Insertion of a Transition Metal Fragment into a Heptaantimonide(3−) Anion: Synthesis and Structure of [Sb7Mo(CO)3]3−

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Reaction of Na_2Sb_7 with $Mo(bipy)(CO)_4$ (bipy = bipyridyl) and 2,2,2-crypt(4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo-[8.8.8]hexacosane) in ethylenediamine results in the formation of $[Na(2,2,2-crypt)]_3$ $[Sb_7Mo(CO)_3]$, whose structure has been determined crystallographically.

Transition metals form a large number of clusters which vary in nature from simple aggregates of metal atoms[1] to extremely complex species formed by transition metal atoms and ligands of various sort such as carbonyls, phosphines, unsaturated organic systems, as well as interstitial atoms.[2] Still, the synthesis of 'naked' clusters of the main group metals, be it neutral or ionic, and having no peripheral ligands such as Sn_9^{4-},[3] Bi_9^{3+},[4] Bi_4^{2-},[5] Sb_7^{3-},[6] Sb_{11}^{3-},[7] and Te_6^{4+}[8] was a major challenge for many years.[9–11] The first indications that transition metals could be incorporated into 'Zintl-ions'[11] came from NMR spectroscopic experiments by Rudolph and coworkers on reactions between $Pt(PPh)_3$, and M_9^{4-} (M = Sn, Pb).[12] The subsequent synthesis of 'Zintl metal carbonylates' such as $[Bi_4Fe_4(CO)_{13}]^{2-}$ [13] and $[Tl_6Fe_{10}(CO)_{36}]^{6-}$ [14] and the isolation and structural characterization of the hexastannide anion $[Sn_6(Cr(CO)_5)_6]^{2-}$,[15] as well as the transition metal nona-stannide and -plumbide clusters $[Sn_9Cr(CO)_3]^{4-}$ and $[Pb_9Cr(CO)_3]^{4-}$ by Haushalter,[16,17] however, are indications of a growing chemistry in this area. We describe here the synthesis and structural characterization of $[Na(2,2,2-crypt)]_3[Sb_7Mo(CO)_3]$ **1** (2,2,2-crypt = 4,7,13,16,21,24-hexa-oxa-1,10-diazobicyclo[8.8.8]hexacosane) containing the $[Sb_7Mo(CO)_3]^{3-}$ anion **2**.

The title compound can be made by treating an ethylene-diamine (en) solution of Na_3Sb_7 with solid $Mo(bipy)(CO)_4$ (molar ratio 1:1.2). Addition of crypt (3 equiv.) and slow evaporation of the solvent affords very air-sensitive red needle-like crystals of **1** in yields of up to 8% (based on Na_3Sb_7). It has been characterized by elemental analysis, IR spectroscopy (ν_{CO}, 1850 and 1760 cm^{-1}), and single-crystal X-ray diffraction. Compound **1** can also be prepared by adding solid $Mo(bipy)(CO)_4$ to a dark-brown en extract of an alloy of the nominal composition NaSb (molar ratio = 1.2:1). After mixing, 3 equiv. of crypt are added. The solution is stirred for 90 min and filtered. Needle-like crystals of **1** are obtained by slow evaporation of the solvent in ca. 4% yield. The crystal structure† contains three well separated (2,2,2-crypt-Na$^+$) cations in addition to the anion **2**, which is shown in Fig. 1. It consist of a Sb7 cage, where the Mo(CO)3 fragment is bridging one of the quadrangular faces. The Mo–Sb distances ($d_{Mo–Sb}$: 2.948 Å) are identical within experimental error and significantly longer than the sum of the covalent radii (2.80 Å).[18]

The insertion of the transition metal fragment reduces the symmetry of the parent Sb_7^{3-} species from C_{3v} to C_s. The symmetry reduction is reflected in the Sb–Sb distances as well. Sb(7), which would be located in the apical position of the parent Sb7 cage has two Sb neighbours at 2.767(9) and 2.769(8) Å distance and another Sb atom 2.707(9) Å apart. Whereas the axial Sb–Sb distances [$d_{Sb(1)–Sb(4)}$: 2.713(9), $d_{Sb(2)–Sb(5)}$: 2.715(9), $d_{Sb(3)–Sb(6)}$: 2.712(9) Å] are virtually identical, one finds distinct differences for the Sb–Sb distances within the triangular base. There are two short Sb–Sb bonds [$d_{Sb(1)–Sb(2)}$: 2.867(9), $d_{Sb(1)–Sb(3)}$: 2.830(9) Å] and one longer Sb–Sb contact [$d_{Sb(2)–Sb(3)}$: 3.289(9) Å], the corresponding Sb–Sb bond distances in the naked Sb_7^{3-} being 2.877 Å. The Sb(2)–Sb(3) distance is significantly longer than a typical Sb–Sb single bond distance (2.81 Å), but it is also much shorter than the Sb–Sb van der Waals distance of 4.40 Å.[18]

The Sb–Sb distance of 2.75 Å in the free Sb_4^{2-} anion[6b] corresponds to a formal bond order of 1.25. The Sb–Sb distances within the Sb_6^{8-} chains in Eu_2Sb_3[19] and Sr_2Sb_3[20] are in the range between 2.887(4) and 3.016(3) Å. An estimate of the bonding interaction using Pauling's relation[21] $d(n) = d(1)$ − 0.6log$n$ gives a Sb–Sb bond order of 0.16. Thus the main structural consequence of incorporating the Mo(CO)3 fragment into the Sb_7^{3-} framework is a lengthening of one basal Sb–Sb bond.

The Sb(3)–Sb(6) bond distance and the metal coordination in the title compound warrant discussion. In general, the attack of a metal fragment at the Y_7^{3-} (or E_4X_3) birdcage can occur in three different positions. (i) The cage contains three topologically distinct atom positions where an electrophilic attack of the metal atom might occur to give an η^1-adduct. (ii) Bond cleavage and insertion of a metal ligand moiety is possible at one of the three types of edges of the cage. (iii) Finally, there are triangular (2x) and quadrangular faces where the attack of the metal fragment might occur.

The easiest possibility is the coordination to the metal through the apical atom as observed in $[Ni(np_3)(P_4Q_3)]$ [np_3 = tris(2-diphenylphosphinoethyl)amine, Q = S, Se].[22] In $P_7[Fe(CO)_2Cp]_3$ the coordination to the metal occurs through the three twofold bridging atoms (corresponding to the X positions in E_4X_3 molecules), which are the cage positions carrying the highest charge.[23] Cleavage of a basal P–P bond by insertion of the metal ligand moiety is found in $[(Pt(\mu-P_4S_3)(PPh_3))_3]$,[24] while a fragmentation of the cage is observed in the remaining cases.[25]

Of particular relevance in the present context is a metallated heptaarsenide anion, $[As_7Cr(CO)_3]^{3-}$, which was reported by Haushalter et al. recently.[26] It contains a cagelike As7 fragment similar to the Sb7 cage of the title compound, which

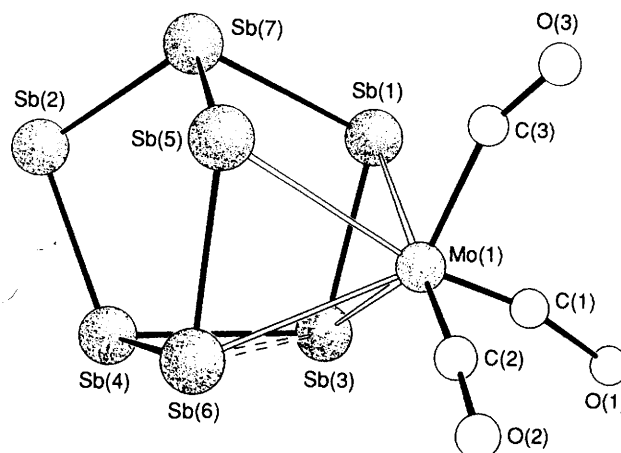Fig. 1 Perspective view of the $[Sb_7Mo(CO)_3]^{3-}$ anion in $[Na(2,2,2-crypt)]_3[Sb_7Mo(CO)_3]$. Pertinent interatomic distances (Å); Mo–Sb(1) 2.951(7), Mo–Sb(3) 2.951(9), Mo–Sb(5) 2.947(9), Mo–Sb(6) 2.942(8), Sb(3)–Sb(4) 2.867(9), Sb(4)–Sb(6) 2.830(9), Sb(3)–Sb(6) 3.289(9), Sb(1)–Sb(3) 2.715(8), Sb(2)–Sb(4) 2.713(9), Sb(5)–Sb(6) 2.712(9), Sb(1)–Sb(7) 2.769(8), Sb(2)–Sb(7) 2.707(9), Sb(5)–Sb(7) 2.767(9), Sb(1)···Sb(5) 3.817(9).
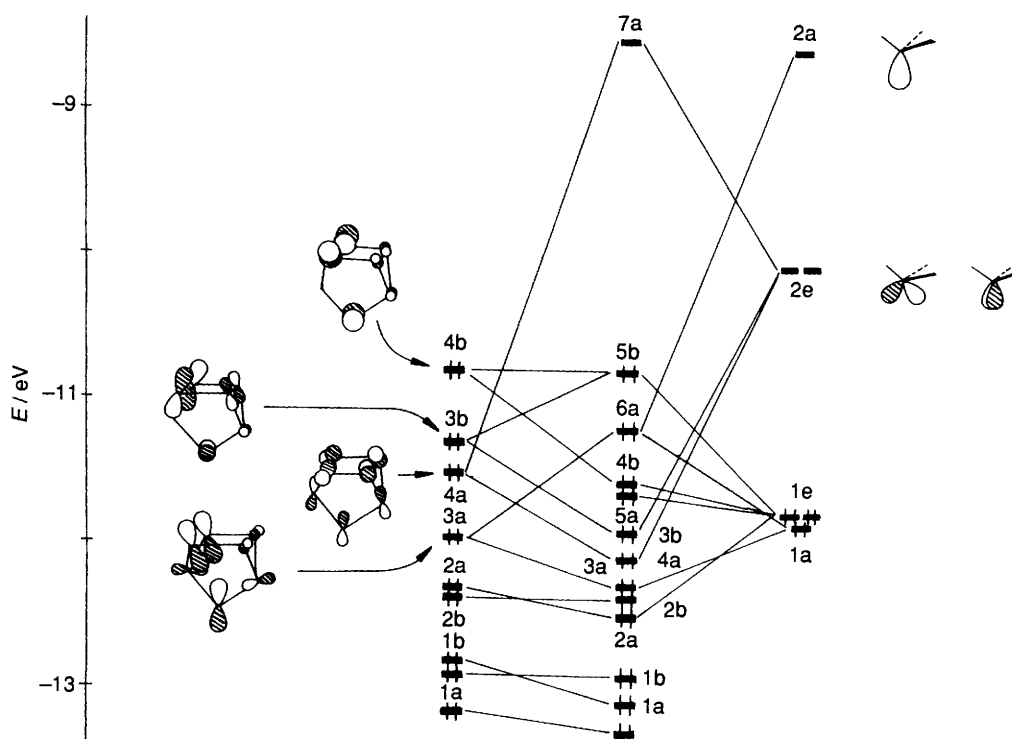
Fig. 2 Diagram for the most important interactions between the fragment molecular orbitals of the Sb_7^{3-} anion (left) and the $Mo(CO)_3$ fragment (right) of the $[Sb_7Mo(CO)_3]^{3-}$ anion (C_s symmetry)

is capped on one quadrangular face by a $Cr(CO)_3$ group. Its principal structural features are similar to those of the $[Sb_7Mo(CO)_3]^{3-}$ anion. The most important difference, however, are As–As distances of 3.09 and 3.29 Å corresponding to the Sb–Sb separations Sb(2)–Sb(3) and Sb(5)–Sb(6). Pauling's relation[21] gives a very small As–As bond orders (0.069 and 0.032), i.e. one might question the presence of As–As bonding at all. Topologically, the formation of $[As_7Cr(CO)_3]^{3-}$ was interpreted as an example for the rearrangement of a nortricyclic As_7^{3-} cluster to a norbornadiene-like fragment bonded to a transition metal centre.[26] From organic chemistry the reverse rearrangement is known to occur easily in $Cr(CO)_n$(norbornadiene) species.[27]

The subtle structural differences between $[Sb_7Mo(CO)_3]^{3-}$ and $[As_7Cr(CO)_3]^{3-}$ as well as the general structural choice for compounds containing Y_7 or E_4X_3 cages can be rationalized using molecular orbital ideas. An interaction diagram‡ for $[Sb_7Mo(CO)_3]^{3-}$, which was constructed by means of extended Hückel calculations[28a] using the fragment orbital formalism,[28b] is shown in Fig. 2.

The calculations were performed on a $[Sb_7Mo(CO)_3]^{3-}$ anion (C_s symmetry based on the experimental geometry), where all basal Sb–Sb distances are kept at 2.9 Å. The $[Sb_7Mo(CO)_3]^{3-}$ anion has been partitioned into a $Mo(CO)_3$ fragment (right side in Fig. 2) and a Sb_7^{3-} cluster (left side in Fig. 2). The orbitals of the $Mo(CO)_3$ fragment are well known. There are three low lying orbitals, a_1 and $1e$ ($2 \times a$ and b under C_s symmetry), originating from metal d_{z^2}, $d_{x^2-y^2}$ and d_{xy}, which are filled for a d^6 system. At somewhat higher energy we find a $2e$ set (a and b under C_s symmetry), mainly metal d_{xz} and d_{yz}, hybridized with p_x and p_y, which makes these orbitals extend away from the ligand. At still higher energy is a $2a_1$ (a under C_s symmetry) hybrid of metal d_{z^2} and s pointing away from the ligand.

The interaction with the Sb_7^{3-} fragment is mainly carried by the $2a_1$ and $2e$ hybrids. The Sb_7^{3-} anion has a number of orbitals with the appropriate symmetry to interact; the interaction of both fragments, however, is determined mainly by the overlap of the frontier orbitals. The frontier orbitals of

the Sb_7^{3-} fragment correspond to Sb lone pairs of Sb–Sb σ-bonding orbitals, respectively. The strongest interactions occur between the $3a$, $4a$ and $3b$ orbitals of the Sb_7^{3-} anion and the appropriate orbitals of the $Mo(CO)_3$ fragment. The $3a$ orbital of the cage and the $1a$ and $2a$ orbitals of the metal fragment are involved in a typical three orbital interaction, the $3a$ and $6a$ orbitals of **2** being the bonding and nonbonding combinations, respectively. Similarly, the $4b$ and $5b$ orbitals of **2** are kept low in energy by mixing in $4b$ contributions of the Sb_7^{3-} anion. The $3b$ orbital of **2** is the bonding combination of the $3b$ orbital of the cage and the $2e_a$ component of the metal fragment. Its $2e_s$ partner interacts strongly with the $4a$ orbital of the Sb_7^{3-} cage.

The latter fragment orbital of the cage has Sb–Sb bonding character. Therefore, one Sb–Sb bond of the cage is weakened by electron transfer to the $Mo(CO)_3$ unit. The result is a partial cleavage of the Sb(3)–Sb(6) bond of the Sb_7 cage in **2**. Since the As $4p$ orbitals are less diffuse than the Sb $5p$ orbitals the overlap of the $Cr(CO)_3$ fragment orbitals with those of the As_7 cage in the $[As_7Cr(CO)_3]^{3-}$ anion is much bigger than the Mo–Sb overlap in **2**. As a result, the As–As bond is cleaved nearly completely whereas only partial bond cleavage is observed in the Sb_7 cage of **2**. For the (still hypothetical) $[Bi_7M(CO)_3]^{3-}$ (M = Cr, Mo, W) anion we expect the corresponding Bi–Bi bond to remain almost unperturbed.

The unexpected η^4-coordination of the Sb_7 cage to the $Mo(CO)_3$ fragment is favoured over the η^1- and η^3-coordination modes for overlap reasons. The bond cleavage within and the associated nortricyclane → norbornadiene rearrangement of the cage are a direct consequence of the η^4 bonding of the $Mo(CO)_3$ fragment. The rearrangement of the cage and bond cleavage are facilitated by strong bonding of the metal fragment to the cage.

Footnotes

† *Crystal data* for [Na(2,2,2-crypt)]$_3$[Sb$_7$Mo(CO)$_3$]: C$_{57}$H$_{108}$N$_6$O$_{21}$ Na$_3$Sb$_7$Mo, M = 2229.77, monoclinic, space group Cc (No. 9), a = 23.29(1), b = 19.85(1), c = 17.29(1) Å, β = 94.59(3), V = 7966(2) Å^3, D_c = 1.86 g cm^{-3}, μ(Mo-Kα) = 1.8 mm^{-1}, Z = 4, λ = 0.71073 Å, crystal needle shape, dimensions 0.23 × 0.10 × 0.20 mm^3, 2θ$_{max}$ = 46°, data collected at 140 K on a Siemens R3 four-circle diffractometer; structure solved and refined using the SHELXTL PLUS program system, empirical absorption correction (transmission factors 0.928–0.531). 5897 Unique reflections of which 4331 are observed [with $I \geq 2\sigma(I)$]. Full-matrix least-squares refinement with hydrogen atoms constrained to chemically reasonable positions. A final R = 0.104, R_w = 0.081 (for the correct enantiomorph) was attained by treating all Mo, Sb, Na, O, and N atoms anisotropically and all C atoms and the O atoms of the carbonyl groups isotropically (564 variables).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Further details concerning the structure determination are available upon request from the Fachinformationszentrum Karlsruhe on quoting the depository number CSD-57625, the authors and the journal citation.

‡ The diagram in Fig. 2 is based on a [Sb$_7$Mo(CO)$_3$]$^{2-}$ anion with idealized C_s-symmetry and the following interatomic distances (Å): Sb(3)–Sb(4) 2.9; Sb(3)–Sb(6) 2.9, Sb(4)–Sb(6) 2.9, Sb(1)–Sb(3) 2.9, Sb(2)–Sb(4) 2.9, Sb(5)–Sb(6) 2.9, Sb(1)–Sb(7) 2.75, Sb(2)–Sb(7) 2.75, Sb(5)–Sb(7) 2.75, Mo–Sb 2.95, Mo–C 1.98.

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