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Some Phosphine Oxide and Arsine Oxide Complexes of Cobalt(II) Nitrate[1a]

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The preparation and characterization of the compounds $Co[(C_6H_5)_3PO]_2(NO_3)_2$, $Co[(C_6H_5)_3AsO]_2(NO_3)_2$, and $Co[(CH_3)_3PO]_2(NO_3)_2$ and their zinc analogs are described. The interpretation of the magnetic properties and the visible and infrared absorption spectra of the cobalt complexes in relation to the distorted six-coordinated structure, which has been found in the last one and is presumed to exist in the first two as well, is also discussed.

Introduction

In a previous communication[2] we reported the preparation and some properties of the compound $\{Co[(C_6H_5)_3PO]_2(NO_3)_2\}$, the magnetic moment of which (4.69 B.M.)[3] was taken to indicate a tetrahedral structure. However, the absorption spectrum of this compound, by reflectance and in solution, over the range 300–1000 mμ differed from the spectra of other tetrahedral cobalt(II) complexes known at that time. The absorption band at ~17,800 cm.$^{-1}$, although similar in general contour to the visible bands of other tetrahedral cobalt(II) complexes, was at rather higher energy than would have been expected, for example, by comparison with the values of ~13,200 cm.$^{-1}$ for $[CoI_4]^{2-}$, where the ligand field strength parameter $\Delta = \sim 2650$ cm.$^{-1}$, and 16,250 cm.$^{-1}$ for the visible band of $[Co(NCS)_4]^{2-}$, where $\Delta = 4550$ cm.$^{-1}$.[4] Moreover, the molar extinction coefficients of the visible band of solutions of the cobalt nitrate complex in methylene chloride (ϵ_m 128) and in nitromethane (ϵ_m 143) were appreciably lower than those (ϵ_m ~400–1700) consistently found for other tetrahedral cobalt(II) complexes.[5-7] On the basis of the evidence then available a tetrahedral structure was, however, postulated for the complex of cobalt nitrate with triphenylphosphine oxide.[2]

Recently, the molecular structure of $Co[(CH_3)_3PO]_2(NO_3)_2$ has been determined by a single-crystal X-ray study[8] with the result that the cobalt in this compound is not tetrahedrally coordinated. Rather, it is surrounded by an irregular arrangement of six oxygen atoms, each nitrate ion serving as a bidentate ligand.

In this paper we report the results of chemical, magnetic, and spectroscopic studies of the cobalt nitrato complexes, $CoL_2(NO_3)_2$ with $L = (C_6H_5)_3PO$, $(C_6H_5)_3AsO$, and $(CH_3)_3PO$, and discuss the interpretation of these data in respect to their known or presumed molecular structures.

Experimental

Preparation of Complexes.—Dinitratobis-(triphenylarsine oxide)-cobalt(II) was obtained by slow addition of triphenylarsine oxide (3.38 g., 0.0105 mole) in cold absolute ethanol (7 ml.) to a vigorously stirred solution of cobalt nitrate hexahydrate (1.46 g., 0.005 mole) in the same solvent (3 ml.). The dark purple-blue complex separated during the addition of the neutral ligand and, when the addition was complete, was filtered, washed with ethanol, and dried under vacuum over sulfuric acid; yield 45%, m.p. 193°.

Anal. Calcd. for $C_{36}H_{30}As_2CoN_2O_8$: C, 52.3; H, 3.65; N, 3.4. Found: C, 52.8; H, 3.6; N, 3.7.

Dinitratobis-(triphenylarsine oxide)-zinc(II).—This white compound was prepared in 80% yield by a method similar to that described for the cobalt(II) complex. In this case, however, the solutions were mixed rapidly while hot and the product crystallized on cooling, m.p. 200°.

Anal. Calcd. for $C_{36}H_{30}As_2N_2O_8Zn$: C, 51.85; H, 3.6; N, 3.4. Found: C, 51.5; H, 3.4; N, 3.6.

Dinitratobis-(triphenylphosphine oxide)-cobalt(II) and -zinc(II) were prepared by procedures similar to those previously described.[9] The purple-red cobalt(II) complex was obtained in 17% yield, m.p. 254°. The white zinc(II) complex was recrystallized from absolute ethanol; yield 33%, m.p. 240°.

Anal. Calcd. for $C_{36}H_{30}N_2O_8P_2Zn$: C, 58.0; H, 4.05. Found: C, 58.25; H, 3.8.

Dinitratobis-(trimethylphosphine oxide)-cobalt(II).—Trimethylphosphine oxide was prepared by the method of Burg and McKee.[10] Three grams (0.033 mole) of $(CH_3)_3PO$ in 5 ml. of CH_3OH and 4.54 g. (0.0156 mole) of $Co(NO_3)_2 \cdot 6H_2O$ in 10 ml. of CH_3OH were mixed in an evaporating dish, which was placed on a steam cone, and a stream of nitrogen was blown over the surface for several hours. The magenta residue, which was mostly tarlike, though some crystals were present, was pumped for several hours in a vacuum desiccator. The still tarry mass was vigorously stirred with 10 ml. of benzene for about 20 min.; the mixture was filtered and the residue dried under vacuum at 25°. By careful evaporation of the benzene filtrate, some small crystals were obtained. The noncrystalline solid was then dissolved in the least volume of 1:1 benzene–methylene chloride and this solution slowly evaporated in a stream of nitrogen, while seed crystals were added from time to time. Reddish purple crystals, m.p. 120–122° after drying under vacuum at 25°, were thus obtained in 40% yield.

Anal. Calcd. for $C_6H_{18}CoP_2N_2O_8$: C, 19.63; H, 4.94; N, 7.63. Found: C, 19.9; H, 5.05; N, 7.68.

Dinitratobis-(trimethylphosphine oxide)-zinc(II).—One gram (0.011 mole) of $(CH_3)_3PO$ in 3 ml. of CH_3OH was added to 1.48 g. (0.005 mole) of $Zn(NO_3)_2 \cdot 6H_2O$ in 5 ml. of CH_3OH. The mixture was heated to boiling and then slowly evaporated in a stream of nitrogen while still warm, affording a warm, viscous residue which crystallized as it cooled further. The complex was recrystallized by dissolving it in a slight excess of benzene and

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(1) (a) Supported by the U. S. Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation; (c) N.S.F. Predoctoral Fellow.

(2) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

(3) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **32**, 1168 (1960).

(4) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(5) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(6) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

(7) M. Goodgame and F. A. Cotton, *ibid.*, **84**, 1543 (1962).

(8) F. A. Cotton and R. H. Soderberg, *ibid.*, **85**, 2402 (1963).

(9) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1878 (1960).

(10) A. B. Burg and W. E. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951).

TABLE I

ELECTRONIC ABSORPTION SPECTRA OF THE COBALT(II) COMPLEXES

Compound	Medium	mμ	cm.$^{-1}$	ϵ molar
$Co[(C_6H_5)_3PO]_2(NO_3)_2$	CH_2Cl_2 (0.1 *M*)	~485 (sh)[a]	~20,600	...
		~527 (sh)	~19,000	...
		558	17,920	138
		840	11,900	6.3
		1325	7,580	13.0
		~1500 (sh)	~6,700	...
$Co[(C_6H_5)_3AsO]_2(NO_3)_2$	CH_2Cl_2 (0.05 *M*)	~535 (sh)	~18,700	...
		573	17,450	212
		~850 (sh)	~11,800	...
		1280	7,810	21.4
		~1500 (sh)	~6,700	...
$Co[(CH_3)_3PO]_2(NO_3)_2$	$CHCl_3$ (0.005 *M*)	525 (sh)	19,050	95
		560	17,850	114
	$CHCl_3$ (0.05 *M*)	840 (sh)	11,900	5.5
		1280	7,800	12.3
		1500	5,660	12.0
	Mull	550	18,200	...
		612 (sh)	16,400	...
		835	12,000	...
		1310	7,620	...

[a] sh, shoulder.

slowly evaporating the solution in a stream of nitrogen at 25°. A slightly yellow, well-crystallized product, m.p. 99–101° after drying under vacuum at 25°, was obtained in 45% yield.

Anal. Calcd. for $C_6H_{18}P_2N_2O_8Zn$: C, 19.29; H, 4.86; N, 7.50. Found: C, 20.0; H, 5.21; N, 7.44.

Infrared Absorption Spectra.—These were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer equipped with a rock-salt prism. Mull spectra were run in Nujol and fluorocarbon oil and solution spectra in CH_2Cl_2.

Electronic Absorption Spectra.—The spectra of the cobalt(II) complexes were measured in methylene chloride solution over the range 350–2500 mμ on a Perkin-Elmer Model 4000 spectrophotometer. The results are shown in Table I and Fig. 1.

Electrolytic Conductance Measurements.—The electrolytic conductances of $\sim 10^{-3}$ *M* solutions of the $(C_6H_5)_3AsO$ and $(CH_3)_3PO$ complexes in nitrobenzene were measured at 25° using conventional equipment. The following molar conductances, in ohm^{-1} mole^{-1}, were obtained: $Co[(C_6H_5)_3AsO]_2(NO_3)_2$, 2.9; $Zn[(C_6H_5)_3AsO]_2(NO_3)_2$, 4.2; $Co[(CH_3)_3PO]_2(NO_3)_2$, 2.3.

X-Ray Powder Data.—These were obtained photographically using Ni-filtered Cu Kα radiation. Use of very small samples minimized fluorescence of the Co compounds.

Magnetic Measurements.—Measurements of bulk susceptibility were made by the Gouy method at temperatures of ~76, ~195, and ~300°K. as described elsewhere.[8] The susceptibility values were corrected for diamagnetism and the reciprocals of the resulting χ_M^{cor} values plotted against absolute temperature. The points defined straight lines within the experimental uncertainties and from these lines the values of θ and μ in the Curie–Weiss equation, $\mu = 2.84[\chi_M^{cor}(T - \theta)]^{1/2}$, were determined.

Discussion

Structural Relationships.—It will first be shown that several lines of physical evidence lead to the conclusion that in all three of the cobalt compounds the arrangement of ligands about the metal atom is probably similar.

Perhaps the best indication of this is provided by the visible and near-infrared spectra given in Table I and in Fig. 1. The spectra of the two phosphine oxide complexes are nearly superimposable and the spectrum of the triphenylarsine oxide complex differs significantly only in its greater intensity from that of the triphenylphosphine oxide complex. Similar intensity differences between analogous phosphine and arsine oxide complexes have been observed before.[11] Finally, when due allowance is made for the effects of the change in phase, both on the molecule itself and on the recording of the spectrum, the mull spectrum of $Co[(CH_3)_3PO]_2(NO_3)_2$ is similar enough to the solution spectrum to indicate that the molecular structure is most likely the same in its essentials in the two cases. Finally, then, the general similarity of all the spectra lead to the conclusion that in all three compounds the nitrate ions are serving as bidentate ligands and that there are thus six oxygen atoms about the cobalt atom in the sort of irregular array found in solid $Co[(CH_3)_3PO]_2(NO_3)_2$.

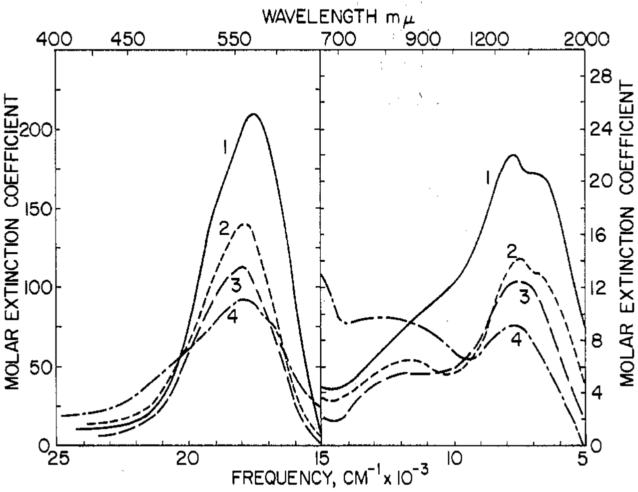

Fig. 1.—Electronic absorption spectra of the cobalt(II) complexes: 1, $Co[(C_6H_5)_3AsO]_2(NO_3)_2$ in CH_2Cl_2; 2, $Co[(C_6H_5)_3PO]_2(NO_3)_2$ in CH_2Cl_2; 3, $Co[(CH_3)_3PO]_2(NO_3)_2$ in $CHCl_3$; 4, $Co[(CH_3)_3PO]_2(NO_3)_2$ mulled in Nujol.

That the complexes remain intact, as molecular entities, in solvents of low polarity is shown by the negligible molar conductances they exhibit even in

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(11) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, **1**, 239 (1962).

dilute ($\sim 10^{-3}$ *M*) nitrobenzene solutions. In addition to the molar conductances reported here, a value of 2.3 ohm^{-1} mole^{-1} has previously been reported[2] for Co$[(C_6H_5)_3PO]_2(NO_3)_2$.

Magnetic data for the crystalline cobalt complexes are identical within experimental error. Thus, as given in Table II, the magnetic moments and θ values obtained by fitting the Curie–Weiss equation to the data are in the ranges $4.56 \leqslant \mu \leqslant 4.65$ B.M. and $-4 \leqslant \theta \leqslant -2$°K. for all three compounds.

By comparison of X-ray powder patterns, it has been found that the crystals of $Co[(C_6H_5)_3PO]_2(NO_3)_2$ and $Zn[(C_6H_5)_3PO]_2(NO_3)_2$ are apparently isomorphous, those of $Co[(C_6H_5)_3AsO]_2(NO_3)_2$ and $Zn[(C_6H_5)_3AsO]_2(NO_3)_2$ are also apparently isomorphous, but the phosphine oxide and arsine oxide compounds show differences indicating different crystal structures. The cobalt and zinc compounds of trimethylphosphine oxide are not isomorphous. From these data, therefore, no similarities (or dissimilarities) in molecular structures of the cobalt complexes can be inferred.

Part of the evidence previously[2] used in assigning a tetrahedral structure to $Co[(C_6H_5)_3PO]_2(NO_3)_2$ was provided by the infrared absorption bands assigned to coordinated nitrate ions. These data are summarized in Table III for all of the Co(II) complexes. The assignments listed at the bottom of the table are those originally suggested by Gatehouse, *et al.*[12] These assignments appear to have been proposed[12] on the implicit assumption that the coordinated nitrate ions examined were attached to the metal atoms through only one oxygen atom; at any rate, it seems safe to assume that in most of the complexes used in the original study,[12] *e.g.*, $[Co(NH_3)_5NO_3]^{2+}$, the coordinated nitrate is monodentate. The work reported here and elsewhere[8] thus leads to the conclusion that it is not in general possible to distinguish between monodentate and bidentate coordinated nitrate ions on the basis of the number and positions of the observed infrared bands alone.

Table II

Magnetic Data[a] for the Cobalt(II) Complexes

Compound	μ	θ
$Co[(CH_3)_3PO]_2(NO_3)_2$	4.65	−2
$Co[(C_6H_5)_3PO]_2(NO_3)_2$	4.56	−4
$Co[(C_6H_5)_3AsO]_2(NO_3)_2$	4.59	−3

[a] μ and θ are defined by the Curie–Weiss law, as explained in the Experimental section.

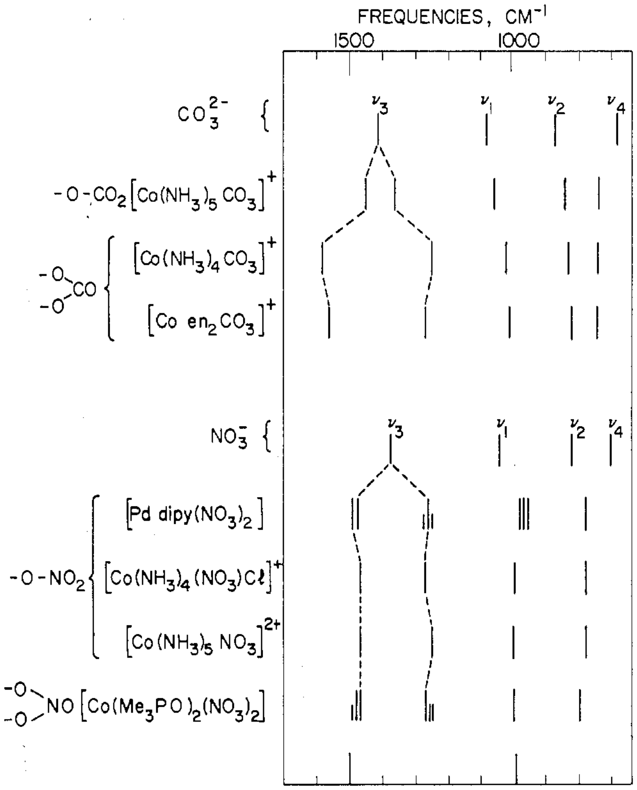

Fig. 2.—Infrared bands of some coordinated nitrate and carbonate ions. Lines of half-height represent unresolved shoulders. ν_1–ν_4 for the free ions have the following significance: ν_1, totally symmetric stretch; ν_2, out-of-plane deformation; ν_3, doubly degenerate stretch; ν_4, in-plane, doubly degenerate bending.

It is interesting to compare these results with those for complexes containing monodentate and bidentate carbonate ions. The comparison is presented graphically in Fig. 2. The infrared data for the carbonate compounds are from the literature.[13] It may be noted that the bidentate nature of the carbonate ion in $[Co(NH_3)_4CO_3]^+$ has recently been proved by X-ray work.[14] The infrared data for the nitrate compounds are from ref. 12. It can be seen that the spectra of monodentate and bidentate carbonate ions exhibit a pronounced difference in magnitude of the splitting of the doubly degenerate CO stretching mode of the free ion.[15] Among the nitrato complexes, there is no significant difference in the spectra of the two types of coordinated nitrate ion. There are at least two possible explanations for this dissimilar behavior under apparently similar circumstances. It is to be noted that the stretching frequencies of the coordinated ions are determined by four force constants: two NO or CO stretching constants and two stretch–stretch interaction constants. Also, whether the ion is monodentate or bidentate, the local symmetry is the same (C_{2v}). Thus, it is quite possible that with only one quantity (the splitting) depending on four parameters, the magnitude of this one quantity might come out the same with two different sets of parameters. On this basis, we might expect the indistinguishability of the spectra of monodentate and bidentate nitrate ions to be more the rule than the exception. Secondly, however, it is to be noted that all the carbonato complexes compared involve the same metal cation, Co^{3+}, while for the nitrato complex, there is variation which *might* be responsible for a purely coincidental similarity in all the splittings. Certainly, data for a Co^{3+} complex containing a bidentate nitrate ion would be of great interest in this connection, but

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(12) B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(13) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

(14) G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 586 (1962); see also ref. 8.

(15) This description of the effect is of course superficial since more extensive dynamical changes must occur upon lowering the symmetry, but it is probably a good first approximation.

TABLE III

INFRARED BANDS OF NITRATE IONS IN THE COMPLEXES

Compound	Phase[a]	Frequencies,[b] cm.$^{-1}$				Note
$[(CH_3)_3PO]_2Co(NO_3)_2$	Solid	1517 (s) 1492 (s) 1469 (s)	1282 (s) 1304 (sh) 1317 (sh)	1024 (m)	812 (w)	*c*
	Soln.	1513 (sh) 1505 (s, b) 1494 (s, b)	1263 (sh) 1275 (sh) 1288 (s)	1021 (m)	813 (w)	*c*
$Co[(C_6H_5)_3PO]_2(NO_3)_2$	Solid	1503 (sh) 1493 (s)	1286 (s)	10 21 (m)	808 (w)	*c*
		1497 (s, b)	1290 (s)	1024 (m)	812 (w)	*d*
	Soln.	1513 (s) 1501 (s) 1493 (s)	1301 (s) ~1270 (sh)	1018 (m)	807 (w)	*c*
		1512 (sh) 1499 (s)	1261 (s, b) 1258 (sh)	1031 (sh) 1025 (m)	812 (w)	*d*
$Co[(C_6H_5)_3AsO]_2(NO_3)_2$	Solid	1470 (s)	1300 (s)	1018 (m)	808 (m)	*c*
	Soln.	1503 (s) 1495 (s) ~1470 (sh)	1304 (s)	1022 (m)	807 (m)	*c*
Assignment	...	Asym. NO_2 str.	Sym. NO_2 str.	NO str.	Nonplane def.	*e*
Range	...	1531–1481	1290–1253	1034–970	800–781	*e*

[a] Solid indicates mull in mineral oil or fluorocarbon oil; solutions were in CH_2Cl_2. [b] s, strong; m, medium; w, weak; sh, shoulder; b, broad. [c] Present work. [d] From ref. 2. [e] See ref. 2 and 12.

we have not discovered any probable example of such a complex in the literature.

Clearly, the problem of correlating the infrared spectra of coordinated nitrate ions (and of course other such ions) with their structural relationship to the cation requires much further study. The preliminary discussion above is given only to indicate that an interesting problem does in fact exist.

Correlation of Electronic Spectra and Magnetic Properties with Structure.—For cobalt(II) complexes which have regular—or nearly regular—octahedral and tetrahedral arrangements of ligands about the metal ion, correlation of observed electronic absorption spectra and magnetic properties has been successful in all general features and, to a considerable extent, in regard to fine details.[16] For an irregular arrangement such as that considered here, comparable success cannot necessarily be expected, because with such low symmetry no helpful restrictions are imposed on the nature or number of electronic states to be considered.

The $Co[(CH_3)_3PO]_2(NO_3)_2$ molecule has no true symmetry elements at all and the only approximate one is a quasi-twofold axis.[8] In particular, the arrangement of the six coordinated oxygen atoms is distinctly acentric. On this basis, the fact that the band intensities are appreciably greater than those in octahedral cobalt(II) complexes, but similar to those in many tetrahedral ones, may be understood.

Also, the appearance of a band at ~18,000 cm.$^{-1}$ is not difficult to understand, since the ground state must be separated by about this amount from some state or states arising out of the ^4P state of the free ion, whatever the detailed arrangement of the coordinated oxygen atoms. However, the absence of any resolved structure or abnormal breadth to this absorption band does make it tempting to assume that the threefold orbital degeneracy of the ^4P state is not greatly split. The most reasonable explanation for this appears to us to be the following one.

In crystalline $Co[(CH_3)_3PO]_2(NO_3)_2$ the angle between the bonds from the cobalt atom to the phosphine oxygen atoms is 106° and that between lines from cobalt to each of the nitrogen atoms is 118°. Finally, the dihedral angle between the planes defined by the pairs of bonds or lines just mentioned is 113°. Thus, if the polyatomic character of the nitrate ions is neglected and they are regarded simply as large diffuse uninegative anions centered at the nitrogen atom positions,[17] then the immediate environment of the cobalt ion may be regarded as having, in a sense, distorted tetrahedral symmetry. The extent of distortion is considerable, but by no means beyond comparison to the distortions found in some other (strictly four-coordinate) "tetrahedral" complexes,[18] and it is also possible that the distortions may be less when the molecules are dissolved in a solvent such as $CHCl_3$. Thus, the six oxygen atoms are so arranged about the cobalt ion that they may have an effect on its d-orbitals qualitatively similar to that produced by a distorted "tetrahedral" array of four ligand atoms. On this basis, all of the resemblances—in absorption band positions and intensities and in magnetic moments—of these bis-phosphine oxide dinitrato complexes to genuine "tetrahedral" complexes of cobalt(II) are understandable.

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(16) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, Book Co., New York, N. Y., 1962, pp. 255–259.

(17) This point of view is not without justification in view of the indications from the internal dimensions of the nitrate ions that there may be very little localized covalent Co–O bonding; see ref. 8.

(18) See, for instance, the structure[19] of bis-(N-propylsalicylaldiminato)-nickel(II), in which bond angles vary between 94 and 125° and the angle between the two O–Ni–N planes is 81°, and the recently re-investigated[20] Cs_3CoCl_5, in which the $CoCl_4^{2-}$ groups have two angles of 106° and four of 111°.

(19) M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1105 (1963).

(20) R. Mason, Imperial College, private communication.