

Fig. 1. Perspective view of the cation with the atomic nomenclature.

C(2)—N(1) is in a distorted half-chair conformation where N(5) and to a lesser extent Cu are the out-of-plane atoms. Since C(15) is disordered there are two possible conformations for the remaining six-membered ring. The ring containing C(15a) has a distorted boat conformation, Cu and C(15a) being the apices of the boat. Alternately the ring containing C(15b) lies almost midway between an envelope [C(16) out-of-plane] and a half-chair [C(16) and N(17) out-of-plane]. In the two similar six-membered chelate rings in [CuL²](ClO₄)₂

there is disorder of five methylene C atoms in addition to two independent ClO₄⁻ groups for each central Cl atom.

The cation is well separated from the ClO₄⁻ anions with no intermolecular or interionic close contacts.

All calculations were performed on a Univac 1106 computer system at the University of Cape Town. We thank the University of Cape Town and the CSIR (Pretoria) for research grants, and the latter for the diffractometer data collection. Crystals were kindly supplied by Dr D. A. Stotter.

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Structure of μ -[1,6-Bis(trifluoro)-3,4-bis(trifluoromethyl)hexene-2-thionato]-tetracarbonyldicobalt, a Product of the Reaction between Hexacarbonyltetrakis(pentafluorobenzenethiolato)dicobalt and Hexafluoro-2-butyne

BY MICHAEL J. BARROW AND GEORGE A. SIM

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

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Abstract. Co₂(C₈F₁₂S)(CO)₄, C₁₂Co₂F₁₂O₄S, orthorhombic, *P*2₁2₁2₁, *a* = 9.635 (6), *b* = 10.497 (6), *c* = 17.411 (8) Å, *U* = 1760.9 Å³, *Z* = 4, *D*_c = 2.21 Mg m⁻³, *F*(000) = 1128, μ (Mo *K*α) = 2.22 mm⁻¹. The structure was refined to an *R* of 0.033 for 2049 reflections. The complex has a flyover structure, with a C₄S bridge between the Co atoms. The bridge is bound to one Co atom through the S atom and an η³-allyl function and to the other Co atom through the CS group and the terminal C atom. The Co—Co separation is 2.552 (1) Å.

Introduction. Hexafluoro-2-butyne reacts with hexacarbonyltetrakis(pentafluorobenzenethiolato)dicobalt

to give several complexes, one of which has the composition [Co₂(CO)₄{C₄(CF₃)₄S}] (Davidson & Sharp, 1975). We undertook an X-ray analysis of this complex to elucidate the molecular structure.

A crystal 0.4 × 0.4 × 0.3 mm was selected for the intensity measurements on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo *K*α radiation. Intensities were measured by the ω-2θ step-scan procedure and of the 2657 independent reflections surveyed, 2049 satisfied the criterion *I* > 3σ(*I*).

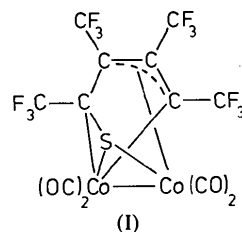
Initial coordinates for the Co atoms were deduced from a Patterson synthesis and the remaining atoms located in electron-density distributions. The atomic parameters were then adjusted by least-squares cal-

culations. Full-matrix refinement, with unit weights and isotropic temperature factors, converged at $R = 0.087$. Anisotropic thermal parameters were then adopted and the calculations reduced R to 0.036.

Anomalous-dispersion corrections were next incorporated. Both enantiomers were tested and R converged at 0.033 for one enantiomer and at 0.043 for the other, which establishes the correct set of atomic coordinates (Table 1).

A difference map computed after the refinement showed only small random peaks ($ca \pm 0.2 e \text{ \AA}^{-3}$). The weighting scheme in the final stages was $w^{-1} = 1 + 0.0011(|F_o| - 18)^2$. All calculations were performed with XRAY 70 (Stewart, Kundell & Baldwin, 1970).*

Discussion. The molecular structure and atom numbering are shown in Fig. 1, bond lengths and angles in Table 2 and intermolecular contacts in Table 3. The results indicate that the complex has the flyover structure (I) with a C₄S bridge between the Co atoms.



The S atom is unsymmetrically placed with respect to the Co atoms, the Co—S distances being 2.141 and 2.367 Å. These distances may be compared with Co—S separations of 2.33 Å in CoBr₂{SC(OEt)NHPPh}₂ (Porta, Tarantelli, Gastaldi & Furlani, 1971), 2.24–2.29 Å in {Co(S₂CSEt)₂(SEt)}₂ (Lewis, Lippard & Zubieta, 1972) and 2.26 Å in Co(NO)(S₂CNMe₂) (Enemark & Feltham, 1972). The sum of the Co and S single-bond radii is 2.20 Å.

The Co—CO lengths in (I) are 1.796–1.839 Å and the other Co—C lengths 1.962–2.072 Å. This distinction is expected; cf. Co—CO distances of 1.72–1.80

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34221 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^5$ for Co, $\times 10^4$ for others)

	x	y	z
Co(1)	31198 (7)	-7239 (6)	63264 (4)
Co(2)	7523 (6)	3659 (6)	62957 (4)
S	2040 (2)	-330 (1)	7375 (1)
C(1)	4362 (8)	1318 (7)	7328 (4)
C(2)	3058 (5)	846 (5)	6936 (3)
C(3)	2152 (5)	1763 (4)	6501 (3)
C(4)	2049 (6)	1577 (4)	5688 (3)
C(5)	2213 (6)	269 (5)	5508 (3)
C(6)	2110 (8)	-257 (7)	4702 (3)
C(7)	2775 (9)	-2415 (6)	6127 (4)
C(8)	-280 (7)	-918 (8)	5891 (4)
C(9)	-746 (7)	1065 (7)	6774 (4)
C(10)	4863 (7)	-656 (6)	5963 (4)
C(11)	1741 (7)	2641 (7)	5119 (4)
C(12)	1700 (8)	2977 (6)	6907 (4)
O(1)	2575 (10)	-3450 (5)	6027 (4)
O(2)	5944 (6)	-630 (7)	5765 (4)
O(3)	-887 (8)	-1697 (7)	5643 (4)
O(4)	-1660 (5)	1455 (6)	7074 (4)
F(1)	5125 (5)	364 (5)	7594 (3)
F(2)	4102 (5)	2070 (5)	7928 (3)
F(3)	5127 (4)	1995 (5)	6843 (3)
F(4)	1330 (6)	2715 (5)	7630 (2)
F(5)	591 (5)	3509 (4)	6578 (3)
F(6)	2690 (6)	3841 (4)	6935 (3)
F(7)	2367 (5)	2426 (4)	4456 (2)
F(8)	401 (4)	2780 (4)	4969 (3)
F(9)	2228 (6)	3743 (3)	5381 (3)
F(10)	3287 (5)	-87 (5)	4320 (2)
F(11)	1088 (5)	258 (5)	4294 (2)
F(12)	1862 (6)	-1504 (4)	4709 (2)

Table 2. Bond lengths (Å) and angles (°)

Co(1)—Co(2)	2.552 (1)	C(4)—C(11)	1.524 (8)
Co(1)—S	2.141 (1)	C(2)—S	1.751 (5)
Co(1)—C(2)	1.962 (5)	C(7)—O(1)	1.117 (8)
Co(1)—C(5)	1.969 (5)	C(8)—O(3)	1.094 (10)
Co(1)—C(7)	1.839 (6)	C(9)—O(4)	1.102 (9)
Co(1)—C(10)	1.796 (7)	C(10)—O(2)	1.098 (9)
Co(2)—S	2.367 (1)	C(1)—F(1)	1.326 (8)
Co(2)—C(3)	2.024 (5)	C(1)—F(2)	1.334 (8)
Co(2)—C(4)	2.072 (5)	C(1)—F(3)	1.326 (8)
Co(2)—C(5)	1.967 (5)	C(6)—F(10)	1.326 (9)
Co(2)—C(8)	1.817 (8)	C(6)—F(11)	1.328 (9)
Co(2)—C(9)	1.821 (7)	C(6)—F(12)	1.331 (8)
C(1)—C(2)	1.513 (9)	C(11)—F(7)	1.322 (8)
C(2)—C(3)	1.504 (7)	C(11)—F(8)	1.324 (8)
C(3)—C(4)	1.432 (7)	C(11)—F(9)	1.329 (8)
C(4)—C(5)	1.417 (7)	C(12)—F(4)	1.337 (8)
C(5)—C(6)	1.513 (8)	C(12)—F(5)	1.336 (9)
C(3)—C(12)	1.521 (8)	C(12)—F(6)	1.317 (9)
C(5)—Co(1)—S	107.4 (2)	C(5)—C(6)—F(10)	111.1 (6)
C(7)—Co(1)—C(10)	98.1 (3)	C(5)—C(6)—F(11)	113.3 (6)
C(5)—Co(2)—S	99.3 (2)	C(5)—C(6)—F(12)	111.2 (5)
C(8)—Co(2)—C(9)	92.4 (3)	C(4)—C(11)—F(7)	110.7 (5)
C(1)—C(2)—S	120.0 (4)	C(4)—C(11)—F(8)	113.5 (6)
C(3)—C(2)—S	110.2 (4)	C(4)—C(11)—F(9)	110.2 (6)
Co(1)—C(7)—O(1)	178.0 (6)	C(3)—C(12)—F(4)	110.0 (5)
Co(1)—C(10)—O(2)	177.5 (7)	C(3)—C(12)—F(5)	112.3 (5)
Co(2)—C(8)—O(3)	179.1 (10)	C(3)—C(12)—F(6)	112.8 (6)
Co(2)—C(9)—O(4)	177.9 (7)	F(1)—C(1)—F(2)	106.1 (5)
C(1)—C(2)—C(3)	120.0 (5)	F(1)—C(1)—F(3)	108.6 (6)
C(2)—C(3)—C(4)	116.8 (4)	F(2)—C(1)—F(3)	106.6 (6)
C(3)—C(4)—C(5)	110.1 (4)	F(10)—C(6)—F(11)	108.2 (5)
C(4)—C(5)—C(6)	123.5 (5)	F(10)—C(6)—F(12)	106.9 (6)
C(12)—C(3)—C(2)	117.9 (5)	F(11)—C(6)—F(12)	105.8 (6)
C(12)—C(3)—C(4)	123.7 (5)	F(7)—C(11)—F(8)	107.0 (6)
C(11)—C(4)—C(3)	123.8 (5)	F(7)—C(11)—F(9)	106.7 (6)
C(11)—C(4)—C(5)	126.1 (5)	F(8)—C(11)—F(9)	108.4 (6)
C(2)—C(1)—F(1)	111.8 (5)	F(4)—C(12)—F(5)	106.1 (6)
C(2)—C(1)—F(2)	113.0 (6)	F(4)—C(12)—F(6)	107.5 (6)
C(2)—C(1)—F(3)	110.5 (5)	F(5)—C(12)—F(6)	107.9 (5)

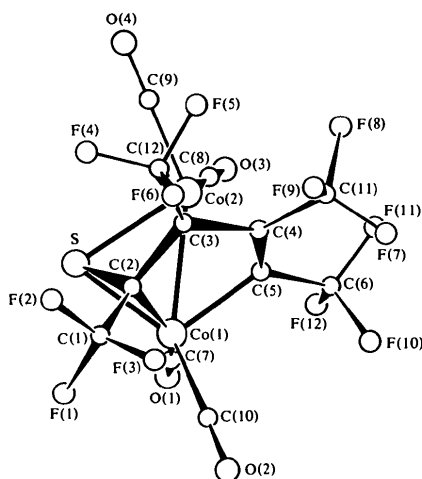


Fig. 1. The molecular structure with the atom labels.

Table 3. Intermolecular contacts (Å)

F(1)...F(6) ^I	2.77 (1)	C(8)...F(4) ^V	3.12 (1)
O(3)...F(12) ^{II}	2.94 (1)	O(1)...F(9) ^{VI}	3.17 (1)
O(4)...F(7) ^{III}	3.06 (1)	O(4)...F(3) ^{VII}	3.17 (1)
O(2)...F(9) ^{IV}	3.07 (1)	F(3)...F(8) ^{IV}	3.18 (1)
F(7)...F(8) ^{IV}	3.10 (1)	F(5)...F(10) ^{III}	3.18 (1)
O(3)...F(4) ^V	3.10 (1)	F(3)...F(7) ^{IV}	3.19 (1)

The superscripts refer to the following transformations of the atomic coordinates:

(I) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$	(V) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(II) $-\frac{1}{2}+x, -\frac{1}{2}-y, 1-z$	(VI) $x, -1+y, z$
(III) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	(VII) $-1+x, y, z$
(IV) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	

Å in Co₃(CO)₈(CMe)(PPh₃) (Brice, Penfold, Robinson & Taylor, 1970), 1.79–1.83 Å in Co₂(CO)₆(C₈H₁₂As₂F₄) (Harrison & Trotter, 1971) and 1.75–1.78 Å in Co₃(CO)₇(C₁₀H₁₅As₂F₄) (Einstein & Jones, 1972), and Co–C distances of 1.99 Å in Co(C₂H₅)(C₁₆H₁₄N₂O₂) (Calligaris, Minichelli, Nardin & Randaccio, 1971),

2.04–2.06 Å in Co{(B₉C₂H₁₀)₂S₂CH} (Churchill & Gold, 1971) and 2.02–2.09 Å in Co(C₈H₁₃)(C₈H₁₂) (Koda, Takenaka & Watanabé, 1971). The Co–Co separation of 2.552 Å in (I) is slightly longer than the values of 2.49–2.51 in Co₃(CO)₈(CMe)(PPh₃), 2.48 in Co₂(CO)₆(C₈H₁₂As₂F₄) and 2.44–2.48 Å in Co₃(CO)₇(C₁₀H₁₅As₂F₄).

The F–C–F angles in the organic ligand (mean 107.1°) are distinctly smaller than the C–C–F angles (mean 111.7°). This result is in accord with the relative electronegativities of C and F.

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Holmium Triacetate Tetrahydrate

BY J. W. BATS, R. KALUS AND H. FUESS

Institut für Kristallographie, Universität Frankfurt/Main, Senckenberg-Anlage 30, 6000 Frankfurt/Main, Federal Republic of Germany

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Abstract. Ho(C₂H₃O₂)₃·4H₂O, triclinic, $P\bar{1}$, $Z = 2$, $a = 9.246(3)$, $b = 9.361(3)$, $c = 10.588(4)$ Å, $\alpha = 90.30(3)$, $\beta = 114.93(2)$, $\gamma = 56.94(2)^\circ$, $V = 665.3(3)$ Å³, $D_c = 2.07$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 6.20$ mm⁻¹; Nb-filtered Mo $K\alpha$ radiation; final $R(F) = 0.053$. The basic structural element consists of a

centrosymmetric dimer with formula Ho₂(C₂H₃O₂)₆·(H₂O)₄. The bonding between dimers consists of hydrogen bonds. The coordination of Ho can be described by a distorted three-vertex trigonal prism with a coordination number of 9. The Ho–O distances range between 2.327 (7) and 2.561 (8) Å. The shortest

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