

evolution of gas and becomes dark red in color. It is possible that some type of ketyl is formed, but the reaction was not investigated further. No other attempts were made to prepare complexes with this ligand.

**Magnetic susceptibilities** of the cobalt and chromium complexes were measured in benzene solution by observing the shift in the proton resonance frequency of benzene due to the presence of the paramagnetic species.<sup>27</sup> A concentric double-walled sample tube was used in which the sample solution was in the inner tube and the pure solvent in the outer annular ring. Proton shifts were measured at 60 Mc. on a Varian Associates A-60 spectrometer and are accurate to  $\pm 1$  c.p.s.

The magnetic moment of solid bis-(diethoxyphosphonylacetyl-methano)-cobalt(II) was also measured by the Gouy method at room temperature using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as a calibrant. In all cases, diamagnetic corrections were made using Pascal's constants.<sup>28</sup>

**Visible and near-infrared spectra** were recorded on a Cary model 14 recording spectrophotometer. Wave lengths are accurate to  $\pm 3 \text{ m}\mu$  and molar extinction coefficients,  $\epsilon$ , are accurate to about  $\pm 5\%$ . Quartz cells of 1 mm., 1 cm., and 10 cm. path length were used for solutions of appropriate concentrations.

**Ultraviolet spectra** were recorded from 350 to 210  $\text{m}\mu$  on a Cary model 11 recording spectrophotometer using 1-cm. quartz

(27) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(28) P. N. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 91.

cells. Band maxima are believed accurate to  $\pm 2 \text{ m}\mu$ . All solutions were prepared in a nitrogen atmosphere and the cells were filled through serum caps as rapidly as possible with a hypodermic syringe.

**Infrared spectra** were recorded on a Perkin-Elmer model 21 double beam spectrophotometer equipped with NaCl optics. Calibration of the frequencies was made with polystyrene film. The recorded locations of band maxima are believed accurate to  $\pm 2 \text{ cm.}^{-1}$ . Solutions were prepared in a nitrogen atmosphere and the cells filled immediately using a hypodermic syringe.

**Nuclear Resonance Spectra.**—Proton resonance spectra were recorded at 60 Mc. on a Varian Associates A-60 high resolution spectrometer equipped with an integrator. Tetramethylsilane was used as an internal standard. Resonance frequencies are believed accurate to  $\pm 0.02$  p.p.m. and the resolution is about 1 c.p.s. Solutions were prepared in a nitrogen atmosphere and used immediately.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR CHEMICAL AND SOLID STATE PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

## The Crystal and Molecular Structure of Bis-(trimethylphosphine oxide)-cobalt(II) Dinitrate

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The crystal structure of bis-(trimethylphosphine oxide)-cobalt(II) dinitrate has been determined using three-dimensional X-ray diffraction data. Although magnetic and spectroscopic data had suggested tetrahedrally coordinated cobalt, it is found that the cobalt is 6-coordinate with a very irregular arrangement of ligand atoms, possessing no strict symmetry elements whatever and only one quasi or approximate one, a 2-fold axis. Among the interesting results are (1) the P-O-Co groups are bent ( $\sim 133^\circ$ ,  $\sim 140^\circ$ ), (2) the P-O bond is longer than in the free  $(\text{CH}_3)_3\text{PO}$  molecule, (3) the nitrate ions are bidentate but little distorted from their inherent  $\text{D}_{3h}$  symmetry.

### Introduction

Recent studies<sup>2</sup> have led to the preparation and characterization by magnetic and spectroscopic studies of compounds of the general type  $\text{Co}(\text{R}_3\text{MO})_2(\text{NO}_3)_2$ , where R may be  $\text{CH}_3$  or  $\text{C}_6\text{H}_5$  and M may be P or As.

A complete X-ray diffraction investigation of the crystal and molecular structures of one of these, namely  $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$ , was undertaken because it was felt that the results would be of interest for three different reasons. (1) There have not previously been any precise data concerning the structures of nitrate complexes. (2) Very little has been reported about the structures of phosphine oxide complexes and more detailed structural data would be desirable. (3) The coordination geometry about the Co(II) ion was of interest in connection with the interpretation of the magnetic and spectroscopic data.

### Structure Determination

**Unit Cell and Space Group.**—Suitable crystals for X-ray work were prepared by slow evaporation of a solution of the complex in a 1:1 mixture of benzene and methylene chloride. The crystals grow as purple parallelepipeds, elongated on one axis. The compound is quite hygroscopic and it was therefore necessary to enclose crystals in thin-walled, soft glass capillary tubes.

From zero layer and several upper layer precession photographs, taken using  $\text{Cu K}\alpha$  and  $\text{Mo K}\alpha$  radiations, the crystals were found to be monoclinic and by superposition of NaCl powder lines on Weissenberg photographs taken later with  $\text{Mo K}\alpha$  radiation the following unit cell dimensions (in  $\text{\AA}$ .) were measured:  $a = 11.70 \pm 0.02$ ,  $b = 12.11 \pm 0.02$ ,  $c = 11.37 \pm 0.02$ ,  $\beta = 93^\circ \pm$

$10'$ . The density measured by flotation was 1.53 g./ml. which indicates 4 molecules (4.02 calcd.) per unit cell. Systematic absences observed on the precession photographs were:  $h0l$ ,  $l \neq 2n$ ;  $0k0$ ,  $l \neq 2n$ . These unambiguously indicate that the space group is  $\text{P}2_1/c$  ( $\text{C}_{2h}^2$ ). With four molecules in the unit cell it follows that all atoms are in general fourfold positions.

**Intensity Measurements.**—A crystal of dimensions  $0.1 \times 0.1 \times 0.15 \text{ mm.}$  was mounted in a capillary tube with its  $c$ -axis parallel to the capillary axis. Equi-inclination Weissenberg photographs were taken for  $0 \leq l \leq 6$  using  $\text{Mo K}\alpha$  radiation. Using another crystal of similar dimensions mounted for rotation about the  $b$ -axis a set of  $h1l$  photographs were taken to tie together intensities on the various  $hkl$  ( $l = 0-6$ ) photographs.

The multiple film technique was used and intensities were measured visually using sets of standard spots prepared from the crystals studied. Approximate corrections were made for spot expansion and contraction on upper layer photographs, as well as the usual Lorentz and polarization corrections. Absorption corrections were neglected in view of the small size of the crystals and the short wave length of the radiation used. In all, 973 data of measurable intensity were collected.

The  $F^2$ -values were placed approximately on an absolute scale and a mean temperature factor obtained using Wilson's method.<sup>3</sup>

**Treatment of Data.**—A three-dimensional Patterson synthesis was calculated using the measured  $F^2$ -values. This synthesis and the several Fourier summations subsequently calculated were done on an IBM 7090 digital computer using Sly, Shoemaker, and Van den Hende's program.<sup>4</sup> A trial and error analysis of the Patterson synthesis indicated positions for the phosphorus atoms (almost in the glide plane) and only two possible sets of positions for the cobalt atoms. One of these alternatives was adopted and structure factors,  $F_{\text{calc}}$ 's, computed from the Co and P positions only, giving for the usual discrepancy index a value of 45%. Signs for the  $F$ 's of 423 of the 530 strongest reflections were then taken to be those just computed. An electron density map was then calculated which showed the  $\text{NO}_3$  groups and the oxygen

(1) (a) Fellow of the Alfred P. Sloan Foundation; (b) National Science Foundation Predoctoral Fellow.

(2) F. A. Cotton, R. H. Soderberg, and D. M. L. Goodgame, *Inorg. Chem.*, in press.

(3) A. J. C. Wilson, *Acta Cryst.*, **2**, 318 (1949).

(4) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, ERFRZ IBM 709-7090 Fourier Program, 1962.

TABLE I

ATOMIC COORDINATES, TEMPERATURE PARAMETERS, AND STANDARD DEVIATIONS FOR ONE  $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$  MOLECULE

No.	Atom	$x/a$	$y/b$	$z/c$	$2B$	$\sigma_x$	$\sigma_y$	$\sigma_z$	$\sigma_{2B}$
1	Co <sub>1</sub>	0.2396	0.4095	0.2566	3.43	0.0002	0.0002	0.0003	0.07
2	P <sub>2</sub>	.0274	.2385	.2750	4.76	.0004	.0005	.0006	.13
3	P <sub>3</sub>	.4474	.2348	.2690	4.28	.0004	.0005	.0006	.12
4	O <sub>4</sub>	.1031	.3247	.2189	5.40	.0012	.0012	.0014	.32
5	O <sub>5</sub>	.3524	.3051	.3231	6.39	.0013	.0013	.0016	.37
6	O <sub>6</sub>	.3007	.4142	.0825	5.27	.0011	.0012	.0015	.32
7	O <sub>7</sub>	.1794	.5341	.1227	6.82	.0013	.0014	.0017	.38
8	O <sub>8</sub>	.2439	.5288	— .0521	9.05	.0017	.0017	.0024	.51
9	O <sub>9</sub>	.1913	.4715	.4265	6.31	.0013	.0013	.0016	.36
10	O <sub>10</sub>	.3230	.5479	.3428	8.39	.0016	.0016	.0021	.47
11	O <sub>11</sub>	.2829	.6054	.5118	11.49	.0021	.0020	.0027	.69
12	N <sub>12</sub>	.2402	.4922	.0468	5.62	.0015	.0016	.0022	.41
13	N <sub>13</sub>	.2691	.5403	.4314	7.48	.0020	.0020	.0026	.53
14	C <sub>14</sub>	.0449	.2341	.4336	7.40	.0021	.0021	.0029	.67
15	C <sub>15</sub>	— .1215	.2695	.2307	7.25	.0021	.0021	.0027	.64
16	C <sub>16</sub>	.0593	.0984	.2289	7.09	.0020	.0021	.0028	.61
17	C <sub>17</sub>	.5608	.3233	.2183	5.48	.0017	.0018	.0023	.51
18	C <sub>18</sub>	.5145	.1489	.3830	6.14	.0019	.0020	.0024	.55
19	C <sub>19</sub>	.3946	.1502	.1496	5.39	.0017	.0018	.0022	.49

atoms of the phosphine oxides, but gave no certain indication of the carbon positions. A structure factor calculation based on all the atoms now located gave an encouraging discrepancy index of only 26% after one cycle of least squares refinement and provided a new and much more reliable set of signs for the observed structure factors; 793 of the latter were now given signs and used for a new electron density map which revealed the carbon atoms along with a few spurious peaks. Structure factors calculated using all atoms, at the coordinates now in hand, gave a discrepancy index of 23% for 835 of the strongest and/or most reliable reflections.

An analogous procedure was also attempted starting with the other set of possible cobalt positions. This led, in the first electron density map, to peaks indicative of six atoms about 2 Å. from Co, but to no other peaks which could be assigned with any confidence to atoms. A second electron density map using signs for structure factors based on these six oxygen atoms as well as the P and Co atoms and including 453 reflections gave some indications of possible positions for additional atoms, but also showed distortion and splitting of the atoms close to Co. In view of these results and the evident feasibility of the other set of Co positions, this alternate choice was assumed to be incorrect.

Three cycles of least squares refinement (diagonal approximation<sup>5</sup>) varying only the atom coordinates lowered the discrepancy index to 17%. After three more cycles in which the isotropic temperature factors for each atom were also allowed to vary, a discrepancy index of 11% was obtained.

Final refinement was done using a full-matrix least squares program, written for the IBM 709/7090 computers by Dr. C. Prewitt of the M.I.T. Geology Department. The very strong 220 reflection and twenty reflections with low  $(\sin \theta)/\lambda$  from upper layer Weissenberg films were omitted, as were all unobserved reflections. Separate scale factors (13 in all) were used for various groups of reflections, divided according to whether spots were extended or contracted on the upper layer ( $hk2-hk6$ ) Weissenberg photographs (10 groups in all) and into groups corresponding to  $hk0$ ,  $hk1$ , and  $h1l$  indices. A total of 948 reflections were used. Individual isotropic temperature factors were used for each atom and the scattering factors were taken from Table 3.3.1.A of the International Tables.<sup>6</sup> Cobalt was taken as  $\text{Co}^+$ . The reflections were weighted according to the weighting function of Cruickshank and Pilling.<sup>7</sup>

Only scale factors were allowed to vary for two cycles, after which three cycles were carried out with all parameters varying. At this point, a bonds and angles calculation showed that bonds which, for chemical though not crystallographic reasons, should presumably be of the same length, had indeed converged. During the last of two more cycles of refinement, changes in atom positions were less than their standard deviations, and the discrepancy index was 10.8%. It was felt that the limits of the data had certainly been reached at this point.<sup>8</sup>

Atomic positions and temperature factors for the atoms of one asymmetric unit are given in Table I, along with the standard deviations calculated in the final cycle of refinement. The numbering of atoms is shown in Fig. 1. In Tables II and III are the interatomic distances and bond angles for the asymmetric unit. Standard deviations for the bond lengths were estimated by the method of Lipson and Cochran.<sup>9</sup>

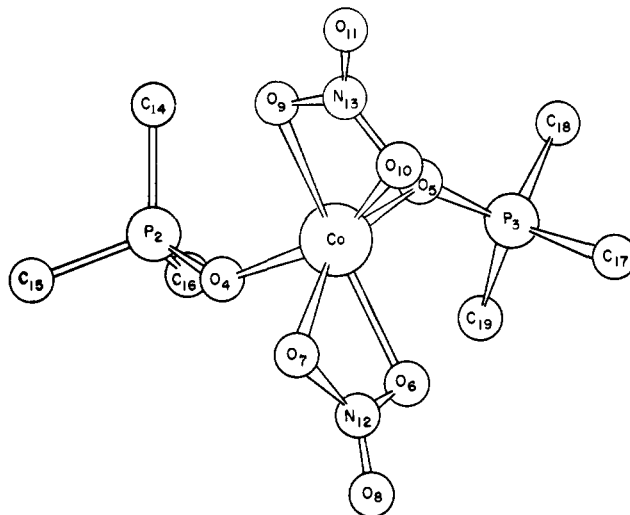


Fig. 1.—The  $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$  molecule viewed down the  $b$ -axis of the unit cell.

As a final check for the correctness of the structure, a three-dimensional Fourier difference synthesis was computed using the 948 reflections considered most reliable as the  $|F_{\text{obs}}|$  value and the atomic positions of Table I to obtain the  $F_{\text{calc}}$  values. The result was very satisfactory, showing no significant peaks or valleys, except minor ones in two places (to be discussed later) where there were indications that an atom was slightly misplaced. In both cases, the indicated shift was reasonable, but no attempt has been made to estimate the indicated shifts quantitatively.

## Discussion

**1. The Trimethylphosphine Oxide Groups.**—The  $(\text{CH}_3)_3\text{PO}$  groups each have the phosphorus atom in essentially the same environment. The averages of the P—C bond lengths in the two ligands are 1.82 and

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(9) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, Ltd., London, 1953, p. 287.

(5) J. H. Van den Hende, "Crystallographic Structure Factor and Least Squares Refinement Program for the IBM 709/7090 Computer," Esso Research and Engineering Co., Linden, N. J., 1961.

(6) "International Tables for Crystallography," Vol. III, K. Lonsdale and N. F. M. Henry, Eds., Kynoch Press, Birmingham, Eng., 1962.

(7) D. W. J. Cruickshank and D. E. Pilling, in "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Eds., Pergamon Press, New York, N. Y., 1961.

(8) A table of calculated and observed structure factors has been de-

TABLE II  
BOND LENGTHS AND STANDARD DEVIATIONS (SD's) IN  
Co[(CH<sub>3</sub>)<sub>3</sub>PO]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>

Bond	Length,		Bond	Length,	
	Å.	SD, Å.		Å.	SD, Å.
Co <sub>1</sub> -O <sub>4</sub> (P)	1.92	0.02	P <sub>3</sub> -O <sub>5</sub>	1.55	0.03
Co <sub>1</sub> -O <sub>5</sub> (P)	1.95	.02	P <sub>3</sub> -C <sub>17</sub>	1.82	.03
Co <sub>1</sub> -O <sub>6</sub> (N)	2.14	.02	P <sub>3</sub> -C <sub>18</sub>	1.81	.03
Co <sub>1</sub> -O <sub>7</sub> (N)	2.23	.02	P <sub>3</sub> -C <sub>19</sub>	1.78	.03
Co <sub>1</sub> -O <sub>8</sub> (N)	2.17	.02	N <sub>12</sub> -O <sub>6</sub>	1.23	.03
Co <sub>1</sub> -O <sub>10</sub> (N)	2.15	.02	N <sub>12</sub> -O <sub>7</sub>	1.25	.03
P <sub>2</sub> -O <sub>4</sub>	1.53	.03	N <sub>12</sub> -O <sub>8</sub>	1.21	.03
P <sub>2</sub> -C <sub>14</sub>	1.81	.03	N <sub>13</sub> -O <sub>9</sub>	1.23	.03
P <sub>2</sub> -C <sub>15</sub>	1.82	.03	N <sub>13</sub> -O <sub>10</sub>	1.22	.03
P <sub>2</sub> -C <sub>16</sub>	1.82	.03	N <sub>13</sub> -O <sub>11</sub>	1.21	.03

TABLE III  
ANGLES IN Co[(CH<sub>3</sub>)<sub>3</sub>PO]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>  
(SD's are approximately 1°)

Interbond angles, deg.			
Bonds to cobalt		Bonds in (CH <sub>3</sub> ) <sub>3</sub> PO, contd.	
O <sub>4</sub> -Co-O <sub>5</sub>	106.1	C <sub>15</sub> -P <sub>2</sub> -C <sub>16</sub>	108.7
O <sub>4</sub> -Co-O <sub>6</sub>	97.0	O <sub>5</sub> -P <sub>3</sub> -C <sub>17</sub>	110.8
O <sub>4</sub> -Co-O <sub>7</sub>	88.9	O <sub>5</sub> -P <sub>3</sub> -C <sub>18</sub>	108.8
O <sub>4</sub> -Co-O <sub>8</sub>	97.5	O <sub>5</sub> -P <sub>3</sub> -C <sub>19</sub>	113.0
O <sub>4</sub> -Co-O <sub>10</sub>	150.2	C <sub>17</sub> -P <sub>3</sub> -C <sub>18</sub>	105.5
O <sub>6</sub> -Co-O <sub>7</sub>	57.2	C <sub>17</sub> -P <sub>3</sub> -C <sub>19</sub>	108.9
O <sub>6</sub> -Co-O <sub>8</sub>	158.1	C <sub>18</sub> -P <sub>3</sub> -C <sub>19</sub>	109.6
O <sub>6</sub> -Co-O <sub>10</sub>	103.6	Bonds in NO <sub>3</sub> -	
O <sub>6</sub> -Co-O <sub>5</sub>	97.1	Co-N <sub>12</sub> -O <sub>6</sub>	177.6
O <sub>7</sub> -Co-O <sub>10</sub>	84.5	Co-N <sub>13</sub> -O <sub>11</sub>	177.8
O <sub>7</sub> -Co-O <sub>5</sub>	152.2	O <sub>7</sub> -N <sub>12</sub> -O <sub>6</sub>	122.9
O <sub>7</sub> -Co-O <sub>8</sub>	106.7	Co-O <sub>6</sub> -N <sub>12</sub>	96.3
O <sub>8</sub> -Co-O <sub>5</sub>	94.6	Co-O <sub>7</sub> -N <sub>12</sub>	91.6
O <sub>8</sub> -Co-O <sub>10</sub>	57.2	Co-O <sub>8</sub> -N <sub>12</sub>	92.7
O <sub>10</sub> -Co-O <sub>5</sub>	92.6	Co-O <sub>10</sub> -N <sub>12</sub>	94.3
Bonds in (CH <sub>3</sub> ) <sub>3</sub> PO		O <sub>6</sub> -N <sub>12</sub> -O <sub>7</sub>	114.7
Co-O <sub>4</sub> -P <sub>2</sub>	139.6	O <sub>6</sub> -N <sub>12</sub> -O <sub>8</sub>	122.2
Co-O <sub>5</sub> -P <sub>2</sub>	133.2	O <sub>8</sub> -N <sub>12</sub> -O <sub>10</sub>	115.3
O <sub>4</sub> -P <sub>2</sub> -C <sub>14</sub>	113.6	O <sub>9</sub> -N <sub>13</sub> -O <sub>11</sub>	122.7
O <sub>4</sub> -P <sub>2</sub> -C <sub>15</sub>	108.1	O <sub>10</sub> -N <sub>13</sub> -O <sub>11</sub>	121.4
O <sub>4</sub> -P <sub>2</sub> -C <sub>16</sub>	112.4	Other angles	
C <sub>14</sub> -P <sub>2</sub> -C <sub>15</sub>	109.7	N <sub>12</sub> -Co-N <sub>13</sub>	118.2
C <sub>14</sub> -P <sub>2</sub> -C <sub>16</sub>	104.2		

Dihedral angle: angle between planes defined by O<sub>4</sub>-Co-O<sub>5</sub> and N<sub>12</sub>-Co-N<sub>13</sub>: 113.0°

1.80 Å. according to Table II. However, the final difference Fourier map suggests that the atom C<sub>19</sub> has been placed a bit too close to P<sub>3</sub>. If it is therefore assumed that the P<sub>3</sub>-C<sub>19</sub> distance (1.78 Å.) given in Table II is probably somewhat too small, we may conclude that all six P-C bond lengths are 1.815 ± 0.02 Å. The average of the two P-O distances is 1.540 ± 0.012. Thus, all six P-C and both P-O bonds are of equal length, within the experimental uncertainties, these lengths and their standard deviations being P-C = 1.82 Å. (SD = 0.03 Å.) and P-O = 1.54 Å. (SD = 0.03 Å.). In addition, all OPC and CPC angles are within 4° or less of the tetrahedral angle and the small deviations, though probably real, have no recognizable significance.

According to a recent X-ray study of (CH<sub>3</sub>)<sub>3</sub>PO,<sup>10</sup> the interatomic distances (uncertainties not known) are P-C = 1.81 Å. and P-O = 1.48 Å. Thus, coordination has not had any discernible effect on the P-C bonds, which is, of course, what one would expect. There is, however, a suggestion of a lengthening of the

P-O bond by about 0.06 Å., but of course the reliability of this number is dubious.

Finally, we note that the two Co-O-P angles are 133 and 140°, each with a probable uncertainty of about 3°.

These results may be compared with those reported by Bränden and Lindquist<sup>11</sup> for SbCl<sub>5</sub>·(CH<sub>3</sub>)<sub>3</sub>PO. Within the rather large uncertainties of their P-C distances (1.84 Å., SD = 0.07; 1.80 Å., SD = 0.08), the P-C distances in the two cases agree. In SbCl<sub>5</sub>·(CH<sub>3</sub>)<sub>3</sub>PO the P-O bond length was found to be 1.61 Å. (SD = 0.02 Å.). This is significantly longer than that in the cobalt complex (1.54 Å., SD = 0.03). The As-O-P angle was found to be 139° (SD = 1.3°) which does not differ significantly from the average (137°) of the two Co-O-P angles found in the cobalt complex.

That the apparent increases in PO bond length from ~1.48 in (CH<sub>3</sub>)<sub>3</sub>PO to ~1.54 in the cobalt complex to ~1.61 in the antimony pentachloride complex are genuine is substantiated by the contravariant trend in the frequencies of those infrared bands which can be assigned as essentially "P-O stretching frequencies." The reported frequencies, in cm.<sup>-1</sup>, are 1158<sup>12</sup> and 1160<sup>2</sup> for (CH<sub>3</sub>)<sub>3</sub>PO, a doublet<sup>2</sup> at 1137 and 1115 for Co-[(CH<sub>3</sub>)<sub>3</sub>PO]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, and 1037<sup>12</sup> for SbCl<sub>5</sub>·(CH<sub>3</sub>)<sub>3</sub>PO; the shifts from the frequency in (CH<sub>3</sub>)<sub>3</sub>PO are thus ~35 and ~120 cm.<sup>-1</sup> for the cobalt and antimony complexes, respectively.

## 2. Structure and Coordination of the Nitrate Ions.—

So far as we know, the results presented here constitute the first fairly accurate report of the geometry and dimensions of the nitrate ion in a coordination complex. Hoard and Stroupe<sup>13</sup> made a very curtailed study leading to a tentative structure for RbUO<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>; in this work the nitrate ions were assumed to be bidentate and some atomic positions were also postulated in accord with packing considerations. More recently, the structure of uranyl nitrate hexahydrate has been studied by two groups whose conclusions are totally inconsistent.<sup>14,15</sup> Vdovenko, *et al.*, concluded that the nitrate ions were not coordinated at all. The work of Fleming and Lynton, on the other hand, indicates the presence of bidentate nitrate ions coordinated, along with two water molecules, to UO<sub>2</sub><sup>2+</sup>. Even if this structure is correct in its general features, the inadequacy of the refinement (which may be remediable) and the disproportionate contribution of the uranium atoms to the structure factors (which cannot be obviated), make it seem unlikely that the positions of the atoms in the nitrate ions are very reliable. Indeed, the rather arresting values reported for several of the interatomic distances seem to bear out this pessimistic prognosis. Fleming and Lynton<sup>16</sup> have also studied UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2(C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>PO. Their conclusion that the nitrate ions are bidentate is probably reliable, but uncertainties in the positions of the light atoms are probably in excess of ±0.1 Å. so that once again no detailed picture of the coordinated nitrate ion emerges.

For the sake of completeness, it should be mentioned that a few crystal structures have been studied in which

(11) C.-I. Bränden and I. Lindquist, *Acta Chem. Scand.*, **15**, 167 (1961); **17**, 353 (1963).

(12) M. Zackrisson and K. I. Alden, *ibid.*, **14**, 994 (1960).

(13) (a) J. L. Hoard and J. D. Stroupe, quoted in "Spectroscopic Properties of Uranium Compounds," G. H. Dieke and A. B. F. Duncan, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 13. (b) This is not to imply that we have any doubt as to the essential correctness of the reported structure. It is also interesting (as pointed out to us by Professor Hoard) that using Zachariasen's treatment [W. H. Zachariasen, *Acta Cryst.*, **7**, 795 (1954)] of the variation in U-O bond distances, one may formulate rubidium uranyl nitrate as a double salt without any well-defined complexing of the uranium by the nitrate ions.

(14) V. M. Vdovenko, *et al.*, *Radiokhim.*, **2**, 24 (1960).

(15) J. E. Fleming and H. Lynton, *Chem. Ind. (London)*, 1416 (1960).

(16) J. E. Fleming and H. Lynton, *ibid.*, 1415 (1960).

(10) H. K. Wang, "Forsvarets forskningsinstitutt, Norge, Intern Rapport IR-K-225," quoted by I. Lindquist, *Nova Acta Reg. Soc. Sci. Upsal.*, *Sev. IV*, **17**, No. 11 (1960); and also in ref. 11.

nitrate ions either form bridges between metal atoms or ions, or can be considered to be part of an essentially ionic array of cations and nitrate ions. Anhydrous copper(II) nitrate contains nitrate ions of both these kinds,<sup>17,18</sup> but for neither have the dimensions of the nitrate ions been reported.  $\text{Cu}(\text{OH})\text{NO}_3$  has also been reported to contain bridging nitrate ions, but no details appear to be available.<sup>19</sup> In silver(I) cyclooctatetraene nitrate, there are bridging nitrate ions, but the degree of covalence to be attributed to the  $\text{Ag}-\text{O}$  bonds is uncertain.<sup>20</sup> Wallwork has carried the determination of the structure of basic beryllium acetate far enough to identify bridging nitrate groups, but further refinement is required to produce accurate structural dimensions. Finally, it may be noted that bidentate nitrate ions have recently been found<sup>21</sup> in  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , but the structural parameters have not been determined very accurately.

In this work, several important structural features of the coordinated nitrate ion have been discovered. Of course no judgment as to whether some or all of these may be considered *general* features of coordinated (bidentate) nitrate ions can be made until more compounds have been studied. In  $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$ , the two nitrate groups are not crystallographically equivalent, but nonetheless they are identical within experimental error in their internal dimensions and their steric relationship to the cobalt ion.

The important structural features of the nitrate coordination are the following five: 1. The nitrate ions are planar within experimental error. Thus the sums of the  $\text{O}-\text{N}-\text{O}$  angles in the two cases are  $360^\circ$  and  $359^\circ$ . 2. The cobalt ion lies in the planes of the nitrate ions. This may be demonstrated in two ways. First, the sums of the internal angles of the quadrilaterals formed by the cobalt ion with the nitrogen atom and the two coordinated oxygen atoms of each nitrate ion are  $359.8^\circ$  and  $359.5^\circ$ . Second, the angles  $\text{Co}-\text{N}_{12}-\text{O}_8$  and  $\text{Co}-\text{N}_{13}-\text{O}_{11}$  are  $177.6^\circ$  and  $177.8^\circ$ , respectively, both of which differ from  $180^\circ$  by less than the estimated un-

certainties. 3. The planar  $\text{Co}-\text{O}-\text{N}-\text{O}$  groups have

essentially  $\text{C}_{2v}$  symmetry. Thus in each such group the  $\text{Co}-\text{O}$  and  $\text{N}-\text{O}$  distances and the  $\text{Co}-\text{O}-\text{N}$  and  $\text{O}-\text{N}-\text{O}$  angles are equal in pairs within experimental error. 4. The  $\text{Co}-\text{O}$  distances are between 2.14 and 2.23 Å. There is, however, an indication in the final difference Fourier map that  $\text{O}_7$  should be a little closer to  $\text{Co}$ . Thus, in computing an average  $\text{Co}-\text{O}$  distance, it might be wise to weight  $\text{Co}-\text{O}_7$  less heavily, say half as much, as the other three. The mean  $\text{Co}-\text{O}$  distance so obtained is 2.16 Å, with a mean deviation of  $\pm 0.02$  Å. 5. Although the  $\text{O}-\text{N}-\text{O}$  angles of the nitrate ion are distorted so that the ones toward the cobalt ion decrease to  $115 \pm 1^\circ$  while the external ones increase correspondingly (to  $122 \pm 1^\circ$ ) the  $\text{N}-\text{O}$  distances remain equal within experimental error at 1.22 Å, with a mean deviation of  $\pm 0.02$  Å. This is equal to the most probable value for

(17) S. C. Wallwork, *Proc. Chem. Soc.*, 311 (1959).

(18) In a private communication, Dr. Wallwork has informed us of some slight modifications in the reported structure of  $\text{Cu}(\text{NO}_3)_2$  and also of the determination of the structure of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{CH}_3\text{NO}_2$ , in which each  $\text{NO}_3^-$  is a bidentate bridging group.

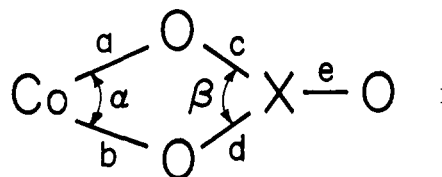
(19) W. Feitknecht, A. Kummer, and J. W. Feitknecht, "Congr. intern. chim. pure et appl., 16<sup>e</sup>, Paris, 1957," Mem. sect. chim. minerale, p. 243 (see *Chem. Abstr.*, **54**, 10620 (1960)).

(20) F. S. Mathews and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 4745 (1958).

(21) G. F. Voloina, I. M. Rumanova, and N. V. Belov, *Krist.*, **6**, 919 (1961); *Chem. Abstr.*, **56**, 11020 (1962); we are indebted to a referee for this reference.

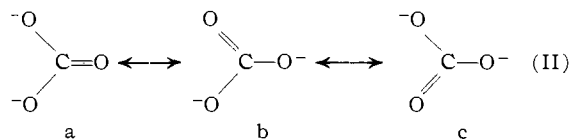
the  $\text{N}-\text{O}$  bond length for the uncoordinated nitrate ion.<sup>22</sup>

The dimensions found here for the  $\text{CoNO}_3$  groupings may be compared with those for the  $\text{CoCO}_3$  grouping found in the  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$  ion,<sup>23</sup> the only other compound in which the structure of a coordinated bidentate ligand of the planar  $\text{XO}_3^{2-}$  type has been accurately determined.<sup>24</sup> There are considerable differences, the most notable ones being those indicated below. The bonds and angles are identified in sketch I.



	In $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$	In $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$
a	1.90 Å.	2.16 Å.
b	$\equiv a$	$\approx a$
c	1.34 Å.	1.22 Å.
d	$\equiv c$	$\approx c$
e	1.24	$\approx c$
$\alpha$	$70.5^\circ$	$57.2^\circ$
$\beta$	$110.4^\circ$	$115.0^\circ$ (av.)

It may be noted that the carbonate ion and in fact the entire  $\text{CoCO}_3$  grouping is planar within the uncertainties in the results. The differences in dimensions *can* be explained invoking only electrostatic forces in each case. Thus, the electrostatic attraction of a tripositive cobalt ion for a dinegative carbonate ion should be very much greater than that of a dipositive cobalt ion for a mononegative nitrate ion. This would result in the carbonate ion being more "squashed against" the metal ion and thus account for the smaller values of the distances a and b and the larger value of the angle  $\alpha$  in the carbonate complex. Furthermore, the greater distortion of the angle  $\beta$  from the value of  $120^\circ$  prevailing in the free carbonate<sup>25</sup> and nitrate<sup>22</sup> ions would also be expected from the stronger electrostatic forces prevailing in the carbonate complex. Finally, the fact that the two types of  $\text{C}-\text{O}$  distances diverge, in opposite directions, very significantly from the distance in the free carbonate ion,<sup>25</sup> 1.29 Å., could also be attributed to electrostatic polarization causing IIa to become much more important than IIb or IIc.



However, we believe that such an extreme electrostatic interpretation, though qualitatively capable of explaining all the facts and difficult to invalidate directly, is unrealistic. It seems likely that there is appreciable covalence in the  $\text{Co}-\text{O}$  bonds in the carbonate complex, but it does seem possible that the  $\text{Co}-\text{O}$  bonds in the nitrate complex may be appreciably ionic. Such distortions of the nitrate ion as do occur can be ex-

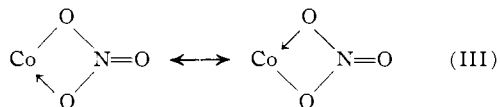
(22) See A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, Oxford, Eng., 1962, p. 627.

(23) G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 586 (1962).

(24) Actually, the final positional parameters of the atoms as reported in ref. 23 were obtained by methods lacking the precision attainable with the best methods now available with high speed computers. In order to make certain that the differences between the nitrate and carbonate situations were real, the structure of  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br}$  was therefore refined using a full-matrix, least squares program, taking the reported<sup>19</sup> atom positions and average thermal parameter as starting parameters. The final refined coordinates did not differ enough from those reported by Barclay and Hoskins to change any interatomic distances by more than 0.01 Å.

(25) R. L. Sass, R. Vidale, and J. Donohue, *Acta Cryst.*, **10**, 567 (1957).

plained without invoking covalence, as shown above, whereas one of the most likely consequences of covalence, as indicated in III, would be to make the distance  $e$  (in I) smaller than the distances  $c$  and  $d$  but this is not observed (as it is in the carbonato complex).



### 3. The Coordination Symmetry of the Cobalt Ion.—

The coordination number of the cobalt ion is six.<sup>26</sup> However, the geometrical arrangement of the six atoms can only be described as irregular. The description "distorted octahedral" would be a misleading euphemism. The space group imposes no symmetry on the molecule and it does not seem to have any quasi or approximate symmetry elements except for a quasi twofold rotation axis colinear with the bisector of the  $O_4$ -Co- $O_5$  angle.

As will be shown elsewhere,<sup>2</sup> the  $\text{Co}(\text{R}_3\text{PO})_2(\text{NO}_3)_2$  complexes have magnetic moments, visible spectra, and infrared spectra which are consistent with a molecular

(26) All intermolecular cobalt to light atom distances are greater than the sum of van der Waals radii.

structure in which the cobalt is tetrahedrally coordinated, and, without the results reported here, the postulation of such a structure would have seemed reasonable. It will be shown<sup>2</sup> that the magnetic and spectroscopic data are also consistent with the structure which has been found. However, the discovery of six-coordinate cobalt, by virtue of nitrate ions being bidentate, in  $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$ , despite the fact that none of the indirect evidence clearly suggested this, raises the important problem of whether similar structural inferences in other cases<sup>27-29</sup> may be similarly in error. X-Ray studies intended to solve this problem are under way.

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(27) F. A. Cotton and T. G. Dunne, *J. Am. Chem. Soc.*, **84**, 2013 (1962).

(28) D. K. Straub, R. S. Drago, and J. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).

(29) J. T. Donoghue and R. S. Drago, *ibid.*, **2**, 572 (1963).