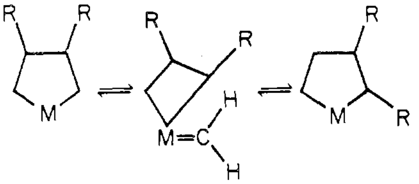
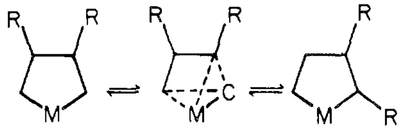
tetrahedrally distorted; the angles around P(1) range from 99.9 (9) to 118.3 (6)° and those around P(2) from 99.4 (8) to 124.0 (6)°. The deviation from planarity of the phenyl rings is given in Table IV.

One of the most interesting features of the structure is the puckering of the tetrahydroplatinole ring. One might expect to find C(40) and C(37) placed symmetrically above and below a plane through the Pt, C(38), and C(39); however, C(37) is 0.76 (2) Å above this plane while C(40) is only 0.40 (2) Å below it. When only the carbon atoms of the ring are considered, C(40) is significantly [1.04 (2) Å] below the plane formed by the other three atoms. A close examination of the packing of molecular units (Figure 2) indicates that puckering does not result from packing requirements. The geometry of the tetrahydroplatinole ring provides an indication of the mechanism whereby rearrangement of metallocycle intermediates in the olefin metathesis reactions occurs. Two analogous mechanisms which are reasonable and which fit the requirements of the observed geometry are



(4)



(5)

In metals with readily accessible, higher coordination numbers,[27,28] the above mechanisms could provide a mode for facile rearrangement. The preparation of similar complexes and characteristic reactions of both these and Pt[P(C_6H_5)$_3$]$_2$-C_4H_8 will be reported.

Registry No. *cis*-Bis(triphenylphosphine)dichloroplatinum(II), 15604-36-1; 1,4-dilithiobutane, 2123-72-0; [bis(triphenylphosphine)tetrahydroplatinole], 40548-16-1.

Acknowledgments. We thank D. Carr and T. K. Brunck for the preparation of single crystals of the complex. Financial support provided to R. H. G. by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and an NSF Traineeship to C. G. B. are acknowledged gratefully.

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(28) E. A. Zurch, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, 92, 528 (1970).

Contribution No. 4609 from the Arthur Amos Noyes Laboratory of
Chemical Physics, California Institute of Technology, Pasadena, California 91109

Crystal Structure of μ-Peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)] Perchlorate

JOHN R. FRITCH, GARY G. CHRISTOPH, and WILLIAM P. SCHAEFER*

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The crystal and molecular structure of μ-peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)] perchlorate, [(en)(dien)Co(O_2)Co(en)(dien)](ClO_4)$_4$, $Co_2C_{12}N_{10}O_{18}H_{42}Cl_4$, has been determined by three-dimensional X-ray crystallographic analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell constants a = 9.062 (2) Å, b = 15.981 (8) Å, c = 11.153 (4) Å, and β = 92.53 (3)°. The calculated density, 1.790 (2) g cm^{-3}, with Z = 2, agrees well with the 1.80 (2) g cm^{-3} measured by flotation. Intensity data were collected with a Datex-automated General Electric diffractometer using iron-filtered cobalt Kα radiation. The structure was solved by the heavy-atom Patterson method and refined by conventional Fourier and least-squares techniques to a final R index of 0.053 for 2130 independent reflections. The O_2 bridge is a peroxide group with the O-O distance 1.488 (6) Å. The Co-O-O-Co linkage is planar, the halves of the cation being related by a center of symmetry centered on the O-O bond. Comparison with other peroxide-bridged compounds suggests that the planarity of the Co-O-O-Co linkage is a consequence of Coulomb repulsion between the two highly charged cobalt centers. The Co-O distance is 1.896 (4) Å and the Co-O-O angle is 110.0 (3)°. The coordination about the cobalt atom is slightly distorted octahedral. The trans effect of the peroxide oxygen atom is apparent in the significant lengthening of the trans Co-N bond relative to the cis Co-N bonds. The terminal nitrogen atoms of the dien ligand are trans to one another.

Introduction

There has been a renewed interest lately in the chemistry and structure of peroxo-bridged dicobalt complexes, although Werner first elucidated their constitution at the turn of the century.[1] In particular, these compounds are of interest because of the ability of some of them to decompose quantitatively to their starting materials, a cobalt(II) species and molecular oxygen. In order to understand the structural basis of the ability of certain of these complexes to function as reversible oxygen carriers it is necessary to have structural data for some of the irreversible oxygen adducts for comparison. As part of our studies on reversible oxygen carriers we have therefore determined the structure of the irreversibly formed complex μ-peroxo-bis[(ethylenediamine)(diethylenetriamine)Co(III)] perchlorate.

In addition to accumulating basic structural information on these compounds we also were intrigued by several particular features of this complex. First, as no structures of μ-peroxo-

(1) A. Werner, *Justus Liebigs Ann. Chem.*, 375, 1 (1910); A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 13, 1 (1970), and references therein.

polyaminedicobalt complexes have yet been reported, we were interested in what steric and electronic effects the polyamine ligands would have on the geometry of the peroxide linkage. Second, the perchlorate salt is very stable both to heat and on exposure to the atmosphere whereas the analogous decaammine nitrate and sulfate salts decompose within 1 or 2 days unless they are kept perfectly dry; we hoped to find a structural basis for this stability. Third, because of conflicting conclusions regarding the relative stability of the several structural isomers of metal-dien complexes,[2,3] we were interested in the configuration of the ligands about the cobalt atom and what import this might hold for the stability of the complex as a whole.

Experimental Section

R. C. Beaumont, Alma College, Alma, Mich., prepared several isomers of the title compound and kindly furnished us with the crystals used in this study. The space group was determined from zero- and upper-level Weissenberg photographs to be $P2_1/n$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$). The equivalent positions in this space group, an unconventional setting of $P2_1/c$, are $\pm(x, y, z;\ ^1/_2 - x,\ ^1/_2 + y,\ ^1/_2 - z)$. The unit-cell parameters were determined by a least-squares fit of diffractometer-measured 2θ values for 12 high-angle reflections. Iron-filtered cobalt Kα radiation was used both for the cell constant measurements and for the data collection. The density of the thick, brown, needlelike crystals was measured by flotation in CCl_4-$CHBr_3$ solution. The pertinent crystal data appear in Table I.

The intensity data were collected on a locally modified, Datex-automated GE XRD-5 goniostat equipped with a NaI(Tl) scintillation counter. The reflections were measured using the θ-2θ scan technique, with a scan rate of 1°/min (a small number of reflections were measured with a 2°/min scan rate) and scan width which varied from 2.0° at $2\theta = 20.0°$ to 3.5° at $2\theta = 152°$. Thirty-second background counts were taken at each end of the scans. Two crystals, ground into spheres of nearly identical diameters and mounted in different random orientations, were used in the data collection. Three reflections were remeasured periodically during the data collection as a check of crystal condition and orientation. The check reflections decreased in intensity by about 10% over the course of the data collection for each of the crystals. A total of 2743 reflections with $2\theta \leqslant 152°$ were measured; of these, 2130 were crystallographically independent and only 39 had F's less than $\sigma(F)$. The disagreement between multiply measured and equivalent reflections was generally less than 1.5% (on F).

Linear corrections for the crystal decay were calculated by a least-squares fit to the check reflection measurements. The variances of individual measurements were derived using the formula

$$\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pS)^2$$

where S, B_1, and B_2 are the scan and background counts, T_S and T_B are the scan and individual background counting times, and p is a factor here taken as 0.02, in the term representing that part of the error which is expected to be proportional to the diffracted intensity. In this term we use the scan counts rather than the more commonly used net intensity[4] as the latter neglects the effect of machine-dependent fluctuations on the backgrounds. The numerical effect of this change is in any case very small.

The two data sets were scaled together and spherical absorption corrections and Lp corrections were applied to the merged set. Because the diameters of the two crystals were equivalent within their variations from true spheres, no significant systematic error is introduced by correcting the merged data for absorption. The maximum absorption correction to a value of F_o was 16% greater than the minimum correction.

Solution and Refinement of the Structure

Table I. Crystal Data for the Formula $Co_2Cl_4C_{12}N_{10}O_{18}H_{42}$

Mol wt 874.2
$a = 9.062$ (2) Å
$b = 15.981$ (8) Å
$c = 11.153$ (4) Å
$\beta = 92.53$ (3)°
$Z = 2$
$V = 1614$ (2) Å^3

$\rho_o = 1.80$ (1) g/cm^3
$\rho_c = 1.790$ (2) g/cm^3
λ(Co Kα) 1.7902 Å
μ(Co Kα) 77.7 cm^{-1}
Crystal 1 diameter 0.027 (1) cm
Crystal 2 diameter 0.026 (1) cm
$\mu R_{av} = 1.01$

The density requires only a half molecule in the asymmetric unit. Inspection of the Patterson map gave the locations of the cobalt atom and its ligand nitrogen and oxygen atoms. Successive structure factor and Fourier calculations[5] revealed first the two independent perchlorate groups and then the remaining heavy atoms in the structure. Several cycles of least-squares refinement, with anisotropic thermal parameters for all the nonhydrogen atoms, resulted in an unweighted R factor of 0.115.[6] At this point the hydrogen atoms were located in difference maps (peaks of 0.5–0.8 e/Å^3). As the thermal motions of the perchlorate oxygen atoms were quite large, we attempted to refine several disordered models. These attempts were unsuccessful; the disordered half oxygen atoms overlapped considerably and the model either refused to refine properly or gave chemically unreasonable results. The final refinement was accordingly carried out in the normal manner. Because of computer memory limitations, the final four least-squares cycles had the parameters separated into two large matrices, with the cross terms between the two blocks neglected. The first block contained the anisotropic thermal parameters, the hydrogen isotropic thermal parameters, the scale factor, and a secondary extinction parameter,[7] while the second block contained all the positional parameters. The final values of the weighted and unweighted R factors and the GOF[6] were 0.13, 0.053, and 4.82. In the last least-squares cycle the shifts in the heavy-atom parameters were all less than $^1/_2$ esd, while those of the hydrogen parameters were all less than 1 esd. Table II lists the final values of the refined parameters and their errors estimated from the diagonal elements of the inverse matrix from the final least-squares cycle. The observed and calculated structure factors are given in a separate table.[8] The final difference Fourier had a number of features of 0.4–0.8 e/Å^3 all associated with the perchlorate oxygen atoms. The only other feature greater than the ±0.3-e/Å^3 general background level was a 0.5-e/Å^3 peak at the cobalt position. The peaks near the oxygen atoms and the high value of the goodness of fit reflect the fact that our ordered model cannot represent the motion of the perchlorate groups well.

Description and Discussion of the Structure

Figure 1 presents the bond distances and angles in the cation. Those for the perchlorate groups appear in Table III. The errors in the cation bond lengths are about 0.004 Å for those involving cobalt, 0.006 Å for those involving the other nonhydrogen atoms, and 0.05 Å for bonds involving hydrogen. The respective errors in the angles are 0.3, 0.4, and 3.0°.

The cation consists of two distorted octahedral cobalt(III) centers linked by a planar peroxide bridge, with a center of symmetry situated at the midpoint of the O–O bond. The O-O distance, 1.49 Å, and the 4+ charge on the binuclear cation require that the O_2 bridge be called a peroxide group. We think that simple Coulomb repulsion between the two

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(2) P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960); F. R. Keene and G. H. Searle, *Inorg. Chem.* **11**, 148 (1972).

(3) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, **19**, 2045 (1966).

(4) W. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957); P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(5) All calculations were performed under the CRYM crystallographic computing system on an IBM 370/165. The scattering factors of Co, Cl, O, N, and C as well as the real part of the anomalous correction for Co and Cl were taken from the "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1952. The scattering factor for hydrogen is that given by R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(6) $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = (\Sigma w|F_o^2 - F_c^2|^2/\Sigma w F_o^4)^{1/2}$, and $w = 1/(\sigma F_o^2)^2$. The quantity minimized in the least-squares was $\Sigma w(F_o^2 - F_c^2)^2$. The "goodness of fit," GOF, is defined as $[\Sigma w(F_o^2 - F_c^2)^2/(N_O - N_P)]^{1/2}$.

(7) The expression for the secondary extinction correction is that given by A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967), eq 3. The maximum percentage change in F_{measd}^2 was 29.1% (110).

(8) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2170.

Table II. Final Values of Positional and Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	301 (1)	929 (0)	3501 (1)	60 (1)	18 (0)	44 (1)	−2 (1)	−1 (1)	8 (1)
O(1)	−561 (3)	147 (2)	4540 (2)	61 (3)	26 (1)	47 (2)	−14 (4)	−21 (4)	21 (3)
N(1)	1319 (4)	1664 (3)	2346 (4)	82 (5)	24 (2)	74 (3)	5 (5)	6 (7)	36 (4)
N(2)	2011 (4)	201 (2)	3371 (4)	79 (5)	26 (2)	69 (4)	11 (5)	16 (7)	28 (4)
N(3)	−948 (4)	400 (3)	2217 (3)	101 (5)	24 (2)	46 (3)	−1 (5)	6 (6)	−2 (4)
N(4)	−1366 (4)	1679 (2)	3649 (3)	80 (5)	22 (1)	48 (3)	−5 (4)	−3 (6)	4 (4)
N(5)	1145 (4)	1511 (2)	4898 (3)	84 (5)	24 (2)	65 (3)	−18 (5)	−39 (6)	9 (4)
C(1)	2583 (7)	1194 (4)	1877 (6)	118 (8)	52 (3)	121 (6)	39 (8)	115 (12)	86 (8)
C(2)	3239 (6)	664 (4)	2853 (6)	92 (6)	48 (3)	144 (7)	40 (8)	97 (11)	77 (8)
C(3)	−2351 (5)	876 (3)	2023 (4)	90 (6)	34 (2)	68 (4)	−13 (6)	−41 (8)	3 (5)
C(4)	−2720 (5)	1252 (3)	3201 (4)	74 (6)	32 (2)	80 (4)	2 (6)	−13 (8)	9 (5)
C(5)	−1342 (6)	2019 (4)	4885 (4)	134 (7)	36 (2)	59 (4)	26 (7)	10 (8)	−23 (5)
C(6)	225 (6)	2250 (3)	5181 (5)	160 (8)	26 (2)	69 (4)	−3 (7)	−37 (9)	−14 (5)
Cl(1)	4447 (1)	1302 (1)	6830 (1)	107 (2)	25 (5)	111 (1)	−5 (1)	−69 (2)	−2 (1)
O(2)	5920 (6)	1386 (4)	6796 (9)	113 (7)	51 (3)	548 (18)	21 (7)	58 (18)	53 (12)
O(3)	3724 (4)	2094 (2)	6618 (4)	147 (6)	26 (1)	131 (4)	30 (5)	−98 (8)	−16 (4)
O(4)	3874 (9)	695 (3)	6111 (8)	487 (16)	41 (2)	370 (12)	107 (11)	−619 (23)	−130 (10)
O(5)	4172 (12)	1036 (6)	7987 (8)	630 (26)	110 (6)	242 (10)	161 (19)	314 (28)	142 (13)
Cl(2)	4371 (1)	3428 (1)	3861 (1)	132 (2)	37 (1)	61 (1)	−34 (2)	−21 (2)	14 (1)
O(6)	4768 (7)	3599 (3)	2688 (4)	372 (12)	65 (3)	78 (4)	−58 (10)	112 (11)	−14 (6)
O(7)	5527 (7)	3293 (6)	4652 (6)	216 (9)	179 (7)	198 (8)	−124 (14)	−214 (14)	177 (12)
O(8)	3369 (7)	2782 (4)	3898 (6)	351 (12)	118 (5)	215 (8)	−324 (13)	−278 (16)	177 (10)
O(9)	3694 (10)	4166 (4)	4220 (6)	570 (21)	80 (4)	226 (9)	101 (15)	400 (23)	16 (10)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(1)	170 (5)	207 (4)	259 (4)	4 (1)	H(12)	187 (5)	452 (3)	675 (4)	3 (1)
H(2)	68 (6)	182 (4)	172 (4)	4 (1)	H(13)	154 (4)	332 (3)	810 (4)	2 (1)
H(3)	313 (7)	151 (4)	166 (6)	6 (2)	H(14)	207 (5)	421 (3)	869 (4)	3 (1)
H(4)	212 (7)	76 (4)	128 (6)	8 (2)	H(15)	367 (5)	295 (3)	822 (4)	2 (1)
H(5)	373 (6)	29 (4)	255 (5)	5 (1)	H(16)	293 (6)	252 (3)	996 (4)	4 (1)
H(6)	394 (8)	101 (4)	373 (6)	7 (2)	H(17)	342 (6)	340 (4)	46 (5)	4 (1)
H(7)	334 (6)	475 (4)	206 (4)	5 (1)	H(18)	46 (5)	273 (3)	466 (4)	4 (1)
H(8)	227 (5)	5 (3)	401 (4)	3 (1)	H(19)	43 (6)	243 (4)	595 (5)	5 (1)
H(9)	114 (5)	8 (3)	750 (4)	3 (1)	H(20)	207 (6)	167 (3)	487 (4)	3 (1)
H(10)	436 (5)	465 (3)	656 (4)	3 (1)	H(21)	128 (5)	110 (3)	547 (4)	4 (1)
H(11)	287 (6)	368 (4)	643 (5)	6 (1)					

[a] The positional and anisotropic thermal parameters have been multiplied by 10^4; the hydrogen positional parameters, by 10^3. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \ldots + \beta_{23}kl)]$. The secondary extinction parameter is $g = 0.0000037$ (6). (See ref 7.)

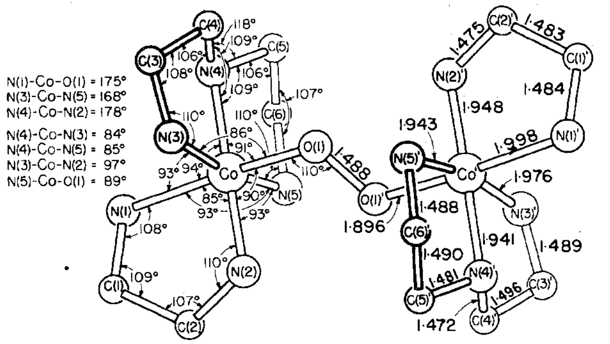

Figure 1. Bond distances and angles in the cation.

charged cobalt centers causes the peroxide bridge to be planar. Table IV summarizes the results of a number of structural studies of peroxide-bridged compounds. In neutral complexes or molecules the peroxide dihedral angles are substantially different from 180°, consistent with the observed[9] and calculated[10] relative conformational energy maximum at that angle for neutral H_2O_2. (This relative maximum is only 1 kcal/mol for H_2O_2, but it is probably higher in molecules where peroxide bridges organic groups or metals.) In charged species both planar and nonplanar peroxide groups have been found, but the nonplanar arrangement appears to occur *only* when the charges on the two centers are neutralized by closely allied and extensively hydrogen-bonded counterions. When the charges are not completely compensated for, the conformational energy minimum occurs at 180°, where the two charged centers have maximal separation. The most striking example is the μ-peroxo-bis[pentaamminecobalt(III)](4+) ion. When this is crystallized as the thiocyanate salt, the cation participates in only two hydrogen bonds, and the peroxo bridge is planar.[11] In the sulfate salt of the same cation, however, nearly all the ammine hydrogen atoms participate in hydrogen bonds, effectively neutralizing the charges on the cobalt centers, and the peroxo bridge has a dihedral angle of 146°.[12] As will be described below, the μ-peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)](4+) cation in this structure participates in only six good hydrogen bonds, four of which are intramolecular. We infer from the high perchlorate thermal motion that the perchlorate counterions are somewhat isolated from the cation by the aliphatic parts of the ligands and are ineffective in neutralizing the concentration of charge; this results in a planar peroxide bridge.

The coordination about the cobalt atoms is approximately octahedral, and the distortions are not unusual for ligands such as en and dien. The three five-membered ligand-cobalt

(9) R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, 36, 1311 (1962); R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *ibid.*, 42, 1931 (1965); C. S. Ewig and D. O. Harris, *ibid.*, 52, 6268 (1970).

(10) T. H. Dunning and N. W. Winter, *Chem. Phys. Lett.*, 11, 194 (1971).

(11) N.-G. Vannerberg, *Acta Crystallogr.*, 18, 449 (1965); F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, submitted for publication in *Acta Crystallogr., Sect. B.*

(12) W. P. Schaefer, *Inorg. Chem.*, 7, 725 (1968).

Table III. Bond Distances, Angles, and Vibration Amplitudes for the Perchlorate Groups

	Distance, Å				Distance, Å		
Atoms	Uncor[a]	TLS	Riding	Atoms	Uncor[a]	TLS	Riding
Cl(1)-O(2)	1.344 (5)	1.39	1.46	Cl(2)-O(6)	1.398 (5)	1.44	1.45
O(3)	1.440 (4)	1.45	1.45	O(7)	1.357 (6)	1.41	1.47
O(4)	1.347 (7)	1.36	1.48	O(8)	1.376 (7)	1.43	1.48
O(5)	1.392 (9)	1.41	1.52	O(9)	1.396 (7)	1.45	1.51

Atoms	Angle,[a] deg	Atoms	Angle,[a] deg
O(2)-Cl(1)-O(3)	110.7 (3)	O(6)-Cl(2)-O(7)	114.6 (4)
O(4)	114.4 (5)	O(8)	111.9 (4)
O(5)	106.0 (6)	O(9)	103.7 (4)
O(3)-Cl(1)-O(4)	112.0 (3)	O(7)-Cl(2)-O(8)	110.7 (5)
O(5)	108.8 (4)	O(9)	106.5 (5)
O(4)-Cl(1)-O(5)	104.6 (5)	O(8)-Cl(2)-O(9)	109.0 (5)
Av	109.4	Av	109.4
Std dev in an obs	3.8	Std dev in an obs	3.9
Av dev from 109.5°	3.0	Av dev from 109.5°	3.0

	Rms amplitudes along the principal axes, Å		
	Axis 1	Axis 2	Axis 3
Cl(1)	0.177	0.189	0.286
O(2)	0.210	0.257	0.589
O(3)	0.171	0.211	0.324
O(4)	0.186	0.247	0.639
O(5)	0.287	0.373	0.573
Cl(2)	0.188	0.196	0.261
O(6)	0.207	0.278	0.406
O(7)	0.216	0.324	0.548
O(8)	0.173	0.272	0.580
O(9)	0.269	0.324	0.545

[a] The estimated standard deviations in these bond lengths and angles were calculated from the diagonal elements of the inverse matrix from the final least-squares cycle. In view of the large calculated corrections and lack of consistency between what are certainly chemically equivalent bonds, we feel that these esd's severely underestimate the real standard deviations in the bond lengths and angles in the perchlorate groups.

Table IV. Dihedral Angles for Peroxo-Bridged Compounds

Compd	Dihedral angle R-O-O-R, deg	Ref
$[(NH_3)_5Co-O_2-Co(NH_3)_5]^{4+}(SO_4^{2-})_2$	146	*a*
$[(DDP)Co-O_2-Co(DDP)]$	149	*b*
$[(NH_3)_5Co-O_2-Co(NH_3)_5]^{4+}(SCN^-)_4$	180	*c*
$[(en)(dien)Co-O_2-Co(en)(dien)]^{4+}(ClO_4^-)_4$	180	*d*
$[(DMF)(salen)Co-O_2-Co(salen)(DMF)]$	110	*e*
H_2O_2 (g)	114	*f*
H_2O_2 (s)	90	*g*
$H_2O_2 \cdot 2H_2O$	130	*h*
2,2′-Dichlorodibenzoyl peroxide	106	*i*
2,2′-Dibromodibenzoyl peroxide	112	*i*
2,2′-Diiododibenzoyl peroxide	111	*i*
4,4′-Dichlorodibenzoyl peroxide	81	*j*
Peroxypelargonic acid	133	*k*
Dibenzoyl peroxide	91	*l*
$[O_3S-O_2-SO_3]^{2-}(NH_4^+)_2$	180	*m*

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rings in each half of the cation all possess the unsymmetrical gauche conformation, consistent with the stability arguments of Corey and Bailar.[13] The terminal nitrogen atoms of the dien ligand are trans to each other. This same arrangement has been observed in a series of dien-Cu complexes[14] and Crayton and Mattern and, more recently, Keene and Searle have concluded, on the basis of chemical evidence, that it is more stable than the all-cis isomer.[2] The opposite conclusion has also been espoused[3] and is similarly supported by physical and steric arguments as well as by several structure determinations,[15] in particular that of $[Co^{II}(en)(dien)Cl]Cl$, in which the dien ligand is in the all-cis configuration.[16] Certainly speculations on the relative isomeric stabilities must be made on a case by case basis, considering both the nature of the metal and the other ligands in the overall energetics of the system.

The Co-N(1) bond is substantially longer than the other four Co-N bonds (in particular Co-N(2)), and it is longer than the same bond in $[Co^{III}(en)_3]^{3+}$ complexes, 1.964 (4) Å[17] and 1.972 (3) Å.[18] Although the ligand-induced distortions from idealized octahedral geometry may contribute to the weakening of Co-N(1), as it does for Co-N(3), the lengthening is primarily due to the effect of the trans O(1). The excellent agreement between chemically equivalent C-N bonds and between C-C bonds precludes the possibility that

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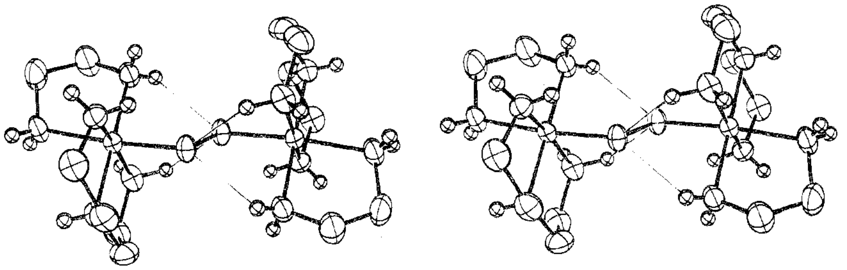

Figure 2. A stereodiagram showing the intramolecular hydrogen bonding and thermal ellipsoids at the 50% probability level, prepared by ORTEP (C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965).

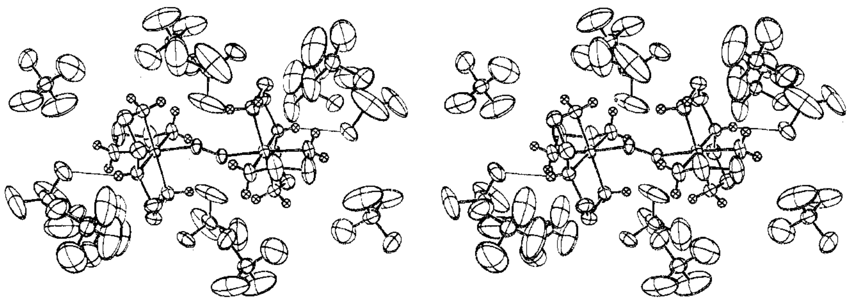

Figure 3. A stereodiagram showing the packing of the perchlorate groups about the cation. Thermal ellipsoids are shown at the 50% probability level.

the variations in the Co-N distances are artifacts; the differences are real and significant.

The plane containing the cobalt atoms and the peroxide bridge is oriented about 45° from the plane of the five-membered Co-en ring. (See Figure 2.) This permits the oxygen atom from one half of the cation to accept hydrogen bonds from N(2) of the en and N(5) of the dien in the other half of the cation, in a manner very similar to that found in the structure of μ-superoxo-bis[pentaamminecobalt(III)] sulfate tris(bisulfate).[19] This intramolecular bonding probably helps to stabilize the planar peroxo bridge, although model-building using CPK space-filling models indicates that similar hydrogen bonds could also be formed if the peroxide bridge were nonplanar to the extent allowed by steric interactions between the halves of the molecule.

Crystals of the perchlorate and nitrate salts of this complex are remarkably stable in air in comparison with salts of the μ-peroxo-bis[pentaamminecobalt(III)] (4+) cation, which decompose or oxidize fairly readily under the same conditions. The activation energy for the thermal decomposition of this complex has been found to be 42.4 kcal/mol, nearly the 50-kcal/mol bond energy of the O_2 linkage in H_2O_2 and organic peroxides.[20] We attribute some of this stability to the four intramolecular hydrogen bonds involving the peroxo bridge. Decomposition on exposure to the atmosphere is probably also hindered by the aliphatic chains of the ligands, which partially shield the bridge and prevent the close approach of oxygen or water molecules which could react with it. Similar stability is shown by μ-O_2-$[(\text{cyclam})\text{Co}^{\text{III}}]_2{}^{4+}$ salts.[21]

Figure 3 shows the arrangement of the perchlorate anions about the cation. Table V lists the inter- and intramolecular close approaches. There is only one good intermolecular hydrogen bond, from N(4) to O(3). The N···O and H···O distances for this bond are the shortest in the structure, the N-H···O angle is appropriate (166°), and O(3) appears to be more firmly fixed in the structure than the other perchlorate oxygen atoms.

Table V. Inter- and Intramolecular Close Contacts

Atoms	Distance, Å A···B	Distance, Å H···B	Distance, Å A–H	Angle AHB, deg
Strong H Bonds				
N(5)-H(21)-O(1′)	2.78	2.10	0.92	130
N(2)-H(8)-O(1′)	2.78	2.31	0.77	120
N(4)-H(15)-O(3′)	3.00	2.26	0.76	166
Weak H Bonds and Close Contacts				
C(4)-H(14)-O(1′)	2.99	2.53	0.94	110
N(1)-H(2)-O(7)	3.06	2.32	0.92	138
N(1)-H(1)-O(8)	3.06	2.34	0.78	152
N(5)-H(21)-O(4)	3.06	2.51	0.92	118
N(5)-H(20)-O(4)	3.06	2.61	0.88	113
N(3)-H(9)-O(6′)	3.07	2.47	0.85	129
N(5)-H(20)-O(8)	3.10	2.42	0.88	136
N(5)-H(20)-O(3)	3.10	2.50	0.88	127
C(6)-H(19)-O(6′)	3.15	2.63	0.91	117
N(1)-H(2)-O(3′)	3.16	2.48	0.92	131
N(2)-H(7)-O(6′)	3.22	2.34	0.92	162
O(3)-O(8′)	3.23			
N(2)-H(7)-O(9′)	3.37	2.59	0.92	143
C(4)-H(14)-O(4′)	3.38	2.53	0.94	149
O(3)-O(7′)	3.39			
C(3)-H(11)-O(3′)	3.42	2.66	1.00	134
C(3)-H(12)-O(5′)	3.47	2.62	0.98	144
C(5)-H(16)-O(7)	3.49	2.55	1.00	158

The apparent thermal motions of these other oxygen atoms are large; the calculated Cl-O bond distances are substantially shorter than the accepted length of 1.446 (3) Å.[22] O(3) is the only oxygen atom which has a Cl-O bond length near this value. We have attempted to interpret the perchlorate oxygen thermal parameters in terms of simple riding motion[23] and, using the Schomaker-Trueblood TLS program,[24] in terms of rigid-body librational and screw motions of the perchlorate groups. The Cl-O distances corrected by the two techniques are given in Table III. In general, they are

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still not satisfactory; the apparent motions of the perchlorate groups are not adequately described by either model. We interpret this to mean that the perchlorate groups are moving anharmonically, and/or these ions are disordered. In support of our argument that the hydrogen bonding in this complex is generally weak, we observe that three of the eight independent perchlorate oxygen atoms have no close approaches to any of the amine hydrogen atoms and yet the apparent thermal motions of these three atoms are no greater than those of the four weakly bonded perchlorate oxygen atoms.

Registry No. $[(en)(dien)Co\text{-}O_2\text{-}Co(en)(dien)]^{4+}(ClO_4^-)_4$, 40685-52-7.

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Contribution No. 2193 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Studies of Boranes. XXXVII. Some Reactions of Triborane(7) and the Structure of Triborane(7)-Carbonyl[1]

JAMES D. GLORE, JEROME W. RATHKE, and RILEY SCHAEFFER*

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The crystal and molecular structure of triborane-carbonyl, $B_3H_7 \cdot CO$, has been determined from three-dimensional X-ray data collected at $-113 \pm 10°$ by counter scan techniques. The compound crystallizes in space group $P1$ with lattice constants $a = 8.304\ (6)$ Å, $b = 5.667\ (3)$ Å, $c = 5.683\ (3)$ Å, $\alpha = 102.48\ (6)°$, $\beta = 75.96\ (7)°$, $\gamma = 104.07\ (6)°$, and a calculated density of $\rho_c = 0.907$ g cm^{-3} for $Z = 2$. All atomic coordinates were located by Patterson and Fourier techniques and full-matrix least-squares refinement of 670 observed reflections provided conventional and weighted R values of 0.0388 and 0.0432, respectively. The structure is described by the *styx* notation 1104. The physical properties of this compound are presented along with some chemistry of its reactive precursor, B_3H_7, notably the formation of B_8H_{18}.

Introduction

The reaction of dimethyl ether-triborane(7) at $-16°$ with boron trifluoride has been studied by Deever and Ritter as a source of the unstable species, B_3H_7.[2,3] Only recently have Paine and Parry used this reaction to prepare triborane(7)-carbonyl by generation of B_3H_7 in the presence of carbon monoxide.[4] Independently of these workers we have generated B_3H_7 at significantly lower temperatures by reaction of BF_3 with the more stable and more easily formed tetrahydrofuran adduct. The reaction is qualitatively similar to that reported with the dimethyl ether adduct except that B_8H_{18} is obtained in high yield. This rare hydride was not observed in the corresponding reaction of dimethyl ether-triborane(7) with BF_3. When the reaction was done in the presence of carbon monoxide, triborane(7)-carbonyl was obtained. A thorough study of the properties of this material and its crystal structure are given in this paper.

Experimental Section

Methods. Standard high-vacuum techniques as described elsewhere[5,6] were used throughout this investigation. Mass spectra were recorded on an AEI Model MS-9 mass spectrometer at 70 eV. ^{11}B and ^1H magnetic resonance spectra were recorded at $-50°$ on a Varian Associates HR 220 spectrometer at 70.6 and 220 MHz, respectively. The "line-narrowed" spectra at 70.6 MHz were obtained by means of a home-built pulse apparatus using a Nicolet 1080 computer to process the data. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer.

Materials. Carbon monoxide and boron trifluoride (Matheson) were purified by distillation through -196 and $-131°$ baths, respectively. Tetrahydrofuran was distilled from lithium aluminum hydride. Tetraborane(10) was prepared from tetramethylammonium triborohydride and polyphosphoric acid.[7]

Preparations. Tetraborane(10) (6.94 mmol) and tetrahydrofuran (28 mmol) were allowed to react in a heavy-walled glass bomb tube of 100-ml volume to form $THF \cdot B_3H_7$ similar to a method described elsewhere.[8] After pumping off excess tetrahydrofuran and B_2H_6 at 0°, BF_3 (13.1 mmol) and CO (35 mmol) were condensed in at $-196°$. The bomb tube was sealed and completely submerged in a $-45°$ bath for 1.5 hr during which time the solid $THF \cdot B_3H_7$ liquefied. Excess CO was removed at $-196°$ and volatile materials were pumped from the tube at $-45°$ for 2 hr and at 0° for 1 additional hr. Infrared spectroscopic examination of the colorless liquid remaining in the bomb, $BF_3 \cdot THF$ (6.45 mmol), showed that it contained no boron hydrides. Triborane-carbonyl (2.14 mmol) passed a $-78°$ bath and formed crystals in a $-112°$ bath. This material was contaminated with B_4H_{10} and B_5H_{11} as judged from the ^{11}B nmr spectrum. Attempts to purify the material further by trap to trap distillation failed because of extensive decomposition during transfer. However, low-temperature column[9] sublimination at $-100°$ gave samples of high purity; typical yields after column fractionation varied from 28 to 30% based on starting B_4H_{10}. Also obtained in the reaction were BF_3 (6.84 mmol), B_4H_{10} (1.30 mmol), B_5H_{11} (0.18 mmol), B_6H_{12} (0.14 mmol), and B_8H_{18} (0.42 mmol). No other carbonyl-boranes and only a trace of B_2H_6 were observed.

When B_3H_7 was generated as above but without addition of CO, 0.378 g of B_4H_{10} gave 0.112 g of B_8H_{18}. Also observed were B_6H_{12}, B_5H_{11}, and B_4H_{10} as well as much smaller amounts of B_5H_9 and B_2H_6. Only 0.029 mmol of H_2 was isolated from the reaction. When the reaction was carried out at 0° with a reaction time of 15 min, 1.14 g of B_4H_{10} resulted in 0.261 g of B_8H_{18}. The lower yield at this temperature is accounted for by decomposition as evidenced by the yellow coloration of the reaction mixture. The boron hydrides isolated in these reactions were identified by their characteristic ir and ^{11}B nmr spectra.

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