

Figure 1. Proposed structure of $B_9H_9Se_2$.

to the $^{11}B_9H_9^{80}Se^{82}Se$ parent ion. The isotope ^{82}Se is present in only 9.19% natural abundance. The probability of having a parent ion with all ^{11}B and all ^{82}Se isotopes is very low. Even though the parent ion peak is relatively intense, the highest expected peak was not observed. The high-resolution mass spectrum contains a peak at m/e 269.9891 which corresponds to $^{11}B_9^{80}H_9^{80}Se^{82}Se$, having a calculated mass of 269.9874. The observed osmometer molecular weight of 266 is in fairly close agreement with the proposed molecular formulation. The 70.6-MHz ^{11}B NMR spectrum contains a 3:4:1:1: pattern of doublets which does not yield much structural information. We postulate that this molecule has an 11-atom nido cage structure as illustrated in Figure 1. The positions of the selenium atoms in the cage structure are uncertain based on the available data. A single-crystal x-ray structure determination of other molecules of this type (e.g., $B_8C_2H_{10}^{2-}$ or $B_{10}H_{10}S^{2-}$) has not been reported. An x-ray structure study of $B_9H_9Se_2$ is in progress.

Transition Metal Derivatives. Treatment of $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ with aqueous potassium hydroxide and $FeCl_2 \cdot 6H_2O$ forms purple $[N(CH_3)_4]_2Fe(B_{10}H_{10}Se)_2$ and green $[N(CH_3)_4]_2Fe(B_{10}H_{10}Te)_2$ in low yield. Attempted purification of the tellurium-iron derivative by column chromatography on silica gel without excluding air gave a yellow-green complex.

The ^{11}B NMR spectrum of this product has signals which occur over a large chemical shift range similar to those of other known iron(III) paramagnetic compounds. Further characterization of this oxidized compound is in progress.

Under aqueous base conditions cobalt(III) chloride and $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ form orange $N(CH_3)_4[Co(B_{10}H_{10}E)_2]$ ($E = Se$ or Te) in low yield. With anhydrous conditions $B_{10}H_{12}E$ ($E = Se$ or Te) are deprotonated by triethylamine in the presence of cyclopentadiene monomer and cobalt(II) chloride to give the yellow compounds $(C_5H_5)_2Co(B_{10}H_{10}E)$ in moderate yields. The ^{11}B NMR spectra of icosahedral heteroatom boranes of the general type $(B_{10}H_{10}E)Co(\text{ligand})$ (where $E = CH^-, As^-, P^-, PR, S, Se,$ or Te)⁵ all have the expected 1:1:2:2:2:2 pattern of resonances. In most cases the area 1 doublets which are due to the boron atoms antipodal to the cobalt and E units are in the low-field part of the spectrum and vary in shielding the most. The ^{11}B NMR spectra of compounds VIII–XI fit well into this general spectral pattern. The 32-MHz ^{11}B NMR spectrum of $Co(B_{10}H_{10}S)_2^-$ reported previously,¹ although not well resolved, is consistent with the spectra obtained for the selenium and tellurium analogues.

All of these compounds have good to moderate thermal stability and chemical stability to moist air. Further synthetic studies in this area are in progress.

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Coordination of Organophosphorus Anions. 6.¹ Characterization of Nitrate Complexes of Cobalt(II), Nickel(II), and Zinc(II). Crystal and Molecular Structure of the Dimeric Nitrate(γ -piperidino β -ketophosphonate)cobalt(II)

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The γ -amino β -ketophosphonate ligand $(C_2H_5O)_2P(O)CH_2COCH_2R$ (R being the amino group $N(CH_3)_2$, $N(C_2H_5)_2$, $N(CH_2)_5$, or $N(CH_2)_4O$) forms dimeric molecular complexes with cobalt(II), nickel(II), and zinc(II) nitrates with the formula $(M(NO_3)_2)_2$. The crystal and molecular structure of $(Co(NO_3)_2)((C_2H_5O)_2P(O)CH_2COCH_2N(CH_2)_5)_2$ is reported. The compound crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.47$ (4) Å, $b = 12.83$ (2) Å, $c = 13.11$ (3) Å, $\beta = 113.15$ (10)°, $V = 1775$ (20) Å³, and $Z = 2$. Observed and calculated densities are 1.47 (3) and 1.49 g cm⁻³, respectively. Full-matrix least-squares refinement has converged with $R = 0.09$ for the 2282 reflections with $\sigma(I)/I < 1$. Each cobalt atom is six coordinated by an asymmetrically bidentate nitrate group and the terdentate OON organic moiety; the two octahedra sharing an edge are linked by means of the oxygen atoms of the carbonyl groups. Physical measurements indicate that similar structures are found for $(M(NO_3)_2)_2$ ($M^{2+} = Co^{2+}, Ni^{2+}, Zn^{2+}$, and L^- with each amino group).

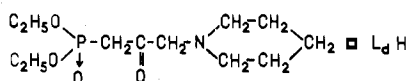
Introduction

In previous studies,²⁻⁴ it was shown that the coordinating behavior of the γ -amino β -ketophosphonates $(C_2H_5O)_2P-$

$(O)CH_2COCH_2R$, designated by LH (L_aH , $R = N(CH_3)_2$; L_bH , $R = N(C_2H_5)_2$; L_cH , $R = NCH_2CH_2OCH_2CH_2$; L_dH , $R = NCH_2CH_2CH_2CH_2$) toward cobalt, nickel, and zinc ions is well demonstrated by the formation of halogeno or

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pseudohalogeno complexes of the type $[MXL]_n$. In particular, we have established that the nature of the central atom M^{2+} and ligand X^- together with the steric characteristics of the amino group R is capable of modifying the dimeric structure from a tetrahedral to a pentacoordinate configuration. This increase in the degree of coordination results from the fact that all the potential donor sites of the organic ligand are then utilized. It therefore appeared reasonable that six coordination might be attained by the presence of a bidentate group X^- . It was particularly interesting to investigate reactions between the ketophosphonates and metal nitrates, since it is well known that the NO_3^- group participates in various types of bonding⁵⁻⁷ and less commonly as an ion. In fact, we have recently been able to isolate ionic complexes of the type $[M_7(OH)_6(L)_6]X_2^{1-}$ and molecular derivatives of stoichiometry $[M(NO_3)L]_n$.⁸ In the former compounds, perchlorate and nitrate groups X^- are both ionic in spite of their very different coordinating ability.^{9,10} This paper deals only with the $[M(NO_3)L]_n$ complexes ($M^{2+} = Co^{2+}, Ni^{2+}, Zn^{2+}$; $L^- = L_a^-, L_b^-, L_c^-, L_d^-$, with $n = 2$). We report here the single-crystal x-ray structural analysis of the compound $[Co(NO_3)L_d]_2$ as well as some physical measurements on related nitrate complexes.



Experimental Section

Preparation of the Co, Ni, and Zn Complexes. The synthesis and characterization of compounds of the type $[M(NO_3)L]_n$ in all their crystallographic forms have been described previously.⁸

Crystallographic Measurements. The crystal of $[Co(NO_3)L_d]_2$ used for the x-ray diffraction work was obtained by recrystallization from a chloroform solution of the complex.

Preliminary diffraction photographs revealed the crystal system to be monoclinic with systematic absences ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$) consistent with the space group $P2_1/c$. The unit cell has dimensions $a = 11.47$ (4) Å, $b = 12.83$ (2) Å, $c = 13.11$ (3) Å, $\beta = 113.15$ (10)°; the unit cell volume based on these dimensions is 1775 (20) Å³. A density of 1.49 g cm⁻³ was calculated for $Z = 2$ with $M = 794.4$ g and this agreed with that of 1.47 (3) g cm⁻³ measured by flotation in a mixture of cyclohexane and bromoform.

Intensity data were collected at room temperature on a Nonius CAD 4 automatic four-circle diffractometer operating in the $\omega/2\theta$ scan mode and using graphite monochromated Mo K α radiation (0.71069 Å); of the 3160 reflections measured, 2282 were retained with $\sigma(I)/I < 1$, where $\sigma(I) = [\text{total counts} + \text{background counts}]^{1/2}$. Values of I were corrected for Lorentz-polarization effects but no absorption corrections were applied. The linear absorption coefficient was 11.4 cm⁻¹. The maximum and minimum transmission factors were 0.91 and 0.79, respectively.

Structure Determination and Refinement. The structure was solved by the multiresolution method with the program MULTAN.¹¹ The phase set with the best figure of merit was used to calculate an E map from which 18 of the 23 nonhydrogen atoms were located. The remaining atoms (four carbons of the two (OC_2H_5) groups and one carbon of the $N(CH_2)_2$ cycle) were located from successive Fourier maps based on the known atom positions. The two terminal carbons of (OC_2H_5) groups were difficult to locate and are characterized by high temperature factors.

The structure was refined by full matrix least squares using a program based on SFLS-5.¹² The atomic scattering factors were calculated from the relation $f_0^2 = A \exp(-a \sin^2 \theta/\lambda^2) + B \exp(-b \sin^2 \theta/\lambda^2) + C^{13}$ where A, B, C, a, b are the constants tabulated by Moore.¹⁴ Anomalous dispersion corrections were applied to the cobalt and phosphorus atoms, with the coefficients $\Delta f'$ and $\Delta f''$ taken from ref 15. A weighting scheme of the form $1/w = \sigma^2(F_o) = (K/4Lp)[\sigma(I)^2/I + p^2I]^{16,17}$ was applied to the data. The final value of p is 0.08. Anisotropic temperature factors were assigned to the cobalt and phosphorus atoms and isotropic ones to the other atoms. No attempt was made to locate hydrogen atoms. The final R value ($R = (\sum |F_o| - K|F_c|)/\sum |F_o|$) and weighted R' value ($R' = [(\sum w|F_o| - K|F_c|)/\sum w|F_o|]^{1/2}$) were 0.09 and 0.10, respectively. The atomic parameters with their standard deviations are listed in Table I and

Table I. Fractional Coordinates with Estimated Standard Deviations in Parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Co	0.6039 (1)	0.5611 (1)	0.1076 (1)
P	0.8440 (2)	0.5914 (2)	0.0549 (2)
N(1)	0.5118 (6)	0.3153 (5)	-0.1260 (5)
N(2)	0.7133 (8)	0.4477 (7)	0.2841 (7)
O(1)	0.5730 (5)	0.5103 (4)	-0.0496 (4)
O(2)	0.7708 (6)	0.6220 (5)	0.1220 (5)
O(3)	0.7128 (7)	0.4119 (6)	0.1971 (6)
O(4)	0.6598 (6)	0.5305 (6)	0.2832 (6)
O(5)	0.7700 (7)	0.4001 (6)	0.3740 (7)
O(6)	0.9856 (6)	0.5725 (5)	0.1284 (5)
O(7)	0.8524 (7)	0.6831 (6)	-0.0224 (6)
C(1)	0.6601 (8)	0.4604 (7)	-0.0719 (7)
C(2)	0.7828 (8)	0.4860 (7)	-0.0337 (7)
C(3)	0.6074 (9)	0.3705 (8)	-0.1548 (8)
C(4)	0.4472 (9)	0.2371 (8)	-0.2199 (8)
C(5)	0.3536 (10)	0.1708 (8)	-0.1950 (8)
C(6)	0.4213 (10)	0.1093 (9)	-0.0846 (9)
C(7)	0.4893 (10)	0.1880 (8)	0.0104 (8)
C(8)	0.5810 (9)	0.2543 (7)	-0.0196 (8)
C(9)	1.0257 (13)	0.5149 (11)	0.2342 (12)
C(10)	1.1374 (16)	0.5848 (13)	0.3129 (14)
C(11)	0.9177 (17)	0.7804 (15)	0.0320 (16)
C(12)	0.9292 (20)	0.8364 (16)	-0.0468 (17)

Table II. Thermal Parameters (Å²) Anisotropic for the Cobalt and Phosphorus Atoms and Isotropic for all Other Atoms

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	58 (1)	54 (8)	41 (8)	1 (1)	15 (7)	-0.4 (9)
P	87 (3)	106 (3)	89 (2)	-14 (2)	36 (2)	7 (2)

	<i>B</i>	<i>B</i>	<i>B</i>
N(1)	4.1 (2)	O(6)	6.8 (3)
N(2)	5.8 (2)	O(7)	5.9 (2)
O(1)	3.8 (1)	C(1)	4.8 (2)
O(2)	5.1 (1)	C(2)	9.4 (4)
O(3)	7.4 (2)	C(3)	12.6 (5)
O(4)	6.4 (2)	C(4)	13.0 (5)
O(5)	8.3 (2)	C(5)	14.6 (7)

temperature factor coefficients in Table II; selected interatomic distances and angles are given in Table III.

Physical Measurements. The methods used for the magnetic and molecular conductance measurements and the recordings of infrared, NMR, and UV-visible spectra have been described previously.⁴ Raman spectra were recorded using a helium-neon laser beam (λ 6328 Å).

Description of the Structure

The complex possesses a dimeric, centrosymmetric structure consisting of two distorted octahedra sharing an edge. In the unit of $[Co(NO_3)L_d]_2$, each cobalt atom is hexacoordinated to a bidentate nitrate group and to the OON terdentate organic moiety; the oxygen atom of each carbonyl group bridges the two cobalt atoms. A view of the dimeric molecule and atomic numbering is given in Figure 1. A projection of the structure along the a axis is shown in Figure 2.

Constraints imposed by the rigidity of the ligands prevent the attainment of a regular arrangement. Each cobalt atom is in a distorted octahedral environment where the oxygen atoms of the two carbonyl groups ($Co^{(1)}-O(1^1)$ 2.056 (6) Å and $Co^{(1)}-O(1^1)$ 2.079 (6) Å) together with one oxygen atom of the asymmetrical bidentate nitrate group ($Co^{(1)}-O(4^1)$ 2.169 (7) Å) and with the oxygen atom of the phosphoryl group of a terdentate ligand ($Co^{(1)}-O(2^1)$ 2.010 (6) Å) define the equatorial plane. Occupying one of the axial sites is the nitrogen atom of the second organic moiety ($Co^{(1)}-N(1^{11})$ 2.150 (7) Å) while the other oxygen atom of the nitrate group ($Co^{(1)}-O(3^1)$ 2.329 (7) Å) completes the metal ion coordination. The $N(1^{11})-Co^{(1)}-O(3^1)$ angle of 141.61 (28)° be-

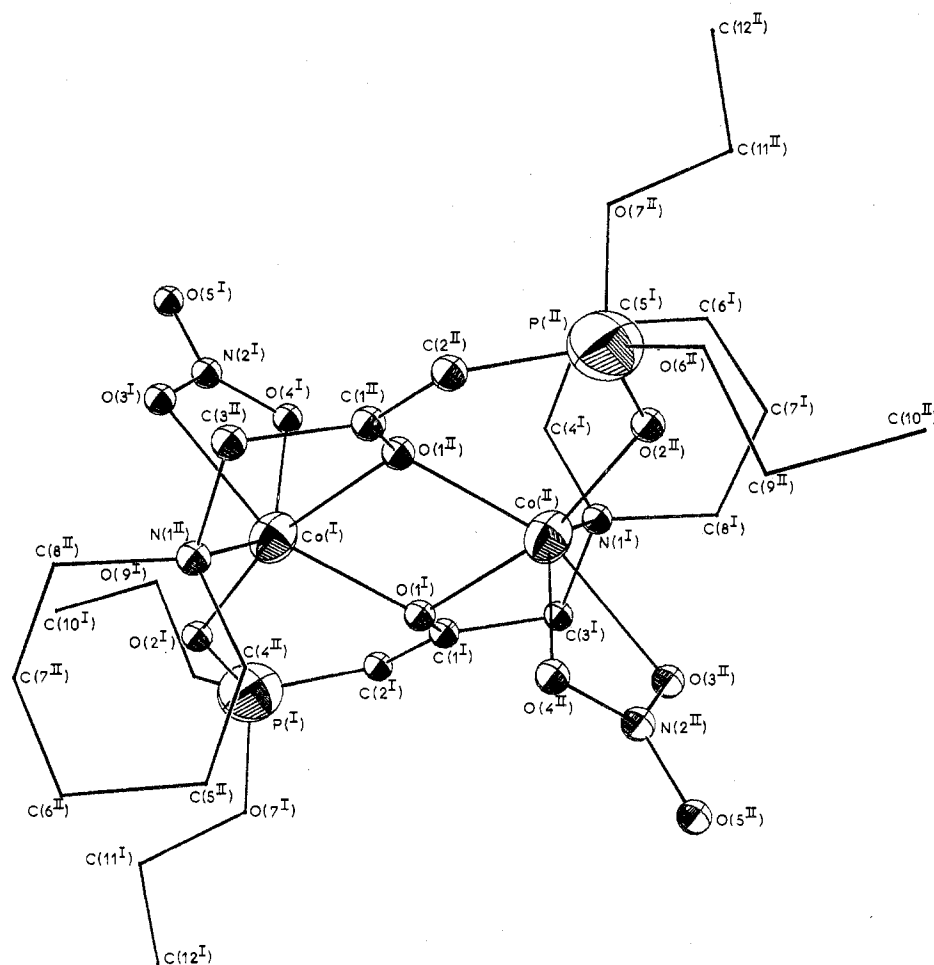


Figure 1. A view of the centrosymmetric dimeric molecule showing the atomic numbering.

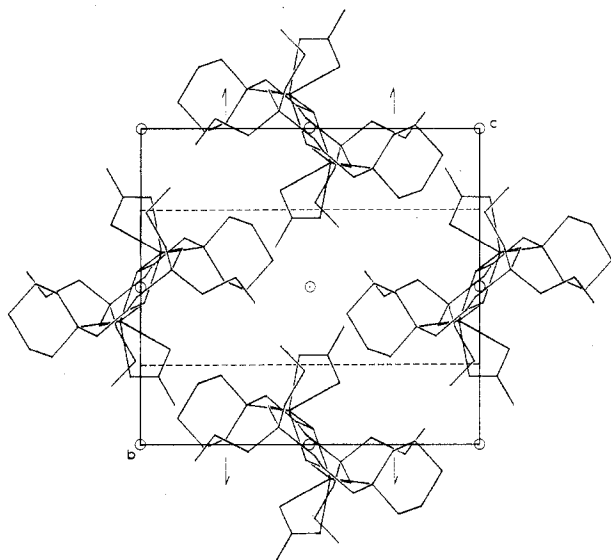


Figure 2. The unit-cell content projected along the *a* direction.

tween the apical positions clearly indicates the marked degree of distortion from a regular geometry. This feature is also evident in the $O(4^I)-Co(1^I)-O(3^I)$ and $O(1^I)-Co(1^I)-O(1^{II})$ angles of $56.13(28)^\circ$ and $74.68(26)^\circ$, respectively, which deviate considerably from the theoretical value of 90° . The cobalt-oxygen bond distances of the OON terdentate donor ligand lie within a small range ($2.05 \pm 0.03 \text{ \AA}$) and agree well with those determined for the trinuclear complex $[Co\{(C_2H_5O)_2P(O)CHCOCH_3\}_2]_3$ ($2.09 \pm 0.05 \text{ \AA}$).¹⁸ As expected

in $[Co(NO_3)L_d]_2$ where dimerization is obtained by shared octahedral edges, the $Co(1^I)-Co(1^{II})$ distance ($3.285(3) \text{ \AA}$) is substantially longer than the metal-metal separations across the shared octahedral faces ($2.916 \pm 0.002 \text{ \AA}$) in the trinuclear complex.¹⁸

The $Co(1^I)-O(3^I)$ and $Co(1^I)-O(4^I)$ bond distances ($2.329(7)$ and $2.169(7) \text{ \AA}$) support the bidentate coordination of the nitrate group and compare favorably with analogous $Co-O$ distances.⁵ The bond length difference $Co-O(NO_3)$ (0.160 \AA) is sufficient to indicate an unsymmetrically coordinated nitrate group, with C_s symmetry. The degree of asymmetry is also reflected in the $Co(1^I)-O(4^I)-N(2^I)$ angle. On going from a symmetrically bidentate coordination to an unsymmetrical one, this angle increases, leading to a unidentate coordination at 110° .¹⁹ The value of $95.99(49)^\circ$ is characteristic of bidentate coordination and approaches the angle of 98.0° found in $[Co(NO_3)_2(C_5H_5N)_3]$ where asymmetry has been suggested on the basis of an x-ray study.²⁰

The planarity of the nitrate ion is preserved (see table IV) and each $O-N-O$ angle is close to 120° . The effect of the coordination is particularly apparent in the $N-O$ bond lengths. The terminal $N-O$ bond ($N(2^I)-O(5^I)$ $1.255(11) \text{ \AA}$) appears to be longer than the two $N-O$ bonds involving the coordinated oxygens ($N(2^I)-O(4^I)$ $1.225(11) \text{ \AA}$ and $N(2^I)-O(3^I)$ $1.232(13) \text{ \AA}$) although the differences are not statistically significant; this apparent lengthening is supported by Raman data (vide infra) and was unexpected for either a monodentate or a bidentate coordination mode of the nitrate group.

In the chelate ring, the observed bond lengths correlate well with those reported in the β -ketophosphonate complex of cobalt.¹⁸ The structure shows that the atoms in the chain from $O(2^I)$ to $N(1^I)$ all lie on the same side of the plane defined

Table III. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses^a

(a) Bond Lengths within a Dimeric Molecule			
Polyhedron around the Cobalt Atom			
Co(I)-O(1 ^I)	2.056 (6)	Co(I)-N(1 ^{II})	2.150 (7)
Co(I)-O(1 ^{II})	2.079 (6)	Co(I)-O(3 ^I)	2.329 (7)
Co(I)-O(2 ^I)	2.010 (6)	Co(I)-O(4 ^I)	2.169 (7)
Nitrate Group			
N(2 ^I)-O(3 ^I)	1.232 (13)	N(2 ^I)-O(5 ^I)	1.255 (11)
N(2 ^I)-O(4 ^I)	1.225 (11)		
Terdentate Ligand			
N(1 ^I)-C(4 ^I)	1.534 (11)	P(1 ^I)-O(7 ^I)	1.583 (9)
C(4 ^I)-C(5 ^I)	1.504 (16)	C(1 ^I)-C(2 ^I)	1.335 (12)
C(5 ^I)-C(6 ^I)	1.561 (14)	C(1 ^I)-C(3 ^I)	1.537 (12)
C(6 ^I)-C(7 ^I)	1.554 (14)	C(1 ^I)-O(1 ^I)	1.314 (12)
C(7 ^I)-C(8 ^I)	1.521 (16)	O(6 ^I)-C(9 ^I)	1.476 (16)
C(8 ^I)-N(1 ^I)	1.522 (10)	O(7 ^I)-C(11 ^I)	1.487 (20)
P(1 ^I)-O(2 ^I)	1.490 (8)	C(9 ^I)-C(10 ^I)	1.572 (20)
P(1 ^I)-C(2 ^I)	1.739 (9)	C(11 ^I)-C(12 ^I)	1.316 (32)
P(1 ^I)-O(6 ^I)	1.546 (6)	C(3 ^I)-N(1 ^I)	1.482 (22)
(b) Separations < 3.65 Å in the Dimeric Molecule			
O(1 ^I) ··· O(1 ^{II})	2.507 (12)	O(4 ^I) ··· C(4 ^{II})	3.208 (13)
O(4 ^I) ··· N(1 ^{II})	2.974 (12)	O(4 ^I) ··· C(1 ^{II})	3.623 (12)
O(4 ^I) ··· C(3 ^{II})	3.132 (13)	Co(I) ··· Co(II)	3.285 (3)
(c) Separations < 3.65 Å between the Dimeric Molecules			
O(4 ^I) ··· C(12 ^{III})	3.45 (20)	O(5 ^I) ··· C(8 ^{IV})	3.60 (13)
O(7 ^I) ··· C(5 ^{VI})	3.51 (20)	N(2 ^I) ··· C(12 ^V)	3.62 (23)
O(5 ^I) ··· C(12 ^V)	3.58 (20)	C(12 ^I) ··· C(10 ^{VII})	3.65 (26)
C(6 ^I) ··· C(6 ^{VIII})	3.59 (27)		
(d) Bond Angles			
Polyhedron around the Cobalt Atom			
N(1 ^{II})-Co(I)-O(1 ^I)	118.59 (25)	O(3 ^I)-Co(I)-O(4 ^I)	56.13 (28)
N(1 ^{II})-Co(I)-O(1 ^{II})	79.06 (26)	N(1 ^{II})-Co(I)-O(3 ^I)	141.61 (28)
N(1 ^{II})-Co(I)-O(4 ^I)	87.22 (27)	O(1 ^I)-Co(I)-O(2 ^I)	89.88 (25)
N(1 ^{II})-Co(I)-O(2 ^I)	108.20 (27)	O(1 ^{II})-Co(I)-O(4 ^I)	98.34 (26)
O(3 ^I)-Co(I)-O(1 ^I)	95.15 (27)	O(2 ^I)-Co(I)-O(4 ^I)	95.70 (27)
O(3 ^I)-Co(I)-O(2 ^I)	88.29 (28)	O(3 ^I)-Co(I)-O(1 ^{II})	94.19 (26)
O(1 ^I)-Co(I)-O(1 ^{II})	74.68 (26)		
Nitrate Group			
O(3 ^I)-N(2 ^I)-O(4 ^I)	119.60 (50)	O(4 ^I)-N(2 ^I)-O(5 ^I)	120.35 (66)
O(3 ^I)-N(2 ^I)-O(5 ^I)	120.04 (60)	Co(I)-O(4 ^I)-N(2 ^I)	95.99 (49)
Terdentate Ligand			
C(8 ^I)-N(1 ^I)-C(4 ^I)	108.18 (62)	O(7 ^I)-P(1 ^I)-C(2 ^I)	105.07 (46)
N(1 ^I)-C(4 ^I)-C(5 ^I)	110.92 (80)	C(1 ^I)-C(2 ^I)-P(1 ^I)	122.05 (77)
C(4 ^I)-C(5 ^I)-C(6 ^I)	110.53 (98)	C(2 ^I)-C(1 ^I)-C(3 ^I)	120.86 (74)
C(5 ^I)-C(6 ^I)-C(7 ^I)	108.89 (93)	C(1 ^I)-C(3 ^I)-N(1 ^I)	107.77 (56)
C(6 ^I)-C(7 ^I)-C(8 ^I)	109.66 (97)	C(3 ^I)-N(1 ^I)-C(8 ^I)	107.88 (65)
C(7 ^I)-C(8 ^I)-N(1 ^I)	111.17 (62)	C(3 ^I)-C(1 ^I)-O(1 ^I)	114.03 (53)
O(2 ^I)-P(1 ^I)-C(2 ^I)	115.45 (46)	O(1 ^I)-C(1 ^I)-C(2 ^I)	125.02 (54)
O(2 ^I)-P(1 ^I)-O(6 ^I)	111.94 (38)	C(3 ^I)-N(1 ^I)-C(4 ^I)	106.50 (55)
O(6 ^I)-P(1 ^I)-O(7 ^I)	101.49 (40)		

^a Roman numeral superscripts refer to the following equivalent positions: (I) x, y, z ; (II) $1-x, 1-y, -z$; (III) $x, 1.5-y, 0.5+z$; (IV) $x, 0.5-y, 0.5+z$; (V) $x, 1.5-y, 0.5+z$; (VI) $1-x, 0.5-y, -0.5-z$; (VII) $x, 1.5-y, z-0.5$; (VIII) $1-x, -y, -z$.

by the atoms Co(I), Co(II), O(1^I), and O(1^{II}). The C-C and C-N distances in the NCH₂CH₂CH₂CH₂CH₂ cycle lie in the range 1.504–1.561 Å. This cycle is not planar, as shown in Table IV and by the packing arrangement in the unit cell in Figure 3. Intramolecular close contacts in the range 2.974 to 3.623 Å are observed between atoms of the nitrate group and those of the piperidino group (see Table III). This feature will be discussed later in connection with the NMR data. There are no unusually short intermolecular contacts.

Structures of $[M(\text{NO}_3)_2\text{L}_2]$, $M^{2+} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$; $L^- = L_a^-, L_b^-, L_c^-, L_d^-$

The present x-ray structural determination of the $[\text{Co}(\text{NO}_3)_2\text{L}_d]_2$ confirms the expected distorted octahedral geometry involving an asymmetrically bidentate nitrate group and a tridentate organic ligand in a dimeric configuration. These results are based on conductivity, magnetic moment, molecular weight, infrared, and electronic spectral mea-

surements. Moreover, the existence of a steric effect is indicated by NMR data.

All the nitrate complexes show at least bidentate metal β -ketophosphonate coordination involving the carbonyl and the phosphoryl groups. As reported previously for complexes containing analogous organic ligands,^{1,4} there was no evidence for a bonded amino group.

The presence of a coordinated nitrate group is evidenced by the number of bands in the infrared spectra; selected data for the $[M(\text{NO}_3)_2\text{L}_b]_2$ complexes are given in Table V. Since these compounds contain only one nitrate group, it was expected that identification of the exact mode of coordination should be easier. The application of the best criterion based on the depolarization ratios of the three highest frequency Raman shifts^{21,22} of the nitrate fundamental frequencies was unsuccessful owing to decomposition of solutions by the laser beam. However, the Raman band at about 1300 cm⁻¹ was weaker than the two bands near 1500 and 1000 cm⁻¹. This

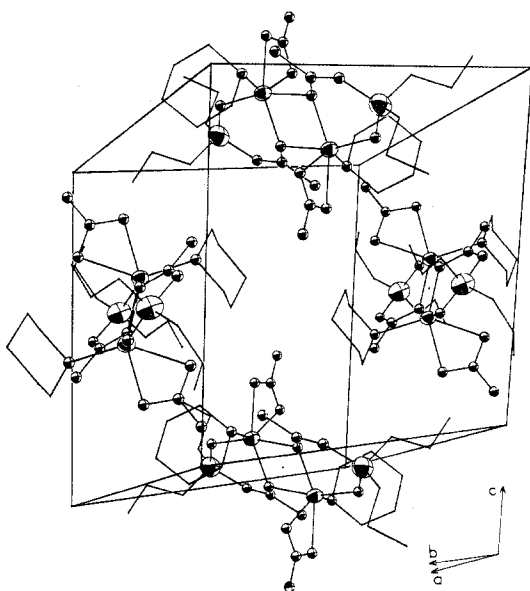


Figure 3. The molecular packing.

Table IV. Least-Squares Planes

(a) Distances (Å) of Atoms from Planes

Plane 1: N(1), C(4)-C(8)
 N(1) 0.171, C(4) -0.307, C(5) 0.241, C(6) -0.216,
 C(7) 0.250, C(8) -0.300

Plane 2: Co, P, O(1), O(2), C(1), C(2)
 Co -0.012, P 0.018, O(1) 0.344, O(2) 0.170, C(1)
 -0.277, C(2) -0.496

Plane 3: N(2), O(3)-O(5)
 N(2) 0.004, O(3) -0.001, O(4) -0.001, O(5) -0.0, Co
 -0.129.

(b) Plane Equations where X , Y , and Z are Coordinates in Å with Reference to Orthogonalized Axes

Plane 1: $0.8206X - 0.5588Y - 0.1195Z = -1.2087$
 Plane 2: $-0.2056X + 0.8280Y - 0.5216Z = 3.988$
 Plane 3: $-0.8554X - 0.4984Y - 0.1411Z = -9.0905$

(c) Dihedral Angles (deg) between Planes
 (1)-(2) 55.31 (1)-(3) 66.01 (2)-(3) 80.60

result suggests a bidentate coordination.⁵ The separation $\Delta\nu'$ in the combination frequencies near 1750 cm^{-1} is compatible with this type of bonding; the values reported in Table V for selected compounds are in the range $38\text{--}56\text{ cm}^{-1}$ as expected for cobalt and nickel bidentate nitrate complexes (the splitting for a monodentate nitrate group is of the order $16\text{--}26\text{ cm}^{-1}$).²³ Since the complexes with L_5^- and L_c^- with respectively two and three crystalline forms have been isolated,⁸ the present data are of value in clarifying the symmetry of the group NO_3 .

Indeed, it appears that for a given metal the $[\text{M}(\text{NO}_3)_2\text{L}_b]_2$ complexes in their δ and ϵ forms give rise to significantly different splittings. The value $\Delta\nu'$ depends on the strength of the metal-nitrate interaction and increases in the order ionic $<$ monodentate $<$ bidentate.²³ Moreover, a nitrate group is asymmetrical with a C_s symmetry as a consequence of arbitrary monodentate or bidentate coordination to a metal ion (vide infra). Thus, there is clearly some degree of asymmetry at least in the ϵ form of $[\text{M}(\text{NO}_3)_2\text{L}_b]_2$. As expected, the value $\Delta\nu'$ depends also on the nature of the metal ion; the sequence $\Delta\nu'(\text{Ni}) > \Delta\nu'(\text{Co}) > \Delta\nu'(\text{Zn})$ is in agreement with that found in the compounds $[\text{M}(\text{NO}_3)_2(\text{py})_3]$ on the basis of infrared absorption²⁴ and x-ray data.²⁰ The specific values $\Delta\nu'$ within each set α $[\text{M}(\text{NO}_3)_2\text{L}_c]_2$, β $[\text{M}(\text{NO}_3)_2\text{L}_d]_2$ with $L^- = L_c^-$ or L_d^- , and γ $[\text{M}(\text{NO}_3)_2\text{L}_c]_2$ also support the C_s structure suggested for the nitrate group. The sequence $\Delta\nu'(\gamma) > \Delta\nu'(\alpha) > \Delta\nu'(\beta)$ provides credence for a tentative assignment of the bands observed at 248 cm^{-1} (γ), 245 cm^{-1} (α), and 241 cm^{-1} (β) in $[\text{Co}(\text{NO}_3)_2\text{L}_c]_2$ to cobalt-oxygen (NO_3) interaction. Indeed, such positions correlate well with the $\nu(\text{Co-O})$ vibration found at 238 cm^{-1} in $[\text{Co}(\text{NO}_3)_2(\text{py})_3]$ with the aid of deuterated pyridine.²⁴ The asymmetric structure for the bidentate nitrate group inferred from the spectroscopic data is confirmed by the foregoing x-ray analysis. Further, the apparent trend in change in the three observed bond lengths N-O can be associated with the unusual sequence²⁵ $I_{1000} > I_{1500} > I_{1300}$ observed for the Raman band intensities.

For each crystalline form studied by mass spectrometry, a fragment containing two units of $[\text{Co}(\text{NO}_3)_2\text{L}_b]$ was observed ($m/e_{\text{exptl}} 770$; $m/e_{\text{th}} 770.4$); this result was indicative of a dimeric structure.

In the nickel complexes, the magnetic data ($\mu = 3.1\text{--}3.2\ \mu_B$ at room temperature) and visible spectra (system band at 0.79 , 1.46 , and 2.45 with a shoulder at $2.21\ \mu\text{m}^{-1}$ in the δ - $[\text{Ni}(\text{NO}_3)_2\text{L}_b]_2$ complex) are in accord with an octahedral configuration.^{26,27} The expected deformation from a regular arrangement is especially evidenced in the cobalt compounds for which magnetic moments of $4.55\text{--}4.60\ \mu_B$ were found; μ lies between 4.7 and $5.2\ \mu_B$ in the absence of distortion.²⁶ This feature is also manifest in the d-d pattern with the splitting of the transitions from ${}^4\text{T}_{1g}(\text{F})$ to ${}^4\text{T}_{2g}(\text{F})$ (bands at 0.67 and $0.86\ \mu\text{m}^{-1}$) and to ${}^4\text{T}_{1g}(\text{P})$ (bands at 1.89 and 2.11 with a shoulder at $2.03\ \mu\text{m}^{-1}$ in δ - $[\text{Co}(\text{NO}_3)_2\text{L}_b]_2$). This spectrum markedly resembles that of $[\text{CoCl}_2(\text{py})_2]_n$,²⁸ in which two apical nitrogen atoms and four basal chlorine atoms surround the cobalt atom in a polymeric chain.²⁹ In both cases, the six-coordinate structure arises from polymerization involving shared edges. The observed bands may thus be assigned to components in a lower symmetry, such as D_{2h} for $[\text{CoCl}_2(\text{py})_2]_n$ or C_{2h} for $[\text{M}(\text{NO}_3)_2\text{L}_b]_2$, in which only the nature of the donor

Table V. Infrared and Raman Frequencies (cm^{-1}) of the Nitrate-Group in the $(\text{M}(\text{NO}_3)_2\text{L}_b)_2$ Complexes

Attribution ^a	$\{\text{M}(\text{NO}_3)_2\text{L}_b\}_2$							
	δ form				ϵ form			
	Ni ²⁺ IR	Co ²⁺ IR	Zn ²⁺		Co ²⁺ IR	Zn ²⁺		
$\nu_1(\text{A}_1)$ (p)	1490	1488	1480	1479 m	1486	1472	1477 mw	
$\nu_4(\text{B}_1)$ (d)	1290	1288	1307	1294 mw	1290	1307	<i>d</i>	
$\Delta(\nu_1 - \nu_4)$	200	200	177	185	196	165		
$\nu_2(\text{A}_1)$ (p)	1030	1027	1032	1031 vs	<i>c</i>	<i>c</i>	1034 vs	
$\nu_6(\text{B}_2)$	810	812	815	815	812	815	809	
$\nu_3(\text{A}_1)$ ^b	751	741 mw	741 w	742	740 w	739 vw	<i>d</i>	
$\nu_3(\text{B}_1)$ ^b	700	701 w	706 sh	708	703 vw	709 sh	712	
$\nu_2 + \nu_3$	1780	1767	1772		1768	1770		
$\nu_2 + \nu_5$	1729	1726	1736		1730	1740		
$\Delta\nu' \{(\nu_2 + \nu_3) - (\nu_2 + \nu_5)\}$	51	41	36		38	30		

^a The $\nu_1, \nu_2, \dots, \nu_6$ attributions are those of Addison³² for a C_{2v} bidentate group. ^b ν_3 and ν_5 are given with an accuracy of $\pm 1\text{ cm}^{-1}$.
^c Masked absorption. ^d Because of its weakness, this absorption cannot be pointed.

Table VI. Selected ^1H NMR Data for the $(\text{Zn}(\text{NO}_3)_2)_2$ Complexes with $\text{L}^- = \text{L}_a^-, \text{L}_b^-$

Compd	δ_3	$J(\text{P}-3)$	δ_4	δ_5	δ_6
L_aH	3.17	22.3	3.25	2.27	
$\{\text{Zn}(\text{NO}_3)_2\text{L}_a\}_2$	4.08	15.0	3.18	2.56	
L_bH	3.22	22.3	3.32	2.58	1.00
$\{\text{Zn}(\text{NO}_3)_2\text{L}_b\}_2$	4.07	14.2	3.23	2.64, 3.03	1.18
				$\Delta\delta_5' = 23.2$	

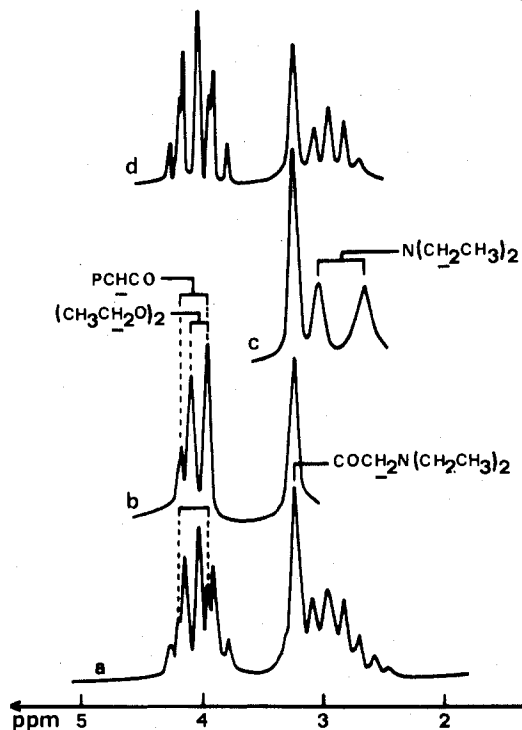


Figure 4. NMR spectra of the $(\text{Zn}(\text{NO}_3)_2)_2$ complex in a CDCl_3 solution: (a) at room temperature; (b) after irradiation of the methyl of the ethoxy groups; (c) after irradiation of the methyl of the diethylamino group; (d) at 333 K.

atoms is taken into account. Although significant differences in position of the energy bands may occur according to the particular crystallographic form or ligand L^- , an analogous stereochemistry is ascribed to all the complexes. This octahedral structure is maintained in chloroform solution.

The NMR spectra of the diamagnetic complexes $[\text{Zn}(\text{NO}_3)_2]_2$ with $\text{L}^- = \text{L}_a^-$ and L_b^- in CDCl_3 solutions were recorded in an attempt to deduce the effect of coordination on protons in position α to the nitrogen atom. As expected (see Table VI), a downfield shift of the resonance δ_5 relative to the uncoordinated ligand³⁰ is observed. However, a significant deshielding of 0.1 ppm in the complexes containing L_a^- occurs with respect to the series of the halogeno complexes $(\text{ZnXL})_2$ with the same L^- ligands, in which the nitrogen atom is not involved in any coordination bonding.³ In the $(\text{ZnXL}_b)_2$ compounds, the contrary effect is observed ($\delta_5' = 2.95$ ppm

for $\text{X}^- = \text{Cl}^-$ and $\delta_5' = 2.84$ ppm for $\text{X}^- = \text{NO}_3^-$); this is not surprising, since it is known that coordination may also affect protons close to the donor center³¹ and leads to a new electronic distribution. The most interesting feature of this study is that intramolecular exchange occurs between the CH_2 groups adjacent to nitrogen in the $(\text{Zn}(\text{NO}_3)_2)_2$ complex. This was established on the basis of dilution, irradiation, and temperature effects (Figure 4). This exchange is peculiar to the complexes containing the diethylamino group, which is bulkier than the dimethylamino group. It would therefore be expected that steric hindrance effects would apply. This interpretation is further supported by the short intramolecular distances revealed by crystallographic analysis of the analogous compound $(\text{Co}(\text{NO}_3)_2)_2$.

Registry No. $[\text{Co}(\text{NO}_3)_2]_2$, 61363-47-1; $[\text{Ni}(\text{NO}_3)_2]_2$, 61363-48-2; $[\text{Co}(\text{NO}_3)_2]_2$, 61363-49-3; $[\text{Zn}(\text{NO}_3)_2]_2$, 61363-50-6; $[\text{Zn}(\text{NO}_3)_2]_2$, 61363-51-7.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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