(Fig. 3). L'isolement des groupes Cu_2O_8 ainsi formés (le plus proche atome de cuivre d'un groupement voisin est situé à 3,77 Å) et la distance relativement faible entre les atomes de cuivre qu'ils contiennent (3,139 Å) conduisent à les considérer comme des clusters. La cohésion entre ces clusters (Fig. 4) est assurée par des tétraèdres CH_3PO_3, l'ensemble constituant des feuillets suivant le plan (100). La Fig. 5 représente une vue de la structure selon l'axe c; elle montre qu'il existe, dans chaque feuillet, un plan moyen contenant les bipyramides compris entre deux plans constitués par les tétraèdres. Ces derniers pointent le sommet occupé par le groupement CH_3 vers le centre de la cavité délimitée par quatre groupements CH_3 du feuillet adjacent, la distance entre les plans moyens dans lesquels se répartissent les atomes de carbone valant 2,016 Å.

Les liaisons hydrogène sont localisées dans les feuillets; la cohésion entre ces derniers doit donc être faible et permet d'envisager l'intercalation de molécules non polaires. En revanche, l'accumulation de groupements hydrophobes CH_3 de part et d'autre de l'espace disponible pour l'intercalation explique, vraisemblablement, l'insolubilité anormale de ce phosphonate dans l'eau.

Références

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.

DARRIET, M., CASSAIGNE, A., DARRIET, J. & NEUZIL, E. (1978). *Acta Cryst.* **B34**, 2105–2110.

DARRIET, M., DARRIET, J., CASSAIGNE, A. & NEUZIL, E. (1975). *Acta Cryst.* **B31**, 469–471.

FENOT, P., DARRIET, J., GARRIGOU-LAGRANGE, C. & CASSAIGNE, A. (1978). *J. Mol. Struct.* **43**, 49–60.

GEBERT, E. & KIHLBORG, L. (1969). *Acta Chem. Scand.* **23**, 221–231.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

NOWOGROCKI, G. (1976). Programme non publié.

POULSEN, S. J. & CALVO, C. (1968). *Can. J. Chem.* **46**, 917–927.

SHANNON, R. D. & CALVO, C. (1973). *Acta Cryst.* **B29**, 1338–1345.

TOMAN, K. (1977). *Acta Cryst.* **B33**, 2628–2631.

TOMAN, K. (1978). *Acta Cryst.* **B34**, 715–721.

WOZNIAK, M. (1977). Thèse, Lille.

trans-Bis(ethylenediamine)hydrogendiacetatocobalt(III) Diperchlorate Monohydrate – A Crystal Structure Containing Symmetrically Hydrogen-Bonded *trans*-Co(en)₂(CH₃CO₂)₂ Cations

By JACQUES ROZIÈRE AND CLAUDE BELIN

Laboratoire des Acides Minéraux LA 79, Université des Sciences et Techniques du Languedoc, place Eugène Bataillon, 34060 Montpellier CEDEX, France

Abstract

The title compound, $[Co(C_2H_8N_2)_2(C_2H_4O_2)(C_2H_3O_2)]$ $(ClO_4)_2 . H_2O$, $C_8H_{23}CoN_4O_4^{2+} . 2ClO_4^- . H_2O$, crystallizes in space group $P\bar{1}$ with $Z = 2$; $a = 8.640$ (2), $b = 8.711$ (2), $c = 14.995$ (4) Å and $\alpha = 91.77$ (2), $\beta = 97.42$ (2), $\gamma = 114.82$ (2)°. Diffraction data were measured over four octants using a four-circle automated diffractometer and monochromatized Mo $K\alpha$ radiation. The structure was solved by heavy-atom and Fourier techniques, then refined by least squares to $R = 0.049$ and $R_w = 0.051$ for 1899 independent observed reflections within $2\theta = 50°$ and for 29 independent (non-hydrogen) atoms with anisotropic thermal parameters and 24 H atoms with isotropic thermal parameters set at 5 Å². The asymmetric unit consists of two non-equivalent centrosymmetric complex cations A and B of formula $[Co(C_2H_8N_2)_2(CH_3CO_2)_2]^+$, two perchlorate anions and a water molecule. Two non-equivalent infinite chains of cations, A and B, are formed through symmetrical hydrogen bonds.

Introduction

The reaction of a trivalent transition-metal chloride with concentrated aqueous solutions of hydrochloric acid and various amine ligands such as ethylene-

diamine (en) has been utilized in the past to prepare complex cations of the type $trans\text{-}M(en)_2X_2^+$ (M = Cr, Rh and Co). The role of these cations in the stabilization of strongly hydrogen-bonded and symmetric species such as the diaquated proton $H_5O_2^+$ or the hydrogen dinitrate ion $(O_2NO.H.ONO_2)^-$ has been recognized by Gillard & Wilkinson (1964) and Gillard & Ugo (1966).

The present research was initiated to determine the nature of the products formed when hydrochloric acid was replaced by a weaker acid such as acetic. Our interest was further stimulated since the compound first reported as $[Co(en)_2(ac)_2]ClO_4.HClO_4$ by Linhard & Stirn (1952) (ac = CH_3CO_2) was supposed to contain the as yet uncharacterized homoconjugated hydrogen diperchlorate anion $(O_3ClO.H.OClO_3)^-$. However it will be shown (see below) that the compound should be reformulated $[Co(en)_2H(ac)_2](ClO_4)_2.H_2O$.

The present structure and the nature of the protonic site are also of interest in relation to the proposed mechanism of acid-catalyzed aquation and ligand displacement in dicarboxylatoamine cobalt(III) complexes (Przystas, Ward & Haim, 1973).

Crystal data and intensity measurements

The compound was prepared from $trans\text{-}[Co(en)_2\text{-}Cl_2]ClO_4$ following the method of Linhard & Stirn (1952). Tabular, violet {010} crystals were grown by slow cooling of saturated hot solutions in commercial ($\simeq$70%) perchloric acid. Preliminary Weissenberg and precession photographs showed the crystal to belong to the triclinic system. Lattice constants were determined by least-squares refinement of the angular positions of 25 reflections collected and centered on an Enraf–Nonius CAD-4 computer-controlled diffractometer (crystal data are given in Table 1). Diffraction data were collected at 295 K up to $2\theta = 50°$ using graphite-

monochromatized Mo $K\alpha_1$ radiation and the ω–2θ scan technique. Scan widths were calculated from the formula $Sw = A + B\tan\theta$ where A depends on the mosaicity and was estimated from the profile analysis of a few low-angle reflections and B compensates for the increase in peak width due to $K\alpha_1$, $K\alpha_2$ splitting. The values of A and B were respectively 1·5 and 0·35. For each reflection the calculated scan angle was extended by 25% at either side to estimate the background count. Three standard reflections were monitored every 60 reflections and showed no significant changes in intensity. Data were corrected for Lorentz and polarization factors and absorption effects. The final data set consisted of 3591 independent reflections of which 1899 had $F_o^2 \geq 3\sigma(F_o^2)$.

Solution and refinement of the structure

The structure was solved in the centrosymmetric space group $P\bar{1}$ using conventional Patterson, Fourier and least-squares refinements assuming the chemical formula given by Linhard & Stirn (1952) to be correct. Scattering factors for neutral atoms and corrections for the anomalous-dispersion effects for Co and Cl were obtained from *International Tables for X-ray Crystallography* (1974).

All atomic positional parameters and isotropic temperature factors were refined by full-matrix least-squares refinements minimizing the function $w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_{count}^2(F^2)/4F^2 + (0.01F)^2$. Initially a difference Fourier map indicated a residual electron density which was included in the model as an O atom of a water molecule of crystallization. A subsequent difference synthesis revealed 23 of the 25 H atoms. These were refined with isotropic temperature factors of 5 Å^2. The positions of the H atoms of the water molecule were difficult to calculate reliably, so they were entirely deleted from the model. The final agreement factors were $R(F) = 0.049$, $R_w(F) = 0.051$; the goodness-of-fit defined as $[\sum w(|F_o| - |F_c|)^2/(N - M)]^{1/2}$, where N is the number of observations (1899) and M is the number of parameters varied (340), was 0·88. Final atomic positional parameters are given in Table 2.*

The crystallographic programs used were *DRF* (a modification of the Zalkin Fourier program), *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinements, *ORFFE* (Busing, Martin & Levy, 1964) for molecular geometry and error functions and *ORTEP* II (Johnson, 1971) for molecular plots.

Table 1. *Summary of crystal data*

Molecular formula $[Co(en)_2H(ac)_2](ClO_4)_2.H_2O$
$M_r = 515.02$
Linear absorption coefficient $\mu^* = 1.284$ mm^{-1}
$D_o = 1.70$ Mg m^{-3}†
$D_c = 1.70$
Crystal dimensions: $0.2 \times 0.08 \times 0.25$ mm
Boundary planes: {100}, {010}, {001}
Space group: $P\bar{1}$
$Z = 2$
Cell constants*: $a = 8.640$ (2), $b = 8.711$ (2), $c = 14.995$ (4) Å
$\qquad\qquad \alpha = 91.77$ (2), $\beta = 97.42$ (2), $\gamma = 114.82$ (2)°
Cell volume = 1011·15 Å^3

* Mo $K\alpha_1$ radiation, $\lambda = 0.71069$ Å.

† Experimental density measurements were obtained by flotation in CCl_4–CBr_4.

Discussion

The structure consists of two discrete crystallo-graphically non-equivalent ClO_4^- anions, non-equivalent centrosymmetric $[Co(NH_2CH_2CH_2NH_2)_2-(CH_3CO_2)_2]^+$ $\{[Co(en)_2(ac)_2]^+\}$ cations, and water

Table 2. Final positional parameters ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for H)

	x	y	z
CoA	0	5000	5000
N(2)A	1091 (8)	4626 (8)	6154 (4)
N(1)A	8137 (8)	2747 (8)	5043 (4)
C(1)A	8743 (11)	1857 (11)	5740 (7)
C(2)A	9780 (11)	3141 (12)	6524 (6)
O(1)A	896 (6)	3850 (6)	4247 (3)
O(2)A	3605 (6)	4962 (7)	4956 (3)
C(3)A	2443 (10)	4021 (10)	4318 (5)
C(4)A	2846 (10)	3036 (11)	3611 (5)
CoB	0	0	0
N(1)B	188 (8)	990 (8)	8837 (4)
N(2)B	2212 (8)	−40 (8)	−91 (4)
C(1)B	1474 (11)	592 (11)	8409 (5)
C(2)B	2966 (11)	961 (11)	9161 (6)
O(1)B	1342 (6)	2152 (6)	693 (3)
O(2)B	49 (7)	3621 (6)	39 (3)
C(3)B	1209 (9)	3520 (9)	611 (5)
C(4)B	2522 (11)	5077 (10)	1204 (6)
ClA	6016 (3)	8515 (3)	3655 (2)
O(3)A	3216 (10)	−154 (9)	6658 (5)
O(4)A	2990 (13)	2315 (14)	6399 (7)
O(5)A	4279 (11)	1301 (10)	5458 (5)
O(6)A	5574 (12)	2439 (11)	6876 (7)
ClB	3107 (3)	6284 (3)	8489 (2)
O(3)B	6118 (9)	2417 (9)	796 (4)
O(4)B	8524 (10)	3792 (13)	1868 (5)
O(5)B	7139 (12)	5286 (9)	1211 (6)
O(6)B	5829 (9)	3373 (9)	2207 (4)
Ow	3291 (8)	−56 (9)	2099 (5)
HB	0	500	0
H(1)B	75 (11)	234 (11)	909 (6)
H(2)B	−46 (11)	86 (11)	866 (6)
H(3)B	89 (11)	−71 (11)	827 (6)
H(4)B	180 (11)	112 (11)	793 (6)
H(5)B	346 (11)	189 (11)	938 (6)
H(6)B	415 (11)	73 (11)	889 (6)
H(7)B	201 (11)	−114 (11)	−17 (6)
H(8)B	305 (11)	37 (11)	47 (6)
H(9)B	315 (11)	458 (11)	161 (6)
H(10)B	279 (11)	582 (11)	92 (6)
H(11)B	194 (11)	542 (11)	154 (6)
HA	500	500	500
H(1)A	721 (11)	283 (11)	513 (6)
H(2)A	774 (11)	221 (11)	431 (6)
H(3)A	814 (11)	108 (11)	594 (6)
H(4)A	912 (11)	162 (11)	523 (6)
H(5)A	33 (11)	265 (11)	694 (6)
H(6)A	924 (11)	348 (11)	678 (6)
H(7)A	197 (11)	446 (11)	613 (6)
H(8)A	164 (11)	582 (11)	656 (6)
H(9)A	354 (11)	216 (11)	399 (6)
H(10)A	211 (11)	267 (11)	310 (6)
H(11)A	403 (11)	422 (11)	345 (6)

molecules. The very short $O \cdots O$ distances across the inversion centers at $0,\frac{1}{2},0$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ suggest the presence of strong hydrogen bonds between acetate groups of neighboring complex cations. Important distances and angles are listed in Tables 3 and 4. The complex cations are linked through the short hydrogen bonds and form two non-equivalent infinite chains $[Co(en)_2H(ac)_2]_n^{2n+}$ extending parallel to the **a** and **b** directions respectively. These chains interact with the perchlorate anions or the water molecule via $NH \cdots O$ hydrogen bonds. However, although the chain along the a axis (chain A) interacts with the two perchlorate anions (A and B), chain (B) along the b axis interacts only with perchlorate (B) and the molecule of water of crystallization (Fig. 1). The perchlorate anions display the expected geometry. The eight values of the Cl—O bond lengths range from 1·337 (7) to 1·433 (6) Å giving a mean distance of 1·402 (10) Å. Owing to the large amount of thermal motion associated with the O atoms, the mean distance is shorter than the expected Cl—O

Table 3. Bond lengths (Å) and angles (°) in the complex cations

	B	A
Co—N(1)	1·957 (6)	1·970 (6)
Co—N(2)	1·946 (6)	1·958 (6)
Co—O(1)	1·929 (5)	1·914 (5)
N(1)—C(1)	1·492 (9)	1·484 (10)
C(1)—C(2)	1·510 (11)	1·501 (12)
N(2)—C(2)	1·491 (9)	1·503 (9)
O(1)—C(3)	1·252 (8)	1·272 (9)
O(2)—C(3)	1·266 (9)	1·274 (9)
C(3)—C(4)	1·527 (11)	1·502 (11)
N(2)—Co—N(1)	94·5 (2)	93·6 (3)
N(2)—Co—O(1)	95·1 (2)	96·1 (2)
N(1)—Co—O(1)	93·4 (2)	94·5 (2)
Co—N(2)—C(2)	109·9 (4)	108·2 (5)
N(2)—C(2)—C(1)	106·0 (6)	107·5 (7)
C(2)—C(1)—N(1)	105·4 (6)	107·0 (7)
C(1)—N(1)—Co	108·2 (4)	108·7 (5)
Co—O(1)—C(3)	128·3 (5)	126·8 (5)
O(1)—C(3)—O(2)	121·4 (7)	122·4 (7)
O(2)—C(3)—C(4)	120·8 (7)	120·7 (7)
C(4)—C(3)—O(1)	117·8 (7)	116·9 (8)

Table 4. Bond lengths (Å) and angles (°) in the perchlorate anion

	B	A
Cl—O(3)	1·414 (6)	1·427 (7)
Cl—O(4)	1·412 (7)	1·337 (7)
Cl—O(5)	1·391 (7)	1·400 (7)
Cl—O(6)	1·433 (6)	1·398 (7)
O(3)—Cl—O(4)	109·3 (5)	110·9 (5)
O(4)—Cl—O(5)	107·8 (6)	111·6 (6)
O(5)—Cl—O(6)	109·3 (5)	117·6 (6)
O(6)—Cl—O(3)	109·7 (4)	109·9 (5)
O(3)—Cl—O(5)	111·1 (5)	108·9 (5)
O(4)—Cl—O(6)	109·6 (5)	107·9 (7)

Table 5. *Hydrogen bonding: distances* (Å) *and angles* (°)

The average standard deviation for H—O distances is 0·07 Å and for O—H—O angles 1°.

| O(2)A—O(2)A | 2·370 (10) | | | | |
O(2)B—O(2)B	2·442 (10)				
Ow—O(6)B	2·878 (9)				
Ow—O(6)A	3·017 (11)	O(6)A—Ow—O(6)B	115·3 (3)		
N(1)A—O(2)A	2·951 (8)	H(1)A—O(2)A	2·31	N(1)A—H(1)A—O(2)A	131
N(1)A—O(5)A	3·200 (10)	H(1)A—O(5)A	2·45	N(1)A—H(1)A—O(5)A	147
N(1)A—O(3)A	3·117 (10)	H(2)A—O(3)A	2·08	N(1)A—H(2)A—O(3)A	150
N(2)A—O(2)A	2·922 (8)	H(7)A—O(2)A	2·31	N(2)A—H(7)A—O(2)A	126
N(2)A—O(4)A	3·079 (9)	H(7)A—O(4)A	2·35	N(2)A—H(7)A—O(4)A	140
N(2)A—O(4)B	3·153 (10)	H(8)A—O(4)B	2·40	N(2)A—H(8)A—O(4)B	126
N(2)A—O(6)B	3·231 (9)	H(8)A—O(6)B	2·50	N(2)A—H(8)A—O(6)B	125
N(1)B—O(2)B	2·925 (8)	H(1)B—O(2)B	2·05	N(1)B—H(1)B—O(2)B	131
N(1)B—O(5)B	3·132 (9)	H(1)B—O(5)B	2·21	N(1)B—H(1)B—O(5)B	137
N(1)B—Ow	2·926 (8)	H(2)B—Ow	2·36	N(1)B—H(2)B—Ow	174
N(2)B—O(2)B	2·936 (8)	H(7)B—O(2)B	2·18	N(2)B—H(7)B—O(2)B	138
N(2)B—O(3)B	3·236 (9)	H(8)B—O(3)B	2·47	N(2)B—H(8)B—O(3)B	133
N(2)B—Ow	3·298 (9)	H(8)B—Ow	2·48	N(2)B—H(8)B—Ow	140
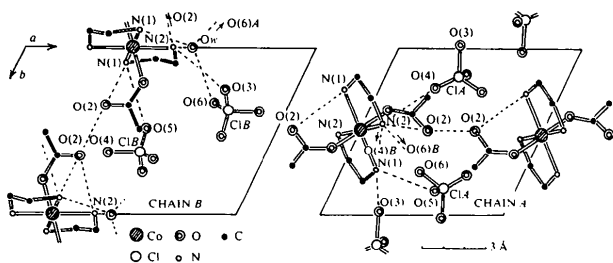
Fig. 1. Projection onto (001) illustrating the packing and the interactions of the complex cations with surrounding ions and molecules.
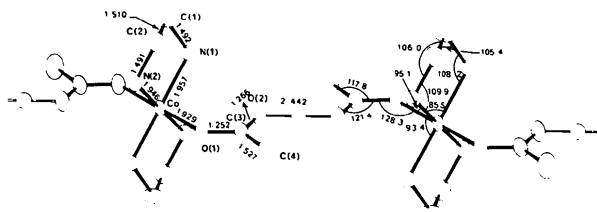
Fig. 2. A perspective view of the isolated chain $[Co(en)_2H(ac)_2]_n^{2n+}$ (B). Interatomic distances (Å) and bond angles (°) are shown.

bond length, in the range 1·426–1·439 Å (Berglund, Thomas & Tellgren, 1975). The shortest lengths, in particular the 1·337 Å distance, might indicate that some disorder is implied for perchlorate (B). In the *trans*-$Co(en)_2(ac)_2^+$ cations, four N atoms from two ethylenediamine ligands and two O atoms of the acetate anions form a disordered octahedral environment around the central Co atom (Fig. 2).

The mean CoN distance is 1·958 (5) Å and the Co—O bond lengths average 1·922 (7) Å.

The two ethylenediamine rings in a complex cation assume a symmetric *gauche* configuration. There is a

pseudo twofold rotation axis, normal to the O(1)CoO(1) axis, relating the acetate groups and the ethylenediamine rings such that the cation approximately conforms to the C_{2h} molecular point group. The dihedral angle α between the plane containing the metal atom, the ring C atoms and that containing the metal atom and the N atoms should be non-zero for ethylenediamine in the *gauche* conformation. In cation (A) α is 27·4 (7)° and in cation (B) it is 29·5 (6)°. In the ethylenediamine groups the four C—N bond lengths have a mean value of 1·493 (4) Å and the two C—C distances average 1·505 (5) Å. If we omit the exceedingly short N(1)—H(2) distance in cation (B) [0·55 (12) Å], the NH and the CH groups in the complex cation show reasonable (for X-rays) average lengths of respectively 0·94 and 0·96 Å. The amino groups of the ethylenediamine rings are involved in an extensive hydrogen-bonding network. In several cases two almost equivalent O contacts are available for an H atom probably leading to bifurcated hydrogen bonds. The hydrogen-bonding scheme is summarized in Table 5. Bond angles around the H atoms average 139° which is not unusual for NH···O interactions (Koetzle & Lehmann, 1976).

The main interest in this structure arises from the very short and apparently symmetrical hydrogen bonds. Similar situations are observed, for instance, in acid salts of carboxylic acids such as sodium hydrogen diacetate (Barrow, Currie, Muir, Speakman & White, 1975; Stevens, Lehmann & Coppens, 1977). The two hydrogen bonds occur in chemically very similar environments; however, their lengths differ significantly [2·442 (10) Å (chain B) and 2·370 (10) Å (chain A)]. Although the difference in length might be accounted for by the closer packing of the complex cations in the a direction, the value of 2·37 Å seems exceedingly short. However, similarly short O···O distances have

been observed in the symmetric diaquahydrogen ion $H_2O.H.OH_2^+$ (Selenius & Delaplane, 1978; Brown, Noe-Spirlet, Busing & Levy, 1977). Unlike those of homoconjugated dicarboxylate anions in Speakman's (1972) type A salts, the two CO distances in the acetate ligands are identical: hydrogen bonding and coordination to the metal atom have similar effects on the C—O bond lengths. The geometry of the carboxylate group is more comparable to that of the acetate acidium ion where the CO groups are equally bonded to two H atoms (Jönsson & Olovsson, 1968).

The planes of the acetate groups are nearly perpendicular to the CoN(1)N(2) planes [93·6 (8)° for cation (A) and 93·0 (8)° for cation (B)] and almost bisect the N(1)CoN(2) outer ring angle. The dihedral angles between the acetate planes and the planes defined by CoN(1)O(1) are 47·0 (6)° [cation (A)] and 46·7 (6)° [cation (B)]. As can be readily seen the orientation of the plane of the acetate ligand is such that the carbonyl O(2) atom comes into a hydrogen-bonding contact with atoms H(1) and H(7): the O atoms involved in the very short OHO bonds also participate in interligand hydrogen bonds with the amino groups of the ethylenediamine ring. This behavior is anomalous with respect to usual type A symmetric hydrogen bonds. This situation has only been encountered in the case of potassium hydrogen *meso*-tartrate (Currie, Speakman, Kanters & Kroon, 1975).

References

BARROW, M. J., CURRIE, M., MUIR, K. W., SPEAKMAN, J. C. & WHITE, D. N. J. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 15–18.

BERGLUND, B., THOMAS, J. O. & TELLGREN, R. (1975). *Acta Cryst.* B31, 1842–1846.

BROWN, G. M., NOE-SPIRLET, M. R., BUSING, W. R. & LEVY, H. A. (1977). *Acta Cryst.* B33, 1038–1046.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

CURRIE, M. C., SPEAKMAN, J. C., KANTERS, J. A. & KROON, J. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 1549–1554.

GILLARD, R. D. & UGO, R. (1966). *J. Chem. Soc.* pp. 549–552.

GILLARD, R. D. & WILKINSON, G. (1964). *J. Chem. Soc.* pp. 1640–1646.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98, 148–150. Birmingham: Kynoch Press.

JOHNSON, C. K. (1971). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

JÖNSSON, P. G. & OLOVSSON, I. (1968). *Acta Cryst.* B24, 559–564.

KOETZLE, T. F. & LEHMANN, M. S. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiment*, Vol. II, pp. 455–469. Amsterdam: North-Holland.

LINHARD, M. & STIRN, G. (1952). *Z. Anorg. Chem.* 268, 105–127.

PRZYSTAS, T. J., WARD, J. R. & HAIM, A. (1973). *Inorg. Chem.* 12, 743–749.

SELENIUS, C. O. & DELAPLANE, R. G. (1978). *Acta Cryst.* B34, 1330–1332.

SPEAKMAN, J. C. (1972). *Struct. Bonding (Berlin)*, 12, 141–199.

STEVENS, F. D., LEHMANN, M. S. & COPPENS, P. (1977). *J. Am. Chem. Soc.* 99, 2829–2831.

The Crystal Structure of μ_4-Antimonio-tetrakis[tricarbonyl(triphenylphosphine)cobalt] Tetraphenylborate–Dichloromethane, $[\{Co(CO)_3PPh_3\}_4 Sb][BPh_4].CH_2Cl_2$

BY R. E. COBBLEDICK AND F. W. B. EINSTEIN

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Abstract

$[\{Co(CO)_3PPh_3\}_4Sb][BPh_4].CH_2Cl_2$ is monoclinic, space group $P2_1/c$, with $a = 16·695$ (6), $b = 38·026$ (14), $c = 15·861$ (6) Å, $\beta = 90·64$ (2)°, $Z = 4$. The structure was refined to an R of 0·060 for 3305 counter reflexions. It consists of discrete $[\{Co(CO)_3PPh_3\}_4Sb]^+$ cations, $[BPh_4]^-$ anions and CH_2Cl_2 solvent of crystallization. In the cation there is tetrahedral geometry about the Sb atom with Sb—Co = 2·593 (3)–2·602 (2) Å (mean Sb—Co = 2·596 Å, mean Co—Sb—Co = 109·5°). The coordination at the Co atoms is trigonal bipyramidal with the CO groups in equatorial positions and the P atoms *trans* to Sb with mean Co—C = 1·74 Å (range 1·71–1·78) and mean Co—P = 2·217 Å (range 2·212–2·226 Å).