Table 3. *Geometrical data for binuclear copper*(II) *chloroacetate complexes*

Ligand	Urea, $OC(NH_2)_2$	Quinoline NC_9H_7	2-Picoline, $NC_5H_4CH_3$	3-Picoline $NC_5H_4CH_3$	Caffeine, $C_8H_{10}N_4O_2$	Mean value
Cu···Cu (Å)	2·65	2·72	2·75	2·69	2·71	2·70 ±0·04
Basal plane—basal plane (Å)	2·23	2·23	2·23	2·23	2·23	2·23 ±0·00
Cu—basal plane (Å)	0·21	0·25	0·26	0·23	0·24	0·24 ±0·02
Sum of bond lengths Cu—O—C—O—Cu (Å)*	6·49	6·44	6·44	6·43	6·46	6·45 ±0·02
Sum of bond angles Cu—O—C—O—Cu (°)*	375·0	374·3	374·9	374·3	374·0	374·5 ±0·4
Cu—O (Å)*	1·97	1·973	1·974	1·974	1·97	1·974 ±0·004
Cu—N (Å)	2·10	2·211	2·161	2·269	2·23	2·19 ±0·07
Reference	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	

References: (*a*) Ivanov, Simonov, Ablov & Milkova (1974); (*b*) Simonov, Ivanov, Ablov, Milkova & Malinovskii (1976*a*); (*c*) Davey & Stephens (1970); (*d*) Simonov, Milkova, Ablov & Malinovskii (1976*b*); (*e*) present work.

* Where more than one chemically equivalent distance or angle is present, the mean value is tabulated.

In Table 3 are compared some geometric parameters of binuclear complexes of the $(ClCH_2COO)_4Cu_2(L)_2$ type (L = neutral ligand). It is evident that the differences in these geometric parameters are not significant, and thus we can consider these to be constant characteristics of such binuclear complexes.

In the title complex, the caffeine N(9) atom is 0·13 (3) Å out of the Cu, C(4), C(8) plane, indicating a slight deviation from sp^2 hybridization. If the Cu—N(9) bond length is compared with Cu—L bond lengths according to Melník (1982), no effect of the ligand geometry on this bond is observed.

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Tetracarbonyl(tri-*tert*-butylstibine)iron, $[Fe(CO)_4\{Sb(C_4H_9)_3\}]$

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Abstract. $M_r = 460{\cdot}98$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}135$ (3), $b = 10{\cdot}209$ (3), $c = 19{\cdot}224$ (5) Å, $U = 1989{\cdot}1$ (10) Å^3, $Z = 4$, $D_x = 1{\cdot}539$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 21{\cdot}15$ cm^{-1}, $F(000) = 928$, $T = 293$ K, $R = 0{\cdot}032$ for 1992 observed reflections. The tri-*tert*-butylstibine molecule occupies an axial position in the trigonal-bipyramidal complex. The axial–axial angle, Sb—Fe—C, is 175·9 (2)°; the average equatorial–equatorial angle is 120·0°; and the average axial–equatorial angle is 90·0°.

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Introduction. Reactions of cyclopolyphosphines and arsines, *cyclo*$(RE)_n$, R = aryl or alkyl, E = P or As, $n = 4$ to 6, with mononuclear metal carbonyls under moderate conditions ($T < 423$ K) lead to a variety of metal chelates retaining monoorgano-substituted RE groups (West, 1977; Rheingold & Fountain, 1984). In an attempt to extend these studies to include reactions of cyclopolystibines, we have investigated the reactions of $Fe(CO)_5$ with tetra-*tert*-butylcyclotetrastibine (Isslieb, Hamann & Schmidt, 1965; Mundt, Becker, Wessely, Breunig & Kischkel, 1982), the only fully characterized cyclostibine known. Instead of the expected products, we observed an extensive disproportionation of the *tert*-BuSb groups to form Sb mirrors and Sb(*tert*-Bu)$_3$; the latter behaved as a simple two-electron donor and substituted for a CO group on $Fe(CO)_5$ to form [Fe(CO)$_4${Sb(*tert*-Bu)$_3$}], the structure of which we now report.

Experimental. 1·33 g *cyclo*(*tert*-BuSb)$_4$ and 0·392 g $Fe(CO)_5$ were combined with 20 ml toluene in a heavy-wall Carius tube; the contents were degassed, evacuated and the tube sealed. After heating for 2 h at 403 K, the tube was cooled to room temperature, the contents evaporated to dryness and extracted with hexane. Pale-yellow crystals of [Fe(CO)$_4${Sb(*tert*-Bu)$_3$}] were obtained on evaporation of the solvent. IR (hexane) carbonyl: 2050, 2018, 1961, 1924 cm^{-1}; ^{1}H NMR (CH_2Cl_2): $\delta = 1{\cdot}54$, singlet; m.p.: 453–463 K (dec.).

Crystal 0·22 × 0·26 × 0·32 mm from hexane mounted on glass fiber. Nicolet $R3$, graphite monochromator, unit cell from least-squares fit of angular settings of 25 reflections ($21 < 2\theta < 25°$). 2155 reflections ($4 \leq 2\theta \leq 52°$) for $0 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 23$. No decay of three standard reflections, semi-empirical absorption correction (transmission 0·47 to 0·50) based on measurements of six equivalent reflections at different azimuthal angles, $R_{\rm int} = 0{\cdot}0086$. 1992 observed unique reflections [$F_o \geq 2{\cdot}5\sigma(F_o)$] from 2132 unique collected. Direct methods (*SOLV*), blocked-cascade least squares, 200 parameters, $w^{-1} = \sigma^2(F) + 0{\cdot}0001\,F^2$, neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), C—H = 0·96 Å, U(H) = 1·2 $U_{\rm eq}$(C), non-H atoms anisotropic, no extinction correction necessary, $R = 0{\cdot}032$, $wR = 0{\cdot}030$, function minimized $\sum w(|F_o|-|F_c|)^2$, final $\Delta/\sigma = 0{\cdot}04$, largest peak in final difference map 0·33 e Å^{-3}, largest trough 0·37 e Å^{-3}, deviation in observation of unit weight = 1·706, *SHELXTL* (Sheldrick, 1984).

Discussion. Most crystallographic studies of $LM(CO)_4$ complexes (M = Fe, Ru or Os; L = Group Va ligand) reveal approximate trigonal-bipyramidal geometry about the metal atom with L occupying an axial position. An exception to this generalization is [Os(CO)$_4$(SbPh$_3$)], in which triphenylstibine occupies an equatorial site (Martin, Einstein & Pomeroy, 1983). To account for this atypical complex two factors were considered. Theoretical studies indicate that in d^8 trigonal-bipyramidal complexes the weaker σ-donor ligand should occupy an equatorial position (Rossi & Hoffmann, 1975; Burdett, 1976); a donor-strength

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	$U_{\rm eq}$*
Sb	2580·2 (4)	−609·1 (4)	6425·7 (2)	37 (1)
Fe	4588·2 (9)	587·2 (10)	5945·5 (5)	47 (1)
C(1)	4269 (8)	−150 (7)	5118 (4)	59 (3)
C(2)	5588 (7)	−179 (7)	6599 (4)	66 (3)
C(3)	6020 (8)	1298 (7)	5607 (4)	68 (3)
C(4)	3850 (7)	2155 (7)	6133 (4)	63 (3)
O(1)	4135 (6)	−555 (7)	4566 (3)	91 (2)
O(2)	6317 (5)	−605 (7)	6994 (3)	94 (2)
O(3)	6973 (5)	1732 (6)	5385 (3)	104 (3)
O(4)	3458 (5)	3164 (5)	6217 (3)	88 (2)
C(11)	2302 (8)	−290 (7)	7566 (3)	54 (2)
C(12)	927 (7)	−729 (9)	7791 (4)	76 (3)
C(13)	3332 (8)	−1088 (8)	7957 (3)	73 (3)
C(14)	2544 (10)	1148 (6)	7709 (3)	71 (3)
C(15)	2731 (7)	−2750 (6)	6273 (3)	51 (2)
C(16)	2451 (9)	−3075 (6)	5507 (3)	74 (3)
C(17)	4151 (7)	−3163 (7)	6427 (4)	71 (3)
C(18)	1765 (8)	−3511 (7)	6733 (4)	74 (3)
C(19)	709 (7)	36 (7)	5922 (4)	58 (3)
C(20)	949 (9)	138 (8)	5147 (4)	74 (3)
C(21)	344 (8)	1395 (7)	6199 (4)	75 (3)
C(22)	−431 (7)	−945 (7)	6077 (4)	73 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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

Sb—Fe	2·547 (1)	Sb—C(11)	2·234 (6)
Sb—C(15)	2·210 (6)	Sb—C(19)	2·229 (7)
Fe—C(1)	1·788 (8)	Fe—C(2)	1·793 (7)
Fe—C(3)	1·748 (8)	Fe—C(4)	1·803 (7)
C(1)—O(1)	1·149 (9)	C(2)—O(2)	1·146 (9)
C(3)—O(3)	1·146 (10)	C(4)—O(4)	1·116 (9)
C(11)—C(12)	1·525 (11)	C(11)—C(13)	1·523 (10)
C(11)—C(14)	1·514 (10)	C(15)—C(16)	1·537 (8)
C(15)—C(17)	1·528 (10)	C(15)—C(18)	1·531 (10)
C(19)—C(20)	1·512 (11)	C(19)—C(21)	1·531 (10)
C(19)—C(22)	1·558 (10)		

Fe—Sb—C(11)	112·8 (2)	Fe—Sb—C(15)	111·8 (2)
C(11)—Sb—C(15)	106·4 (2)	Fe—Sb—C(19)	112·4 (2)
C(11)—Sb—C(19)	106·0 (3)	C(15)—Sb—C(19)	107·1 (2)
Sb—Fe—C(1)	88·6 (3)	Sb—Fe—C(2)	89·3 (2)
C(1)—Fe—C(2)	122·8 (3)	Sb—Fe—C(3)	175·9 (2)
C(1)—Fe—C(3)	89·6 (4)	C(2)—Fe—C(3)	88·5 (3)
Sb—Fe—C(4)	91·2 (2)	C(1)—Fe—C(4)	118·4 (3)
C(2)—Fe—C(4)	118·8 (3)	C(3)—Fe—C(4)	92·9 (3)
Fe—C(1)—O(1)	174·6 (7)	Fe—C(2)—O(2)	174·0 (7)
Fe—C(3)—O(3)	178·2 (7)	Fe—C(4)—O(4)	174·9 (7)
Sb—C(11)—C(12)	110·5 (4)	Sb—C(11)—C(13)	108·7 (4)
C(12)—C(11)—C(13)	109·2 (6)	Sb—C(11)—C(14)	107·4 (4)
C(12)—C(11)—C(14)	112·4 (7)	C(13)—C(11)—C(14)	108·5 (6)
Sb—C(15)—C(16)	109·1 (4)	Sb—C(15)—C(17)	108·2 (4)
C(16)—C(15)—C(17)	107·4 (6)	Sb—C(15)—C(18)	112·4 (4)
C(16)—C(15)—C(18)	109·0 (6)	C(17)—C(15)—C(18)	110·5 (5)
Sb—C(19)—C(20)	108·1 (5)	Sb—C(19)—C(21)	108·8 (5)
C(20)—C(19)—C(21)	108·6 (6)	Sb—C(19)—C(22)	111·0 (5)
C(20)—C(19)—C(22)	110·6 (6)	C(21)—C(19)—C(22)	109·7 (6)

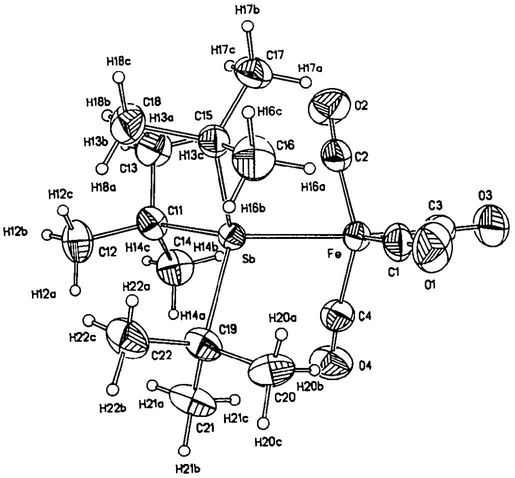

Fig. 1. Molecular structure and labeling scheme for $[Fe(CO)_4\{Sb(\textit{tert}\text{-}Bu)_3\}]$ showing 50% probability thermal ellipsoids and H atoms with arbitrary radii.

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 $[Fe(CO)_4\{Sb(\textit{tert}\text{-}Bu)_3\}]$. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular structure is shown in Fig. 1. The $(\textit{tert}\text{-}Bu)_3Sb$ molecule occupies an axial site; both the σ-donor capacity and steric demands for $(\textit{tert}\text{-}Bu)_3Sb$ 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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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42171 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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. $M_r = 613·2$, triclinic, $P\bar{1}$, $a = 8·286$ (1), $b = 10·474$ (2), $c = 14·922$ (2) Å, $\alpha = 102·45$ (2), $\beta = 94·52$ (2), $\gamma = 109·58$ (2)°, $V = 1175·3$ Å^3, $Z = 2$, $D_x = 1·733$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·41$ mm^{-1}, $F(000) = 638$, $T = 291$ K, $R = 0·028$ 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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