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Crystal and Molecular Structure of Pentakis(4-methyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane)cobalt(I)(acetonitrile)trinitratocobalt(II), $\{Co[P(OCH_2)_3CMe]_5\}[Co(NO_3)_3NCMe]$

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Unlike PR_3 ligands which readily form $ONCo(PR_3)_3$ upon reaction with $Co(NO_3)_2$ in *i*-PrOH, $P(OCH_2)_3CMe$ (L) induces disproportionation of divalent cobalt to form red $[CoL_5]_2[Co(NO_3)_4]$ (**1**) and purple $[CoL_6]_2[Co(NO_3)_4]_3$ (**2**). Evidence for the nitrosyl complex $ONCo[P(CH_2O)_3CMe]_3$ (**3**) is presented in the case of the caged phosphine ligand, however. Attempted recrystallization of **1** from hot acetonitrile results in the formation of red $[CoL_5][Co(NO_3)_3NCMe]$ (**4**) and yellow $[CoL_5]NO_3$. The crystal and molecular structure of the title compound **4** was determined from three-dimensional single-crystal x-ray data. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 22.578$ (3), $b = 17.224$ (5), and $c = 25.961$ (9) Å and eight molecules per unit cell. The structure was solved by conventional heavy-atom techniques and refined on *F* by least-squares methods to weighted and unweighted *R* factors of 0.091 and 0.111, respectively, for 3944 independent nonzero reflections. The cation consists of a near-perfect trigonal-bipyramidal array of P atoms around the monovalent cobalt with an average CoP distance of 2.128 (3) Å. Distances and angles associated with the ligand are very comparable to those recently reported for $P(OCH_2)_3CH_2Br$. The anion has a novel heptacoordinate cobalt(II) geometry which incorporates three bidentate nitrates and an acetonitrile molecule. The axial OCoN angle is 178.9° while the OCoO angles in the somewhat distorted equatorial plane range from 57.9 to 93.4°. The axial (2.160 Å) and equatorial (average 2.165 Å) CoO bond distances are nearly equal.

Introduction

In a recent communication[1] Bressan and Rigo reported the new synthesis of $ONCo(PR_2R')_3$ complexes (R′ = alkyl or H) via reaction 1. In an effort to synthesize the isoelectronic and

$$Co(NO_3)_2{\cdot}6H_2O + PR_2R' \xrightarrow{i\text{-PrOH}} ONCo(PR_2R')_3 + OPR_3 \qquad (1)$$

isostructural cobalt analogue of the $ONNi[P(OCH_2)_3CMe]_3^+$ cation whose molecular structure[2] and infrared properties[3] we reported recently, we sought to prepare $ONCo[P(OCH_2)_3CMe]_3$ by this route. Under the conditions described for this reaction,[1] however, we show in this paper that Co(II) disproportionates to give $[CoL_5]_2[Co(NO_3)_4]$ (**1**) and $[CoL_6]_2[Co(NO_3)_4]_3$ (**2**) while the isomeric phosphine $P(CH_2O)_3CMe$ forms $ONCo[P(CH_2O)_3CMe]_3$ (**3**) as expected. We also report the further reaction of **1** with acetonitrile to give the title compound **4** and the structure of **4** obtained by diffraction means is described.

Experimental Section

Ether and acetonitrile were distilled from $LiAlH_4$ and CaH_2, respectively. Infrared spectra were obtained with a Beckman IR-4250 instrument using sodium chloride optics and visible spectra were recorded on a Cary 14 spectrophotometer. Phosphorus-31 NMR spectra were measured on a Bruker HX-90 spectrometer operating in the Fourier transform mode. Routine ^{1}H NMR spectra were obtained on either a Varian Associates A-60 or a Hitachi Perkin-Elmer R20-B spectrometer. Conductivity measurements were made on an Industrial Instruments Inc. Model RC 16B2 conductivity bridge. Carbon, hydrogen, and nitrogen analyses were carried out by Chemalytics, Inc., Tempe, Ariz., and cobalt analyses were performed by previously reported spectrophotometric methods[4] using cobalt tris(acetylacetonate)[5] as a secondary standard.

The ligands $P(OCH_2)_3CMe$[6] and $P(CH_2O)_3CMe$[7] were prepared by methods reported elsewhere.

$\{Co[P(OCH_2)_3CMe]_5\}_2[Co(NO_3)_4]$ (1) and $\{Co[P(OCH_2)_3CMe]_6\}_2[Co(NO_3)_4]_3$ (2). To 1.18 g (4.05 mmol) of $Co(NO_3)_2{\cdot}6H_2O$ dissolved in 14 mL of acetone was added 8.1 mL of 2,2-dimethoxypropane. The violet solution was stirred for 15 min whereupon 3.00 g (20.2 mmol) of ligand was added all at once. The solution was allowed to stir during which time a red-violet precipitate slowly separated. After $^1/_2$ h, the precipitate was filtered under a partial pressure N_2 atmosphere leaving a deep red filtrate. In a partial pressure N_2 filled drybag, the purple-red precipitate was transferred to a flask and 35 mL of acetonitrile was slowly added with stirring which caused the remaining solid to turn purple. The purple powder was filtered from the red solution and when ether was added to the filtrate to the cloud point, a small amount of additional purple powder was precipitated. All of the purple powder was recrystallized by dissolving the powder in 95 mL of acetonitrile, followed by addition of ether to the cloud point. After cooling of the mixture to 0 °C overnight, purple crystals of **2** were produced in 25% yield. Their ^{1}H NMR spectrum is nearly identical with that found for the fluoroborate analogue.[8]

Anal. Calcd for $C_{60}H_{108}Co_3O_{72}N_{12}P_6$: C, 25.59; H, 3.87; N, 5.97; Co, 10.46. Found: C, 25.90; H, 3.83; N, 5.69; Co, 10.04.

Cooling the original red filtrate for 12 h at 0 °C gave **1** in 23% yield as a very hygroscopic red powder. The ^{31}P NMR and ^{1}H NMR spectra of this compound are consistent with that found for the $\{Co[P(OCH_2)_3CCH_3]_5\}^+$ cation.[9] IR and UV–visible spectra and the conductivity of this complex are very comparable to those of the $P(OMe)_3$ analogue reported earlier.[10]

$ONCo[P(CH_2O)_3CMe]_3$ (3). To 1.46 g (5.0 mmol) of $Co(NO_3)_2{\cdot}6H_2O$ dissolved in 30 mL of 2-propanol was added 3.7 g (25 mmol) of $P(CH_2O)_3CMe$. The resulting mixture was heated under an inert atmosphere to 55 °C for 15 min during which time the solution turned deep red. Removal of the solvent under vacuum left an extremely viscous red oil which defied recrystallization. An IR spectrum taken in a Nujol mull of the oil exhibited a sharp nitrosyl band at 1753 cm^{-1}.

$\{Co[P(OCH_2)_3CCH_3]_5\}[Co(NO_3)_3NCMe]$ (4). A saturated blood red hot acetonitrile solution of **1** on slow cooling to room temperature overnight gave clear red crystals of **4**. Filtration under nitrogen and concentration of the filtrate by boiling off about one-third of the solvent under an inert atmosphere produced a second crop of **4** on slow cooling to room temperature (52% total yield). Addition of ether to the cloud point of the filtrate and cooling to 0 °C yielded a mixture of **4** and $\{CoP(OCH_2)_3CMe]_5\}NO_3$. The latter yellow compound can be precipitated in pure form from the bright yellow filtrate in 9% yield by flooding with ether. Both the ^{31}P NMR and ^{1}H NMR spectra of this compound and **4** reveal the presence of the $\{Co[P(OCH_2)_3CCH_3]_5\}^+$ cation.[9] Moreover, an acetonitrile proton peak is also evident in the ^{1}H NMR spectrum of **4** in CH_2Cl_2 solution.

Collection and Reduction of X-Ray Data. A suitable needlelike crystal of **4** measuring approximately 0.3 × 0.3 × 0.1 mm was mounted in a 0.3-mm sealed Lindemann capillary tube under an inert atmosphere. The crystal was then mounted on a four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[11] Three ω-oscillation photographs were taken at various χ and ϕ settings from which 15 strong independent reflections were selected. By use of an automatic indexing program,[12] the coordinates of these reflections produced a reduced cell and reduced cell scalars which were consistent with orthorhombic symmetry. This was confirmed by inspection of ω-oscillation photographs taken about each of the three axes in turn since all axes showed mirror symmetry. Within experimental error, the observed layer line spacings agreed with those predicted for this cell by the indexing program.

The lattice constants were obtained from a least-squares refinement using the Nelson–Riley extrapolation function[13] based on the precise $\pm 2\theta$ ($|2\theta| > 20°$) measurements of 15 strong independent reflections. At 27 °C and with Mo Kα radiation (λ 0.7107 Å) they are $a = 22.578$ (3), $b = 17.224$ (5), and $c = 25.961$ (9) Å. The observed density of 1.54 ± 0.02 g/cm^3 determined by the flotation method (CCl_4–$CHCl_3$) is in good agreement with the calculated value of 1.536 g/cm^3 for eight molecules per unit cell.

The data were collected at 27 °C with graphite-monochromated Mo Kα radiation. All data within a 2θ sphere of 42° in the *hkl* octant were measured using an ω-stepscan technique.

As a general check on electronic and crystal stability, the intensities of four standard reflections, (12,10,0), (16,0,0), (0,16,0), and (0,0,12), were remeasured every 75 reflections. These standards were not observed to vary significantly throughout the entire period of data collection (~4 days); hence, a decomposition correction was unnecessary. A total of 6548 reflections were recorded in this manner. Examination of the data revealed only the following systematic absences: $0kl$ when $l = 2n$, $h0l$ when $h = 2n$, and $hk0$ when $k = 2n$. These absences uniquely determine the space group as *Pcab*. The data were reindexed to bring it to the standard *Pbca* (D_{2h}^{14}) designation via the transformation ($h\bar{l}k$). Data reduction was performed to obtain a data set which contained 3944 reflections which were judged observed ($F_o \geq 3F_o$). The space group assignment was confirmed by subsequent solution and refinement of the structure. An absorption coefficient of 6.05 cm^{-1} was calculated using the μ/ρ values published in ref 14. The intensity data were not corrected for this absorption.

Solution and Refinement of the Structure. The positions of the two cobalts and the five phosphorus atoms were determined routinely by using a weighted tangent approach.[15] After two cycles of least-squares refinement[16] with the isotropic thermal parameters held at 3.0 Å^2 and by varying the scale factor, the discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ were 0.543 and 0.592, respectively. A Fourier map was generated at the conclusion of the second cycle and from it the positions of 27 of the smaller atoms in the trigonal-bipyrmaidal unit were found. Two more cycles yielded the two molecules of acetonitrile of crystallization. The entire structure was subjected to two cycles of varying the isotropic thermal parameters whereupon it was segmented for anisotropic refinement. The positional coordinates and the anisotropic thermal parameters were varied for two cycles for each of the following segments: $Co[P(OCH_2)_3CCH_3]_3$, wherein the three ligands were those containing P(1), P(2), and P(3); $Co[P(OCH_2)_3CCH_3]_2$, containing P(4) and P(5); $Co(MeCN)(NO_3)_3 \cdot 2MeCN$; $Co[P(OCH_2)_3CCH_3]_3$, containing P(1), P(3), and P(5); and $Co[P(OCH_2)_3CCH_3]_2$, containing P(2) and P(4). A final refinement of two cycles varying only the positional coordinates for all of the atoms yielded the necessary data for calculating the structural parameters as well as final discrepancy factors of $R_1 = 0.091$ and $R_2 = 0.111$. The hydrogen atoms were not located. The atomic scattering factors used in the refinement were those of Hanson et al.[17] for the neutral atoms and the real and imaginary corrections[16] for anomalous dispersion for cobalt were also included in the calculations. The final positional and anisotropic thermal parameters of the atoms are shown in Table I. The final observed and calculated structure factor amplitudes for the 3944 reflections have been tabulated.[18] Inspection of a final, difference electron density synthesis revealed no unaccountably large residual electron density. There were no anomalously close intermolecular contacts in the final model.

Discussion

Apparently the formation of nitrosyl complexes according to reaction 1 is limited to phosphines which are less electronegative than phosphite esters. As has been shown earlier,[19] phosphites (L) favor disproportionation of cobalt(II) as shown in reaction 2. The formation of the diamagnetic trigonal-bipyramidal Co(I) and octahedral Co(III) cations is probably associated with the strong ligand field stabilization afforded by ligands which because of their electronegative substituents are able to accept π density from the metal. Interestingly, $P(CH_2O)_3CMe$, a phosphine isomer of the phosphite $P(OCH_2)_3CMe$, undergoes reaction 1 and this can be accounted for by the decreased electronegativity of phosphorus expected on reversing the OCH_2 groups. That these oxygens do have an effect, however, is indicated by the NO stretching frequency observed for this complex (1753 cm^{-1}) which lies at considerably higher frequency than those for the secondary and tertiary phosphine analogues (1620–1690 cm^{-1}) described by Bressan and Rigo.[1]

$$2Co^{2+} + 11L \rightarrow CoL_5^{+} + CoL_6^{3+} \qquad (2)$$

The displacement of a coordinated nitrate in **1** by an acetonitrile solvent molecule can be represented by reaction 3 since both products were identified. The isolation of **4** permitted for the first time the determination of the structure of the five-coordinate Co(phosphite)$_5^+$ cation since previous attempts in our laboratories using a variety of other anions failed to give suitable crystals.[20] Cations of the type Co(phosphite)$_5^+$ exhibit a single ^{31}P NMR chemical shift at room temperature[9,21] which resolves to an A_3B_2 pattern at low temperature.[22] This behavior has been interpreted in terms of the fluxional character of five-coordinate d^8 systems, in which a relatively rigid trigonal-bipyramidal form is stabilized at lower temperatures.[22]

$$\underset{1}{[CoL_5]_2[Co(NO_3)_4]} + MeCN \rightarrow \underset{4}{[CoL_5][Co(NO_3)_3NCMe]} + [CoL_5]NO_3 \qquad (3)$$

Our x-ray structural investigation of **4** demonstrates the persistence of the trigonal-bipyramidal geometry for the Co(phosphite)$_5^+$ cation in the solid state (Figure 1); the bond distances are given in Table II and pertinent bond angles are listed in Tables III and IV. The average Co–P distance of 2.128 (3) Å is somewhat shorter than most of the Ni–P distances found in Ni(II) complexes of phosphites including those of the caged type (2.14–2.24 Å[23,24]). This distance is also considerably shorter than the sum of the single-bond covalent radii of phosphorus (1.10 Å) and cobalt(I) (~1.4 Å), the latter being estimated from the near-invariance of octahedral covalent radii in isoelectronic metal ions (e.g., the radius of Ni(II) is 1.39 Å; those of Fe(II) and Co(III) are ~1.2 Å) and the progression in these radii from 1.22 Å for Co(III) and 1.32 Å for Co(II).[25] Interestingly, the equatorial phosphorus atoms are just within a van der Waals diameter (3.8 Å) of one another (3.690 (5) Å) whereas they are within an average of

Table I. Final Positional and Anisotropic Temperature Factors for $\{Co[P(OCH_2)_3CMe]_5\}[Co(NO_3)_3NCMe]^a$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.7891 (1)	0.1777 (1)	0.6029 (1)	14 (0)	21 (1)	13 (0)	0 (0)	0 (0)	0 (0)
Co(2)	0.1470 (1)	0.4705 (1)	0.6374 (1)	25 (0)	40 (1)	15 (0)	−2 (1)	0 (0)	−1 (0)
P(1)	0.8336 (1)	0.2835 (2)	0.6204 (1)	15 (1)	19 (1)	14 (1)	0 (1)	1 (0)	0 (1)
P(2)	0.8317 (1)	0.0712 (2)	0.6229 (1)	13 (1)	20 (1)	13 (1)	0 (1)	0 (0)	0 (1)
P(3)	0.7048 (1)	0.1780 (2)	0.5667 (1)	15 (1)	22 (1)	12 (1)	0 (1)	0 (0)	0 (1)
P(4)	0.8294 (1)	0.1739 (2)	0.5291 (1)	16 (1)	21 (1)	13 (1)	0 (1)	0 (1)	0 (1)
P(5)	0.7498 (1)	0.1787 (2)	0.6774 (1)	15 (1)	21 (1)	12 (1)	0 (1)	0 (1)	0 (1)
O(1)	0.0954 (4)	0.4265 (6)	0.7010 (3)	31 (3)	66 (5)	16 (2)	−7 (3)	1 (2)	0 (3)
O(2)	0.0982 (4)	0.3672 (6)	0.6291 (4)	35 (3)	60 (5)	22 (2)	−9 (3)	0 (2)	−2 (3)
O(3)	0.0477 (5)	0.3166 (6)	0.6923 (5)	33 (3)	59 (5)	38 (3)	−22 (3)	0 (2)	12 (3)
O(4)	0.2202 (5)	0.3812 (6)	0.6479 (4)	37 (3)	49 (5)	25 (2)	−1 (2)	4 (2)	−8 (3)
O(5)	0.2175 (4)	0.4878 (6)	0.6888 (4)	29 (3)	51 (5)	24 (2)	3 (3)	−6 (2)	−6 (3)
O(6)	0.2898 (5)	0.4095 (8)	0.7012 (5)	39 (4)	89 (8)	40 (3)	7 (4)	−8 (3)	6 (4)
O(7)	0.1116 (4)	0.5816 (6)	0.6501 (4)	32 (3)	45 (5)	32 (3)	4 (3)	−5 (2)	−3 (3)
O(8)	0.0679 (4)	0.5168 (7)	0.5908 (4)	30 (3)	65 (6)	30 (3)	−10 (3)	1 (2)	−1 (3)
O(9)	0.0401 (5)	0.6362 (7)	0.6093 (5)	30 (3)	72 (6)	45 (3)	12 (4)	−2 (3)	21 (4)
O(11)	0.8948 (4)	0.3001 (5)	0.5928 (4)	20 (3)	47 (4)	40 (3)	−7 (3)	9 (2)	−22 (3)
O(12)	0.7991 (4)	0.3617 (5)	0.6090 (5)	23 (2)	18 (3)	50 (3)	0 (2)	−6 (2)	7 (3)
O(13)	0.8538 (5)	0.2960 (6)	0.6788 (4)	56 (4)	56 (5)	18 (2)	−35 (4)	−6 (2)	4 (2)
O(21)	0.8945 (3)	0.0796 (5)	0.6502 (3)	15 (2)	34 (3)	23 (2)	−3 (2)	−5 (1)	1 (2)
O(22)	0.7984 (3)	0.0153 (4)	0.6618 (4)	17 (2)	29 (4)	29 (2)	4 (2)	5 (2)	12 (2)
O(23)	0.8471 (4)	0.0107 (5)	0.5776 (3)	44 (3)	40 (4)	11 (1)	19 (3)	−3 (2)	−1 (2)
O(31)	0.6995 (4)	0.2244 (5)	0.5141 (3)	21 (2)	48 (4)	19 (2)	−2 (2)	−4 (2)	10 (2)
O(32)	0.6794 (3)	0.0944 (4)	0.5502 (3)	21 (2)	29 (3)	26 (2)	7 (2)	−4 (2)	−3 (2)
O(33)	0.6487 (4)	0.2130 (5)	0.5976 (3)	26 (2)	54 (4)	14 (2)	11 (3)	0 (2)	−9 (2)
O(41)	0.8986 (3)	0.1551 (5)	0.5271 (3)	15 (2)	42 (4)	17 (2)	0 (2)	0 (1)	−4 (2)
O(42)	0.8039 (4)	0.1096 (5)	0.4909 (3)	25 (2)	39 (4)	15 (2)	−6 (3)	2 (2)	−1 (2)
O(43)	0.8256 (4)	0.2507 (5)	0.4949 (3)	28 (2)	37 (4)	17 (2)	1 (3)	3 (2)	3 (2)
O(51)	0.7954 (3)	0.1655 (4)	0.7231 (3)	15 (2)	40 (4)	12 (1)	0 (2)	0 (1)	4 (2)
O(52)	0.7013 (3)	0.1149 (4)	0.6888 (3)	18 (2)	29 (3)	17 (2)	−2 (2)	0 (2)	−3 (2)
O(53)	0.7164 (3)	0.2556 (4)	0.6943 (3)	25 (2)	20 (3)	17 (2)	5 (2)	1 (2)	2 (2)
N(1)	0.0782 (5)	0.3670 (8)	0.6744 (5)	24 (3)	67 (8)	23 (3)	−4 (4)	−5 (3)	10 (4)
N(2)	0.2439 (5)	0.4248 (7)	0.6799 (5)	29 (4)	50 (7)	22 (3)	0 (4)	1 (3)	11 (4)
N(3)	0.0712 (5)	0.5786 (8)	0.6149 (5)	28 (4)	56 (7)	26 (3)	−4 (5)	4 (3)	8 (4)
N(4)	0.1971 (5)	0.5105 (7)	0.5768 (5)	22 (3)	46 (6)	26 (3)	−3 (3)	5 (2)	0 (3)
N(5)	1.0289 (9)	0.3838 (14)	0.2431 (8)	50 (7)	148 (18)	53 (6)	−4 (9)	2 (6)	−29 (8)
N(6)	0.5730 (11)	0.4207 (13)	0.4510 (9)	95 (11)	111 (15)	64 (8)	−27 (10)	−20 (7)	−21 (8)
C(1)	0.2248 (7)	0.5393 (8)	0.5447 (6)	32 (4)	32 (6)	25 (3)	1 (4)	−1 (3)	−5 (4)
C(2)	0.2605 (7)	0.5776 (9)	0.5044 (6)	35 (4)	48 (7)	24 (3)	0 (5)	7 (3)	9 (4)
C(3)	0.9885 (9)	0.3429 (15)	0.2533 (8)	32 (6)	125 (18)	31 (5)	12 (8)	0 (5)	−24 (8)
C(4)	0.9378 (8)	0.3010 (12)	0.2585 (8)	32 (5)	96 (12)	39 (5)	−16 (7)	1 (4)	−3 (6)
C(5)	0.5458 (8)	0.3794 (11)	0.4237 (9)	43 (6)	58 (10)	43 (6)	2 (6)	10 (5)	23 (7)
C(6)	0.5155 (7)	0.3314 (10)	0.3892 (7)	30 (4)	56 (8)	31 (4)	2 (5)	−6 (3)	−9 (5)
C(11)	0.9254 (6)	0.3714 (9)	0.6033 (7)	25 (4)	64 (9)	44 (5)	−17 (5)	16 (4)	−35 (5)
C(12)	0.8300 (6)	0.4338 (8)	0.6218 (10)	21 (4)	17 (5)	101 (9)	0 (4)	−22 (5)	−3 (6)
C(13)	0.8851 (11)	0.3694 (11)	0.6911 (6)	93 (10)	69 (10)	20 (3)	−58 (8)	−1 (5)	−6 (5)
C(14)	0.8902 (5)	0.4176 (7)	0.6433 (5)	15 (3)	27 (5)	20 (3)	2 (3)	7 (2)	2 (3)
C(15)	0.9242 (7)	0.4950 (7)	0.6579 (7)	31 (4)	26 (5)	40 (4)	−17 (4)	6 (4)	−8 (4)
C(21)	0.9243 (6)	0.0079 (7)	0.6659 (7)	24 (4)	28 (6)	43 (4)	4 (4)	−14 (3)	8 (4)
C(22)	0.8273 (6)	−0.0574 (7)	0.6780 (6)	20 (3)	31 (5)	34 (4)	9 (3)	8 (3)	13 (4)
C(23)	0.8774 (9)	−0.0615 (8)	0.5920 (5)	76 (7)	43 (7)	13 (3)	44 (6)	−3 (3)	5 (3)
C(24)	0.8878 (5)	−0.0626 (6)	0.6503 (5)	16 (3)	15 (4)	21 (3)	1 (3)	1 (2)	3 (3)
C(25)	0.9201 (6)	−0.1370 (7)	0.6661 (5)	24 (3)	37 (6)	20 (3)	10 (4)	6 (2)	10 (3)
C(31)	0.6413 (6)	0.2210 (10)	0.4855 (6)	18 (3)	82 (9)	28 (4)	−6 (5)	−6 (3)	19 (5)
C(32)	0.6216 (6)	0.0908 (8)	0.5237 (6)	19 (3)	43 (7)	36 (4)	5 (4)	−15 (3)	−1 (4)
C(33)	0.5915 (6)	0.2118 (10)	0.5705 (5)	18 (3)	90 (9)	16 (3)	12 (5)	−7 (2)	−12 (4)
C(34)	0.5996 (5)	0.1725 (8)	0.5185 (4)	12 (3)	52 (6)	14 (2)	5 (4)	−4 (2)	−3 (3)
C(35)	0.5376 (6)	0.1707 (8)	0.4912 (5)	22 (3)	44 (6)	21 (3)	2 (4)	−5 (2)	−4 (4)
C(41)	0.9254 (6)	0.1488 (10)	0.4753 (5)	20 (4)	100 (11)	13 (3)	−10 (5)	4 (3)	−14 (4)
C(42)	0.8312 (6)	0.1049 (10)	0.4402 (5)	26 (4)	79 (9)	14 (3)	−24 (5)	5 (3)	−12 (4)
C(43)	0.8508 (9)	0.2462 (9)	0.4433 (6)	69 (8)	46 (8)	23 (4)	14 (6)	28 (4)	13 (4)
C(44)	0.8790 (5)	0.1670 (7)	0.4352 (5)	18 (3)	47 (7)	14 (2)	−8 (4)	3 (2)	−3 (3)
C(45)	0.9082 (7)	0.1612 (11)	0.3802 (6)	38 (5)	85 (11)	17 (3)	2 (6)	12 (3)	−3 (5)
C(51)	0.7734 (5)	0.1772 (8)	0.7756 (4)	22 (3)	52 (7)	12 (2)	−6 (4)	0 (2)	−1 (4)
C(52)	0.6853 (5)	0.1073 (7)	0.7437 (4)	23 (3)	34 (5)	12 (2)	−4 (4)	7 (2)	−5 (3)
C(53)	0.6853 (6)	0.2515 (8)	0.7439 (5)	35 (4)	40 (6)	13 (2)	10 (4)	6 (3)	0 (3)
C(54)	0.7058 (5)	0.1793 (7)	0.7730 (4)	22 (3)	40 (6)	11 (2)	1 (4)	−1 (2)	−2 (3)
C(55)	0.6796 (7)	0.1791 (9)	0.8279 (5)	34 (4)	63 (8)	16 (3)	2 (5)	11 (3)	7 (4)

[a] The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All β values are × 10^4.

3.010 (5) Å of the axial phosphorus atoms. Similar relationships hold in the isoelectronic $Ni[P(OCH)_3(CH_2)_3]_5^{2+}$ structure[26] suggesting that the axial bonding is stronger than equatorial in these systems since the MP bond lengths are the same in the cation of **4** and MP_{ax} is somewhat shorter than MP_{eq} in the nickel complex. The average OPO and POC bond angles of 101.2 (5) and 117.1 (7)° are very comparable to the corresponding angles in the $[AgL_4]^+$ and $[ONNiL_3]^+$ complexes of $P(OCH_2)_3CCH_3$.[2] Indeed these angles in the free ligand change very little upon complexation to a metal as is

Table II. Intramolecular Bond Distances (Å) in the $\{Co[P(OCH_2)_3CMe]_5\}^+$ Cation

	Z				
	1	2	3	4	5
Co(1)-P(*Z*)	2.131 (3)	2.135 (3)	2.123 (3)	2.123 (3)	2.129 (3)
P(*Z*)-O(*Z*1)	1.582 (9)	1.591 (8)	1.587 (8)	1.597 (8)	1.587 (7)
P(*Z*)-O(*Z*2)	1.584 (8)	1.584 (8)	1.608 (8)	1.593 (8)	1.580 (8)
P(*Z*)-O(*Z*3)	1.597 (10)	1.611 (11)	1.616 (8)	1.595 (9)	1.585 (8)
O(*Z*1)-C(*Z*1)	1.44 (2)	1.47 (1)	1.51 (1)	1.48 (1)	1.47 (1)
O(*Z*2)-C(*Z*2)	1.46 (2)	1.47 (1)	1.48 (1)	1.46 (1)	1.47 (1)
O(*Z*3)-C(*Z*3)	1.48 (2)	1.47 (1)	1.47 (1)	1.46 (2)	1.47 (1)
C(*Z*1)-C(*Z*4)	1.53 (2)	1.52 (2)	1.52 (2)	1.51 (2)	1.53 (2)
C(*Z*2)-C(*Z*4)	1.50 (2)	1.55 (2)	1.50 (2)	1.52 (2)	1.53 (2)
C(*Z*3)-C(*Z*4)	1.50 (2)	1.53 (2)	1.52 (2)	1.52 (2)	1.53 (2)
C(*Z*4)-C(*Z*5)	1.58 (2)	1.53 (2)	1.57 (2)	1.58 (2)	1.54 (2)

Table III. Angles (deg) in the $Co(PO_3)_5$ Moiety of the Cation

	Z				
	1	2	3	4	5
Co(1)-P(*Z*)-O(*Z*1)	118.0 (3)	115.6 (3)	116.7 (3)	117.1 (3)	114.0 (3)
Co(1)-P(*Z*)-O(*Z*2)	117.0 (3)	117.6 (3)	115.8 (3)	115.3 (3)	116.9 (3)
Co(1)-P(*Z*)-O(*Z*3)	116.9 (4)	118.4 (3)	119.0 (3)	117.0 (3)	117.2 (3)

P(1)-Co(1)-P(2)	118.0 (1)	P(1)-Co(1)-P(5)	89.8 (1)
P(1)-Co(1)-P(3)	121.0 (1)	P(2)-Co(1)-P(4)	90.0 (1)
P(2)-Co(1)-P(3)	121.0 (1)	P(2)-Co(1)-P(5)	88.5 (1)
P(4)-Co(1)-P(5)	178.5 (1)	P(3)-Co(1)-P(4)	89.2 (1)
P(1)-Co(1)-P(4)	90.9 (1)	P(3)-Co(1)-P(5)	91.6 (1)

Table IV. Angles (deg) in the $P(OCH_2)_3CMe$ Ligands

	Z				
	1	2	3	4	5
P(*Z*)-O(*Z*1)-C(*Z*1)	119.3 (8)	117.1 (7)	118.0 (8)	116.4 (7)	117.1 (7)
P(*Z*)-O(*Z*2)-C(*Z*2)	116.3 (8)	119.2 (7)	118.5 (7)	116.7 (7)	114.3 (7)
P(*Z*)-O(*Z*3)-C(*Z*3)	117.1 (9)	117.6 (7)	116.5 (7)	116.5 (8)	115.5 (7)
O(*Z*1)-P(*Z*)-O(*Z*1)	101.0 (5)	101.3 (5)	101.2 (5)	101.1 (4)	102.2 (4)
O(*Z*1)-P(*Z*)-O(*Z*3)	99.0 (6)	101.0 (5)	100.4 (5)	101.7 (4)	102.8 (4)
O(*Z*2)-P(*Z*)-O(*Z*3)	101.7 (6)	100.5 (5)	100.8 (5)	102.1 (5)	101.5 (4)
O(*Z*1)-C(*Z*1)-C(*Z*4)	108.8 (10)	110.5 (9)	106.4 (10)	109.1 (10)	107.5 (9)
O(*Z*2)-C(*Z*2)-C(*Z*4)	111.1 (10)	107.9 (9)	107.2 (10)	109.7 (10)	109.6 (9)
O(*Z*3)-C(*Z*3)-C(*Z*4)	109.3 (11)	109.5 (10)	109.0 (9)	109.8 (10)	109.2 (9)
C(*Z*1)-C(*Z*4)-C(*Z*2)	108.4 (14)	108.0 (11)	111.2 (11)	106.6 (11)	107.8 (10)
C(*Z*1)-C(*Z*4)-C(*Z*3)	108.3 (13)	109.7 (12)	109.2 (12)	112.4 (12)	110.1 (11)
C(*Z*2)-C(*Z*4)-C(*Z*3)	110.1 (14)	108.8 (12)	112.1 (11)	108.8 (12)	108.9 (10)
C(*Z*1)-C(*Z*4)-C(*Z*5)	110.3 (10)	109.8 (10)	108.0 (10)	108.7 (10)	110.0 (10)
C(*Z*2)-C(*Z*4)-C(*Z*5)	111.9 (10)	110.1 (9)	108.6 (10)	109.2 (11)	110.0 (11)
C(*Z*3)-C(*Z*4)-C(*Z*5)	107.8 (12)	110.4 (10)	107.5 (9)	111.1 (11)	110.1 (10)

shown from the recent molecular structure determination of $P(OCH_2)_3CH_2Br$[27] in which the OPO and POC angles are 100.1 (2) and 117.5 (3)°, respectively. The bond distances in the ligand in **4** are also comparable to the corresponding distances in the complexes reported previously[2] and in $P(OCH_2)_3CH_2Br$.[27] From the structural data available it appears that no significant structural changes are induced on complexation of this caged ligand to metals. In contrast, the formation of the phosphate $O{=}P(OCH_2)_3CMe$ does result in a significant increase in the OPO angle (103.2°) and a decrease in POC angle (115.3°) and these changes are ascribable to rehybridization effects expected on formation of the phosphoryl linkage.[27]

Heretofore, reported x-ray structural investigations of five-coordinate CoL_5^+ species have been restricted to isocyanide ligands which include CNMe,[28] CNC_6H_5,[29] CNC_6H_4-Cl-*p*,[30] and $CNC_6H_2(CH_3)_3$-2,4,6.[31] Except for packing considerations, there appears to be no clear-cut correlation of the variation in expected bonding properties of these ligands with the square-pyramidal and trigonal-bipyramidal geometries found for the cations.[29] Indeed $Ni(CN)_5^{3-}$ has been found to exhibit both geometries in the solid state.[32] In contrast, phosphorus esters appear to stabilize the trigonal-bipyramidal configuration in five-coordinate d^8 systems[23,24,26,33] except for the mixed ligand complex *trans*-$Ni(CN)_2[P(OEt)_2C_6H_5]_3$ which appears to be substantially distorted from this geometry.[33,34]

Table V. Angles (deg) in the $[Co(NO_3)_3NCMe]^-$ Anion

Co(2)-N(4)-C(1)	174.0 (11)	O(5)-N(2)-O(6)	120.9 (14)
N(4)-C(1)-C(2)	178.8 (15)	O(7)-Co(2)-O(8)	58.1 (4)
N(4)-Co(2)-O(1)	178.9 (5)	Co(2)-O(7)-N(3)	97.0 (8)
N(4)-Co(2)-O(2)	119.6 (4)	Co(2)-O(8)-N(3)	89.1 (9)
N(4)-Co(2)-N(1)	149.0 (4)	O(7)-N(3)-O(8)	115.8 (13)
N(4)-Co(2)-O(4)	85.3 (4)	O(7)-N(3)-O(9)	117.3 (14)
N(4)-Co(2)-O(5)	91.2 (4)	O(8)-N(3)-O(9)	127.0 (15)
N(4)-Co(2)-N(2)	87.9 (4)	O(1)-Co(2)-O(4)	93.6 (4)
N(4)-Co(2)-O(7)	91.4 (4)	O(1)-Co(2)-O(5)	88.4 (4)
N(4)-Co(2)-O(8)	84.8 (4)	O(1)-Co(2)-O(7)	89.6 (4)
N(4)-Co(2)-N(3)	87.2 (4)	O(1)-Co(2)-O(8)	96.0 (4)
O(1)-Co(2)-O(2)	59.9 (4)	O(2)-Co(2)-O(4)	79.7 (4)
Co(2)-O(1)-N(1)	91.7 (7)	O(2)-Co(2)-O(5)	125.6 (4)
Co(2)-O(2)-N(1)	95.4 (8)	O(2)-Co(2)-O(7)	126.0 (4)
O(1)-N(1)-O(2)	113.0 (11)	O(2)-Co(2)-O(8)	80.4 (4)
O(1)-N(1)-O(3)	122.4 (13)	O(4)-Co(2)-O(7)	150.9 (4)
O(2)-N(1)-O(3)	124.6 (14)	O(4)-Co(2)-O(8)	149.5 (4)
O(4)-Co(2)-O(5)	57.9 (4)	O(5)-Co(2)-O(7)	93.4 (4)
Co(2)-O(4)-N(2)	89.1 (8)	O(5)-Co(2)-O(8)	151.0 (4)
Co(2)-O(5)-N(2)	97.0 (8)	N(1)-Co(2)-N(2)	98.2 (4)
O(4)-N(2)-O(5)	116.0 (12)	N(1)-Co(2)-N(3)	100.6 (4)
O(4)-N(2)-O(6)	123.1 (14)	N(2)-Co(2)-N(3)	151.2 (4)

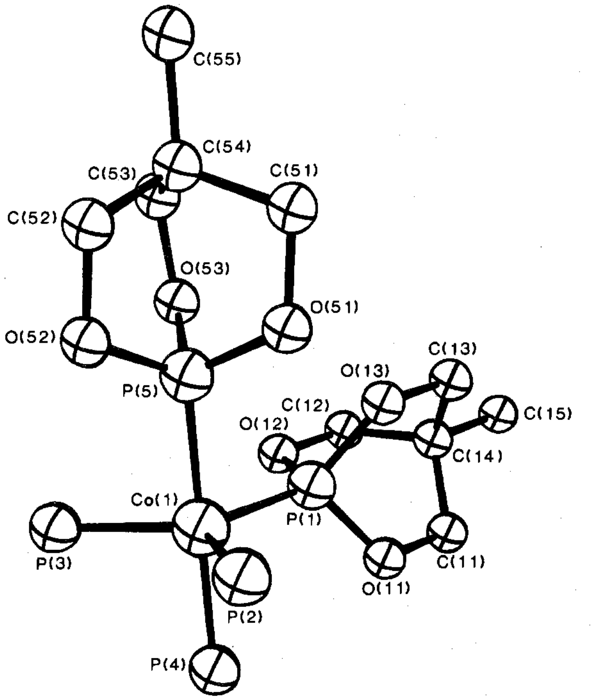

Figure 1. Computer drawing of the $Co[P(OCH_2)_3CCH_3]_5^+$ cation showing two of the five ligands.

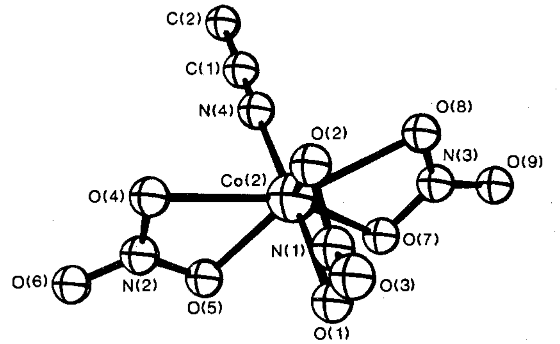

Figure 2. Computer drawing of the $[Co(NO_3)_3NCCH_3]^-$ anion.

The geometry of the $[Co(NO_3)_3NCCH_3]^-$ anion of **4** approximates that of a pentagonal bipyramid with N(4) and O(1) lying on the axis and the plane formed by C(2), C(1), N(4), Co(2), O(2), O(3), N(1), and O(1) forming a quasi-mirror plane (Figure 2). The bond angles and distances associated with this new anion are set forth in Tables V and VI, respectively. The nonplanarity of the equatorial oxygens implied by the sum of the equatorial OCoO bond angles of (369.5°) appears to stem from the axially chelating nitrate. The small O(2)Co(2)O(1) angle in this moiety (59.9°) coupled with its apparently strong proclivity to form a realtively undistorted axial O(1)Co(2)N(4) angle of 178.9° results in an N(4)-Co(2)O(2) angle of 119.6° which is significantly larger than the expected 90°. The N(4)Co(2)O(4), -O(5), -O(7), and -O(8) angles are, however, very near 90° (88.2° average) and both equatorially chelating nitrates are only very slightly twisted (4.2° for $N(2)O_3$ and 4.4° $N(3)O_3$) such that O(4) and O(8) are slightly above a least-squares plane containing cobalt and all of the equatorial oxygens (0.42 and 0.43 Å, respectively) while O(5) and O(7) are slightly below (0.21 and 0.23 Å, respectively). Co(2) is 0.094 Å above this plane and O(2) appears 0.53 Å below. The axial atoms are nearly collinear, with the largest distortion being the Co(2)N(4)C(1) angle (174°).

The geometry of this anion has been found in several neutral tetravalent metal complexes of the type $M(chel)_3Z$ where M is Zr or Sn, chel is a β-diketonate or tropolonate ligand and Z is a halide or η-cyclopentadienide.[35] Because of the substantially larger "bite" of a β-diketonate (2.7–2.9 Å[36]) compared to that of nitrate in the present structure (2.13 Å), the equatorial oxygens in the $Zr(acac)_3Cl$ structure have a 2.57-Å average contact distance which is 0.11–0.34 Å less than the van der Waals diameter of oxygen (2.80 Å).[35] The corresponding contacts in the anion of the present structure average 3.24 Å between ligands and 2.13 Å within them. The smaller distance demanded by the relatively small bite of the nitrate and the axially binding tendency of O(1) combine to allow the equatorial plane to remain relatively uncrowded.

Table VI. Intramolecular Bond Distances (Å) in the $[Co(NO_3)_3NCMe]^-$ Anion and in the MeCN of Crystallization[a]

Co(2)-O(1)	2.160 (8)	Co(2)-O(8)	2.299 (11)
Co(2)-O(2)	2.104 (10)	O(7)-N(3)	1.292 (14)
O(1)-N(1)	1.296 (14)	O(8)-N(3)	1.238 (14)
O(2)-N(1)	1.258 (14)	N(3)-O(9)	1.224 (14)
N(1)-O(3)	1.202 (13)	Co(2)-N(4)	2.054 (12)
Co(2)-O(4)	2.274 (10)	N(4)-C(1)	1.156 (16)
Co(2)-O(5)	2.098 (9)	C(1)-C(2)	1.477 (19)
O(4)-N(2)	1.243 (14)	N(5)-C(3)	1.18 (3)
O(5)-N(2)	1.260 (14)	C(3)-C(4)	1.36 (3)
N(2)-O(6)	1.202 (14)	N(6)-C(5)	1.18 (2)
Co(2)-O(7)	2.100 (10)	C(5)-C(6)	1.40 (2)

[a] The last four entries pertain to the two MeCN molecules of crystallization.

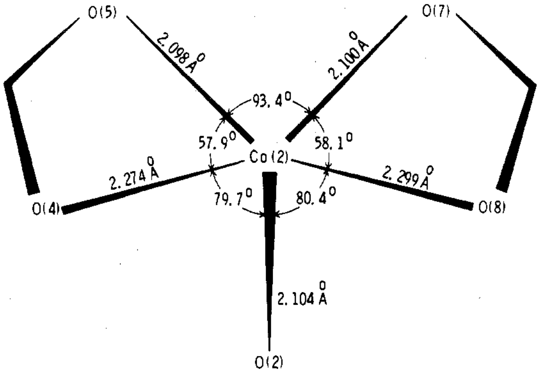

Figure 3. Approximate relative orientation of the nonaxial atoms as viewed down the axis defined by C(2) and O(1) of the $[Co(NO_3)_3NCCH_3]^-$ anion.

The CoO bond distances in the $[Co(NO_3)_3NCCH_3]^-$ anion given in Table VI reveal no significant difference in CoO_{eq} (2.165 Å average) and CoO_{ax} (2.160 Å). In $Zr(acac)_3Cl$ the axial ZrO distance is about 3% shorter than the corresponding equatorial bond length and this was rationalized as stemming in part from the more crowded oxygens in the pentagonal plane.[35] This idea is supported by the constancy of our CoO lengths since the pentagonal plane in $[Co(NO_3)_3CNCH_3]^-$ is not as sterically encumbered for reasons discussed earlier.

An interesting feature of the pentagonal plane becomes apparent from its top view depicted in Figure 3. Even though O(2) is further below the plane than O(5) and O(7), the coordination angles of O(2) with O(4) and O(8) are distinctly smaller than the O(5)Co(2)O(7) angle, and the Co(2)O(4) and Co(2)O(8) distances are perceptibly larger than Co(2)O(5) and Co(2)O(7). These observations in conjunction with the twists of the equatorial nitrate planes which raise O(4) and O(8) slightly above the equatorial plane suggest that electronic rather than steric factors are operative in what can be described as a crowding of O(4) and O(8) against the pseudoequatorial oxygen (O(2)) of the unique nitrate. It should be noted, however, that O(8) and O(4) approximately maintain their van der Waals distance from O(2) (2.82 Å on the average).

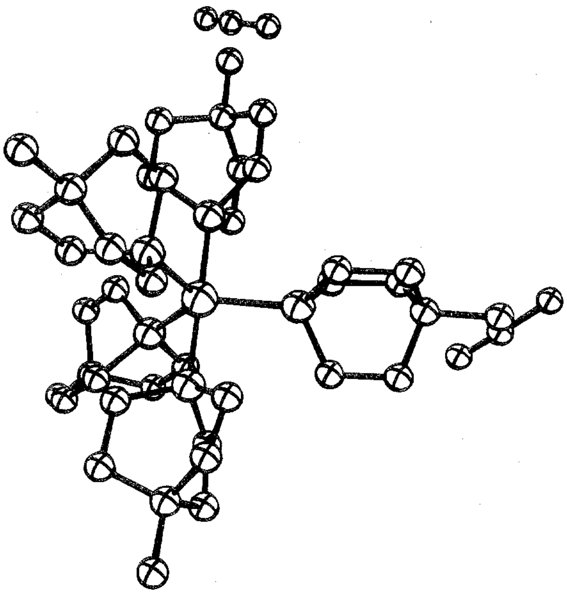

Figure 4. Computer drawing of the $Co[P(OCH_2)_3CCH_3]_5^+$ cation and the relative positions of the two acetonitriles of crystallization.

Using the definition that an M–O bond length difference of 0.2–0.7 Å for a bidentate nitrate constitutes unsymmetrical chelation,[37] we conclude that the two equatorial nitrates in the $[Co(NO_3)_3NCCH_3]^-$ anion are only marginally unsymmetrically bound (Δ(CoO) being 0.17–0.19 Å) while the unique nitrate is quite symmetrically attached (Δ(CoO) = 0.06 Å). Because of the frequent observance of unsymmetrically bound nitrates in $M(NO_3)_4{}^{n-}$ complexes having unpaired electrons, this distortion has been ascribed to nonspherical electron distributions.[37,38] Such distortions as well as the crowding of the equatorial nitrates against the equatorial oxygen of the unique nitrate may well be associated with the nonspherical electron distribution stemming from the paramagnetism of the d^7 Co(II) atom. The magnetic susceptibility of 4.22 μ_B measured for **4** from 105 to 300 K is consistent with the presence of 3 unpaired electrons in pentagonal bipyramidal symmetry.

The only other close contacts in the anion arise from N(4) of the coordinated acetonitrile with O(4), O(5), O(7), and O(8) for which the average distance is 2.94 (2) Å and the van der Waals contact is 2.9 Å. The NO_3 groups are quite planar, the average departure of the atoms being 0.007, 0.001, and 0.006 Å for $N(1)O_3$, $N(2)O_3$ and $N(3)O_3$. A least-squares plane through the atoms of both equatorial nitrates and Co(2) reveals only small deviations of the atoms involved, which range from 0.014 to 0.133 Å with an average of 0.098 Å. No abnormal intermolecular contacts were observed. The location of the two acetonitriles of crystallization with respect to the cation is shown in Figure 4.

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Registry No. 1, 62264-33-9; **2**, 62264-32-8; **3**, 62288-62-4; **4**, 62264-31-7; $\{Co[P(OCH_2)_3CMe]_5\}NO_3$, 62264-29-3.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. Bressan and P. Rigo, *J. Chem. Soc., Chem. Commun.*, 553 (1974).
(2) J. H. Meiners, C. J. Rix, J. C. Clardy, and J. G. Verkade, *Inorg. Chem.*, **14**, 705 (1975).
(3) J. O. Albright, F. L. Tanzella, and J. G. Verkade, *J. Coord. Chem.*, **6**, 225 (1976).
(4) L. P. Pepkowitz and J. L. Marley, *Anal. Chem.*, **27**, 1330 (1955).
(5) R. A. Chalmers and M. Umar, *Anal. Chim. Acta*, **42**, 357 (1968).
(6) J. G. Verkade, T. J. Hutteman, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).
(7) E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 168 (1968).
(8) C. A. Tolman, L. W. Yarbrough, and J. G. Verkade, *Inorg. Chem.*, **16**, 479 (1977).
(9) K. J. Coskran, R. D. Bertrand, and J. G. Verkade, *J. Am. Chem. Soc.*, **89**, 4535 (1967).
(10) K. J. Coskran, T. J. Huttemann, and J. G. Verkade, *Adv. Chem. Ser.*, **No. 62**, 590 (1966).
(11) W. J. Rohrbaugh and R. A. Jacobson, *Inorg. Chem.*, **13**, 2535 (1974).
(12) R. A. Jacobson, "An Algorithm for Automatic Indexing and Bravais Lattice Selection. The programs Blind and Alice", U.S. Atomic Energy Commission Report IS-3469, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1974.
(13) D. E. Williams, "LCR-2, a Fortran Lattice Constant Refinement Program", U.S. Atomic Energy Commission Report IS-1052, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1964.
(14) "International Tables for X-Ray Crystallography", Vol. III, 2nd ed, Kynoch Press, Birmingham, England, 1962.
(15) P. Main, M. Woolfson, and G. Germain, "MULTAN", Department of Physics, University of York, York, England, 1971.
(16) The following crystallographic programs were used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT, and Friedel", USAEC Report IS-2625, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program", USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(17) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(18) Supplementary material.
(19) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).
(20) J. H. Meiners, J. R. Swain, and J. G. Verkade, unpublished observations.
(21) J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **2**, 944 (1963).
(22) J. P. Jesson and P. Meakin, *J. Am. Chem. Soc.*, **96**, 5760 (1974).
(23) L. J. Vande Griend, J. C. Clardy, and J. G. Verkade, *Inorg. Chem.*, **14**, 710 (1975).
(24) D. S. Milbrath, J. P. Springer, J. C. Clardy, and J. G. Verkade, *Inorg. Chem.*, **14**, 2665 (1975).
(25) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
(26) E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, **4**, 407 (1970).
(27) D. S. Milbrath, J. P. Springer, J. C. Clardy, and J. G. Verkade, *J. Am. Chem. Soc.*, **98**, 5493 (1976).
(28) F. A. Cotton, J. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965).
(29) L. D. Brown, D. R. Greig, and K. N. Raymond, *Inorg. Chem.*, **14**, 645 (1975).
(30) S. H. Simonsen and W. C. Bryson, Abstracts, 29th Southwest Regional Meeting of the American Chemical Society, El Paso, Tex., Dec 1973, No. 184.
(31) W. C. Bryson and S. H. Simonsen, Abstracts, 30th Southwest Regional Meeting of the American Chemical Society, Austin Tex., December 1974 No. 240.
(32) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, **13**, 2387 (1974).
(33) J. C. Clardy, D. A. Allison, and J. G. Verkade, *Inorg. Chem.*, **11**, 2804 (1972).
(34) It should be noted that $HCo[P(OEt)_2C_6H_5]_4$ is also a distorted trigonal bipyramid [D. O. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *J. Chem. Soc. D*, 322 (1971)] and that $HCo[P(OC_6H_5)_3]_4$ is isomorphous with $Ni[P(OC_6H_5)_3]_4$ which is tetrahedral [J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 96 (1970)].
(35) R. B. Von Dreele, J. J. Stezowski, and R. C. Fay, *J. Am. Chem. Soc.*, **93**, 2887 (1971), and references therein.
(36) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1961).
(37) C. C. Addison, N. Logan, S. C. Wallwork, and G. D. Garner, *Q. Rev., Chem. Soc.*, **25**, 289 (1971).
(38) F. W. B. Einstein, D. W. Johnson, and D. Sutton, *Can. J. Chem.*, **50**, 3332 (1972). In this article the structure of $Mn(NO_3)_3(bpy)$ was determined by x-ray means. The coordination geometry is somewhat different from that of $Co(NO_3)_3NCCH_3$ in that one NO_3 is monodentate axial while the bpy ligand spans an axial and equatorial site.