Contribution from the Department of Chemistry, Simon
Fraser University, Burnaby 2, British Columbia, Canada

Crystal Structure of a Complex Containing an Antimony–Iron σ Bond, $[Cl_2Sb\{Fe(CO)_2(h^5\text{-}C_5H_5)\}_2][Sb_2Cl_7]$

FREDERICK W. B. EINSTEIN* and RAYMOND D. G. JONES

The crystal structure of $[Cl_2Sb\{Fe(CO)_2(h^5\text{-}C_5H_5)\}_2][Sb_2Cl_7]$ has been determined from three-dimensional X-ray diffraction data collected by a computer-controlled diffractometer using Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/n$; the unit cell contains 8 molecules and has dimensions $a = 15.849$ (2), $b = 11.968$ (2), $c = 31.338$ (5) Å, and $\beta = 92.33$ (1)°; $d_m = 2.2$ (1) and $d_c = 2.32$ g/cm³ for 8 molecules. The structure was solved by direct methods and refined by full-matrix least-squares techniques to R and R_w of 0.056 for 5097 observed reflections ($2\theta \leqslant 45°$). Each asymmetric unit contains two $[Cl_2Sb\{Fe(CO)_2(h^5\text{-}C_5H_5)\}_2]^+$ cations and an anion grouping of formula $Sb_4Cl_{14}^{2-}$. The two independent cations are similar in geometry. In each cation, two chlorine atoms and two iron atoms form a grossly distorted tetrahedron about antimony with (average) Sb–Fe = 2.440 and Sb–Cl = 2.42 Å. Each iron atom can be considered to have octahedral coordination. The anionic grouping has the range of antimony–chlorine interatomic contacts 2.354–2.975 Å and can be considered to contain $SbCl_3$, $SbCl_4^-$, and $Sb_2Cl_7^-$. However if short contacts to 3.55 Å are considered, the antimony and chlorine atoms form infinite ribbons parallel to the ab plane, each antimony having six chlorine near neighbors which form a distorted octahedron about each antimony. The cations lie between these ribbons.

Introduction

Many compounds of transition metals are known where a group Va atom acts as a donor toward the metal atom. However, until recently, no compounds containing a transition metal–group Va atom σ bond had been characterized. $(CF_3)_2AsFe(CO)_2(h^5\text{-}C_5H_5)$ and $(CF_3)_2AsMo(CO)_3(h^5\text{-}C_5H_5)$,[1] $(C_6F_5)_2AsFe(CO)_2(h^5\text{-}C_5H_5)$ and $(C_6F_5)_2AsMo(CO)_3(h^5\text{-}C_5H_5)$,[2] and $Cl_2SbCo(CO)_4$ and $Bi[Co(CO)_4]_3$[3] are all believed to have such a σ bond. Dahl and his coworkers have definitely shown the existence of these types of bonds from X-ray diffraction studies of $As_3Co(CO)_3$,[4] $As_2Co_2(CO)_5P(C_6H_5)_3$ and $As_2Co_2(CO)_6$,[5] $Sb_4Co_4(CO)_{12}$,[6] and $[\{Fe(h^5\text{-}C_5H_5)(CO)_2\}_3SbCl]_2[FeCl_4]\cdot CH_2Cl$.[7] Cullen and his coworkers have prepared several additional compounds from reaction of $[Fe(CO)_2(h^5\text{-}C_5H_5)]_2$ with arsenic, antimony, and bismuth trihalides,[8] and these also contain a transition metal–group Va atom σ bond.

Recently it has been shown that $CsSb_2F_7$ contains the $Sb_2F_7^-$ entity[9] whereas KSb_2F_7 has SbF_3 and SbF_4^- units.[10] For the latter compound, if antimony–fluorine contacts to ~2.5 Å are considered, the "$Sb_2F_7^-$ unit" is actually infinite chains of alternate octahedral and trigonal-bipyramidal coordination polyhedra. Accordingly, the compound we decided to study, $[Cl_2Sb\{Fe(CO)_2(h^5\text{-}C_5H_5)\}_2]^+[Sb_2Cl_7]^-$,[8] did not necessarily contain $Sb_2Cl_7^-$ ions.

Experimental Section

Crystals of the compound which were crystallized from dichloromethane were red-brown plates, slightly elongated in the a direction. Since the compound was air and possibly light sensitive, the crystals

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(5) A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 5633 (1969).

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(9) R. R. Ryan, S. H. Mastin, and A. C. Larson, *Inorg. Chem.*, **10**, 2793 (1971).

(10) S. H. Mastin and R. R. Ryan, *Inorg. Chem.*, **10**, 1757 (1971).

were sealed in Lindemann glass capillaries under nitrogen. Weissenberg photographs of nets $0kl$–$3kl$ and precession photographs of zones $hk0$ and $h0l$, taken with Cu Kα radiation, indicated that the crystals were monoclinic. The following spectra were systematically absent: $h0l$ for $h + l = 2n + 1$; $0k0$ for $k = 2n + 1$. The space group is uniquely determined as $P2_1/n$ $[\pm(x, y, z), \pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)]$, a nonstandard orientation of $P2_1/c$.

Crystal Data. $[Cl_2Sb\{Fe(CO)_2(h^5\text{-}C_5H_5)\}_2][Sb_2Cl_7]$, mol wt = 1038.1, crystals are monoclinic, $P2_1/n$, with cell dimensions $a = 15.849$ (2), $b = 11.968$ (2), $c = 31.338$ (5) Å, and $\beta = 92.33$ (1)°. $U = 5939.02$ Å³. The measured density is 2.2 (1) g/cm³ (flotation in $ZnBr_2$ solution) while the calculated density is 2.32 g/cm³ for 8 molecules per unit cell. Hence there are two molecules in the asymmetric unit. $F(000) = 3872$, λ(Cu Kα) is 1.5418 Å, λ(Mo Kα$_1$) is 0.70926 Å, and μ(Mo Kα) = 40.3 cm⁻¹.

A plate-shaped crystal was cut to dimensions 0.22 × 0.17 × 0.48 mm and sealed in a Lindemann glass capillary under an atmosphere of nitrogen. This one crystal was used to measure the cell dimensions and the intensity data and was mounted with the long direction slightly offset from the ϕ axis of the diffractometer in order to minimize intrinsic multiple reflections. Cell dimensions were obtained at 24° by the least-squares analysis of the 2θ values [$2\theta > 31°$; the function minimized was $\Sigma(\Delta\theta)^2$] of 18 reflections which had been accurately centered on a computer-controlled Picker diffractometer.[11] Mo Kα$_1$ radiation was used and the takeoff angle was 1°. The errors in the cell dimensions are those determined in the least-squares process.

Integrated intensities for one quadrant were determined using the θ–2θ scan technique with Mo Kα radiation (niobium filtered) and a scintillation counter equipped with pulse height analysis. The takeoff angle was 2.5°. Each reflection was scanned for 0.9° (extended for spectral dispersion) at a scan rate of 2° min⁻¹ in 2θ. At each end of the scan range, the background scattering was counted for 10 sec. Every 75 reflections, two standard reflections were measured and the maximum deviation of any individual standard from the mean was 3%. This variation was random and indicates that the crystal did not undergo any significant decomposition during data collection. It was found that some 100 reflections in approximately the same region of reciprocal space suffered from some overlap with adjacent reflections. The intensities for these reflections were rescanned using a smaller detector aperture and scaled to the other data.[12] In this manner, intensities for 7760 reflections with $2\theta \leqslant 45°$ were measured.

(11) The programs for preliminary crystallographic calculations and diffractometer control were written by Dr. P. G. Lenhert, Vanderbilt University. The data reduction program was written by Dr. M. M. Gilbert of this laboratory. All other programs used are listed in F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, **11**, 395 (1972).

(12) Because of the long c axis, it is possible that some reflections suffered marginally from overlap with adjacent reflections. Reflections were monitored for unequal background counts and peak asymmetry and it is estimated that errors in intensity due to overlap were insignificant for all reflections.
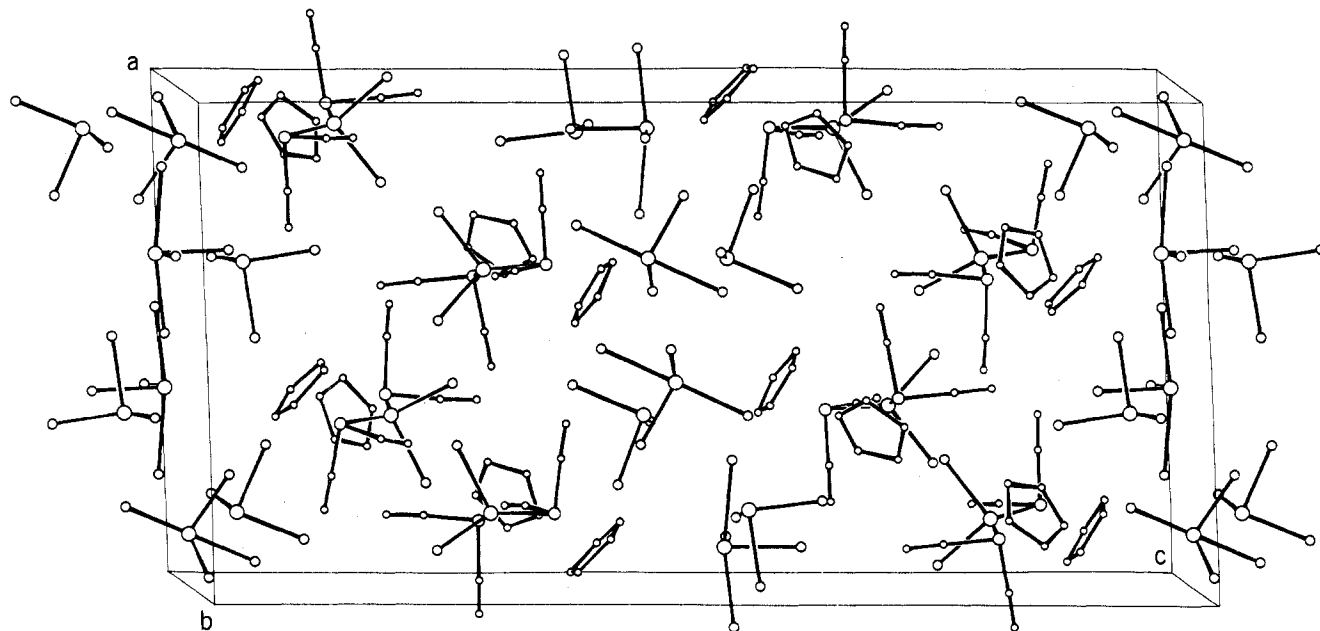
Figure 1. A packing diagram showing the contents of the unit cell. The alternation of the anion grouping and cations along the c axis is readily seen.
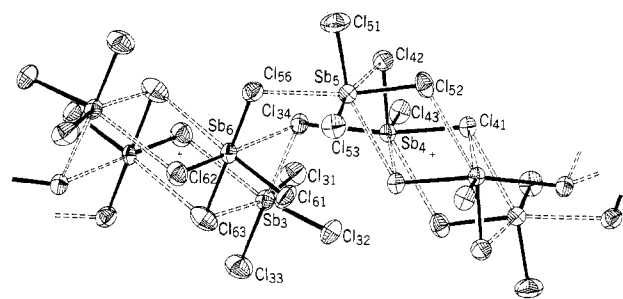

Figure 2. A diagram showing the antimony–chlorine ribbons. The significance of the full and broken lines is explained in the text. The left "+" corresponds to the center of symmetry at $(0, \frac{1}{2}, 0)$ while that to the right is the center of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$; 30% probability thermal ellipsoids are shown for the atoms.

Intensities were corrected for background (normalized to the scan time) and for the Lorentz–polarization factor. No absorption correction was applied and it is estimated that the maximum possible error in intensity due to this neglect is ~10%. For each reflection, the esd in the intensity, σ_I, was determined from $\sigma_I = \{TC + (t_s/t_b)^2(B_1 + B_2) + (kI)^2\}^{1/2}$ where TC is total count, B_1 and B_2 are the background counts at each end of the scan range, t_s is the scan time, t_b is the background-count time, and k is a constant set equal to 0.03.[13] If $I < 2.3\sigma_I$, I = net intensity, the reflection was considered unobserved. The number of observed reflections was 5097.

Structure Determination. Structure solution was initiated using the symbolic addition procedure.[14,15] Since it had been noticed in an oscillation photograph about the a axis that the intensities of reflections on odd-layer lines were much weaker than those on even-layer lines, it was no surprise to find that reflections in parity groups e- - had larger E values than those in o- - parity groups. (e stands for an even number; o stands for an odd number.) It was decided to determine signs for the large E values in e- - groups first and subsequently use these signs to phase the o- - reflections, a technique which had been used successfully before.[16] For the e- - groups, $\overline{6}63$ ($E = +4.41$) and $2,11,8$ ($E = +4.12$) were chosen to define the origin while the sign of $4,0,16$ ($E = +2.86$) could be assigned from Sayre relationships. An additional reflection, 651 ($|E| = 3.55$), was included in the starting set, first with sign $+1$ and second with sign -1. Both starting sets allowed assignment of phases for e- - reflections with $|E| > 2.0$. The highest 40 E values in each set were

(13) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(14) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

(15) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(16) F. W. B. Einstein, E. Enwall, D. M. Morris, and D. Sutton, *Inorg. Chem.*, **10**, 678 (1971).
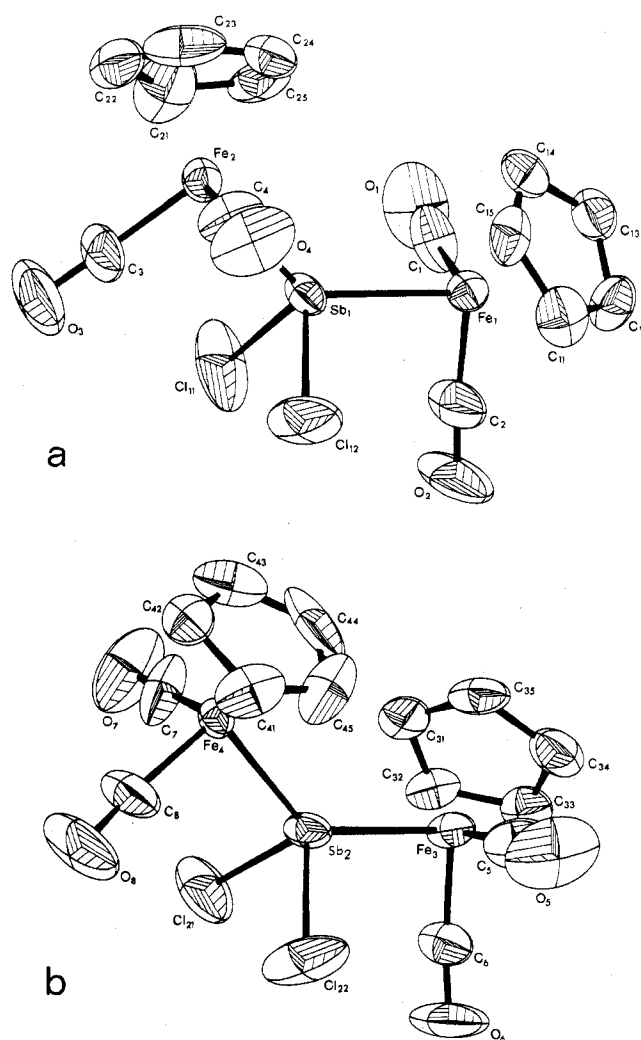

Figure 3. A diagram showing the two independent cations; 30% probability thermal ellipsoids are shown for the atoms.

then used to phase the o- - groups with $\overline{5}60$ having $E = +2.63$. For the o- - groups, reflections with $|E| > 1.6$ were used.

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Table I. Atomic Parameters

(A) Atomic Coordinates in Fractional Coordinates

Atom	x	y	z
Sb(1)	0.62043 (7)[a]	0.29264 (9)	0.31023 (3)
Fe(1)	0.5937 (1)	0.0915 (2)	0.30905 (7)
Fe(2)	0.6391 (1)	0.4328 (2)	0.36664 (7)
Cl(11)	0.5242 (6)	0.3644 (6)	0.2600 (2)
Cl(12)	0.7369 (5)	0.3118 (6)	0.2671 (2)
C(11)	0.7097 (12)	0.0061 (21)	0.3157 (8)
C(12)	0.6401 (12)	−0.0710 (16)	0.3119 (7)
C(13)	0.5892 (13)	−0.0529 (17)	0.3472 (7)
C(14)	0.6242 (17)	0.0402 (19)	0.3711 (6)
C(15)	0.6968 (14)	0.0716 (16)	0.3519 (8)
C(21)	0.5249 (16)	0.4550 (35)	0.3926 (9)
C(22)	0.5819 (26)	0.5286 (20)	0.4129 (10)
C(23)	0.6463 (21)	0.4673 (44)	0.4315 (7)
C(24)	0.6259 (29)	0.3548 (36)	0.4248 (10)
C(25)	0.5511 (28)	0.3496 (31)	0.4012 (10)
C(1)	0.4846 (12)	0.1096 (17)	0.3178 (7)
O(1)	0.4160 (9)	0.1174 (16)	0.3230 (6)
C(2)	0.5830 (17)	0.0917 (18)	0.2537 (7)
O(2)	0.5750 (16)	0.0862 (15)	0.2167 (5)
C(3)	0.6340 (14)	0.5448 (17)	0.3302 (7)
O(3)	0.6286 (14)	0.6167 (14)	0.3069 (6)
C(4)	0.7488 (12)	0.4209 (18)	0.3654 (6)
O(4)	0.8207 (8)	0.4108 (16)	0.3652 (5)
Sb(2)	0.13609 (8)	0.29550 (9)	0.30963 (3)
Fe(3)	0.1075 (2)	0.0969 (2)	0.30593 (7)
Fe(4)	0.1445 (1)	0.4342 (2)	0.36695 (7)
Cl(21)	0.2712 (4)	0.3065 (5)	0.2777 (2)
Cl(22)	0.0675 (6)	0.3756 (5)	0.2510 (2)
C(31)	0.1984 (13)	0.0708 (14)	0.3569 (6)
C(32)	0.2178 (12)	0.0013 (18)	0.3210 (6)
C(33)	0.1472 (14)	−0.0678 (14)	0.3118 (5)
C(34)	0.0850 (12)	−0.0449 (18)	0.3410 (7)
C(35)	0.1150 (15)	0.0452 (17)	0.3689 (5)
C(41)	0.0322 (14)	0.5099 (24)	0.3846 (7)
C(42)	0.1004 (15)	0.5330 (16)	0.4172 (7)
C(43)	0.1288 (18)	0.4332 (32)	0.4316 (7)
C(44)	0.0812 (27)	0.3512 (27)	0.4118 (12)
C(45)	0.0251 (14)	0.3923 (35)	0.3827 (10)
C(5)	−0.0094 (14)	0.1234 (18)	0.3035 (6)
O(5)	−0.0750 (9)	0.1440 (20)	0.3013 (6)
C(6)	0.1177 (12)	0.0930 (13)	0.2511 (6)
O(6)	0.1193 (12)	0.0868 (12)	0.2143 (4)
C(7)	0.2510 (12)	0.4005 (19)	0.3763 (8)
O(7)	0.3190 (9)	0.3798 (17)	0.3835 (6)
C(8)	0.1669 (16)	0.5456 (17)	0.3323 (6)
O(8)	0.1725 (16)	0.6176 (14)	0.3088 (6)
Sb(3)	0.13636 (6)	0.27835 (9)	0.05688 (3)
Sb(4)	0.39136 (6)	0.37092 (8)	−0.01450 (3)
Cl(34)	0.2188 (2)	0.3834 (4)	−0.0242 (1)
Cl(31)	0.1614 (3)	0.0884 (4)	0.0420 (1)
Cl(32)	0.2728 (3)	0.3106 (5)	0.0865 (1)
Cl(33)	0.0801 (3)	0.2423 (4)	0.1249 (2)
Cl(41)	0.5498 (2)	−0.3728 (3)	−0.0212 (1)
Cl(42)	0.3874 (2)	−0.4151 (4)	−0.0890 (1)
Cl(43)	0.3843 (3)	0.1778 (3)	−0.0354 (1)
Sb(5)	0.36314 (6)	0.69938 (8)	−0.07085 (3)
Sb(6)	0.11570 (6)	0.60726 (8)	−0.00683 (3)
Cl(56)	0.1753 (3)	0.7035 (4)	−0.0732 (1)
Cl(51)	0.3422 (4)	0.7334 (5)	−0.1438 (1)
Cl(52)	0.5144 (3)	0.6971 (4)	−0.0800 (1)
Cl(53)	0.3648 (3)	0.8862 (4)	−0.0489 (1)
Cl(61)	0.2369 (3)	0.6642 (4)	0.0327 (1)
Cl(62)	0.0396 (3)	0.7752 (5)	0.0047 (1)
Cl(63)	0.0542 (3)	0.5255 (5)	0.0626 (2)

[a] In this table and all subsequent tables, the number in parentheses is the esd in the least significant digit(s). [b] Of the form $\exp[-2\pi^2 \cdot$

For each set of signs, an electron density map was calculated, F_o's being used as coefficients in lieu of E's. The set having 651 with sign +1 gave a reasonable model, six antimony, four iron, and two chlorine atoms being located in the map. Structure factors calculated for these atoms gave $R = 0.34$ for data to $2\theta = 30°$. All nonhydrogen atoms were located in two subsequent Fourier maps and refinement of position and isotropic thermal parameters led to $R = 0.11$ for data to $2\theta = 35°$. Each reflection was given unit weight and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Subsequently, all atoms were given anisotropic temperature factors and weights $w = 1/\sigma_F^2$, where $\sigma_F = \sigma_I/(Lp)2F_o$, and refinement converged to $R = 0.056$ and $R_w = 0.056^{17}$ for all observed data.[18] The maximum parameter shift at convergence was $<0.4\sigma$ and the error of fit was 1.8. There were no significant variations of $w(|F_o| -$

(17) $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

Table I. (*Continued*)

(B) Anisotropic Thermal Parameters (A^2)[b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	0.0797 (8)	0.0560 (7)	0.0511 (6)	−0.0114 (7)	−0.0118 (6)	0.0136 (6)
Fe(1)	0.068 (2)	0.059 (2)	0.052 (1)	−0.009 (1)	−0.011 (1)	−0.000 (1)
Fe(2)	0.073 (2)	0.049 (2)	0.071 (2)	−0.005 (1)	−0.001 (1)	0.003 (1)
Cl(11)	0.331 (10)	0.105 (5)	0.212 (8)	0.013 (6)	−0.199 (8)	0.034 (5)
Cl(12)	0.221 (8)	0.160 (6)	0.132 (5)	−0.095 (6)	0.100 (5)	−0.017 (5)
C(11)	0.073 (14)	0.106 (19)	0.151 (22)	0.011 (14)	0.022 (14)	0.013 (17)
C(12)	0.076 (14)	0.074 (14)	0.129 (18)	0.006 (11)	0.020 (13)	−0.016 (13)
C(13)	0.111 (16)	0.073 (15)	0.099 (16)	0.003 (13)	−0.007 (14)	0.017 (13)
C(14)	0.161 (22)	0.090 (18)	0.065 (15)	0.032 (17)	−0.016 (15)	0.021 (13)
C(15)	0.087 (16)	0.076 (15)	0.107 (18)	0.034 (13)	−0.042 (14)	0.003 (14)
C(21)	0.100 (19)	0.131 (25)	0.205 (31)	−0.021 (21)	0.057 (19)	−0.021 (25)
C(22)	0.178 (30)	0.084 (19)	0.124 (23)	−0.043 (22)	0.064 (20)	−0.024 (17)
C(23)	0.159 (28)	0.234 (43)	0.054 (15)	−0.025 (30)	−0.001 (15)	−0.028 (22)
C(24)	0.229 (42)	0.124 (27)	0.092 (23)	0.062 (31)	0.073 (23)	0.040 (22)
C(25)	0.237 (42)	0.094 (23)	0.126 (26)	−0.061 (28)	0.124 (26)	−0.033 (21)
C(1)	0.068 (13)	0.081 (15)	0.156 (20)	−0.017 (13)	−0.018 (14)	0.031 (13)
O(1)	0.062 (9)	0.161 (16)	0.281 (22)	−0.016 (12)	−0.012 (13)	0.029 (15)
C(2)	0.252 (19)	0.098 (18)	0.081 (16)	−0.078 (18)	0.007 (18)	−0.001 (15)
O(2)	0.486 (35)	0.160 (17)	0.052 (9)	−0.135 (19)	−0.013 (15)	0.006 (11)
C(3)	0.173 (22)	0.056 (14)	0.110 (17)	−0.047 (15)	−0.019 (15)	0.010 (12)
O(3)	0.327 (26)	0.084 (13)	0.190 (19)	−0.046 (14)	−0.031 (17)	0.065 (13)
C(4)	0.063 (13)	0.143 (20)	0.101 (16)	−0.014 (14)	−0.016 (12)	−0.033 (14)
O(4)	0.062 (9)	0.244 (20)	0.178 (15)	−0.026 (12)	−0.019 (10)	−0.049 (14)
Sb(2)	0.1163 (10)	0.0460 (7)	0.0477 (6)	0.0082 (7)	0.0049 (6)	0.0068 (6)
Fe(3)	0.112 (2)	0.056 (2)	0.047 (1)	0.011 (1)	−0.011 (1)	−0.002 (1)
Fe(4)	0.066 (2)	0.047 (1)	0.065 (2)	−0.004 (1)	0.012 (1)	−0.002 (1)
Cl(21)	0.182 (6)	0.136 (6)	0.161 (6)	−0.025 (5)	0.109 (5)	0.003 (5)
Cl(22)	0.369 (11)	0.096 (5)	0.116 (5)	0.085 (6)	−0.116 (6)	−0.000 (4)
C(31)	0.109 (16)	0.062 (12)	0.076 (14)	0.009 (12)	−0.034 (12)	0.027 (11)
C(32)	0.092 (15)	0.106 (16)	0.071 (13)	0.011 (13)	−0.005 (11)	−0.007 (12)
C(33)	0.115 (16)	0.052 (11)	0.071 (13)	0.017 (11)	−0.004 (12)	0.008 (9)
C(34)	0.106 (16)	0.099 (17)	0.094 (15)	−0.006 (14)	0.006 (13)	0.038 (14)
C(35)	0.144 (20)	0.076 (14)	0.050 (11)	0.028 (14)	−0.009 (13)	0.006 (10)
C(41)	0.086 (16)	0.156 (24)	0.113 (18)	0.058 (16)	0.018 (13)	−0.043 (17)
C(42)	0.116 (18)	0.071 (14)	0.089 (15)	0.011 (13)	0.023 (13)	−0.016 (12)
C(43)	0.152 (26)	0.183 (30)	0.079 (16)	0.042 (25)	0.030 (16)	0.024 (20)
C(44)	0.248 (47)	0.108 (24)	0.195 (42)	−0.024 (28)	0.155 (35)	0.027 (25)
C(45)	0.066 (16)	0.227 (39)	0.186 (31)	−0.037 (19)	0.061 (16)	−0.144 (30)
C(5)	0.120 (18)	0.123 (18)	0.096 (15)	0.058 (16)	−0.027 (14)	0.007 (13)
O(5)	0.070 (10)	0.355 (28)	0.209 (18)	0.079 (15)	−0.046 (11)	−0.008 (18)
C(6)	0.146 (17)	0.056 (12)	0.069 (12)	0.012 (11)	0.019 (12)	−0.005 (10)
O(6)	0.332 (24)	0.127 (13)	0.043 (8)	0.009 (13)	0.014 (11)	0.003 (9)
C(7)	0.067 (14)	0.122 (19)	0.193 (24)	−0.025 (15)	0.011 (16)	−0.075 (17)
O(7)	0.090 (12)	0.208 (20)	0.261 (21)	0.021 (14)	−0.016 (14)	−0.097 (16)
C(8)	0.243 (27)	0.067 (15)	0.082 (15)	−0.017 (16)	0.060 (16)	−0.001 (12)
O(8)	0.455 (34)	0.084 (13)	0.178 (18)	−0.033 (17)	0.114 (20)	0.044 (12)
Sb(3)	0.0485 (6)	0.0660 (8)	0.0682 (7)	−0.0027 (6)	−0.0005 (5)	0.0088 (6)
Sb(4)	0.0419 (6)	0.0383 (6)	0.0609 (6)	−0.0051 (5)	−0.0003 (5)	−0.0033 (5)
Cl(34)	0.053 (2)	0.079 (3)	0.077 (3)	0.004 (2)	−0.002 (2)	−0.002 (2)
Cl(31)	0.121 (4)	0.074 (3)	0.105 (4)	0.008 (3)	−0.016 (3)	−0.010 (3)
Cl(32)	0.066 (3)	0.128 (5)	0.106 (4)	−0.021 (3)	−0.020 (3)	−0.017 (3)
Cl(33)	0.129 (5)	0.113 (4)	0.088 (4)	0.000 (4)	0.035 (3)	0.023 (3)
Cl(41)	0.048 (2)	0.068 (3)	0.076 (3)	0.003 (2)	0.006 (2)	−0.000 (2)
Cl(42)	0.064 (3)	0.082 (3)	0.070 (3)	−0.005 (2)	0.001 (2)	−0.015 (2)
Cl(43)	0.078 (3)	0.040 (2)	0.099 (3)	−0.005 (2)	−0.007 (2)	−0.008 (2)
Sb(5)	0.0588 (7)	0.0490 (7)	0.0606 (7)	−0.0041 (6)	0.0049 (5)	−0.0002 (6)
Sb(6)	0.0364 (6)	0.0531 (7)	0.0709 (7)	−0.0020 (5)	0.0015 (5)	−0.0002 (6)
Cl(56)	0.078 (3)	0.077 (3)	0.072 (3)	0.007 (3)	−0.008 (2)	0.005 (2)
Cl(51)	0.129 (5)	0.158 (5)	0.062 (3)	−0.035 (4)	0.000 (3)	−0.016 (3)
Cl(52)	0.057 (3)	0.083 (3)	0.107 (4)	−0.013 (2)	0.018 (2)	−0.009 (3)
Cl(53)	0.102 (4)	0.050 (3)	0.112 (4)	−0.003 (3)	0.006 (3)	−0.007 (3)
Cl(61)	0.063 (3)	0.126 (4)	0.088 (3)	−0.015 (3)	−0.027 (2)	−0.008 (3)
Cl(62)	0.085 (3)	0.080 (3)	0.112 (4)	−0.028 (3)	−0.004 (3)	−0.019 (3)
Cl(63)	0.133 (5)	0.108 (4)	0.107 (4)	−0.008 (4)	−0.048 (4)	0.006 (3)

$(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$

$|F_c|)^2$ for ranges of F_O and $(\sin\theta)\lambda^{-1}$. Some very low-angle reflections had poor agreement (not extinction effects) and the indices of these reflections could be correlated with peaks, in a final difference map, of height 1.9 e A^{-3} near Fe(2) and 1.6 e A^{-3} near Sb(2). Other peaks in this map had maximum heights of ~1 e A^{-3} near iron and antimony atoms (the peak height of the smallest carbon atom was 3.1 e A^{-3}). Because of the large thermal motion of the cyclopentadienyl groups, no attempt was made to locate hydrogen atoms on these groups.

Scattering factors for the neutral atoms were taken from ref 19a

(18) Since our refinement program did not allow all parameters to be varied in one cycle; generally the parameters for the anions and each cation were refined in turn.

(19) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); D. T. Cromer, *ibid.*, **18**, 17 (1965).

Table II. Molecular Geometry

	(A) Cation				(B) Anion		
	(i) Interatomic Distances, Å				(i) Interatomic Distances,[b] Å		
Sb(1)–Fe(1)	2.444 (2)	Sb(2)–Fe(3)	2.422 (3)	Sb(3)–Cl(31)	2.357 (5)	Sb(4)–Cl(41)	2.529 (4)
Sb(1)–Fe(2)	2.446 (2)	Sb(2)–Fe(4)	2.446 (2)		2.382[a]		2.538[a]
Sb(1)–Cl(11)	2.312 (6)	Sb(2)–Cl(21)	2.403 (6)	Sb(3)–Cl(32)	2.350 (4)	Sb(4)–Cl(42)	2.393 (4)
	2.418[a]		2.460[a]		2.375[a]		2.408[a]
Sb(1)–Cl(12)	2.343 (6)	Sb(2)–Cl(22)	2.306 (5)	Sb(3)–Cl(33)	2.382 (5)	Sb(4)–Cl(43)	2.338 (4)
	2.410[a]		2.390[a]		2.412[a]		2.354[a]
Fe(1)–C(1)	1.78 (2)	Fe(3)–C(5)	1.88 (2)	Sb(3)···Cl(34)	3.165 (4)	Sb(4)–Cl(34)	2.744 (4)
Fe(1)–C(2)	1.74 (2)	Fe(3)–C(6)	1.73 (2)	Sb(3)···Cl(62)[I]	3.386 (6)	Sb(4)···Cl(41)[II]	3.382 (5)
Fe(2)–C(3)	1.76 (2)	Fe(4)–C(7)	1.75 (2)	Sb(3)···Cl(63)	3.240 (5)	Sb(4)···Cl(52)[II]	3.363 (5)
Fe(2)–C(4)	1.75 (2)	Fe(4)–C(8)	1.77 (2)	Sb(5)–Cl(51)	2.334 (5)	Sb(6)–Cl(61)	2.345 (4)
					2.372[a]		2.370[a]
C(1)–O(1)	1.11 (2)	C(5)–O(5)	1.07 (2)	Sb(5)–Cl(52)	2.427 (4)	Sb(6)–Cl(62)	2.379 (4)
C(2)–O(2)	1.16 (2)	C(6)–O(6)	1.16 (2)		2.444[a]		2.403[a]
C(3)–O(3)	1.13 (2)	C(7)–O(7)	1.12 (2)	Sb(5)–Cl(53)	2.339 (4)	Sb(6)–Cl(63)	2.611 (5)
C(4)–O(4)	1.15 (2)	C(8)–O(8)	1.14 (2)		2.360[a]		2.644[a]
Fe(1)–C(11)	2.11 (2)	Fe(3)–C(31)	2.13 (2)	Sb(5)···Cl(56)	2.975 (4)	Sb(6)–Cl(56)	2.590 (4)
Fe(1)–C(12)	2.11 (2)	Fe(3)–C(32)	2.08 (2)	Sb(5)···Cl(41)[II]	3.263 (4)	Sb(6)···Cl(63)[I]	3.528 (6)
Fe(1)–C(13)	2.09 (2)	Fe(3)–C(33)	2.07 (2)	Sb(5)···Cl(42)	3.474 (5)	Sb(6)···Cl(34)	3.197 (4)
Fe(1)–C(14)	2.08 (2)	Fe(3)–C(34)	2.13 (2)				
Fe(1)–C(15)	2.08 (2)	Fe(3)–C(35)	2.06 (2)	(ii) Interatomic Angles, Deg			
Fe(2)–C(21)	2.03 (2)	Fe(4)–C(41)	2.09 (2)	Cl(31)–Sb(3)–Cl(32)	94.4 (2)	Cl(41)–Sb(4)–Cl(42)	84.5 (2)
Fe(2)–C(22)	2.07 (2)	Fe(4)–C(42)	2.05 (2)	Cl(31)–Sb(3)–Cl(33)	94.3 (2)	Cl(41)–Sb(4)–Cl(43)	92.2 (2)
Fe(2)–C(23)	2.06 (2)	Fe(4)–C(43)	2.04 (2)	Cl(31)–Sb(3)–Cl(34)	98.4 (2)	Cl(41)–Sb(4)–Cl(34)	168.3 (2)
Fe(2)–C(24)	2.09 (2)	Fe(4)–C(44)	2.11 (2)	Cl(31)–Sb(3)–Cl(62)[I]	81.2 (2)	Cl(41)–Sb(4)–Cl(41)[II]	76.0 (2)
Fe(2)–C(25)	2.07 (2)	Fe(4)–C(45)	2.02 (2)	Cl(31)–Sb(3)–Cl(63)	164.3 (2)	Cl(41)–Sb(4)–Cl(52)[II]	70.6 (2)
C(11)–C(12)	1.44 (2)	C(31)–C(32)	1.44 (2)	Cl(32)–Sb(3)–Cl(33)	92.8 (2)	Cl(42)–Sb(4)–Cl(43)	94.4 (2)
C(11)–C(15)	1.40 (2)	C(31)–C(35)	1.42 (2)	Cl(32)–Sb(3)–Cl(34)	81.3 (2)	Cl(42)–Sb(4)–Cl(34)	83.9 (2)
C(12)–C(13)	1.41 (2)	C(32)–C(33)	1.41 (2)	Cl(32)–Sb(3)–Cl(62)[I]	168.2 (2)	Cl(42)–Sb(4)–Cl(41)[II]	96.8 (2)
C(13)–C(14)	1.44 (2)	C(33)–C(34)	1.40 (2)	Cl(32)–Sb(3)–Cl(63)	101.2 (2)	Cl(42)–Sb(4)–Cl(52)[II]	155.0 (2)
C(14)–C(15)	1.37 (2)	C(34)–C(35)	1.46 (2)	Cl(33)–Sb(3)–Cl(34)	166.4 (2)	Cl(43)–Sb(4)–Cl(34)	89.8 (2)
C(21)–C(22)	1.40 (2)	C(41)–C(42)	1.48 (3)	Cl(33)–Sb(3)–Cl(62)[I]	98.4 (2)	Cl(43)–Sb(4)–Cl(41)[II]	162.9 (2)
C(21)–C(25)	1.35 (3)	C(41)–C(45)	1.41 (4)	Cl(33)–Sb(3)–Cl(63)	87.1 (2)	Cl(43)–Sb(4)–Cl(52)[II]	84.7 (2)
C(22)–C(23)	1.37 (2)	C(42)–C(43)	1.35 (2)	Cl(34)–Sb(3)–Cl(62)[I]	88.6 (2)	Cl(34)–Sb(4)–Cl(41)[II]	104.3 (2)
C(23)–C(24)	1.40 (2)	C(43)–C(44)	1.37 (4)	Cl(34)–Sb(3)–Cl(63)	82.1 (2)	Cl(34)–Sb(4)–Cl(52)[II]	121.1 (2)
C(24)–C(25)	1.37 (2)	C(44)–C(45)	1.34 (4)	Cl(62)[I]–Sb(3)–Cl(63)	83.0 (2)	Cl(41)[II]–Sb(4)–Cl(52)[II]	79.7 (2)
(ii) Interatomic Angles, Deg				Cl(51)–Sb(5)–Cl(52)	89.3 (2)	Cl(61)–Sb(6)–Cl(62)	94.8 (2)
Cl(11)–Sb(1)–Cl(12)	94.8 (3)	Cl(21)–Sb(2)–Cl(22)	92.6 (3)	Cl(51)–Sb(5)–Cl(53)	96.9 (2)	Cl(61)–Sb(6)–Cl(63)	89.6 (2)
Cl(11)–Sb(1)–Fe(1)	104.3 (2)	Cl(21)–Sb(2)–Fe(3)	101.7 (2)	Cl(51)–Sb(5)–Cl(56)	82.5 (2)	Cl(61)–Sb(6)–Cl(56)	88.7 (2)
Cl(11)–Sb(1)–Fe(2)	107.1 (2)	Cl(21)–Sb(2)–Fe(4)	104.3 (2)	Cl(51)–Sb(5)–Cl(41)[II]	162.0 (2)	Cl(61)–Sb(6)–Cl(63)[I]	176.2 (2)
Cl(12)–Sb(1)–Fe(1)	103.2 (2)	Cl(22)–Sb(2)–Fe(3)	106.8 (2)	Cl(51)–Sb(5)–Cl(42)	91.3 (2)	Cl(61)–Sb(6)–Cl(34)	85.4 (2)
Cl(12)–Sb(1)–Fe(2)	106.0 (2)	Cl(22)–Sb(2)–Fe(4)	108.2 (2)	Cl(52)–Sb(5)–Cl(53)	92.6 (2)	Cl(62)–Sb(6)–Cl(63)	88.9 (2)
Fe(1)–Sb(1)–Fe(2)	134.60 (8)	Fe(3)–Sb(2)–Fe(4)	134.90 (8)	Cl(52)–Sb(5)–Cl(56)	171.7 (2)	Cl(62)–Sb(6)–Cl(56)	87.1 (2)
				Cl(52)–Sb(5)–Cl(41)[II]	73.6 (2)	Cl(62)–Sb(6)–Cl(63)[I]	96.1 (2)
Sb(1)–Fe(1)–C(1)	92.7 (7)	Sb(2)–Fe(3)–C(5)	91.1 (7)	Cl(52)–Sb(5)–Cl(42)	81.6 (2)	Cl(62)–Sb(6)–Cl(34)	178.8 (2)
Sb(1)–Fe(1)–C(2)	91.7 (7)	Sb(2)–Fe(3)–C(6)	92.8 (6)	Cl(53)–Sb(5)–Cl(56)	89.5 (2)	Cl(63)–Sb(6)–Cl(56)	175.6 (2)
C(1)–Fe(1)–C(2)	95.6 (9)	C(5)–Fe(3)–C(6)	95.6 (9)	Cl(53)–Sb(5)–Cl(41)[II]	89.7 (2)	Cl(63)–Sb(6)–Cl(63)[I]	89.8 (2)
Sb(1)–Fe(2)–C(3)	93.0 (7)	Sb(2)–Fe(4)–C(7)	89.4 (7)	Cl(53)–Sb(5)–Cl(42)	169.9 (2)	Cl(63)–Sb(6)–Cl(34)	92.2 (2)
Sb(1)–Fe(2)–C(4)	91.1 (7)	Sb(2)–Fe(4)–C(8)	93.8 (6)	Cl(56)–Sb(5)–Cl(41)[II]	114.4 (2)	Cl(56)–Sb(6)–Cl(63)[I]	95.7 (2)
C(3)–Fe(2)–C(4)	93.8 (9)	C(7)–Fe(4)–C(8)	93.4 (11)	Cl(56)–Sb(5)–Cl(42)	97.4 (2)	Cl(56)–Sb(6)–Cl(34)	91.7 (2)
				Cl(41)[II]–Sb(5)–Cl(42)	80.8 (2)	Cl(63)[I]–Sb(6)–Cl(34)	86.1 (2)
Fe(1)–C(1)–O(1)	178 (2)	Fe(3)–C(5)–O(5)	176 (3)	Sb(3)–Cl(34)–Sb(4)	109.3 (1)	Sb(5)–Cl(56)–Sb(6)	111.7 (1)
Fe(1)–C(2)–O(2)	177 (2)	Fe(3)–C(6)–O(6)	175 (2)				
Fe(2)–C(3)–O(3)	178 (2)	Fe(4)–C(7)–O(7)	178 (2)				
Fe(2)–C(4)–O(4)	178 (2)	Fe(4)–C(8)–O(8)	173 (3)				
C(12)–C(11)–C(15)	107 (2)	C(32)–C(31)–C(35)	108 (2)				
C(11)–C(12)–C(13)	107 (2)	C(31)–C(32)–C(33)	108 (2)				
C(12)–C(13)–C(14)	108 (2)	C(32)–C(33)–C(34)	109 (2)				
C(13)–C(14)–C(15)	107 (2)	C(33)–C(34)–C(35)	108 (2)				
C(14)–C(15)–C(11)	111 (2)	C(34)–C(35)–C(31)	107 (2)				
C(22)–C(21)–C(25)	108 (2)	C(42)–C(41)–C(45)	106 (2)				
C(21)–C(22)–C(23)	108 (2)	C(41)–C(42)–C(43)	107 (2)				
C(22)–C(23)–C(24)	107 (2)	C(42)–C(43)–C(44)	108 (3)				
C(23)–C(24)–C(25)	108 (2)	C(43)–C(44)–C(45)	112 (3)				
C(24)–C(25)–C(21)	108 (2)	C(44)–C(45)–C(41)	108 (3)				

[a] Distance corrected for thermal motion using the riding-motion model. [b] Superscript I: Atomic coordinates are related to those in Table I by a center of symmetry (0, $^1/_2$, 0). Superscript II: Atomic coordinates are related to those in Table I by a center of symmetry at ($^1/_2$, $^1/_2$, 0).

while anomalous dispersion corrections for antimony and iron were those listed in ref 19b.

Results. The final atomic parameters are shown in Table I.[20] Table II lists the interatomic distances and angles, some of the distances having been corrected for riding motion[21] where this correction seemed appropriate. Since not all parameters could be refined in one least-squares cycle, the errors in the interatomic distances and

Table III. Equations to Planes through Selected Atomic Groupings of the form $AX + BY + CZ + D = 0^a$

Atoms defining plane[b]	Plane	A	B	C	D	χ^2
C(11) through C(15)	I	−0.5130	0.6510	−0.5594	11.045	2.59
C(21) through C(25)	II	0.5427	0.0188	−0.8397	5.996	1.52
C(31) through C(35)	III	−0.3554	0.6884	−0.6323	7.428	1.96
C(41) through C(45)	IV	0.7026	−0.0316	−0.7109	8.739	0.92

[a] X, Y, and Z are in angstroms and are parallel to a, b, and c^*. [b] Fe(1) lies 1.711 Å above plane I; Fe(2) lies 1.697 Å above plane II; Fe(3) lies 1.702 Å above plane III; Fe(4) lies 1.687 Å above plane IV.

angles will be underestimated. In Table III, the equations to selected planar groupings are tabulated. Figure 1 shows the arrangement of the molecules in the unit cell while Figures 2 and 3 show the anion and cation groupings and indicate the atomic labeling used.

Discussion

The asymmetric unit contains two cations, [Cl₂Sb{Fe(h⁵-C₅H₅)(CO)₂}₂]⁺ (I), and an anion grouping of formula [Sb₄-Cl₁₄]²⁻. As can be seen from Figure 3, the two crystallographically independent cations are similar in shape. Inspection of Figures 1 and 2 shows that the antimony–chlorine groupings form ribbons parallel to the *ab* plane. The cations sit between these ribbons. All chlorine (anion)···carbon (π-cyclopentadienyl) contacts are >3.3 Å while the chlorine (anion)···oxygen (carbonyl) contacts are >3.4 Å.

The Cation. The two independent cations have within the limits of error similar bond lengths and bond angles. As a result, except where otherwise stated, bond lengths and bond angles have been averaged over the two cations but the esd's are those associated with the individual measurements.

If the antimony atom in the cation is considered to be Sb(V), then each iron atom is formally in the zero oxidation state. Electron bookkeeping for the iron atom shows five electrons are donated from the π-cyclopentadienyl group, two electrons are donated from each of two carbonyl groups, and one electron is donated from antimony in forming the Sb–Fe σ bond, a total of ten electrons which is consistent with a krypton configuration. The carbonyl groups and the antimony atom form angles of ~90° with one another about each iron atom and hence the iron atom has approximately octahedral coordination, the π-cyclopentadienyl moiety being considered tridentate. The Fe–C(carbonyl) is 1.77 (2) Å and Fe–C(π-cyclopentadienyl) is 2.08 (2) Å while C–C in the π-cyclopentadienyl group is 1.40 (2) Å. These values compare favorably with values found in similar fragments.[7,22] Since the bond lengths in the π-cyclopentadienyl groups have not been corrected for the large thermal motion, the values quoted will be somewhat short.

The arrangement of the iron and chlorine atoms about the antimony atom leads to a very distorted tetrahedron. Although the angle Cl–Sb–Fe, 105.2 (2)°, is just less than the tetrahedral value, the angles Cl–Sb–Cl, 93.7 (3)°, and Fe–Sb–Fe, 134.8 (1)°, differ markedly from the ideal value. The large value for the angle Fe–Sb–Fe is probably associated with steric repulsion of the two bulky [Fe(h⁵-C₅H₅)(CO)₂] groups. Dahl[7] has reviewed the series of compounds

[Fe(h⁵-C₅H₅)(CO)₂]ₙSnCl₄₋ₙ, n = 0–3, and has shown that systematic changes occur in the Sn–Cl and Sn–Fe bond lengths and the Cl–Sn–Cl, Cl–Sn–Fe, and Fe–Sn–Fe bond angles as n changes [see Table VI of ref 7 and the discussion therein]. Moreover, he has found that if allowance is made for the shorter covalent radius of antimony (0.04 Å),[23] the greater positive charge localization on antimony, and the greater covalency of Sb–Cl bonds with respect to similar properties of tin, the bond lengths and bond angles about antimony in [{Fe(h⁵-C₅H₅)(CO)₂}₃SbCl]⁺ (II) are similar to those found about tin in the analogous tin compound {Fe-(h⁵-C₅H₅)(CO)₂}₂{Mo(h⁵-C₅H₅)(CO)₃}SnCl (III).[22g,24] Dahl also predicted that trends in the antimony series will follow that of the tin series. These predictions have been confirmed in this structural analysis. For I, Sb–Fe = 2.440 (2) and Sb–Cl = 2.419 (6) Å; Cl–Sb–Cl = 93.7 (3), Cl–Sb–Fe = 105.2 (2), and Fe–Sb–Fe = 134.8 (1)°. The values in the analogous tin compound [Fe(h⁵-C₅H₅)(CO)₂]₂SnCl₂ (IV) are 2.492 (8) and 2.43 (1) Å and 94.1 (6), 107.2 (individual esd 0.3°), and 128.6 (3)°.[22f] There is one discrepancy—Sn–Cl > Sb–Cl by ~0.01 Å whereas in II and III Sn–Cl > Sb–Cl by ~0.1 Å. This anomaly could be a result of the Sb–Cl being overestimated by the riding motion correction or of the fact that no corrections were made in IV where only isotropic refinement of parameters was carried out, or a combination of both.

The Anion Group. A survey of some structures containing antimony and chlorine reveals that Sb–Cl bond lengths generally lie between 2.3 and 2.4 Å.[25] Using this range as a guide for a chlorine bonded to antimony, the "anion group" in each asymmetric unit contains two SbCl₃ groups [Sb(3) and Sb(5)] and two SbCl₄⁻ ions [Sb(4) and Sb(6)]. It will be noted that the upper limit for a Sb–Cl bond distance has been extended beyond 2.4 Å, to 2.744 (4) Å in the case of Sb(4)–Cl(34). However, since Cl(56) is 2.590 (4) Å from Sb(6) and 2.975 (4) Å from Sb(5), we believe this symmetry in the bridging bonds does not preclude describing the Sb(5), Sb(6) grouping as an Sb₂Cl₇⁻ ion.

A more searching analysis of antimony–chlorine interatomic distances in Table IIB reveals there is a large spread in values. If we consider interatomic distances to 3.55 Å, each antimony atom has six chlorine "near neighbors." Some of these chlorine atoms are bonded in the electron-pair sense (shown as full lines in Figure 2) while others are more distant (shown as broken lines in Figure 2) but by no means without significant electronic interaction with the antimony atoms. (The sum of the van der Waals radii of

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(25) (a) A. Demalde, A. Mangia, M. Nardelli, G. Pelizzi, and M. E. Y. Tani, *Acta Crystallogr., Sect. B*, 28, 147 (1972); (b) R. Hulme and J. T. Szymanski, *ibid.*, 25, 753 (1969); (c) J-M. Le Carpentier and R. Weiss, *C. R. Acad. Sci., Ser. C*, 265, 797 (1967); (d) R. Weiss and B. Chevrier, *Chem. Commun.*, 145 (1967); (e) L. Brun and C-I. Branden, *Acta Crystallogr.*, 20, 749 (1966); (f) C-I. Branden and I. Lindqvist, *Acta Chem. Scand.*, 17, 353 (1963); (g) S. M. Ohlberg, *J. Amer. Chem. Soc.*, 81, 811 (1959); (h) I. Lindqvist and A. Niggli, *J. Inorg. Nucl. Chem.*, 2, 345 (1956).
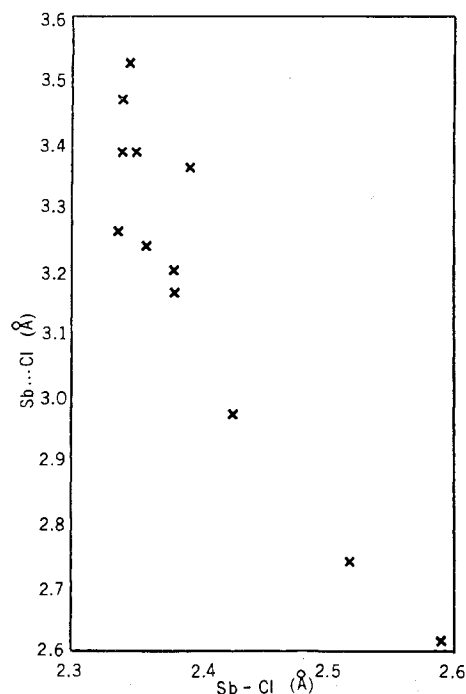
Figure 4. A plot of the two trans Sb–Cl contacts for each of the four octahedral antimony(III) atoms.

Figure 5. A plot of Sb–Cl bond lengths *vs.* Sb· · ·Cl contacts for each shared chlorine atom in the anion. Circles refer to data from ref 25a. X's refer to this work. Superscript a: these chlorine atoms also have a longer contact. Superscript b: This chlorine atom is the one proposed as the bridging chlorine in an $Sb_2Cl_7^-$ ion.

antimony and chlorine is 4.0 Å.[26]). These "near neighbors" allow each antimony to have very distorted octahedral coordination and lead to formation of continuous ribbons of antimony and chlorine atoms parallel to the *ab* plane. In other antimony halide compounds, higher coordination numbers than those implied by the molecular formula have been achieved by consideration of longer contacts which are considerably less than the sum of the van der Waals radii of the atoms involved. In SbF_3,[27] each antimony atom has three fluorine atoms at 1.92 Å and three others at 2.61 Å (sum of van der Waals radii of antimony and fluorine is 3.55 Å[26]) which results in a distorted octahedral arrangement about antimony. In KSb_2F_7,[10] the basic antimony–halogen units are SbF_3 and SbF_4^- but longer contacts of 2.41 and 2.57 Å are found. For $SbCl_3$,[25b] each antimony has three other chlorine atoms at ~3.5 Å.

Some evidence for an electronic interaction in the longer interatomic distances is also provided in the variation in length of the bonded antimony–chlorine distances. The chlorine atoms bonded to Sb(3) are not involved in other contacts with antimony less than 3.55 Å and the Sb(3)–Cl range from 2.375 (4) to 2.412 (5) Å. For Sb(4), the bonded chlorines are Cl(43), Cl(42), Cl(41), and Cl(34) and the distance to each is 2.354 (4), 2.408 (4), 2.529 (4), and 2.744 (4) Å, respectively. These chlorine atoms are, in order, involved in zero, one, two, and two interactions with other antimony atoms and, hence, as the numer of interactions increases, the bond length increases.

Figure 4 shows a plot of the all trans Sb–Cl contacts for

(26) See ref 23, p 260.
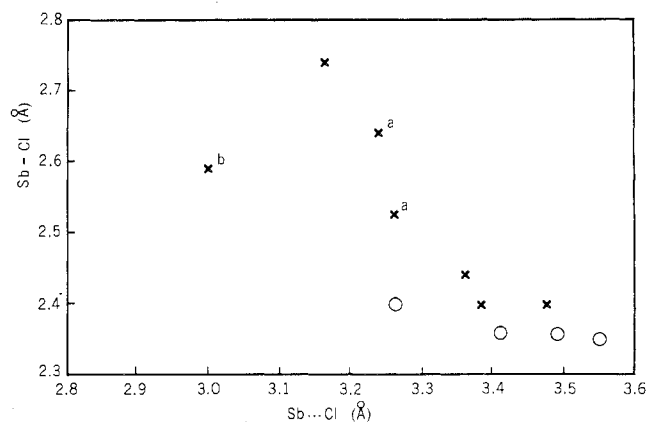(27) A. J. Edwards, *J. Chem. Soc. A*, 2751 (1970).

each of the four octahedral antimony atoms. A systematic trend is clear with a symmetrical situation at ~2.60 Å; this would presumably correspond to a formal bond order of $^1/_2$ (assuming that there is no significant π component in bonds of this type). At the simplest molecular orbital level one could regard each pair of trans bonds of this type as simple four-electron three-center bonds involving the p orbitals on the antimony and chlorine atoms.

Figure 5 shows a plot of the antimony–chlorine bond distance *vs.* antimony–chlorine contact to 3.55 Å for each shared chlorine atom in the anion. It can be seen that the points lie on a smooth curve except that for Cl(56). We suggest that the fact that Cl(56) lies off the curve supports our argument for an $Sb_2Cl_7^-$ ion involving this chlorine as the bridge.

The nature and strength of the interaction is difficult to access. In π molecular complexes of $SbCl_3$ with phenanthrene[25a] and naphthalene,[25b] it was observed that the Sb–Cl bond trans to the direction of the interaction of antimony with the aromatic center was lengthened by ~0.02–0.05 Å with respect to the cis Sb–Cl bonds. Although this lengthening was some type of trans effect, which is not predominant for this case, the magnitude of the resultant change was much less than is observed for this anionic grouping. Since the interaction in π molecular complexes is fairly strong, one might postulate that the antimony–chlorine interactions joining the $SbCl_3$ and $SbCl_4^-$ groups here are fairly strong. (Since the type of interaction in each compound is different, direct comparison cannot be made).