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The Crystal and Molecular Structure of Tetraphenylarsonium Tetranitratocobaltate(II); an Eight-Coordinate Cobalt(II) Complex[1]

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Tetraphenylarsonium tetranitratocobaltate(II), $[As(C_6H_5)_4]_2[Co(NO_3)_4]$, crystallizes in the space group C2/c with four formula units in a monoclinic cell of dimensions $a = 23.47 \pm 0.03$, $b = 11.34 \pm 0.01$, $c = 18.57 \pm 0.02$ A, and $\beta = 107.0 \pm 0.1°$. The structure of this first example of eight-coordinate cobalt was determined from a three-dimensional X-ray study of a single crystal. The anion, which consists of cobalt(II) coordinated by four bidentate nitrate groups, has the idealized point group symmetry of D_{2d}. The eight cobalt–oxygen bonds may be divided into two sets; the four short bonds, 2.03–2.11 A, define an elongated bisphenoid, with a vertical angle of 47°, while the four longer bonds, two 2.36 and two 2.54 A, define a severely flattened, irregular bisphenoid—very nearly a square—with a vertical angle of 81°. It is shown that this structure accounts satisfactorily for the resemblance of the visible spectrum and magnetic susceptibility to those typical for a tetrahedral Co(II) complex. It is also shown that the circumstances attending the attainment of an exceptionally high coordination number in this case lead to a generalization concerning circumstances in which unusually high coordination numbers may be expected elsewhere.

Introduction

Several years ago, compounds containing the tetranitratocobaltate(II) ion, $[Co(NO_3)_4]^{2-}$, were reported from two laboratories.[2,3] On the basis of its magnetic moment and its visible and infrared spectra, this complex ion was assigned a tetrahedral structure. However, as a result of subsequent investigations[4,5] of the compounds $Co(R_3MO)_2(NO_3)_2$, R = CH_3 or C_6H_5, M = P or As, it was suggested that bidentate nitrate ions might also occur in $[Co(NO_3)_4]^{2-}$ with the over-all arrangement of oxygen atoms about the metal ion being such as to produce a ligand field of approximately tetrahedral symmetry, even though the actual disposition of oxygen atoms would not have this shape. This suggestion has been confirmed by a single crystal X-ray structure determination of tetraphenylarsonium tetranitratocobaltate(II), $[As(C_6H_5)_4]_2[Co(NO_3)_4]$, which is reported here.

Experimental Section

The complex was prepared by mixing stoichiometric quantities of $As(C_6H_5)_4Cl$, $AgNO_3$, and $CoCl_2$ in acetonitrile. After separating the insoluble AgCl by decantation, the solution was condensed to an oil by evaporation, and the remaining acetonitrile was extracted into ether. The complex was then recrystallized from a chloroform solution by addition of CCl_4.

Anal. Calcd for $C_{48}H_{40}N_4O_{12}As_2Co$: C, 53.69; H, 3.75; N, 5.21. Found: C, 53.67; H, 3.87; N, 5.28.

A single crystal, in the form of a thin plate of approximate dimensions 0.25 × 0.25 × 0.10 mm and mounted about the b^* axis, was used for collecting the intensity data. Intensities were measured, using Mo $K\alpha$ radiation, on a General Electric XRD-5 goniostat equipped with a scintillation counter. Measurements were made by the moving crystal–moving counter method of Furnas,[6] with the modification that background measurements were made at the lowest and highest values of the scan. Each of the background measurements was for one-half the time of the scan and their sum was subtracted from the total of scan counts to give an observed intensity.

Approximately 2900 independent reflections were measured with 40-sec scans over a range of 2.66° for $2\theta > 15°$, while for $2\theta < 15°$ the range was determined such that only the $K\alpha_1$–$K\alpha_2$ doublet was measured. No corrections were made for absorption—the linear absorption coefficient, μ, being 19 cm^{-1}.

The diffractometer settings for all the reflections in the sphere $2\theta_{Mo} \leq 44°$ as well as the reciprocal Lorentz and polarization factors were computed with Professor D. P. Shoemaker's 709/7090 program GONIO-MIXG2. Electron density summations were carried out using the Fourier program ERFR-2.[7] The structure was refined by the full-matrix least-squares refinement program of Prewitt (SFLSQ-3).[8] The function minimized was $\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2$, where F_o and F_c are the observed and calculated structure factors, respectively, and w is the weighting factor. The reflections were given equal weights until the value of the residual, R, defined as

$$\sum w||F_o| - |F_c||/\sum w|F_o|$$

dropped to 0.12, after which we used a weighting scheme. With $|F_o|$ on the scale of Table II, in which the final F_c and $|F_o|$ are compared, the weighting scheme had the form $F_o \leq 45$, $w = (F_o/52)^2$; $45 < F_o < 100$, $w = 0.55 + F_o/220$; $F_o \geq 100$, $w = 1.0$. Atomic scattering factors were taken as those given by Ibers[9] for Co^{2+}, As^+, N^-, C, O.

Results

Unit Cell and Space Group.—The violet crystals contain four formula units $[As(C_6H_5)_4]_2[Co(NO_3)_4]$ in a monoclinic cell with dimensions $a = 23.47 \pm 0.03$, $b = 11.34 \pm 0.01$, $c = 18.57 \pm 0.02$ A, $\beta = 107.0 \pm 0.1°$, $V = 4726$ A^3. The density calculated from the X-ray data is 1.52 g/cc, in comparison with the value of 1.47 g/cc found by flotation in bromobenzene at 36.5°. Precession photographs established the following conditions for systematic absences: for hkl, $h + k \neq 2n$; for $h0l$, $l \neq 2n$. These conditions are in agree-

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[1] Research supported by a grant from the U. S. Army Research Office.

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

[3] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).

[4] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

[5] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).

[6] T. G. Furnas, Jr., "Single Crystal Orienter Instruction Manual," X-Ray Department, General Electric, 1957.

[7] W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090, ERFR-2,"

[8] C. T. Prewitt, "A Full-Matrix Crystallographic Least-Squares Program for the IBM 709/7090," 1962.

[9] J. A. Ibers in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p 202.

TABLE I

POSITIONAL AND THERMAL PARAMETERS ($\beta_{ij} \times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATION (σ) FOR $[(C_6H_5)_4As]_2[Co(NO_3)_4]$

Atom	x/a(σ)	y/b(σ)	z/c(σ)	$\beta_{11}(\sigma)$[a]	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Co	0.5000	0.834(1)	0.2500	44(1)	92(4)	59(2)	0	19(1)	0
O_1	0.5579(6)	0.954(1)	0.2299(8)	41(4)	212(20)	83(7)	-3(8)	25(4)	13(10)
O_2	0.6419(6)	0.941(1)	0.2060(8)	41(4)	228(20)	90(7)	-16(8)	23(4)	-9(11)
O_3	0.5920(8)	0.792(1)	0.2276(9)	81(6)	120(16)	106(9)	-37(9)	24(6)	-6(11)
O_4	0.5350(6)	0.703(1)	0.3310(7)	51(4)	164(16)	63(6)	-17(7)	10(4)	6(9)
O_5	0.5596(12)	0.863(2)	0.3868(12)	134(11)	168(20)	134(12)	21(14)	38(9)	-52(12)
O_6	0.5808(8)	0.693(2)	0.4457(8)	77(6)	356(24)	61(6)	24(13)	14(4)	41(13)
N_1	0.6006(6)	0.895(2)	0.2210(8)	19(3)	252(28)	53(8)	-15(8)	16(3)	-13(11)
N_2	0.5611(7)	0.756(2)	0.3898(9)	41(4)	208(24)	51(6)	24(9)	25(4)	9(10)
C_{11}[b]	0.8832(6)	0.766(1)	0.0881(8)	21(4)	72(12)	38(6)	-15(8)	-2(3)	4(7)
C_{12}	0.8745(6)	0.810(2)	0.0151(8)	23(4)	100(16)	39(6)	-14(8)	9(4)	-1(6)
C_{13}	0.9051(7)	0.767(1)	-0.0347(9)	23(5)	112(16)	52(8)	-8(8)	7(3)	-8(6)
C_{14}	0.9451(7)	0.674(2)	-0.0140(10)	25(5)	140(24)	66(9)	-28(9)	15(5)	-50(10)
C_{15}	0.9543(8)	0.626(2)	0.0607(11)	33(5)	104(16)	74(8)	-8(8)	23(6)	-17(6)
C_{16}	0.9246(7)	0.666(2)	0.1107(9)	27(5)	112(16)	56(8)	-14(8)	15(4)	8(5)
C_{21}	0.8903(6)	0.837(1)	0.2521(8)	23(4)	92(16)	32(6)	-6(8)	0(5)	-10(6)
C_{22}	0.9260(7)	0.935(2)	0.2673(10)	28(4)	92(16)	60(8)	-23(6)	-4(5)	-6(10)
C_{23}	0.9564(8)	0.958(2)	0.3443(10)	37(5)	116(16)	50(8)	-14(8)	9(5)	-20(8)
C_{24}	0.9543(7)	0.881(2)	0.4013(9)	22(4)	164(24)	46(6)	-22(6)	-4(4)	32(8)
C_{25}	0.9204(8)	0.776(2)	0.3836(9)	33(4)	144(24)	43(7)	-9(8)	-10(3)	-11(10)
C_{26}	0.8900(7)	0.750(1)	0.3056(9)	26(5)	104(16)	48(6)	-1(8)	0(3)	31(15)
C_{31}	0.7884(6)	0.680(1)	0.1529(8)	26(6)	80(16)	33(6)	2(7)	-9(3)	11(14)
C_{32}	0.7461(6)	0.695(2)	0.2001(8)	20(4)	108(16)	43(7)	3(8)	4(3)	14(6)
C_{33}	0.7064(8)	0.606(2)	0.2029(10)	28(5)	144(20)	55(8)	-12(8)	2(5)	15(11)
C_{34}	0.7083(9)	0.550(2)	0.1587(11)	36(5)	124(20)	60(9)	-18(9)	-11(6)	35(10)
C_{35}	0.7489(8)	0.488(1)	0.1144(10)	32(5)	84(16)	60(8)	-16(7)	2(5)	5(10)
C_{36}	0.7875(7)	0.578(1)	0.1123(9)	30(5)	80(16)	53(8)	5(7)	-1(5)	1(9)
C_{41}	0.7936(7)	0.946(1)	0.1126(8)	27(4)	96(12)	28(5)	-5(6)	5(3)	-1(7)
C_{42}	0.8211(7)	1.053(1)	0.1122(10)	27(5)	88(16)	67(9)	-8(7)	-3(5)	21(10)
C_{43}	0.7882(7)	1.155(1)	0.0899(10)	27(4)	76(16)	65(8)	6(7)	3(5)	9(9)
C_{44}	0.7262(8)	1.149(1)	0.0735(9)	43(5)	76(16)	42(7)	-1(8)	6(5)	4(8)
C_{45}	0.7003(6)	1.044(2)	0.0721(9)	24(4)	144(20)	40(7)	9(8)	2(4)	3(10)
C_{46}	0.7304(6)	0.939(1)	0.0947(9)	19(4)	104(16)	41(6)	11(7)	2(4)	-4(8)
As	0.8401(1)	0.806(1)	0.1509(1)	19(1)	64(4)	31(1)	2(1)	4(1)	-1(1)

[a] Due to computer limitations all 302 parameters could not be varied simultaneously, hence the standard deviations for the thermal parameters are estimates based on previous cycles of refinement. [b] C_{ij} corresponds to the jth carbon of the ith phenyl.

ment with either the centric space group C2/c (C_{2h}^6) or the noncentric space group Cc (C_s^4). The existence of the latter was assumed until all the atom positions definitely showed the twofold axis which is necessary for the centric space group C2/c.

Determination of Structure.—After the 2870 observed intensities had been corrected for Lorentz and polarization effects, a three-dimensional Patterson synthesis was computed. Plausible positions for the three crystallographically independent heavy atoms (As, As, Co), all in fourfold general positions, $(0, 0, 0; {}^1/_2, {}^1/_2, 0) + (x, y, z; x, \bar{y}, {}^1/_2 + z)$, were located from the Patterson function by considering the possible metal–metal vectors. Since it was impossible to differentiate between cobalt and arsenic at this point, the first three-dimensional electron density Fourier was calculated with phases based on three gallium atoms. This function readily revealed the approximate locations of several of the phenyl groups, which in turn differentiated between the cobalt and the arsenic atoms. Continued Fourier refinement eventually resulted in the final location of all 67 heavy atoms. It was obvious at this point that the noncentric space group Cc should be replaced by the centric space group C2/c. This increased symmetry allowed the 67 sets of fourfold general positions to be reduced to 33 sets of eightfold general positions and one set of fourfold special positions. The cobalt was thus assigned the special position $(0, 0, 0; {}^1/_2, {}^1/_2, 0) \pm (0, y, {}^1/_4)$ and all the other atoms were given the general positions $(0, 0, 0; {}^1/_2, {}^1/_2, 0) \pm (x, y, z; x, \bar{y}, {}^1/_2 + z)$.

A least-squares refinement with all 34 of the atoms, each having an isotropic temperature factor of the form $\exp -(B_t \sin^2 \theta/\lambda^2)$, and using 2870 reflections, each with unit weight, resulted in a residual, R, of 0.15 after five cycles. At this point it was discovered that in setting up the least-squares program an error had been made in one of the cell constants. Correction of this error and two more cycles of refinement resulted in an R of 0.12. The next cycle of refinement, in which greater weight was given to the intermediate reflections, caused a further decrease of R to 0.11. Refinement was continued with anisotropic temperature factors of the form $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. Although a full-matrix least-squares program was used, computational limitations necessitated the following procedure which is, in effect, a block diagonal approximation. In each of three successive cycles only one class of parameters was varied while the others were held fixed. The classes of parameters were (1) all atom

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS ×19.21 FOR $[(C_6H_5)_4As]_2[Co(NO_3)_4]$

positional parameters, (2) all principal components of the temperature factor tensors, (3) all off-diagonal elements of the temperature factor tensors. These cycles were followed by three more in each of which all parameters for a given third of the atoms were varied, those for the remaining two-thirds being held fixed. It was then apparent that convergence of all parameters to their final values had been reached, the final residual, R, being 0.098. The atom parameters from the last cycle are listed in Table I. The observed and calculated structure factors are compared in Table II. The standard deviations are obtained from the usual least-squares formula $\sigma^2_{(j)} = a_{jj}(\Sigma w\Delta^2)(m - n)$, where a_{jj} is the appropriate element of the matrix inverse to the normal equation matrix.

The use of anisotropic temperature parameters is probably of marginal value under the circumstances, but they do appear to be reasonable and thus their inclusion probably leads to some slight increase in the accuracy of the positional parameters. The nitrate ions show an appreciable anisotropy in their thermal motion, as indicated by the root-mean square amplitudes given in Table III. As one might expect, the greatest oxygen amplitudes are those parallel and perpendicular to the planes of the nitrate ions.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATIONS (IN A)

Atom	Max	Int	Min
Co	0.34	0.24	0.30
O_1	0.39	0.36	0.30
O_2	0.40	0.27	0.30
O_3	0.48	0.41	0.25
O_4	0.39	0.31	0.30
O_5	0.59	0.49	0.29
O_6	0.50	0.45	0.29
N_1	0.41	0.29	0.20
N_2	0.40	0.31	0.24

Discussion

Coordination of Cobalt(II).—A perspective view of the $[Co(NO_3)_4]^{2-}$ ion is given in Figure 1. Bond angles and bond distances are given in Table IV. Although crystallographically the symmetry of the anion is only C_2, the structure comes very close to having D_{2d} symmetry.

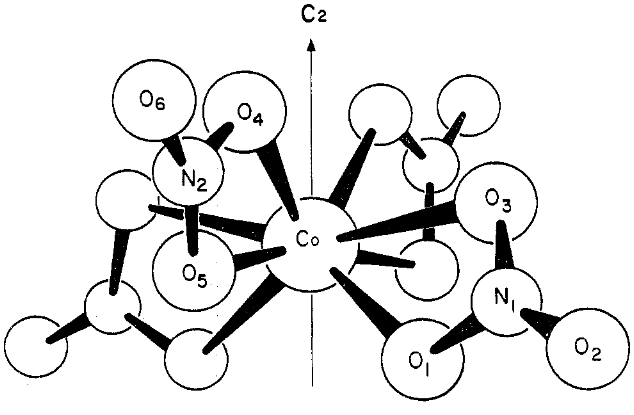

Figure 1.—A perspective view of the $[Co(NO_3)_4]^{2-}$ ion. Atoms are numbered as in Table I.

The eight bonded oxygen atoms may be divided into two sets, the four atoms of each set being related by the idealized $\bar{4}$ axis which is coincident with the twofold axis shown in Figure 1. The eight oxygen atoms may be visualized as occupying the corners of the D_{2d} dodecahedron shown in Figure 2. The A positions correspond to the short Co–O bonds and the B positions to the longer ones. The ratio of the mean Co–O_A to mean Co–O_B bond lengths is 0.83 compared to 0.96 for the $[CrO_8]^{3-}$ complex[10] and 1.10 for the bis(diarsine)

TABLE IV

INTERATOMIC DISTANCES AND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS

Interatomic distances, A		Angles, deg	
Co–O_1	2.03 (2)	O_1–Co–O_3	54 (1)
Co–O_4	2.11 (1)	O_4–Co–O_5	52 (1)
Co–O_3	2.36 (2)	O_1–Co–C_2[a]	48 (1)
Co–O_5	2.54 (2)	O_4–Co–C_2[a]	45 (1)
O_1–N_1	1.25 (2)	O_1–N_1–O_3	110 (2)
O_2–N_1	1.20 (2)	O_3–N_1–O_2	128 (2)
O_3–N_1	1.20 (3)	O_1–N_1–O_2	122 (2)
O_4–N_2	1.25 (2)	O_4–N_2–O_5	117 (2)
O_5–N_2	1.21 (3)	O_5–N_2–O_6	128 (2)
O_6–N_2	1.24 (3)	O_4–N_2–O_6	115 (2)
As–C_{11}[b]	1.81 (1)	C_{11}–As–C_{21}	112 (1)
As–C_{21}	1.94 (1)	C_{11}–As–C_{31}	108 (1)
As–C_{31}	1.89 (2)	C_{11}–As–C_{41}	109 (1)
As–C_{41}	1.94 (1)	C_{21}–As–C_{31}	109 (1)
C_{11}–C_{12}	1.40 (2)	C_{21}–As–C_{41}	109 (1)
C_{12}–C_{13}	1.41 (2)	C_{31}–As–C_{41}	110 (1)
C_{13}–C_{14}	1.39 (2)	C_{11}–C_{12}–C_{13}	123 (2)
C_{14}–C_{15}	1.45 (3)	C_{12}–C_{13}–C_{14}	121 (2)
C_{15}–C_{16}	1.39 (3)	C_{13}–C_{14}–C_{15}	117 (2)
C_{16}–C_{11}	1.47 (2)	C_{14}–C_{15}–C_{16}	124 (2)
C_{21}–C_{22}	1.37 (2)	C_{15}–C_{16}–C_{11}	119 (2)
C_{22}–C_{23}	1.42 (3)	C_{16}–C_{11}–C_{12}	117 (1)
C_{23}–C_{24}	1.39 (3)	C_{21}–C_{22}–C_{23}	117 (2)
C_{24}–C_{25}	1.41 (3)	C_{22}–C_{23}–C_{24}	122 (2)
C_{25}–C_{26}	1.45 (2)	C_{23}–C_{24}–C_{25}	120 (2)
C_{26}–C_{21}	1.41 (2)	C_{24}–C_{25}–C_{26}	120 (2)
C_{31}–C_{32}	1.52 (2)	C_{25}–C_{26}–C_{21}	117 (1)
C_{32}–C_{33}	1.39 (2)	C_{26}–C_{21}–C_{22}	123 (1)
C_{33}–C_{34}	1.45 (3)	C_{31}–C_{32}–C_{33}	120 (1)
C_{34}–C_{35}	1.43 (3)	C_{32}–C_{33}–C_{34}	116 (2)
C_{35}–C_{36}	1.37 (2)	C_{33}–C_{34}–C_{35}	123 (2)
C_{36}–C_{31}	1.38 (2)	C_{34}–C_{35}–C_{36}	120 (2)
C_{41}–C_{42}	1.37 (2)	C_{35}–C_{36}–C_{31}	120 (2)
C_{42}–C_{43}	1.39 (2)	C_{36}–C_{31}–C_{32}	121 (1)
C_{43}–C_{44}	1.40 (3)	C_{41}–C_{42}–C_{43}	121 (2)
C_{44}–C_{45}	1.33 (2)	C_{42}–C_{43}–C_{44}	119 (2)
C_{45}–C_{46}	1.39 (2)	C_{43}–C_{44}–C_{45}	119 (2)
C_{46}–C_{41}	1.43 (2)	C_{44}–C_{45}–C_{46}	125 (1)
		C_{45}–C_{46}–C_{41}	115 (1)
		C_{46}–C_{41}–C_{42}	121 (1)

[a] C_2 is the twofold axis shown in Figure 1. [b] C_{ij} corresponds to the jth carbon of the ith phenyl.

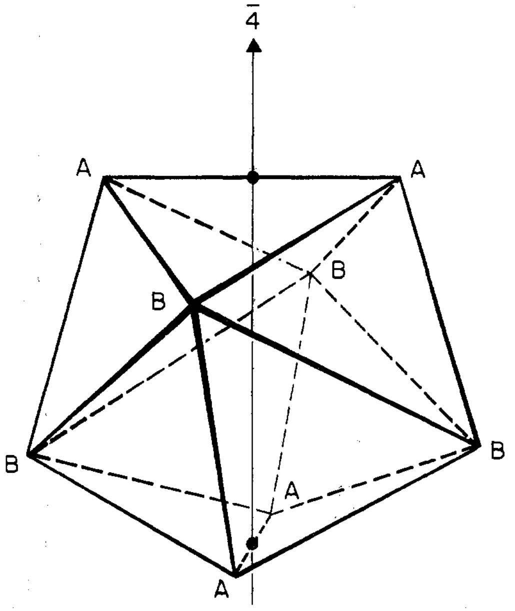

Figure 2.—D_{2d} dodecahedron ($\bar{4}2m$).

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[10] J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

adducts of $TiCl_4$ and VCl_4.[11] These varying ratios are most probably due to steric factors and/or crystal packing considerations.

The Nitrate Groups.—The effect of coordination upon the structures of the nitrate ions is slight. Both are planar within the limits of error, the sum of the three ONO angles being 360° in each case. The mean of the N–O distances involving the oxygen atoms which form the shorter bonds to cobalt (1.25 ± 0.02A) is greater than the mean of the four N–O distances involving oxygen atoms which form long bonds to cobalt or are not bonded to cobalt (1.21 ± 0.03A), but the difference is of doubtful significance in a statistical sense, since Δ/σ is only 0.8. In several cases[12] where nitrate groups are attached by covalent bonds through one oxygen atom, the N–O distance involving the bonded oxygen atom has been about 1.41 A while the mean of the other two N–O distances has been about 1.20 A. The mean of all six N–O distances in the present case is 1.22 ± 0.02 A, which agrees well with the distance[13] in ionic nitrates, 1.22 ± 0.01 A, and no single N–O distance differs from the mean by a significant amount. In fact, the only distortion of the nitrate ions which appears to be significant in a statistical sense (*i.e.*, physically real) and in a chemical sense is the fact that the ONO angles subtended by the oxygen atoms which are coordinated to the cobalt atom are 110 and 117°, while the others are 115, 122, 128, and 128°. A similar distortion was previously found[4] in $Co[(CH_3)_3PO]_2(NO_3)_2$ and can probably be attributed primarily to electrostatic perturbation of the nitrate ion by the Co(II) ion. In summary, the shape and dimensions of the nitrate ions are not inconsistent with the presumption that the bonding is mainly ionic, although they do not actually prove such a description of the bonding.

The Tetraphenylarsonium Ions.—The four crystallographically independent phenyl groups are hexagonal within experimental error. The mean C–C distance is 1.41 ± 0.04 A. The four As–C distances have a mean value (with standard deviation of the mean) of 1.90 ± 0.05 A. This implies a covalent radius for the quaternary arsenic atom of 1.15 ± 0.05 A, when a single bond radius of 0.75 A is used for sp^2 hybridized carbon,[14] in agreement with the accepted value of 1.18 A.[15] The distances of the various carbon atoms from their least-squares planes are shown in Table V.

Table V

Best Plane Parameters and Distances of Atoms from the Mean Plane

Plane no.	Direction cosines[a]	Atom	Distance, A
(1)	(L) 0.1868	Co	0.000
	(M) 0.0638	O_1	0.010
	(N) 0.9803	O_2	−0.023
		O_3	0.005
		N_1	0.009
(2)	(L) −0.9673	Co	0.000
	(M) 0.0095	O_4	−0.019
	(N) 0.2535	O_5	−0.015
		O_6	0.060
		N_2	−0.031
(3)	(L) 0.6640	C_{11}	0.014
	(M) 0.6502	C_{12}	−0.009
	(N) 0.3693	C_{13}	0.002
		C_{14}	−0.002
		C_{15}	0.008
		C_{16}	−0.014
(4)	(L) −0.8690	C_{21}	0.053
	(M) 0.4792	C_{22}	−0.040
	(N) 0.1234	C_{23}	0.001
		C_{24}	0.017
		C_{25}	0.018
		C_{26}	−0.048
(5)	(L) 0.4716	C_{31}	0.003
	(M) −0.4034	C_{32}	−0.002
	(N) 0.7841	C_{33}	0.002
		C_{34}	−0.001
		C_{35}	0.001
		C_{36}	−0.002
(6)	(L) −0.2488	C_{41}	−0.010
	(M) 0.1581	C_{42}	0.013
	(N) 0.9556	C_{43}	−0.020
		C_{44}	0.030
		C_{45}	−0.031
		C_{46}	0.013

[a] Direction cosines are given relative to the orthogonalized crystal axes (*a*, *b*, *ab*).

Electronic Structure of the Cobalt Ion.—When the preparation of the $[Co(NO_3)_4]^{2-}$ ion was first reported,[2,3] it was inferred from the appearance of the visible spectrum and the magnetic moment[16] that a tetrahedrally coordinated Co(II) ion was present. While this investigation has shown that that is not so, the actual structure of the coordination shell is fundamentally though not superficially related to the previously assumed tetrahedral structure.

As noted, oxygen atoms lie roughly at the vertices of a dodecahedron with D_{2d} symmetry. Since D_{2d} is a subgroup to T_d, the *symmetry* of the actual coordination must evidently be a distorted form of tetrahedral symmetry, whatever the difference in the physical *structure* may be.

However, a more detailed *structural* relationship also exists. This may be seen by noting that the dodecahedron consists of two interpenetrating bisphenoids (a tetrahedron distorted to D_{2d} symmetry), whose relative orientations are such that they have a common S_4 axis and the same pair of vertical symmetry planes. In fact, each of the four A–B lines (Figure 2) lying in and thus defining these symmetry planes contains one vertex of a tetrahedron.

In the present case, this interpretation may be considered in a semiquantitative sense. If we assume, very crudely, that the contribution made by each of the

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(16) The magnetic susceptibility has now been measured over a temperature range of 77–300°K (J. G. Bergman, Ph.D. Thesis, Massachusetts Institute of Technology, 1965). The molar susceptibilities, corrected for diamagnetism (555×10^{-6} cgs unit) and temperature-independent paramagnetism (451×10^{-6} cgs unit) measured at 77, 195, 265, and 300°K, fit the Curie–Weiss law ($\mu = 2.84(\chi_M^{cor} xT)^{1/2}$ with $\mu = 4.60 \pm 0.05$ BM and $\theta = 12 \pm 1°$).

coordinated oxygen atoms to the ligand field potential is inversely proportional to its distance from the cobalt ion, we may select "centers of gravity" of the electrostatic potential on each of the four A–B lines (Figure 2). It is found that these four points define a bisphenoid with an average vertical angle of 107°, that is, very nearly a regular tetrahedron. In this way, the "tetrahedral mimicry" in the spectral and magnetic properties is very neatly explained. This viewpoint is qualitatively similar to that previously proposed[5,6] for the $Co(OMR_3)_2(NO_3)_2$ complexes.

Discussion of the High Coordination Number.—There does not appear to be any other case in which Co(II) has a coordination number of eight, and it is therefore of interest to consider whether there are any special features of the present situation which are responsible for its occurrence here.

We believe that the most important factor is that, because of the internal structure of the nitrate ion, four of the O · · · O distances are very short (~2.1 A). It is therefore possible to fit such a large number of oxygen atoms around the cobalt ion, keeping the other O · · · O contacts at or near the normal sum of the nonbonded radii while simultaneously maintaining close Co–O distances. We may add to this observation the one made earlier, namely, that the mean positions of the close pairs of ligand atoms lie approximately at the vertices of a tetrahedron, which is one of the common coordination polyhedra for the metal ion concerned.

There would seem to be no reason why such a combination of structural features could not occur with other metal ions, and, in fact, several other examples may be cited.

With the nitrate ion itself, there is the nearly isostructural $Ti(NO_3)_4$ molecule, recently described by Addison, *et al.*[17] Even more interesting, because it represents the same principles operating in the framework of a different and higher set of coordination numbers, is the structure of $Mg_3Ce_2(NO_3)_{12} \cdot 24H_2O$,[18] in which each Ce(IV) ion is surrounded by six bidentate nitrate ions. The oxygen atoms lie at the vertices of a distorted icosahedron, and the actual coordination number of the ceric ion is 12, a rather high value for an ion of radius ~0.9 A. In this case, the midpoints of the intranitrate O · · · O lines lie approximately at the vertices of an octahedron, a common coordination polyhedron.

The structures of several peroxo complexes might also be mentioned, most notably that of the $[Cr(O_2)_4]^{3-}$ ion,[19] which has a D_{2d} structure very much like those of $[Co(NO_3)_4]^{2-}$ and $Ti(NO_3)_4$. Again, the fact that some interligand distances are constrained to be very short (~1.4 A) permits a high coordination number (the Cr(V) ion must be quite small for a coordination number of eight) and the mean positions of the close pairs of ligand atoms approximately define a common coordination polyhedron (a tetrahedron) corresponding to a more normal coordination number for the ion in question.

It seems reasonable to expect that the principles manifested in the $[Co(NO_3)_4]^{2-}$ structure and the others just cited should also be exemplified in other compounds and that they might serve to design some new complexes with high coordination numbers.

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The Reaction of Molten Magnesium Cyclopentadienide with Fluorides and Other Metal Halides

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Molten magnesium cyclopentadienide in the absence of solvent reacts with a large number of metal halides, and in particular fluorides, to give cyclopentadienyl metal compounds, frequently in good yield. The reaction is particularly suited to the preparation of the cyclopentadienyls of thorium, uranium, scandium, and the rare earths from their fluorides, which are readily accessible and relatively stable to moisture.

Introduction

Magnesium cyclopentadienide ($MgCp_2$) is a readily sublimable white solid which melts at 177° to a clear, mobile liquid boiling at 222°.[1] Although it is thermodynamically somewhat more stable than ferrocene, the high free energies of formation of the magnesium

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