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$[Fe_2(Sb_2S_6)(CO)_6]^{2+}$: A Cationic Group 15/16 Metal Cluster

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Cationic main group clusters have been known for over 150 years,[1−3] and in the past two decades many of their structures have come to light.[4,5] However, very little is known of their fundamental reaction chemistry. In particular, their reactions with transition metals are almost unknown. Recently some scattered reports appeared in the literature describing complexes of cationic main group clusters with transition metal carbonyls. These include $[W_2(CO)_{10}Se_4][SbF_6]_2$,[6] $[W(CO)_4(Te_3)][SbF_6]_2$,[7] $[Mo(CO)_4(Te_3)][SbF_6]_2$, $[FeW(CO)_8(Se_2)][SbF_6]_2$,[8] and $[Co_2(CO)_6(S_2)][AsF_6]_2$.[9] Note that these complexes contain only homoleptic group 16 cationic clusters. This relatively small number of clusters is in marked contrast to the very rich chemistry of metal complexes with main group anions.[10−13]

We have begun to explore systematically the reactions of polyatomic chalcogen cations with transition metal carbonyls. We have found that sulfur and selenium cations react with various iron carbonyls in liquid SO_2, to form the new cationic clusters $[Fe_3(S_2)_2(CO)_{10}][SbF_6]_2$, $[Fe_3(Se_2)_2(CO)_{10}][SbF_6]_2$, and $[Fe_4(Se_2)_3(CO)_{12}][SbF_6]_2\cdot 3SO_2$.[14] Now we wish to report an extension of this work, namely the isolation and characterization of $[Fe_2(Sb_2S_6)(CO)_6][SbF_6]_2\cdot 2SO_2$ (**I**), containing a novel antimony sulfur cationic cage. It is well-known that anionic group 15/16 clusters readily form complexes with transition metals.[15] However, this is the first metal carbonyl cluster containing a mixed main group *cationic* cluster.

When $[S_8][Sb_2F_{11}]_2$ is reacted with 3 equiv of either $Fe(CO)_5$ or $Fe_2(CO)_9$ in SO_2,[16] there is an initial formation of the previously described $[Fe_3(S_2)_2(CO)_{10}][SbF_6]_2$[14] as orange needles (eq 1), but upon standing at room temperature, this product redissolves, forming an orange solution, which in a few days deposits orange cubes (eq 2).

$$3Fe(CO)_5 + S_8(Sb_2F_{11})_2 \xrightarrow{SO_2} [Fe_3(S_2)_2(CO)_{10}][SbF_6]_2 + \text{byproducts} \quad (1)$$

$$[Fe_3(S_2)_2(CO)_{10}][SbF_6]_2 \xrightarrow{SO_2} [Fe_2(CO)_6(Sb_2S_6)][SbF_6]_2\cdot 2SO_2 + \text{byproducts} \quad (2)$$

A single-crystal X-ray diffraction study was undertaken,[17] revealing the cagelike structure of the title compound (Figure 1). The unit cell contains two structurally similar but crystallographically unique $[Fe_2(Sb_2S_6)(CO)_6]^{2+}$ clusters, along with their four SbF_6^- counteranions. There are also two SO_2 molecules of crystallization in the lattice per cation cluster. The structure of the cation cluster is quite unusual, with an $Fe(CO)_3$ fragment connected to each end of an Sb_2S_6 cage. Each iron center is pseudooctahedral, having an η^1 sulfur bond, an η^2-bound S_2 from the cage, and three carbonyls to complete its coordination sphere. There is an inversion center at the centroid position of the central Sb_2S_2 ring and a noncrystallographic 2-fold rotation axis parallel to, and passing through, the antimony atoms of this central four-membered ring. Alternatively, the cluster can be viewed as two distorted trigonal prisms sharing an edge between the two antimony atoms.

The two clusters per asymmetric unit are virtually identical, and for brevity, only one will discussed. The η^1 sulfur−iron bonds, $Fe(1)-S(1) = 2.350(4)$ Å and $Fe(2)-S(4) = 2.384(4)$ Å, are quite long. For example, the η^1 Fe−S bond distances in $[CpFeS_2]_2$ are 2.10 Å.[18] Typically Fe−S single bonds range from 2.18 to 2.26 Å.[19] The Fe−S bond distances of the η^2-bound S_2 unit range from 2.284(3) to 2.293(3) Å and are much closer to normal η^2-S_2 Fe−S bond distances (typically 2.22−2.27 Å[18,20]). The Fe−C bond distances in the title complex range from 1.81 to 1.87 Å, which are within reasonable limits for iron-bound carbonyl ligands. The angles around the iron center are somewhat distorted with respect to the η^2-bound S_2 atoms. The S−Fe−S bond angles [53.3(1)°] are acute but are not out of the ordinary for η^2-bound S_2 units.

In the central cage, the antimony centers have a distorted trigonal bipyramidal geometry, with lone pairs in an equatorial position, as expected for formal Sb(III) centers. The apical bound sulfur atoms have bond angles of 149.15(9)°. The central planar Sb_2S_2 rings in the title compound have typical Sb−S

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(16) Experimental work: The starting $[S_8][Sb_2F_{11}]_2$[34] (0.150g) was stirred for 30 min with 3 equiv of $Fe(CO)_5$ (0.05 mL) predissolved in 10 mL of SO_2 at room temperature. The reaction mixture was then filtered, and the filtrate was allowed to stand undisturbed to deposit orange cubes of the product in *ca.* 25% yield (0.050 g). IR (Nujol mull, cm^{-1}): 2119, 2086, 2069, 2018. Anal. (Atlantic Microlabs, Norcross, GA). Calcd for $Fe_2Sb_4S_8F_{12}C_6O_{10}$: C, 5.76; H, 0.00. Found: C, 5.51; H, 0.14.
(17) X-ray crystallographic data for $[Fe_2(Sb_2S_6)(CO)_6][SbF_6]_2\cdot 2SO_2$: orange hexagon (0.50 × 0.30 × 0.25 mm), MW = 1315.21, triclinic, space group $P\bar{1}$ (No. 2) at 173 K; $a = 12.072(5)$ Å, $b = 14.622(6)$ Å; $c = 10.120(4)$ Å, $\alpha = 90.23(4)°$, $\beta = 111.75(3)°$, $\gamma = 112.96(3)°$, $V = 1504(1)$ Å^3, $Z = 2$, $d(\text{calc}) = 2.90$ g/cm^3. Data were collected on Rigaku AFC7R rotating-anode diffractometer, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $\omega-2\theta$ scan, scan range $2.0 < \theta < 24.98°$, data collected h,$\pm k$,$\pm l$ (12,±16,±11). Total reflections of 4330 collected, 4056 unique, 3950 observed, $I > 3\sigma(I)$, $R_{\text{merg}} = 12.46\%$, $\mu = 5.142$ mm^{-1}, empirical absorption correction (transmission factors 0.707−1.695). Structure was determined using direct methods (SHELXS-86[35]) and refined using teXsan.[36] All atoms were refined anisotropically; $R = 0.0590$, $R_w = 0.0930$.
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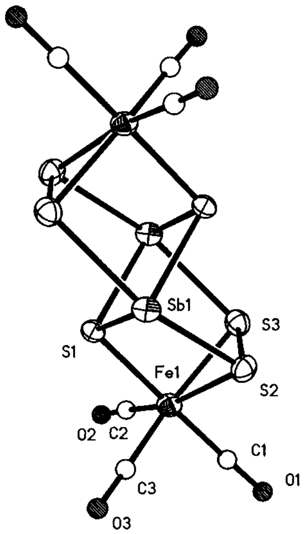

Figure 1. ORTEP view (50% probability ellipsoids) of one of the two similar but unique cations of $[Fe_2(Sb_2S_6)(CO)_6][SbF_6]_2 \cdot 2SO_2$. Important bond distances (Å) and angles (deg): Sb(1)−S(1) = 2.513(3), Sb(1)−S(1A) = 2.507(3), Sb(1)−S(2) = 2.713(3), Sb(1)−S(3) = 2.675(4), Fe(1)−S(1) = 2.350(4), Fe(1)−S(2) = 2.284(3), Fe(1)−S(3) = 2.288(3), S(2)−S(3) = 2.052(4); S(1)−Sb(1)−S(1A) = 92.15(9), S(1)−Sb(1)−S(2) = 77.1(1), S(1)−Sb(1)−S(3) = 82.7(1), S(2)−Sb(1)−S(3A) = 149.15(9), Sb(1)−S(1)−Sb(1A) = 87.85(9), Sb(1)−S(1)−Fe(1) = 95.7(1), Sb(1)−S(2)−Fe(1) = 92.0(1), Sb(1)−S(2)−S(3) = 105.5(1), S(1)−Fe(1)−S(2) = 89.4(1), S(1)−Fe(1)−S(3) = 88.2(1), S(2)−Fe(1)−S(3) = 53.3(1), Fe(1)−S(2)−S(3) = 63.4(1), Fe(1)−S(3)−S(2) = 63.2(1).

bond distances, ranging from 2.496(3) to 2.513(2) Å. However, the axial Sb−S bond lengths are somewhat longer, ranging from 2.675(4) to 2.734(3) Å. Since there have been no cationic antimony chalcogenide clusters previously reported, either as isolated clusters or as metal complexes, direct comparison is difficult. However, antimony−sulfur bonds in representative anions typically range from 2.40 to 2.65 Å.[21−23] The distances of the homoleptic bonds between the axial sulfur atoms, S(2)−S(3) = 2.052(4) Å and S(5)−S(6) = 2.055(4) Å, are typical of S−S single bonds. The S−S bonds in coordinated metal disulfides normally range from 1.96 to 2.05 Å.[18,24−27] The $[SbF_6]^-$ counterions and SO_2 molecules of solvation are normal in all respects and will not be mentioned further.

An IR spectrum of the air-sensitive orange cubes taken as a Nujol mull contains metal carbonyl bands which are shifted to substantially higher wavenumbers. The epicenter of the bands is approximately 70 cm^{-1} higher than that for the starting iron carbonyl. This behavior is typical of cationic chalcogen metal carbonyl clusters.[1−4,9,14] The crystalline product is stable under an argon atmosphere at room temperature but decomposes rapidly in CH_3CN, AsF_3, or CH_2Cl_2 to insoluble solids.

This new cationic cluster is unique because of the incorporation of antimony atoms into the cage structure. There is one previous report of isolated arsenic−sulfur and −selenium cationic clusters, obtained from direct oxidation of the neutral binary clusters by SbF_5.[28] However, no antimony incorporation is observed, and no further chemistry has been reported with these cationic cages. Group 15/16 fragments have been observed as ligands in $[Co(Triphos)(P_2X)][BF_4]$ (X = S, Se)[29] and $[(Triphos)Co(As_2X)][BF_4]$ (X = Se, Te).[30] However, in these cases, the three membered main group rings are best considered neutral, with the formal charge being placed on the transition metal center.

The only apparent source of antimony in the cluster is the starting counteranion, $[Sb_2F_{11}]^-$. It appears that Sb(V)−F bonds have been completely replaced by Sb(III)−S bonds, in a complicated internal reaction, which at this point is still a puzzle. It is observed that prolonged exposure of the intermediate, $[Fe_3(S_2)_2(CO)_{10}]^{2+}$, to the byproducts of the original reaction mixture is necessary for product formation. Several attempts were made to elucidate another pathway for the formation of the product. Previously prepared $[Fe_3(X_2)_2(CO)_{10}][SbF_6]_2$ (X = S, Se) was reacted with MF_5 (M = Sb, As) stoichiometrically, in SO_2. However, this only led to obvious decomposition of the parent compounds, with elemental chalcogen being formed along with the neutral $Fe_3X_2(CO)_9$. The chalcogen cation was reacted *in situ* with 1 equiv of MF_5 and iron carbonyl, but this also led to the formation of elemental chalcogen and the neutral $Fe_3X_2(CO)_9$. Pre-reaction of iron carbonyl with the corresponding chalcogen cation, followed by addition of MF_5 to the reaction solution, led to the same decomposition products. In our hands, the only route to $[Fe_2(Sb_2S_6)(CO)_6]^{2+}$ is through the use of $[S_8][Sb_2F_{11}]_2$. The presence of $[Sb_2F_{11}]^-$ is crucial to the formation of the product. If $[S_8][SbF_6]_2$ is used as a starting material, the title compound is not formed. The "trapped" SbF_5 in $[Sb_2F_{11}]^-$ apparently plays a part in the formation of the final product, but its exact role is still unclear. The $[Sb_2F_{11}]^-$ anion has been shown previously to be a complex chemical entity in SO_2, with formation of a number of different higher nuclearity antimony fluorides.[31−33]

Thus, an unusual new molecule $[Fe_2(Sb_2S_6)(CO)_6][SbF_6]_2 \cdot 2SO_2$, which is the first compound containing a mixed group 15/16 cationic cluster has been prepared. The group 15 atoms have apparently been introduced via a complicated internal redox process.

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Supporting Information Available: Complete tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, and anisotropic thermal parameters along with a view of the packing in unit cell of the title compound (6 pages). Ordering information is given on any current masthead page.

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