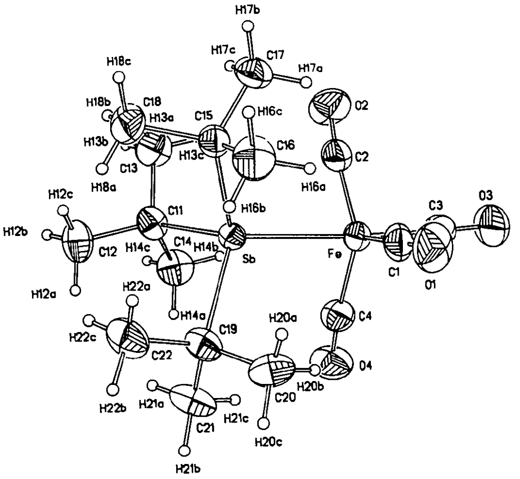

Fig. 1. Molecular structure and labeling scheme for $[Fe(CO)_4\{Sb(tert\text{-}Bu)_3\}]$ showing 50% probability thermal ellipsoids and H atoms with arbitrary radii.

order $Ph_3P > Ph_3As > CO > Ph_3Sb$ could explain the exceptional behavior of Ph_3Sb. Alternatively, it has been shown that sterically demanding R_3E groups favor axial positions (Lichtenberger & Brown, 1977).

Both considerations accurately predict the structure we obtain for $[Fe(CO)_4\{Sb(tert\text{-}Bu)_3\}]$. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular structure is shown in Fig. 1. The $(tert\text{-}Bu)_3Sb$ molecule occupies an axial site; both the σ-donor capacity and steric demands for $(tert\text{-}Bu)_3Sb$ exceed those for Ph_3Sb. The Fe-atom coordination geometry conforms to that expected for a trigonal-bipyramidal structure: the axial–axial angle, Sb—Fe—C(3), is 175·9 (2)°; the average equatorial–equatorial angle is 120·0°; and the average axial–equatorial angle is 90·0°. The closest intramolecular contacts between the stibine molecule and the carbonyl are H(13*c*)—O(2) 2·65, H(16*a*)—O(1) 2·67 and H(21*c*)—O(4) 2·70 Å, and are considerably shorter than the closest contact in $[Os(CO)_4(SbPh_3)]$, 3·04 Å (Martin *et al.*, 1983). The Sb—C bonds are staggered relative to the equatorial Fe—C bonds.

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Structure of Hexaamminecobalt(III) Tris(malonato)ferrate(III) Pentahydrate, $[Co(NH_3)_6][Fe(C_3H_2O_4)_3].5H_2O$

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Abstract. $M_r = 613{\cdot}2$, triclinic, $P\bar{1}$, $a = 8{\cdot}286\ (1)$, $b = 10{\cdot}474\ (2)$, $c = 14{\cdot}922\ (2)$ Å, $\alpha = 102{\cdot}45\ (2)$, $\beta = 94{\cdot}52\ (2)$, $\gamma = 109{\cdot}58\ (2)°$, $V = 1175{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}733$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}41$ mm^{-1}, $F(000) = 638$, $T = 291$ K, $R = 0{\cdot}028$ for 3743 observed reflections. All three six-membered chelate rings of the anion have boat conformations. Essentially octahedrally coordinated Fe is bonded to O at distances of 1·962 (1)–2·022 (1) Å. The cation is centrosymmetric, with Co octahedrally coordinated, Co—N 1·957 (2)–1·970 (2) Å. An extensive hydrogen-bonding network links malonate O atoms and water molecules.

Introduction. The complex was prepared from $[Co(NH_3)_6]Cl_3$, $FeCl_3$ and disodium malonate in

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aqueous solution at room temperature (Powell & Ware, 1984). The anion is known to be photosensitive in solution (Ghosh & Mitra, 1928; van Eldick & van der Berg, 1970), and also undergoes photodecomposition in the solid state, to give Fe^{II} products (Powell & Ware, 1984). This photosensitivity is of interest for non-silver photographic printing processes (Kosar, 1965; Callaby & Brotto, 1970). The anion has also been studied as a model in EXAFS and Mössbauer investigations of polycarboxylate–iron(III) complexes, and as a model for siderophores such as enterobactins, which act as iron transporters in biological systems (Brown, Fronczek, Isied, Nibert & Raymond, 1976; Isied, Kuo & Raymond, 1976). A precise crystal structure of this simple representative of the wide class of polycarboxylate–iron(III) complexes was required as an aid in interpreting the results of these studies.

Experimental. Crystal mounted on glass fibre, 0·23 × 0·29 × 0·54 mm, Stoe–Siemens AED diffractometer, unit-cell parameters from 2θ values of 24 reflections ($20 < 2\theta < 25°$). 6160 reflections measured with $2\theta < 50°$, h −9→3, k −12→12, l −17→17, on-line profile-fitting (Clegg, 1981), no significant intensity variation for three standard reflections, semi-empirical absorption corrections based on ellipsoid model and sets of equivalent reflections measured at different azimuthal angles, transmission 0·65–0·71. 4136 unique reflections ($R_{\rm int} = 0{\cdot}017$), 3743 with $F > 4\sigma(F)$ used in analysis. Structure solved from Patterson and difference syntheses, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0{\cdot}0001F^2$, H atoms constrained to give C—H = 0·96 Å, O—H = N—H = 0·87 Å, $H—X—H = 109{\cdot}5°$, $U({\rm H}) = 1{\cdot}2U_{\rm eq}(X)$, anisotropic thermal parameters for non-H atoms, extinction $x = 3{\cdot}8\,(2) \times 10^{-6}$ $[F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}]$, scattering factors from *International Tables for X-ray Crystallography* (1974). 344 parameters, $R = 0{\cdot}028$, $wR = 0{\cdot}033$, slope of normal probability plot = 1·32, max. $\Delta/\sigma = 0{\cdot}024$, mean = 0·006, largest peak in final difference map = 0·29 e Å^{-3}, largest hole = −0·32 e Å^{-3}. Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1,* molecular-geometry parameters in Table 2. The structure of the anion is shown in Fig. 1.

The cation has the expected octahedral Co coordination. The Fe atom in the anion is also essentially octahedrally coordinated, but each of the O—Fe—O angles within the chelate rings is slightly below 90°. The

Table 1. *Atomic coordinates* (×10^4, Fe ×10^5) *and equivalent isotropic thermal parameters* (Å^2 ×10^4) *with e.s.d.'s in parentheses*

$U_{\rm eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	$U_{\rm eq}$
Co(1)	0	0	0	215 (2)
N(11)	817 (3)	1385 (2)	−724 (1)	283 (7)
N(12)	2361 (2)	−17 (2)	272 (1)	303 (8)
N(13)	548 (3)	1501 (2)	1149 (1)	320 (8)
Co(2)	0	5000	5000	212 (2)
N(21)	388 (3)	3325 (2)	5186 (1)	304 (8)
N(22)	1363 (3)	5008 (2)	3983 (1)	316 (8)
N(23)	−2132 (3)	3783 (2)	4116 (1)	336 (8)
Fe	51769 (4)	21961 (3)	79062 (2)	237 (1)
O(11)	5694 (2)	2259 (2)	6615 (1)	313 (7)
O(12)	6917 (2)	1274 (2)	8013 (1)	287 (6)
O(13)	6760 (2)	1707 (2)	5339 (1)	378 (7)
O(14)	8182 (2)	−232 (2)	7515 (1)	364 (7)
C(11)	6329 (3)	1485 (2)	6080 (2)	266 (9)
C(12)	7260 (3)	440 (2)	7360 (2)	258 (8)
C(13)	6489 (3)	219 (2)	6358 (2)	289 (9)
O(21)	4688 (2)	2164 (2)	9182 (1)	310 (6)
O(22)	6898 (2)	4096 (2)	8419 (1)	334 (6)
O(23)	4419 (2)	3119 (2)	10593 (1)	392 (7)
O(24)	8919 (2)	5900 (2)	9412 (1)	373 (7)
C(21)	5254 (3)	3133 (2)	9947 (2)	258 (9)
C(22)	7638 (3)	4795 (2)	9250 (2)	277 (9)
C(23)	7009 (3)	4271 (3)	10067 (2)	363 (10)
O(31)	3277 (2)	2901 (2)	7642 (1)	339 (7)
O(32)	3337 (2)	249 (2)	7490 (1)	321 (6)
O(33)	667 (2)	2765 (2)	7064 (1)	435 (8)
O(34)	970 (2)	−1448 (2)	6665 (1)	432 (7)
C(31)	1808 (3)	2261 (2)	7098 (2)	302 (9)
C(32)	1938 (3)	−206 (2)	6895 (2)	283 (9)
C(33)	1508 (3)	841 (2)	6450 (2)	316 (9)
O(4)	6853 (3)	1662 (2)	1390 (1)	592 (10)
O(5)	3254 (3)	2994 (2)	3687 (1)	449 (8)
O(6)	4143 (3)	3751 (2)	5598 (1)	509 (9)
O(7)	9281 (3)	4520 (2)	2179 (1)	459 (9)
O(8)	5392 (3)	4140 (2)	2521 (1)	493 (9)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co(1)—N(11)	1·965 (2)	Co(1)—N(12)	1·973 (2)
Co(1)—N(13)	1·963 (2)	Co(2)—N(21)	1·957 (2)
Co(2)—N(22)	1·962 (2)	Co(2)—N(23)	1·970 (2)
Fe—O(11)	2·016 (2)	Fe—O(12)	2·000 (2)
Fe—O(21)	1·982 (2)	Fe—O(22)	1·962 (1)
Fe—O(31)	1·996 (2)	Fe—O(32)	2·022 (1)
O(11)—C(11)	1·282 (3)	O(12)—C(12)	1·279 (3)
O(13)—C(11)	1·232 (3)	O(14)—C(12)	1·240 (3)
C(11)—C(13)	1·514 (4)	C(12)—C(13)	1·516 (3)
O(21)—C(21)	1·284 (2)	O(22)—C(22)	1·280 (3)
O(23)—C(21)	1·230 (3)	O(24)—C(22)	1·241 (2)
C(21)—C(23)	1·508 (3)	C(22)—C(23)	1·502 (4)
O(31)—C(31)	1·286 (3)	O(32)—C(32)	1·282 (3)
O(33)—C(31)	1·230 (4)	O(34)—C(32)	1·232 (3)
C(31)—C(33)	1·518 (3)	C(32)—C(33)	1·520 (4)

N(11)—Co(1)—N(12)	91·1 (1)	N(11)—Co(1)—N(13)	90·9 (1)
N(12)—Co(1)—N(13)	88·2 (1)	N(21)—Co(2)—N(22)	89·6 (1)
N(21)—Co(2)—N(23)	89·2 (1)	N(22)—Co(2)—N(23)	90·4 (1)
O(11)—Fe—O(12)	87·6 (1)	O(11)—Fe—O(21)	179·2 (1)
O(12)—Fe—O(21)	92·5 (1)	O(11)—Fe—O(22)	90·6 (1)
O(12)—Fe—O(22)	93·8 (1)	O(21)—Fe—O(22)	88·6 (1)
O(11)—Fe—O(31)	87·9 (1)	O(12)—Fe—O(31)	172·1 (1)
O(21)—Fe—O(31)	92·0 (1)	O(22)—Fe—O(31)	92·8 (1)
O(11)—Fe—O(32)	94·4 (1)	O(12)—Fe—O(32)	87·2 (1)
O(21)—Fe—O(32)	86·4 (1)	O(22)—Fe—O(32)	174·9 (1)
O(31)—Fe—O(32)	86·6 (1)	Fe—O(11)—C(11)	128·2 (2)
Fe—O(12)—C(12)	127·2 (2)	O(11)—C(11)—O(13)	122·7 (2)
O(11)—C(11)—C(13)	118·2 (2)	O(13)—C(11)—C(13)	119·1 (2)
O(12)—C(12)—O(14)	122·3 (2)	O(12)—C(12)—C(13)	119·9 (2)
O(14)—C(12)—C(13)	117·8 (2)	C(11)—C(13)—C(12)	117·0 (2)
Fe—O(21)—C(21)	130·4 (1)	Fe—O(22)—C(22)	132·4 (2)
O(21)—C(21)—O(23)	121·2 (2)	O(21)—C(21)—C(23)	119·2 (2)
O(23)—C(21)—C(23)	119·6 (2)	O(22)—C(22)—O(24)	121·8 (2)
O(22)—C(22)—C(23)	120·6 (2)	O(24)—C(22)—C(23)	117·6 (2)
C(21)—C(23)—C(22)	120·3 (2)	Fe—O(31)—C(31)	129·2 (2)
Fe—O(32)—C(32)	129·1 (2)	O(31)—C(31)—O(33)	123·0 (2)
O(31)—C(31)—C(33)	117·9 (2)	O(33)—C(31)—C(33)	119·1 (2)
O(32)—C(32)—O(34)	122·5 (3)	O(32)—C(32)—C(33)	117·7 (2)
O(34)—C(32)—C(33)	119·7 (2)	C(31)—C(33)—C(32)	116·0 (2)

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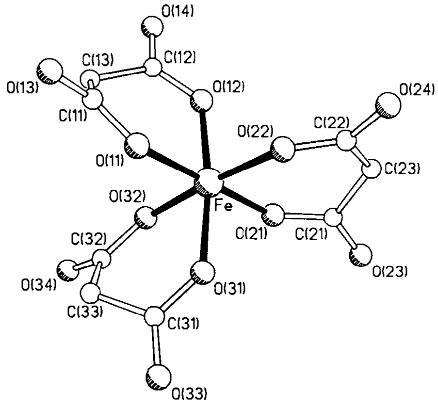

Fig. 1. Structure of the $[Fe(malonate)_3]^{3-}$ anion, viewed along the approximate threefold axis. H atoms are omitted.

anion has approximate D_3 symmetry, as is anticipated for the various classes of compounds for which this is taken as a model.

Each of the three six-membered chelate rings has a boat conformation, the Fe and opposite C atoms both lying on the same side of the mean plane of the other four atoms (Fig. 1). This contrasts with the tris(malonato)manganate(III) ion {studied in $K_3[Mn(malonate)_3].2H_2O$}, for which two rings are boats and the third, lying across a crystallographic twofold rotation axis, has the two O atoms above and below the exact plane of the other four atoms (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977).

The water molecules are involved in extensive hydrogen bonding with the O atoms of the malonate ligands.

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Structure of Bis[*N*,*N*-bis(2-hydroxyethyl)dithiocarbamato]copper(II), $[Cu(C_5H_{10}NO_2S_2)_2]$

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Abstract. $M_r = 423{\cdot}5$, triclinic, $P\bar{1}$, $a = 11{\cdot}946\ (3)$, $b = 7{\cdot}826\ (3)$, $c = 9{\cdot}789\ (4)$ Å, $\alpha = 69{\cdot}65\ (3)$, $\beta = 83{\cdot}06\ (3)$, $\gamma = 81{\cdot}78\ (3)^\circ$, $V = 846{\cdot}66$ Å^3, $Z = 2$, $D_x = 1{\cdot}66$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}706$ mm^{-1}, $F(000) = 434$, $T = 293$ K, $R = 0{\cdot}086$ for 1654 unique observed reflections. The pair of centrosymmetrically related molecules form a dimer. Intradimer short contacts observed [Cu···Cu: 3·451 (2), Cu···S: 2·773 (4) Å] are the shortest reported so far in dimeric Cu^{II} dithiocarbamate complexes. The copper

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