compound $[CoL_6](ClO_4)_3$ is expected to be diamagnetic on the basis of its $d^6$ electronic configuration since in a strong octahedral field the six electrons will be paired in the $t_{2g}$ level. It is remarkable that this complex and the corresponding nitrate are colorless; they are the first known cases of colorless cobalt(III) complexes. If it can be assumed that the bands at 325 and 280 mμ are the spin-allowed $^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{1g}(t_{2g})^5(e_g)$ and $^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{2g}(t_{2g})^5(e_g)$ transitions, respectively, the following calculation yields a value for $Dq$. Assuming that the ratio of the parameters $F_2/F_4 = 9.3$ for the $Co(en)_3^{+3}$ ion[16] is also valid for the $[CoL]_6^{+3}$ complex, a value of 72.4 cm.$^{-1}$ for $F_4$ is obtained upon solving simultaneously the equations for the strong-field approximation[16]

$$\Delta E(^1T_{1g}-{}^1A_{1g}) = -35F_4 + 10Dq$$

and

$$\Delta E(^1T_{2g}-{}^1A_{1g}) = 16F_2 - 115F_4 + 10Dq$$

The value 3320 cm.$^{-1}$ for $Dq$ which can then be obtained from these equations is very close to that of the $[Co(CN)_6]^{-3}$ ion which is 3350 cm.$^{-1}$.[17] The analogous band positions in the spectrum of $[Co(CN)_6]^{-3}$ at 310 and 255 mμ[18] are at slightly higher energies than in $[CoL_6]^{+3}$. The intense bands at 253 mμ (ε 17,000) and 224 mμ (ε 35,000) are undoubtedly due to charge-transfer transitions. Although the bands in $[CoL_6]^{+3}$ could conceivably be due to $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^3T_{2g}$ transitions, the spin-forbidden character of these excitations would be expected to yield very much smaller extinction coefficients as in the case of the very weak 420 mμ band (ε 0.5) assigned to such a spin-forbidden transition in $[Co(CN)_6]^{-3}$.[18] In addition to the fact that $Dq$ of $P(OCH_2)_3CCH_3$ is comparable to that of cyanide ion in the cobalt(III) complex, the lower mutual repulsion of the d-electrons in the excited singlet states for the $[CoL_6]^{+3}$ ion (5000 cm.$^{-1}$) as compared to that in the $[Co(CN)_6]^{-3}$ ion (6500 cm.$^{-1}$) indicates that the bicyclic phosphite has a greater nephelauxetic effect than cyanide ion.

The stability and high coordination number of the complexes described in this work compared to the lack of complexes involving trialkyl phosphites is undoubtedly due in large measure to the high symmetry of L and its low ligand–ligand repulsion. Perhaps appreciable metal–phosphorus bond order is gained by d-π → p-π bonding from the metal orbitals to those on phosphorus, especially in the case of cobalt(I) and nickel(II) complexes. Thus back π-bonding in addition to the σ-bonding by the lone-pair electrons on phosphorus may make the ligand field for L comparable to that of the cyanide ion. It is also noteworthy that L can stabilize high and low oxidation states as in the $[CoL_6]^{+3}$ and $[CoL_5]^{+1}$ ions, respectively.

**Acknowledgments.**—The authors are grateful to the National Science Foundation and the Research Corporation for financial assistance. They also thank Messrs. T. J. Huttemann and E. J. Boros for some of the analytical data.

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(14) R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

(15) R. Barnes and J. Hoffman, private communication.

(16) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, pp. 259–261.

(17) J. S. Griffith, "The Theory of the Transition-Metal Ions," Cambridge University Press, Cambridge, 1961, p. 310.

(18) S. Kida, J. Fujita, K. Nakamoto, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 79 (1958).