Novel Antimony Cluster Displaying a Quadruply Bridging Chloride. *X*-Ray Crystal Structure of $\{[Fe(\eta\text{-}C_5H_5)_2]_2[Sb_4Cl_{12}O]\}_2\cdot 2C_6H_6$

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Summary The product of the reaction between $SbCl_3$ and $Fe(\eta\text{-}C_5H_5)_2$ in benzene is shown by *X*-ray crystallography to possess an octameric unit $[Sb_4Cl_{12}O]_2^{4-}$, with terminal and bridging chloride groups and bridging oxo-groups; the ferricenium cations are shown to adopt the eclipsed configurations.

OXIDATION of ferrocene in the presence of group 5 trihalides has been shown to lead to a wide variety of ionic products containing the ferricenium cation and highly aggregated halogeno-group 5 anions.[1,2] Solutions of $BiCl_3$ or $BiBr_3$ and ferrocene when photolysed produce $[Fe(\eta\text{-}C_5H_5)_2]BiX_4$ containing infinitely extended edge-sharing irregular BiX_6^{3-} octahedra.

We now report that photolysis of benzene solutions of ferrocene and antimony trichloride in the presence of oxygen also produces dark blue needle-like crystals that are soluble in water (with decomposition), but unlike the extended association found for the tetrahalogenobismuthate anions, the anions are octameric clusters and contain oxygen bridges between metal centres in addition to chlorine bridges.

Preliminary mechanistic studies strongly suggest that the photoactive species is formed by electrophilic attack of the $SbCl_2^+$ ion on ferrocene to form the dichloroantimonoferrocenonium ion $[Cl_2SbFe(\eta\text{-}C_5H_5)_2]^+$ which, upon activation, is oxidized to the ferricenium ion by dissolved oxygen. Despite a wide range of initial molar ratios of ferrocene to $SbCl_3$ investigated, the product herein described is the sole ferrocene derivative observed.

Crystals of $[Fe(\eta\text{-}C_5H_5)_2]_4[Sb_4Cl_{12}O]_2\cdot 2C_6H_6$ are triclinic, *M* 2757·2, with $a = 15{\cdot}889(6)$, $b = 12{\cdot}764(5)$, $c = 12{\cdot}726(5)$ Å, $\alpha = 83{\cdot}42(4)$, $\beta = 114{\cdot}32(6)$, and $\gamma = 116{\cdot}34(6)°$, space group $P\bar{1}$, $Z = 1$, D_c 2·18, D_m 2·20 g cm^{-3}, F_{000} 1300. The structural analysis is based on 3180 independent reflections ($I_{obs}) > 2{\cdot}58\sigma(I_{obs})$ (Mo-K_α, $\mu = 40{\cdot}13$ cm^{-1}) and *R* is currently 0·089. The essential stereochemistry of the octameric unit is shown in Figure 1 and the e.s.d.'s in the bond lengths average 0·002 (Sb–Sb), 0·003 (Sb–Cl), 0·02 (Fe–C), and 0·03 Å (C–C).†

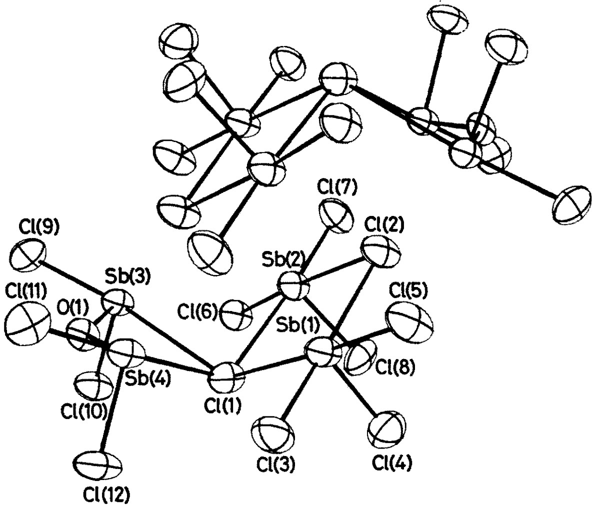

FIGURE 1. Perspective view of the centrosymmetrically related tetrameric units $[Sb_4Cl_{12}O]^{2-}$. The position of the centre of symmetry is indicated.

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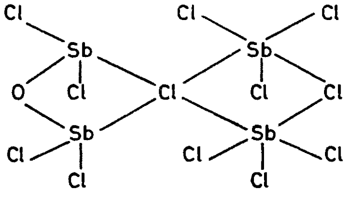
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Figure 1 demonstrates the unusual geometry of the two centrosymmetrically related tetramers which comprise the octameric unit [see also diagram (A)]. There are two distinct antimony co-ordination environments; that about Sb(1) and Sb(2) is essentially square pyramidal, each antimony being co-ordinated to three terminal chloride atoms at an average distance of 2·374 Å, a doubly bridging chloride at 3·00 Å, and the quadruply bridging chloride at 3·149 and 3·012 Å, while that about Sb(3) and Sb(4) is pseudo-trigonal bipyramidal, the stereochemically active lone-pair sharing the basal plane with the bridging-oxo group at 1·92 Å and the terminal Cl at 2·374 Å, and the apical positions defined by terminal Cl atoms at 2·372 Å and the quadruply bridging chloride at 3·192 and 3·031 Å. The oxo-bridged antimony atoms exhibit an unusually close contact distance of 3·457 Å, as compared to the more common non-bonding distances of 4·210, 4·040, 4·016, and 4·069 Å for Sb(1)–Sb(2), Sb(1)–Sb(4), Sb(1)–Sb(2′), and Sb(2)–Sb(3), respectively. The tetrameric units are connected by significant interactions of Sb(3) and Sb(4) with Cl(2′), 3·344 and 3·232 Å, respectively.



(A)

The octameric units $[Sb_4Cl_{12}O]_2^{4-}$ are discrete, displaying no significant interactions with neighbouring clusters. The ferricenium cations and the benzene solvent molecules occupy channels between the octamers (Figure 2). Unlike the staggered ring configuration of ferrocene itself, the ferricenium cations possess cyclopentadiene rings in the eclipsed configuration with an average twist angle α of 3·6° and a dihedral angle of 5° between the planes formed by the rings. The average distance of the iron from the ring centroids is 1·68 Å. The eclipsed configuration has been observed in previously determined ferricenium-ion structures.[1–5]

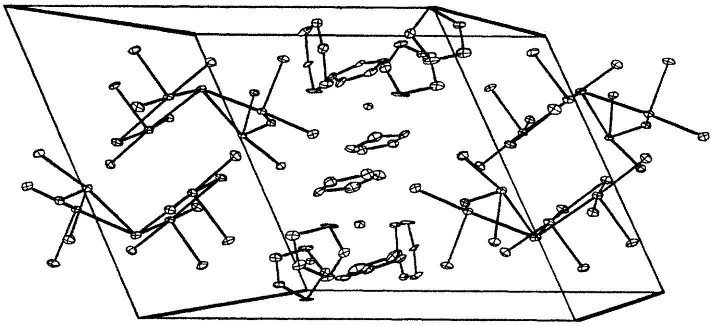


FIGURE 2. Packing diagram showing positions of two adjacent unit cells and illustrating the eclipsed configuration of the rings of the ferricenium cation, $[Fe(\eta\text{-}C_5H_5)_2]^+$. The channel occupied by the ferricenium cations and the benzene molecules of crystallization is also depicted.

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