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Synthesis, Structure, and Bonding of a Cubanelike Sb_4Cl_4 Molecular Complex, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$, Containing Quadruply Bridging Chlorine Atoms

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The $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ charge-transfer complex is a by-product in the reaction of $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ with $SbCl_3$. In the solid state, this 4:4 molecular complex between $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ and $SbCl_3$ possesses a Sb_4Cl_4 cubanelike framework with four antimony and four chlorine atoms occupying alternate corners of a tetragonally distorted cube; the mean value of the Cl→Sb bonds which constitute the 12 edges of the cube is 3.27 Å. The structural features of the bridging chlorine and antimony atoms are examined relative to (1) the rare bonding mode of the quadruply bridging chlorine atoms which are tetrahedrally coordinated to four metal atoms and (2) an assessment of the extent of steric activity of the lone valence electron pair of each hexacoordinate Sb(III). Crystals of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ are orthorhombic with four formula species in a unit cell of symmetry *Aba2* (nonstandard axial setting of *C2ca*) and dimensions $a = 15.282$ (3), $b = 15.215$ (3), and $c = 23.191$ (6) Å. The structure was solved by the heavy-atom method and refined to $R_1 = 5.1\%$ and $R_2 = 3.6\%$ based on 1614 independent intensities with $I \geq 2\sigma(I)$.

Introduction

The ability of antimony trichloride to form molecular complexes (also called electron donor–acceptor complexes or charge-transfer complexes)[2] has been known for many years. As early as 1882, Smith and Davies[3,4] reported a complex between antimony trichloride and naphthalene. In the solid state the antimony trihalides have a great tendency either to combine with additional halide ions to give anionic complexes (e.g., the $SbCl_5^{2-}$ dianion[5]) or to form neutral adducts when electron donors are available.[4,6]

This paper describes the preparation and characterization of an unusual 4:4 iron–antimony complex formed from $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ and $SbCl_3$, which with a cubanelike Sb_4Cl_4 core exemplifies a rare instance of halogen atoms tetrahedrally bonded to four metal atoms (i.e., other kinds of species containing tetrahedrally coordinated chlorine atoms include ClO_4^- and ClO_3F in which the chlorine atom is bonded to electronegative nonmetallic atoms and cuprous chloride which possesses the zinc blende structure). The synthesis and structural characterization of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ were connected to our research on transition metal–antimony complexes[1,7] as part of a systematic study to obtain new metal cluster systems. Subsequent to an initial presentation[1] of the results given here, Cullen and co-workers[8] have described an extensive investigation of the reactions of antimony trihalides with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ from which they obtained a number of species including both neutral and ionic complexes. One of their isolated products was another electron donor–acceptor complex between $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ and $SbCl_3$, viz., a 4:2 iron–antimony complex of composition $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_2$; its molecular geometry was established by Einstein and MacGregor[9] from an x-ray diffraction study which revealed the chlorine atoms of the four $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ groups to be bridged to either one or two hexacoordinate antimony atoms.[10] This work has provided an opportunity to examine closely the bonding nature of the bridging chlorine and the antimony atoms in these molecular

complexes including an assessment of the extent of steric activity of the lone valence electron pairs of the hexacoordinate Sb(III) atoms.

Experimental Section

Preparation and Properties. The reaction of $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ with $SbCl_3$ in THF yields a variety of compounds.[1,7b] When the reaction mixture was sublimed under vacuum at room temperature, an orange substance wetted by the THF was obtained on the cold finger. It was redissolved in hexane, dried, and resublimed at room temperature to give red crystals of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ in low yields. The crystals once obtained could not be resublimed at room temperature. Evidence that the adduct was formed by the cosublimation of the intermediate product $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ and the unreacted $SbCl_3$ starting material is given by the fact that $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ was found abundantly in the reaction mixture. The isolated solid is stable in dry air but, being very hygroscopic, is readily destroyed by humidity. It has a melting point of 84 °C dec, compared to 73.4 °C for $SbCl_3$[11] and 87 °C for $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$.[12]

A mass spectrum[13] of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ was obtained from an AEI Model MS-902 mass spectrometer under operating conditions of 70 eV of electron energy and a probe temperature of 40 °C with samples introduced into the ion source by a direct-inlet system. Besides the major m/e peaks corresponding to $SbCl_3^+$, $SbCl_2^+$, $SbCl^+$, Sb^+, $Fe(C_5H_5)(CO)_2Cl^+$, $Fe(C_5H_5)(CO)Cl^+$, $Fe(C_5H_5)Cl^+$, $Fe(C_5H_5)(CO)_2^+$, $Fe(C_5H_5)(CO)^+$, $Fe(C_5H_5)^+$, $Fe(C_3H_3)^+$, Fe^+, and CO^+, smaller peaks with correct isotopic abundance could be assigned to $Fe(C_5H_5)(CO)_2SbCl_2^+$, $Fe(C_5H_5)(CO)SbCl_2^+$, and $Fe(C_5H_5)SbCl_2^+$ species.

Single-Crystal X-Ray Data Collection. A suitable crystal with morphology approximating a bicapped tetragonally flattened octahedron was coated with Canadian balsam and mounted on the end of a glass fiber. This crystal was kept in a nitrogen atmosphere until the balsam dried before exposure to air.

Preliminary precession and Weissenberg photographs showed D_{2h}-*mmm* Laue symmetry characteristic of the orthorhombic system. This crystal of approximate dimensions 0.15 (corresponding to the c direction as the rotation axis) × 0.20 × 0.17 mm was then transferred to a General Electric full-circle Datex-controlled diffractometer; the crystal alignment and the collection and treatment of the intensity
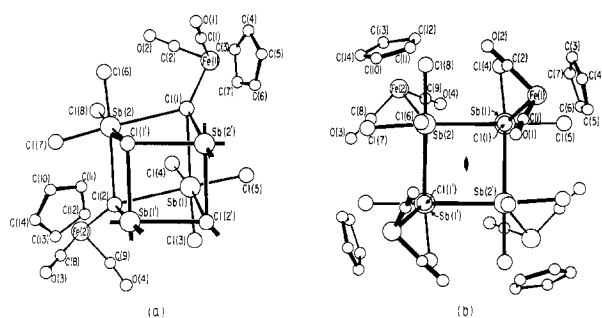
Figure 1. (a) General view and atomic numbering scheme of the $[Fe(\eta^5-C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ molecular complex. For clarity, only half of the terminal ligands to the Sb_4Cl_4 framework are shown. (b) View down the crystallographic twofold axis of the molecule which ideally conforms to $S_4-\bar{4}$ symmetry.

data have been previously described.[7b] All intensity data were recorded via the $\theta-2\theta$ scan technique with symmetric 2θ scans at $2°/\text{min}$ rate and with stationary-crystal, stationary-counter background counts of 15 s taken at the beginning and the end of each scan. The radiation used was Zr-filtered Mo $K\alpha$ (λ 0.710 69 Å). Data were collected to $2\theta \leq 47°$ with a uniform scan range of $1.75°$. Since calculated transmission coefficients[14] (based on a linear absorption coefficient[15a] for Mo $K\alpha$ radiation of 38.9 cm^{-1}) ranged from 0.52 to 0.62 (corresponding to only a $\pm 4\%$ fluctuation in the $|F_o|$'s), absorption corrections were neglected. Of the 2056 crystallographically independent reflections (comprising one octant), the 1614 reflections for which $I_o \geq 2\sigma(I)$ were used in the structural analysis and least-squares refinement.

Unit Cell and Space Group. Lattice constants (measured at ~ 22 °C) and their estimated uncertainties were determined by least-squares refinement of the angle settings of 24 selected reflections.[14] These orthorhombic cell parameters are $a = 15.282$ (3) Å, $b = 15.215$ (3) Å, $c = 23.191$ (6) Å; the volume of the unit cell is 5394 $Å^3$. The density of 2.19 g/cm^3 calculated on the basis of four tetrameric molecules per cell ($Z = 4$) agrees well with the experimental value of 2.17 g/cm^3 determined by the flotation method. The total number of electrons per unit cell, $F(000)$, is 3328.

Systematic absences of $\{hkl\}$ for $k + l = 2n + 1$, $\{0kl\}$ for $k = 2n + 1$, and $\{h0l\}$ for $h = 2n + 1$ indicate the possible space groups as either $Aba2$ (C_{2v}^{17}, No. 41; nonstandard axial setting of $C2ca$) or $Abam$ (D_{2h}^{18}, No. 64; nonstandard axial setting of $Cmca$). The choice of the noncentrosymmetric space group $Aba2$ was later verified by the successful refinement of the determined structure. Its solution required the location of 2 antimony, 2 iron, 8 chlorine, 4 oxygen, 14 carbon, and ideally 10 hydrogen atoms (corresponding to half of a tetrameric molecule) each occupying the following general eightfold set of positions: $(0, 0, 0; 0, 1/2, 1/2) + (x, y, z; \bar{x}, \bar{y}, z; 1/2 - x, 1/2 + y, z; 1/2 + x, 1/2 - y, z)$.

Determination of the Structure. The structure was solved by the application of the usual Patterson and heavy-atom Fourier techniques. An interpretation of a computed three-dimensional sharpened Patterson map[14] revealed the fractional coordinates of the two independent

antimony atoms. With the z coordinate of one antimony atom fixed in order to define the origin along the c axis, two cycles of least-squares refinement[14] based on these initial fractional coordinates of the antimony atoms resulted in an R_1 of 34.7% and an R_2 of 43.5%.[16] A composite of Fourier syntheses and least-squares refinement[17] led to the location and refinement of the remaining nonhydrogen atoms. The thermal parameters of the antimony, iron, and chlorine atoms were refined anisotropically while those of the oxygen and carbon atoms were refined isotropically. The final descrepancy factors were $R_1 = 5.2\%$ and $R_2 = 3.6\%$ with no parameters changing in the last cycle by more than 0.25σ. A three-dimensional Fourier difference map based on this anisotropic–isotropic refinement showed no unusual features. No attempt was made to identify the hydrogen atoms of the cyclopentadienyl rings. Equations of least-squares planes for the cyclopentadienyl rings were determined by a least-squares method.[14]

The positional and thermal parameters with their esd's obtained from the output of the last least-squares cycle are presented in Table I. Interatomic distances and bond angles together with their esd's are listed in Table II. The observed and calculated structure factors are given elsewhere (supplementary material).

Results and Discussion

General Description of the Crystal Structure. Crystalline $[Fe(\eta^5-C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ is constructed of discrete molecules whose geometry, which is constrained by a crystallographic twofold axis, is displayed in Figure 1. In this 4:4 iron–antimony complex the antimony atoms of four $SbCl_3$ units and the chlorine atoms of four $Fe(\eta^5-C_5H_5)(CO)_2Cl$ units occupy alternate apices of a distorted cube. The Sb–Cl bonds which constitute the 12 edges of the resulting cubic Sb_4Cl_4 core have lengths ranging from 3.175 (5) to 3.375 (5) Å with the mean value of 3.24 Å, which is ca. 0.35 Å shorter than the nonbonding Sb⋯Cl van der Waals distance[18,19a] reflecting definite charge-transfer interactions between these atoms in the solid state.

A stereoscopic view of the unit cell is shown in Figure 2. All intermolecular distances are normal van der Waals contacts with the shortest one being 3.29 Å for an O(1)⋯C(13) separation.

The $Fe(\eta^5-C_5H_5)(CO)_2Cl$ Moiety. Each iron atom of the two crystallographically independent $Fe(\eta^5-C_5H_5)(CO)_2Cl$ fragments in this tetrameric molecule exhibits an approximate octahedral-like environment with one chlorine atom and two carbonyl groups occupying three positions and the η^5-cyclopentadienyl ring (assumed to sterically function as a tridentate ligand) occupying the three other sites. The bond angles of the monodentate ligands are expectedly clustered near 90° with a mean value of 94.2° for the Cl–Fe–CO bond angles and a mean value of 90.9° for the OC–Fe–CO bond angles in the two independent $Fe(\eta^5-C_5H_5)(CO)_2Cl$ moieties.

The two independent Fe–Cl bond lengths are 2.301 (5) and 2.320 (5) Å. The mean Fe–CO and C–O bond lengths of 1.74 and 1.16 Å, respectively, and the average Fe–C–O bond angle
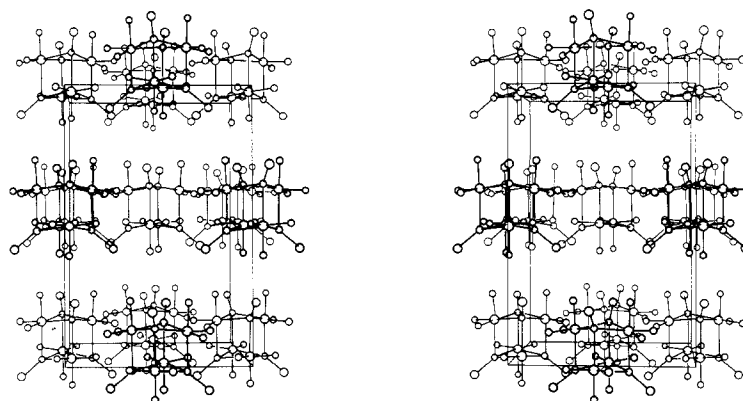

Figure 2. Stereoscopic view of the orthorhombic unit cell showing the packing arrangment of the four discrete $[Fe(\eta^5-C_5H_5)(CO)_2Cl]_4-[SbCl_3]_4$ molecules per cell.

Table I. Final Atomic Parameters with Estimated Standard Deviations[a]

Atom	x	y	z	B, Å^2
Sb(1)	0.0308 (1)	0.3537 (1)	0.0000	b
Sb(2)[c]	0.3561 (1)	0.0312 (1)	0.1284 (1)	b
Fe(1)	0.0491 (2)	0.2416 (2)	0.2107 (1)	b
Fe(2)[c]	0.2584 (2)	0.0390 (2)	0.4185 (1)	b
Cl(1)	0.0314 (3)	0.3542 (3)	0.1455 (2)	b
Cl(2)	0.1434 (3)	0.0273 (3)	0.4833 (2)	b
Cl(3)	0.0311 (4)	0.3448 (4)	−0.1008 (3)	b
Cl(4)	0.1658 (3)	0.2827 (3)	0.0102 (3)	b
Cl(5)	−0.0512 (4)	0.2225 (3)	0.0090 (3)	b
Cl(6)	0.3474 (4)	0.0378 (4)	0.2299 (3)	b
Cl(7)	0.2843 (3)	0.1656 (3)	0.1148 (3)	b
Cl(8)	0.2262 (3)	−0.0534 (4)	0.1228 (3)	b
O(1)	−0.0069 (12)	0.3441 (11)	0.3101 (9)	9.6 (5)
O(2)	0.2286 (13)	0.2828 (10)	0.2374 (8)	10.4 (5)
O(3)	0.2160 (10)	0.2178 (12)	0.3824 (8)	9.8 (5)
O(4)	0.1663 (10)	−0.0302 (11)	0.3197 (9)	9.2 (5)
C(1)	0.0150 (15)	0.3060 (15)	0.2691 (10)	6.5 (5)
C(2)	0.1567 (16)	0.2652 (16)	0.2258 (11)	7.5 (6)
C(3)	0.0845 (12)	0.1107 (11)	0.2008 (8)	4.7 (4)
C(4)	0.0224 (13)	0.1189 (13)	0.2468 (9)	5.9 (5)
C(5)	−0.0541 (13)	0.1509 (13)	0.2205 (9)	6.0 (5)
C(6)	−0.0375 (13)	0.1624 (12)	0.1630 (9)	5.6 (5)
C(7)	0.0521 (11)	0.1383 (11)	0.1505 (8)	5.0 (4)
C(8)	0.2317 (17)	0.1450 (17)	0.3978 (11)	8.1 (6)
C(9)	0.1985 (16)	−0.0053 (15)	0.3604 (11)	7.7 (6)
C(10)	0.3585 (12)	0.0469 (11)	0.4820 (8)	4.5 (4)
C(11)	0.3343 (11)	−0.0444 (11)	0.4744 (8)	4.6 (4)
C(12)	0.3474 (12)	−0.0677 (12)	0.4170 (9)	5.4 (5)
C(13)	0.3830 (12)	0.0090 (12)	0.3850 (8)	4.6 (4)
C(14)	0.3879 (12)	0.0776 (12)	0.4275 (8)	4.9 (4)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sb(1)	453 (6)	420 (6)	159 (3)	−10 (7)	−14 (4)	−44 (4)
Sb(2)	398 (6)	470 (6)	157 (3)	21 (7)	31 (4)	11 (4)
Fe(1)	449 (14)	448 (14)	188 (6)	11 (13)	21 (8)	5 (8)
Fe(2)	465 (14)	370 (12)	180 (6)	10 (14)	−7 (8)	14 (8)
Cl(1)	527 (27)	423 (25)	198 (13)	−118 (24)	−5 (14)	41 (13)
Cl(2)	442 (26)	484 (27)	211 (13)	60 (24)	53 (13)	4 (13)
Cl(3)	1165 (49)	1006 (44)	162 (13)	−211 (44)	7 (21)	−76 (19)
Cl(4)	536 (28)	516 (25)	449 (19)	95 (22)	−72 (20)	−54 (19)
Cl(5)	803 (36)	609 (31)	318 (16)	−306 (29)	−4 (22)	−75 (19)
Cl(6)	846 (39)	1099 (45)	158 (13)	−191 (39)	39 (18)	4 (19)
Cl(7)	587 (28)	563 (30)	394 (18)	183 (24)	59 (18)	81 (18)
Cl(8)	619 (30)	758 (33)	287 (14)	−226 (26)	26 (19)	26 (20)

[a] In this and the following table the estimated standard deviations of the least significant figures are given in parentheses. [b] Anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ were used for the antimony, iron, and chlorine atoms; the resulting thermal coefficients (×10^5) are given in the second part of this table. [c] Sb(2), Cl(6), Cl(7), and Cl(8) atoms discussed in the text as well as illustrated in the figures were generated from the coordinates in this table by the symmetry operation $^1/_2 - x$, $^1/_2 + y$, z; Fe(2), Cl(2), O(3), O(4), C(8), C(9), C(10), C(11), C(12), C(13), and C(14) atoms were generated by x, $^1/_2 + y$, $-^1/_2 + z$. The "prime" set was obtained by the crystallographic twofold axis $2_c(0, b/2)$ from the "unprime" set.

of 176.0° are consistent with values obtained from the 4:2 iron–antimony complex[9] and other molecules containing Fe(η^5-C₅H₅)(CO)₂ groups.[20] Although various orientations of the cyclopentadienyl ligands with respect to the one chlorine and two carbonyl ligands of each iron are possible, it was found (Figure 3) that the two Fe(η^5-C₅H₅)(CO)₂Cl fragments are essentially mirror images of each other. The carbon atoms of the cyclopentadienyl rings are coplanar within 0.01 Å. The Fe–C distances of 2.11 Å (average) and the C–C ring distances of 1.42 Å (average) are not different from those in other cyclopentadienyliron dicarbonyl complexes.[20]

The SbCl₃ Moiety. The geometry of the two independent SbCl₃ moieties in the 4:4 iron–antimony complex does not differ significantly from that of the corresponding fragments in the pure crystalline SbCl₃[21,22] and in the 4:2 iron–antimony complex.[9] The Sb–Cl distances range from 2.340 (5) to 2.370 (5) Å with a mean value of 2.353 Å which is 0.03 Å shorter than the corresponding mean value of 2.383 Å in the 4:2 iron–antimony complex.[9] In each SbCl₃ part of the 4:4

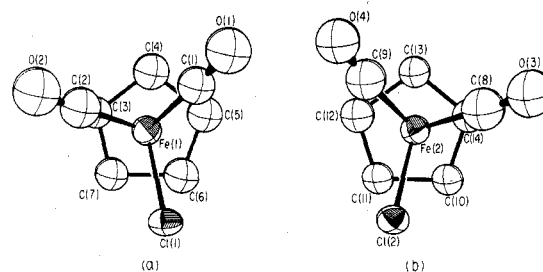**Figure 3.** Local environment about each of the two crystallographically independent iron atoms projected normal to the plane of the cyclopentadienyl ring. All atoms are represented by 40% probability ellipsoids of thermal displacement.

iron–antimony complex the Sb–Cl bonds are almost orthogonal to one another.

It is informative that the Sb–Cl bond lengths and Cl–Sb–Cl bond angles of the SbCl₃ molecule in the gaseous state were

Table II. Interatomic Distances and Bond Angles[a]

A. Intramolecular Bonding Distances (Å)

Sb(1)–Cl(1)	3.375 (5)		Fe(1)–C(3)	2.08 (2)
Sb(2)–Cl(2)	3.366 (5)		Fe(1)–C(4)	2.09 (2)
	Av 3.371		Fe(1)–C(5)	2.11 (2)
			Fe(1)–C(6)	2.10 (2)
Sb(1)–Cl(2)	3.175 (5) ⎱		Fe(1)–C(7)	2.10 (2)
Sb(2)–Cl(1')	3.221 (5) ⎰			Av 2.10
Sb(1)–Cl(2')	3.243 (5) ⎱			
Sb(2)–Cl(1)	3.219 (4) ⎰		Fe(2)–C(10)	2.13 (2)
	Av 3.215		Fe(2)–C(11)	2.15 (2)
			Fe(2)–C(12)	2.12 (2)
Sb(1)–Cl(3)	2.342 (6)		Fe(2)–C(13)	2.11 (2)
Sb(2)–Cl(6)	2.359 (6)		Fe(2)–C(14)	2.08 (2)
	Av 2.351			Av 2.12
Sb(1)–Cl(4)	2.340 (5) ⎱		C(3)–C(4)	1.43 (2)
Sb(2)–Cl(7)	2.343 (5) ⎰		C(4)–C(5)	1.41 (2)
Sb(1)–Cl(5)	2.366 (5) ⎱		C(5)–C(6)	1.37 (3)
Sb(2)–Cl(8)	2.370 (5) ⎰		C(6)–C(7)	1.45 (2)
	Av 2.355		C(7)–C(3)	1.34 (2)
				Av 1.40
Fe(1)–Cl(1)	2.301 (5)			
Fe(2)–Cl(2)	2.320 (5)		C(10)–C(11)	1.45 (2)
	Av 2.311		C(11)–C(12)	1.39 (2)
			C(12)–C(13)	1.49 (2)
Fe(1)–C(1)	1.75 (2)		C(13)–C(14)	1.44 (2)
Fe(1)–C(2)	1.72 (3)		C(14)–C(10)	1.42 (2)
Fe(2)–C(8)	1.73 (3)			Av 1.44
Fe(2)–C(9)	1.76 (3)			
	Av 1.74			
C(1)–O(1)	1.16 (2)			
C(2)–O(2)	1.16 (2)			
C(8)–O(3)	1.19 (3)			
C(9)–O(4)	1.13 (2)			
	Av 1.16			

B. Intramolecular Bond Angles (deg)

Cl(2)–Sb(1)–Cl(2')	88.0 (1)		Sb(2)–Cl(1)–Sb(2')	88.6 (1)
Cl(1)–Sb(2)–Cl(1')	89.7 (1)		Sb(1)–Cl(2)–Sb(1')	90.3 (1)
	Av 88.9			Av 89.4
Cl(1)–Sb(1)–Cl(2)	96.8 (1) ⎱		Sb(1)–Cl(1)–Sb(2)	83.1 (1) ⎱
Cl(2)–Sb(2)–Cl(1')	97.5 (1) ⎰		Sb(1')–Cl(2)–Sb(2)	82.7 (1) ⎰
Cl(1)–Sb(1)–Cl(2')	96.9 (1) ⎱		Sb(1)–Cl(1)–Sb(2')	82.9 (1) ⎱
Cl(1)–Sb(2)–Cl(2)	96.1 (1) ⎰		Sb(1)–Cl(2)–Sb(2)	83.9 (1) ⎰
	Av 96.8			Av 83.2
Cl(4)–Sb(1)–Cl(5)	93.9 (2)		Fe(1)–Cl(1)–Sb(1)	131.0 (2)
Cl(7)–Sb(2)–Cl(8)	94.3 (2)		Fe(2)–Cl(2)–Sb(2)	130.1 (2)
	Av 94.1			Av 130.6
Cl(3)–Sb(1)–Cl(4)	94.2 (2) ⎱		Fe(1)–Cl(1)–Sb(2)	129.9 (2) ⎱
Cl(6)–Sb(2)–Cl(7)	94.1 (2) ⎰		Fe(2)–Cl(2)–Sb(1')	131.0 (2) ⎰
Cl(3)–Sb(1)–Cl(5)	92.3 (2) ⎱		Fe(1)–Cl(1)–Sb(2')	125.6 (2) ⎱
Cl(6)–Sb(2)–Cl(8)	91.7 (2) ⎰		Fe(2)–Cl(2)–Sb(1)	123.6 (2) ⎰
	Av 93.1			Av 127.5
Cl(3)–Sb(1)–Cl(2)	85.7 (2) ⎱		Cl(1)–Fe(1)–C(1)	93.2 (7)
Cl(6)–Sb(2)–Cl(1')	84.4 (2) ⎰		Cl(2)–Fe(2)–C(9)	94.1 (8)
Cl(3)–Sb(1)–Cl(2')	85.7 (2) ⎱		Cl(1)–Fe(1)–C(2)	95.2 (9)
Cl(6)–Sb(2)–Cl(1)	86.7 (2) ⎰		Cl(2)–Fe(2)–C(8)	94.1 (9)
	Av 85.6			Av 94.2
Cl(4)–Sb(1)–Cl(2)	85.4 (1) ⎱		Fe(1)–C(1)–O(1)	175.6 (22)
Cl(7)–Sb(2)–Cl(1')	86.2 (2) ⎰		Fe(1)–C(2)–O(2)	177.8 (25)
Cl(5)–Sb(1)–Cl(2')	92.7 (2) ⎱		Fe(2)–C(8)–O(3)	177.5 (24)
Cl(8)–Sb(2)–Cl(1)	90.0 (2) ⎰		Fe(2)–C(9)–O(4)	173.0 (23)
	Av 88.6 (av)			Av 176.0
Cl(4)–Sb(1)–Cl(1)	84.1 (2) ⎱		C(3)–C(4)–C(5)	104.9 (18)
Cl(7)–Sb(2)–Cl(2)	83.2 (2) ⎰		C(4)–C(5)–C(6)	108.2 (18)
Cl(5)–Sb(1)–Cl(1)	85.1 (2) ⎱		C(5)–C(6)–C(7)	109.8 (17)
Cl(8)–Sb(2)–Cl(2)	86.4 (2) ⎰		C(6)–C(7)–C(3)	104.7 (16)
	Av 84.7		C(7)–C(3)–C(4)	112.2 (17)
				Av 108.0
Cl(3)–Sb(1)–Cl(1)	176.8 (2)			
Cl(6)–Sb(2)–Cl(2)	176.6 (2)		C(10)–C(11)–C(12)	108.9 (16)
	Av 176.7		C(11)–C(12)–C(13)	109.3 (17)
			C(12)–C(13)–C(14)	104.2 (16)
Cl(4)–Sb(1)–Cl(2')	173.4 (2) ⎱		C(13)–C(14)–C(10)	110.8 (16)
Cl(7)–Sb(2)–Cl(1)	175.7 (2) ⎰		C(14)–C(10)–C(11)	106.8 (15)
Cl(5)–Sb(1)–Cl(2)	177.9 (2) ⎱			Av 108.0
Cl(8)–Sb(2)–Cl(1')	176.1 (2) ⎰			
	Av 175.8			

Table II *(Continued)*

C. Intramolecular Nonbonding Distances (Å)

Cl(3)···Cl(4)	3.428 (9) ⎱	Cl(2)···C(9)	3.01 (2)
Cl(6)···Cl(7)	3.441 (8) ⎰	Cl(2)···C(10)	3.30 (2)
Cl(3)···Cl(5)	3.396 (9) ⎱	Cl(2)···C(11)	3.12 (2)
Cl(6)···Cl(8)	3.394 (9) ⎰	C(1)···C(2)	2.47 (3)
	Av 3.415	C(1)···C(4)	2.90 (3)
		C(1)···C(5)	2.82 (3)
Cl(4)···Cl(5)	3.440 (7)	C(1)···C(6)	3.39 (3)
Cl(7)···Cl(8)	3.454 (7)	C(2)···C(3)	2.66 (3)
	Av 3.447	C(2)···C(4)	3.07 (3)
Cl(3)···O(4)	3.36 (2)	C(2)···C(7)	3.05 (3)
Cl(6)···O(1)	3.41 (2)	C(8)···C(9)	2.50 (4)
Cl(1)···C(1)	2.97 (2)	C(8)···C(10)	3.13 (3)
Cl(1)···C(2)	2.99 (3)	C(8)···C(13)	3.12 (3)
Cl(1)···C(6)	3.13 (2)	C(8)···C(14)	2.69 (3)
Cl(1)···C(7)	3.30 (2)	C(9)···C(12)	2.79 (3)
Cl(2)···C(8)	2.99 (3)	C(9)···C(13)	2.89 (3)

a Averaged for the $(FeCl)_4(SbCl_3)_4$ fragment of the $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$ molecule on the basis of assumed tetragonal $D_{2d}\text{-}\overline{4}2m$ symmetry; the braces represent the symmetry-equivalent distances and angles based on an $S_4\text{-}\overline{4}$ geometry (i.e., with the S_4 axis being coincident with the crystallographic twofold axis) ideally possessed by the entire molecule.

determined on the basis of trigonal C_{3v} symmetry to be 2.37 (2) Å and 96 (4)°, respectively, from electron diffraction[23] and 2.325 (5) Å and 99.5 (1.5)°, respectively, from microwave spectroscopy.[24] A comparison of the more precise microwave values with those of the above-mentioned SbCl₃-coordinated complexes suggests that such coordination of the SbCl₃ fragment produces little change in the Sb–Cl bond lengths along with an expected decrease in the Cl–Sb–Cl bond angles toward 90°. It is concluded that these particular variations are consistent with the premise that the unshared electron pair in the trigonal-pyramidal SbCl₃ molecule does not markedly influence the SbCl₃ geometry via its steric activity upon the SbCl₃ forming hexacoordinate Sb(III) complexes (vide infra).

Geometry of the Sb₄Cl₄ Cubanelike Framework. In the 4:4 iron–antimony complex the antimony atoms of the four SbCl₃ molecules and the chlorine atoms of the four $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ fragments occupy the alternate corners of a distorted cube (Figure 1). This linkage of each chlorine atom to one iron and three antimony atoms produces a bonding tetrahedral environment, while the coordination of each antimony to three terminal and three bridging chlorine atoms gives rise to an octahedral arrangement. Although the resulting $(Fe\text{-}Cl)_4(SbCl_3)_4$ fragment of crystallographically required C_2-2 site symmetry may be idealized to cubic T_d-43m symmetry, the Sb₄Cl₄ core is somewhat elongated along the crystallographic twofold axis, giving rise to an idealized tetragonal D_{2d}-42m geometry. This distortion is reflected by the two longitudinal Sb(1)–Cl(1) and Sb(2)–Cl(2) bond distances of 3.375 (5) and 3.366 (5) Å, respectively, being longer than the four lateral Sb–Cl bond distances which range from 3.175 (5) to 3.243 (5) Å. The Cl–Sb–Cl and Sb–Cl–Sb bond angles in the Sb₄Cl₄ framework also vary in accord with D_{2d} symmetry; the Cl(2)–Sb(1)–Cl(2′) and Cl(1)–Sb(2)–Cl(1′) angles of 88.0 (1) and 89.7 (1)°, respectively, are distinctly smaller than the other four independent Cl–Sb–Cl angles (Table II) of range 96.1 (1)–97.5 (1)°, while the Sb(2)–Cl(1)–Sb(2′) and Sb(1)–Cl(2)–Sb(1′) angles of 88.6 (1) and 90.3 (1)°, respectively, are considerably larger than the other four independent Sb–Cl–Sb angles (Table II) which vary from 82.7 (1) to 83.9 (1)°.

An examination of the intramolecular distances and bond angles of the entire molecule (Table II) shows that the idealized D_{2d} geometry of the Sb₄Cl₄ core is lowered by inclusion of the terminal ligands to S_4-4 with the crystallographic axis coincident with the S_4 axis. This distortion from a D_{2d} toward a tetragonal S_4 geometry is clearly evidenced in Table II both from the Fe–Cl–Sb bond angles and from the Cl–Sb–Cl bond angles of the terminal chlorine ligands. The 2° smaller Cl(3)–Sb(1)–Cl(5) and Cl(6)–Sb(2)–Cl(8) bond

angles compared to Cl(3)–Sb(1)–Cl(4) and Cl(6)–Sb(2)–Cl(7) bond angles may be attributed to intramolecular steric overcrowding involving primarily the carbonyl ligands.

Comparison of the 4:4 and 4:2 Iron–Antimony Structures and Resulting Bonding Implications. An unusual feature of the 4:4 iron–antimony complex with a cubanelike Sb₄Cl₄ core is the rare bonding mode of the bridging chlorine ligands in being tetrahedrally coordinated to four metal atoms—viz., one iron and three antimony atoms. All seven valence electrons of each chlorine atom participate in the bonding, with one valence electron used to form an Fe–Cl σ bond and with the remaining three electron pairs involved in the formation of Cl→Sb σ bonds.

A comparison of the structural features of the 4:4 and 4:2 iron–antimony complexes shows that the Fe–Cl(bridging) bond lengths are relatively insensitive to the number of Cl→Sb bonds formed by each bridging chlorine atom in that the Fe–Cl distances appear to increase only by 0.01–0.02 Å with each additional Cl→Sb bond. In the 4:2 iron–antimony complex,[9] the mean value of 2.286 Å for the two independent Fe–Cl-(doubly bridging) bond distances (corresponding to each chlorine atom forming only one Cl→Sb bond) of 2.279 (9) and 2.292 (10) Å is only 0.01 Å shorter than the mean value of 2.296 Å for the two independent Fe–Cl(triply bridging) bond distances (corresponding to each chlorine atoms forming two Cl→Sb bonds) of 2.280 (10) and 2.312 (9) Å. In turn, this latter mean value is only 0.02 Å shorter than the corresponding mean value of 2.316 Å found in the 4:4 iron–antimony complex for the independent Fe–Cl(quadruply bridging) bond distances of 2.301 (5) and 2.330 (5) Å. The relative bond length insensitivity to the mode of chlorine bridging in these complexes suggests that the presumed increase in total Cl→Sb charge transfer with increased number of Cl to Sb linkages does not apparently diminish to any great extent the σ and π Cl→Fe donation (which would have the effect of weakening the Fe–Cl bond as evidenced by a bond length increase).

On the other hand, the total charge received by each SbCl₃ fragment in the 4:4 iron–antimony complex from the Cl→Sb bonding is presumably smaller than that in the 4:2 iron–antimony complex in that the donor:acceptor ratio is 1:1 in the former and 2:1 in the latter. This charge difference is evidenced by the larger average value of 3.27 Å for the Sb–Cl(bridging) distances and the smaller mean value of 2.35 Å for the Sb–Cl(terminal) distances in the 4:4 iron–antimony complex in comparison with the corresponding values of 3.15 and 2.38 Å, respectively, in the 4:2 iron–antimony complex, a fact which is also in accord with the inverse relationship between the trans-related Sb–Cl distances observed in other

compounds.[2b,9] In this connection, in the 4:2 iron–antimony complex the two independent Sb–Cl(doubly bridging) distances of 3.025 (9) and 3.052 (9) Å are shorter than the four independent Sb–Cl(triply bridging) distances of 3.089 (9), 3.196 (9), 3.257 (9), and 3.307 (9) Å, an indication that the former bonds are stronger. These observations can be rationalized by the same argument considered above in that each doubly bridging chlorine atom only donates its electron density to one antimony atom (resulting in a stronger Cl→Sb bond) whereas each triply bridging chlorine atom donates a smaller electron charge to each of two antimony atoms.

In the 4:4 and the 4:2 iron–antimony complexes, each Sb(III) is octahedrally coordinated via three Sb–Cl(terminal) σ bonds and three Sb–Cl(bridging) bonds such that there is no clear-cut evidence for any pronounced steric activity of the lone electron pair. Except for the case of these two complexes, the steric activity of the lone pair has been consistently observed in previously known *neutral* adducts of $SbCl_3$ such as the 1:1 $SbCl_3$–aniline adduct,[6] the 2:1 $SbCl_3$–naphthalene adduct,[4] and the 2:1 SbI_3–1,4-dithiane addition compound.[25] These molecular complexes possess vacant sites which can be allocated to the nonbonding electron pair of the antimony atoms. In the $SbCl_3$–aniline complexes,[6] the antimony atom was considered to possess a trigonal-bipyramidal electron pair arrangement with a nitrogen electron pair at one axial position and with one of the equatorial positions occupied by the nonbonding pair. Similarly, in the 2:1 complex between $SbCl_3$ and naphthalene,[4] the antimony atom was viewed as having a distorted trigonal-bipyramidal environment with two chlorine atoms and the lone electron pair located at equatorial positions and with the third chlorine atom and the π system of the naphthalene molecule occupying the two axial positions. In a similar fashion, the antimony atoms in the 2:1 addition compound SbI_3–1,4-dithiane[25] were each regarded to be octahedrally surrounded by three iodine atoms, two sulfur atoms, and the unshared electron pair.

Crystalline $SbCl_3$ was first considered as discrete molecules by Lindquist and Niggli,[21] although the authors pointed out that there are intermolecular Sb⋯Cl distances of 3.5 Å. A subsequent determination by Peterson[22] showed several Sb–Cl separations shorter than van der Waals contacts of 4.0 Å (Pauling's tabulation[19a]), but if one accepts the more reasonable value of 3.60 Å suggested by Hulme and Szymanski[18] for a Sb⋯Cl contact distance, there would be only two significant Cl→Sb charge-transfer interactions with Sb–Cl separations of 3.50 Å. Our calculations based on positional parameters reported by Petersen,[22] showed that the two longer Sb–Cl bonds of 2.36 Å are trans to the two charge-transfer Sb–Cl interactions, while the shorter one of 2.30 Å is trans to the presumed electron pair site in a resulting octahedral electron pair arrangement about each antimony atom, in accord with the observations of bond lengthening due to trans charge-transfer interactions in other molecular complexes.[2b,9] The electron pair arrangement about the Sb(III) in crystalline $SbCl_3$ can therefore be considered as analogous to that about the Sb(III) in the $SbCl_5^{2-}$ dianion.[5] This $Sb^{III}Cl_5^{2-}$ dianion, unlike its neutral $Sb^{V}Cl_5$ counterpart which has a trigonal-bipyramidal configuration,[26] possesses an octahedral electron pair distribution with the nonbonding electron pair assumed to occupy an axial site.

There is no observable vacant site which can be attributed to the unshared electron pair of each octahedral Sb(III) in the 4:4 iron–antimony complex. This breakdown of the valence-shell electron-pair repulsion concept[27] (which predicts that the lone pair should be sterically active and should therefore give rise to a seven-coordinated arrangement[28,29] with the lone pair occupying a distinct site) has previously been observed only for a number of antimony(III) halide anions

including the SbX_6^{3-} trianions (X = Cl^{30}, Br^{31}), the $[Sb_2Br_9]^{3-}$ trianion,[32] and the $[SbCl_4]_n^{n-}$ polyanion,[33] in all of which each Sb(III) possesses one nonbonding and six bonding valence-shell electron pairs. In the solid state, the SbX_6^{3-} trianions and the electronically equivalent homologues such as the TeX_6^{2-} dianions (X = Cl,[34] Br^{35}) all apparently have O_h symmetry with a sterically inactive lone pair.[36–38] In order to rationalize the observed regular octahedral geometry, Beach[39] suggested that the unshared pair of electrons occupies the spherical 5s orbital while the s orbital responsible for the bond formation is the outer 6s orbital; this proposal was utilized[39] to rationalize the longer bond distances in these octahedral complexes compared to the sum of covalent radii. Gillespie[27b] pointed out that, due to considerable ligand–ligand repulsion, the lone pair in being placed inside the valence shell would contribute to the shielding of the bonding electron pairs from the central nucleus and hence would effectively decrease the electronegativity of the central atom and increase the bond lengths. It is noteworthy that when the crowding effect of the ligand is reduced, as in the case of multidentate ligands, the lone pair resumes its "active" steric function—viz., in the $[Sb(C_2O_4)_3]^{3-}$ trianion which possesses a pentagonal-bipyramidal electron pair configuration with the lone pair presumed to occupy one axial site.[40]

In view of the steric crowding around the Sb atoms in the 4:4 and 4:2 iron–antimony complexes, it may be presumed that the lone pair likewise is sterically deactivated through its occupying primarily the inner 5s orbital with the other 6s orbital available for charge donation from the bridging chlorine atoms.

References and Notes

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Å range and with the three bridging chlorine atoms at much longer distances between 3.03 (1) and 3.31 (1) Å.

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(13) We are indebted to Dr. A. S. Foust for running the mass spectra.

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(16) $R_1 = [\sum ||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2 = [\sum w_i ||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\sum w_i ||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.

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Mechanisms of Substitution of Ligand-Bridged Diiron Hexacarbonyl Complexes. μ-Butatriene-bis(tricarbonyliron) Complexes: Crystallographic Determination of the Structure of a Carbonyl Substitution Product and Evidence for a Carbonyl-Inserted Intermediate

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μ-Butatriene-bis(tricarbonyliron) complexes react with phosphines and phosphites to substitute the carbonyl ligand trans to the iron–iron bond. The addition of an incoming ligand without loss of a carbonyl moiety can be demonstrated in some cases by isolation and characterization of the adduct. Such adducts lose carbon monoxide upon heating. Kinetic data are reported for the carbonyl substitution reactions of triphenylphosphine and triphenyl phosphite with μ-butatriene-bis(tricarbonyliron), μ-tetraphenylbutatriene-bis(tricarbonyliron), and μ-di(biphenyl-2,2'-ylidene)-bis(tricarbonyliron) and for the addition without carbonyl displacement of tri-*n*-butylphosphine to μ-tetraphenylbutatriene-bis(tricarbonyliron). The mechanisms of these reactions are discussed. The crystal and molecular structure of one of these products, μ-butatriene-(triphenylphosphine)pentacarbonyldiiron, has been determined by x-ray crystallography. Four molecular units of $Fe_2PO_5C_{27}H_{19}$ (mol wt 566) are distributed in a monoclinic cell ($P2_1/c$) with $a = 11.277$ (4) Å, $b = 13.349$ (6) Å, $c = 17.604$ (7) Å, and $\beta = 107.64$ (1)° and a volume of 2526 Å³. The structure was refined to a residual of 0.063 (based on F) using 1403 diffractometer-collected reflection intensities. Each iron atom is in an octahedral environment which is completed by an iron–iron bond of 2.627 Å. The bridging butatriene ligand retains a planar carbon skeleton but is twisted end for end by 90° in a manner which suggests π-allyl bonding to each iron atom. The phosphine substituent is observed to be trans to the iron–iron bond.

Introduction

Previous reports document the kinetics and mechanisms of the reactions of organosulfur-,[2] organonitrogen-,[3] and organophosphorus-bridged[4] bis(tricarbonyliron) complexes with Lewis bases. Butatriene–bis(tricarbonyliron) complexes have structures[5] which are similar to the structures of the sulfur-,[6] nitrogen-,[7] and phosphorus-bridged[8] complexes. The structure of di(biphenyl-2,2'-ylidene)butatrienebis(tricarbonyliron),[5] $Fe_2(CO)_6(\mu$-$C_{28}H_{16})$, consists of two $Fe(CO)_3$ groups con-

nected by an iron–iron bond as well as by the bridging butatriene group. One interesting feature of the structure is that the ends of the butatriene bridging group extend over one side of the octahedral faces containing the two central butatriene carbon atoms and the carbonyl ligands trans to the iron–iron bond. This feature results from the formation of a π-allylic bond from the butatriene group to each of the iron atoms.

The kinetic data for the nitrogen-[3] and sulfur-bridged[2] complexes can be rationalized by a bimolecular substitution