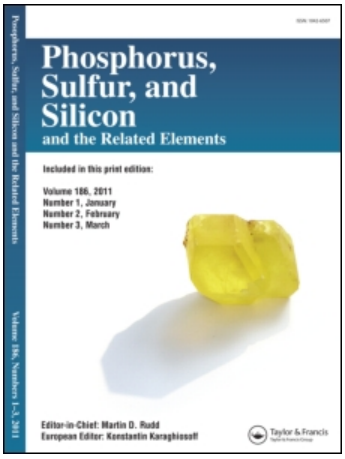

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Chemistry of Anionic Antimony Selenides

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To cite this Article Martin, T. M. , Schimek, G. L. , Mlsna, D. A. and Kolis, J. W.(1994) 'The Chemistry of Anionic Antimony Selenides', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 93 — 103
To link to this Article: DOI: 10.1080/10426509408021802
URL: http://dx.doi.org/10.1080/10426509408021802

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 93-103
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THE CHEMISTRY OF ANIONIC ANTIMONY SELENIDES: SYNTHESIS AND STRUCTURE OF SALTS OF $[Sb_4Se_6]^{2-}$ AND $[Fe_2(CO)_4(SbSe_4)_2]^{2-}$

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Abstract The reaction of $[HFe(CO)_4]^-$ with various binary antimony selenides was investigated. In the presence of Sb_2Se_3 the organometallic anion acts as a reducing agent leading to formation of $[Sb_4Se_6]^{2-}$ which has a crown shaped geometry with a transannular Sb-Sb bond. Reaction with Sb_2Se_5 leads to incorporation of iron carbonyl with formation of a dimer of formula $[Fe_2(CO)_4(SbSe_4)_2]^{2-}$. The cluster contains two $Fe(CO)_2$ fragments bridged by $SbSe_4^{3-}$ units. The main group anions are not tetrathiometallates, but rather a trivalent Sb bound to two selenides and a diselenide. Both compounds were structurally characterized as their $[PPh_4]^+$ salts. Crystal data for $[PPh_4]_2[Sb_4Se_6]$, triclinic, P-1, a = 10.124(2)Å, b = 14.670(2)Å, c = 17.352(2)Å, α = 96.42(2)°, β = 95.78(2)°, γ = 97.09(2)°, V = 2524.2(7)Å^3, Z = 2, R = 0.0377, R_w = 0.0465; crystal data for $[PPh_4]_2[Fe_2(CO)_4(SbSe_4)_2]$, monoclinic, $P2_1/n$, a = 15.552(5)Å, b = 110.279(3)Å, c = 18.159(6)Å, β = 101.72(3)°, V = 2819(1)Å^3, Z = 2, R = 0.0372, R_w = 0.0395.

INTRODUCTION

The chemistry of the polychalcogenides is quite extensive, [1] but their structural chemistry is somewhat limited by their tendency to retain the divalent state. The introduction of one or more trivalent centers greatly increases the topological complexity of the main group fragment and enhances the possibility of more extensive cage and cluster formation. Futhermore, the coordination chemistry of such species has the potential to lead to a vast array of new bonding and structural types. The most straightforward way to introduce a trivalent center to a main group cluster is to simply use group 15 elements.[2] Accordingly, we have begun a systematic investigation of the chemistry of the mixed 15/16 anionic clusters and their coordination chemistry with transition metals.

A number of interesting papers describing the chemistry of molecular 15/16 anions have appeared but the work has been somewhat sporadic until the last several years.[3] Most of the work has focused on the group 15 sulfides,[4] although several interesting molecular anions of the heavier elements (As, Sb, Se, Te) have recently appeared.[5] Workers in our group have isolated a number of new group 15 selenides such as $P_2Se_8^{2-}$ [6] and $As_4Se_6^{2-}$,[7]

and have used them to prepare a number of transition metal complexes. We have found that metal carbonyls are particularly useful sources of transition metal centers with polynuclear anions,[8] and have prepared a number of new metal main group hybrid clusters, including $[Fe_2(CO)_4(PSe_5)_2]^{2-}$, [6] $[M(CO)_2(As_3Se_3)_2]^{2-}$ (M = Mo,W),[9] $[Fe(CO)(As_3Se_3)_2]^{2-}$, $[Mn(CO)_3(As_3Se_5)]^{2-}$ and $[Fe_2(CO)_4(AsTe_4)_2]^{2-}$.[10]

We extended our investigations to the chemistry of antimony chalcogenides and found that reduction of various binary antimony sulfides leads to the formation of a number of molecular antimony sulfides including $[Sb_4S_6]^{2-}$ and $[Sb_6S_6]^{2-}$.[11] The reduction of the antimony selenides, Sb_2Se_3, Sb_4Se_4 or Sb_2Se_5, also leads to a very rich chemistry as well, and careful choice of reducing agents leads to a number of different products. For example, reduction of Sb_4Se_4 or Sb_2Se_3 with an alkali metal such as potassium, leads to formation of the highly insoluble $[Sb_{12}Se_{20}]^{4-}$ in good yield.[12] In this paper, we describe the reactions of Sb_2Se_3 and Sb_2Se_5 with the organometallic reducing agent $[HFe(CO)_4]^-$. It was found that Sb_2Se_3 reacts to form the new anion $[Sb_4Se_6]^{2-}$, while reaction with Sb_2Se_5 results in the incorporation of iron carbonyl fragments to form $[Fe_2(CO)_4(SbSe_4)_2]^{2-}$, the first metal complex of an antimony selenide fragment. The structures of both of these complexes are described.

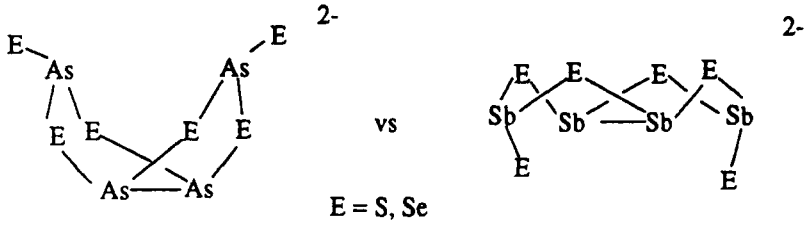
Table I. Crystallographic Data

	I	II
formula	$C_{48}H_{40}P_2Sb_4Se_6$	$C_{52}H_{40}O_4P_2Fe_2Sb_2Se_8$
fw	1639.5	1777.6
cryst syst	triclinic	monoclinic
space group	P-1	$P2_1/n$
a, Å	10.124(2)	15.422(5)
b, Å	14.670(2)	10.279(3)
c, Å	17.352(2)	18.159(6)
a, deg	96.42(2)	
b, deg	95.78(2)	101.72(3)
g, deg	97.09(2)	
V, Å^3	2524.2(7)	2818.7(14)
Z	2	2
D_{calc}, g cm^{-3}	2.157	2.094
T, °C	25	25
l, Å	0.71073	0.71073
m, mm^{-1}	6.540	6.717
transm coeff	0.69-1.00	0.56-1.00
no. of obsd data ($I>3s(I)$)	4153	1584
no. variables	542	197
$R(F_O)$	0.0377	0.0372
$R_w(F_O)$	0.0465	0.0395

RESULTS

Structure of $[(C_6H_5)_4P]_2[Sb_4Se_6]$ (II)

The dianion, $[Sb_4Se_6]^{2-}$ (Figure 1), while having the same empirical formula as its arsenic selenide and sulfide analogs, has a different structure. The cluster has a "crown type " arrangement of atoms similar to S_8, however there is an Sb-Sb bond across the center and one exocyclic Sb-Se bonds at each end. This conformation is different from the $[As_4E_6]^{2-}$ species which has a "basket-type" arrangement with the As-As bond at the the base of the "basket" and the two ends folded upward acting as the handles.[4e,7]



Both distinct types of antimony atoms exhibit trigonal pyramidal geometry in $[Sb_4Se_6]^{2-}$. For example, each Se-Sb-Se angle for Sb(1) is *ca.* 95°. The distances within the complex are comparable to those in **II** (vida infra). The exocyclic Sb(1)-Se(1) distance of 2.470(2)Å is short

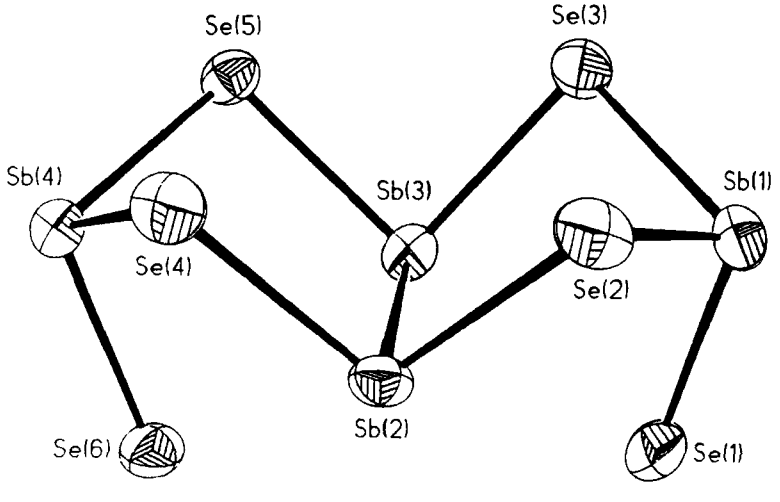
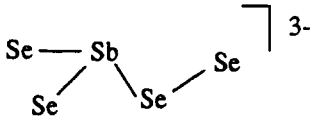


Figure 1. Thermal ellipsoid plot of $[Sb_4Se_6]^{2-}$, **I**, with 35% probability ellipsoids

for an Sb-Se single bond suggesting that some double bond character may be present. The other Sb-Se bond distances average 2.593(1)Å and are typical for Sb-Se single bonds. The transannular Sb-Sb distance of 2.858(1)Å is somewhat long for an Sb-Sb distance but still indicates a bonding interaction between Sb(2)-Sb(3). This structural type has also been observed for the corresponding sulfide analog as well, although it crystallizes in a different crystal system (monoclinic for the sulfide versus triclinic for the selenide).[11] At this time we have no ready explanation for different orientation of the arsenic relative to the antimony clusters.

Structure of $[(C_6H_5)_4P]_2[Fe_2(CO)_4(SbSe_4)_2]$ (II).

The structure of II consists of well separated dianions of $[Fe_2(CO)_4(SbSe_4)_2]^{2-}$ and $[PPh_4]^+$ cations with an inversion center located between the two iron atoms. The anions are dimers of iron carbonyl fragmetns which are bridged by $SbSe_4^{3-}$ groups (Figure 2). The $SbSe_4^{3-}$ groups are not tetrethiometallates as might be expected, but rather consist of trivalent antimony atoms with one diselenide fragment attached 

. This ligand is similar to that in a corresponding arsenic telluride complex, $[Fe_2(CO)_4(AsTe_4)_2]^{2-}$.[10] However, such an arrangement is more surprising for antimony, given its greater tendency to assume a pentavalent

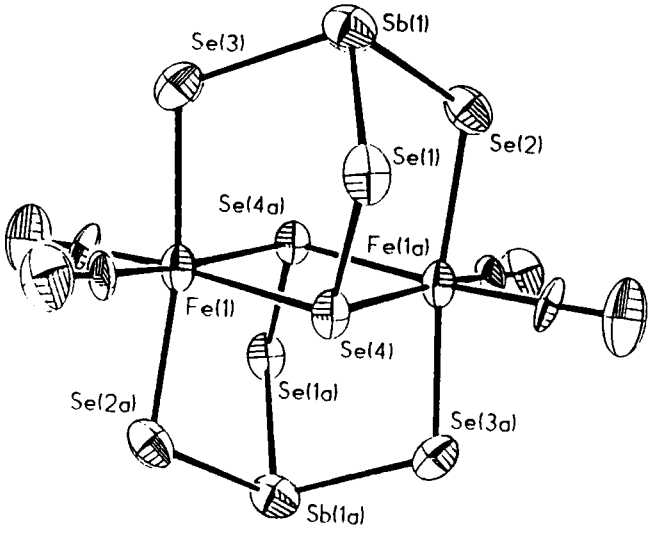


Figure 2. Thermal ellipsoid plot of $[Fe2(CO)4(SbSe_4)_2]^{2-}$, II, with 35% probability ellipsoids

Table II. Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2x10^3$) for $Sb_4Se_6^{2-}$

	x	*y*	*z*	U_{eq}
Sb(1)	864(1)	2030(1)	8097(1)	54(1)
Sb(2)	4652(1)	2594(1)	8426(1)	42(1)
Sb(3)	3605(1)	2119(1)	6820(1)	42(1)
Sb(4)	7118(1)	1581(1)	7252(1)	47(1)
Se(1)	1845(2)	3537(1)	7752(1)	66(1)
Se(2)	2775(1)	1686(1)	9085(1)	53(1)
Se(3)	1523(1)	944(1)	6966(1)	52(1)
Se(4)	6203(1)	1328(1)	8561(1)	53(1)
Se(5)	4954(1)	778(1)	6420(1)	46(1)
Se(6)	6755(1)	3221(1)	7237(1)	58(1)
P(1)	4161(3)	-2353(2)	6468(2)	40(1)
P(2)	8919(3)	6684(2)	8468(2)	35(1)
C(1)	4290(13)	-3559(8)	6259(7)	44(5)
C(2)	3188(14)	-4211(9)	6283(7)	56(6)
C(3)	3232(17)	-5141(9)	6160(8)	65(6)
C(4)	4400(19)	-5434(9)	5990(8)	67(7)
C(5)	5540(17)	-4810(9)	5973(7)	62(6)
C(6)	5491(14)	-3866(8)	6107(7)	51(5)
C(7)	2793(11)	-2106(7)	5803(7)	38(4)
C(8)	2490(12)	-2654(8)	5074(7)	45(5)
C(9)	1480(13)	-2436(9)	4554(7)	51(5)
C(10)	876(13)	-1693(9)	4737(9)	59(6)
C(11)	1206(14)	-1126(9)	5440(9)	63(6)
C(12)	2176(12)	-1354(8)	5978(8)	48(5)
C(13)	5677(11)	-1687(7)	6287(7)	40(5)
C(14)	5868(13)	-1453(9)	5564(7)	52(5)
C(15)	7034(15)	-891(10)	5466(8)	71(6)
C(16)	7992(14)	-601(9)	6066(8)	58(6)
C(17)	7831(13)	-871(9)	6777(8)	57(6)
C(18)	6685(13)	-1409(8)	6912(8)	53(5)
C(19)	3902(12)	-2057(8)	7472(7)	46(5)
C(20)	4002(13)	-1133(8)	7772(8)	53(5)
C(21)	3901(13)	-898(9)	8558(8)	58(6)
C(22)	3668(14)	-1571(10)	9039(8)	62(6)
C(23)	3569(13)	-2484(9)	8743(8)	54(6)
C(24)	3674(12)	-2729(9)	7963(8)	51(5)
C(25)	8963(11)	7922(7)	8648(6)	35(4)
C(26)	10170(13)	8470(8)	8628(8)	56(5)
C(27)	10247(15)	9429(8)	8804(8)	64(6)
C(28)	9144(16)	9814(8)	8978(8)	58(6)
C(29)	7961(15)	9278(8)	9000(8)	56(6)
C(30)	7867(12)	8314(7)	8835(7)	39(4)
C(31)	10147(10)	6372(7)	9164(7)	34(4)
C(32)	10419(13)	6897(8)	9896(8)	54(5)
C(33)	11284(13)	6635(9)	10467(8)	56(5)
C(34)	11853(12)	5865(9)	10327(8)	46(5)
C(35)	11599(12)	5328(8)	9625(8)	44(5)
C(36)	10731(12)	5566(7)	9049(7)	42(4)

	x	*y*	*z*	U_{eq}	
C(37)	7278(11)	6149(7)	8609(6)	31(4)	
C(38)	6856(12)	6286(7)	9333(6)	37(4)	
C(39)	5619(12)	5879(7)	9449(7)	43(5)	
C(40)	4810(12)	5319(8)	8856(7)	41(5)	
C(41)	5245(12)	5156(7)	8147(7)	41(5)	
C(42)	6476(12)	5582(7)	8007(6)	40(4)	
C(43)	9214(10)	6342(7)	7488(7)	36(4)	
C(44)	9231(13)	5430(8)	7199(8)	52(5)	
C(45)	9355(14)	5181(9)	6431(8)	60(6)	
C(46)	9466(14)	5840(12)	5926(9)	72(7)	
C(47)	9460(16)	6750(11)	6193(9)	78(7)	
C(48)	9344(13)	7018(9)	6969(8)	57(6)	

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

Table III. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$) for $[Fe(SbSe_4)(CO)_2]^{2-}$

	x	*y*	*z*	U_{eq}
Sb(1)	9020(1)	1862(1)	188(1)	58(1)
Se(1)	8265(1)	3156(2)	-962(1)	50(1)
Se(2)	10552(1)	2042(2)	-88(1)	56(1)
Se(3)	8939(1)	3692(2)	1117(1)	55(1)
Se(4)	9214(1)	5030(2)	-744(1)	39(1)
Fe(1)	9263(2)	5749(2)	540(1)	39(1)
P(1)	339(3)	2692(4)	3809(2)	39(2)
C(1)	8096(12)	6027(15)	290(10)	49(8)
C(2)	9449(10)	6394(17)	1466(9)	46(7)
O(1)	7357(8)	6178(12)	146(7)	66(5)
O(2)	9590(8)	6824(14)	2060(7)	86(6)
C(44)	2151(11)	5599(16)	4298(10)	56(5)
C(21)	1269(10)	1811(15)	5199(9)	46(4)
C(34)	1390(14)	-560(20)	3058(12)	84(7)
C(45)	1543(11)	4639(15)	4360(9)	50(5)
C(20)	466(10)	2241(14)	4765(8)	42(4)
C(40)	1082(10)	3973(15)	3728(9)	45(4)
C(23)	681(11)	1703(15)	6329(10)	52(5)
C(24)	-104(11)	2174(15)	5914(9)	51(5)
C(11)	-981(11)	4553(15)	3471(9)	51(5)
C(25)	-217(11)	2455(15)	5147(9)	48(5)
C(10)	-783(10)	3258(15)	3494(9)	42(4)
C(42)	1797(12)	5325(17)	2970(11)	68(6)
C(31)	147(13)	1286(20)	2527(12)	84(7)
C(43)	2274(12)	5934(17)	3599(10)	66(6)
C(41)	1226(12)	4334(17)	3018(10)	60(5)
C(22)	1393(11)	1518(15)	5960(9)	51(5)
C(30)	560(10)	1364(15)	3256(9)	43(4)
C(35)	1152(12)	435(16)	3502(10)	58(5)
C(12)	-1842(13)	4990(20)	3304(10)	76(6)
C(32)	319(15)	245(22)	2043(13)	98(7)
C(14)	-2323(14)	2774(20)	3208(11)	83(7)
C(33)	954(14)	-576(21)	2322(12)	93(7)
C(13)	-2495(14)	4047(20)	3205(11)	80(6)
C(15)	-1466(11)	2332(17)	3364(10)	60(5)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

tate relative to that of arsenic. It should be noted that if a formal charge of 3- is assigned to the ıtimony selenide ligand, then each iron center is in a 2+ formal oxidation state.

The trivalent Sb atoms are in a pyramidal geometry, as expected. The Sb-Se bonds average .535(2)Å which is slightly short for Sb-Se single bonds (see above) although they can vary ıidely. The Se-Se distance is 2.402(3)Å which is a reasonable Se-Se bond distance. The central on selenide ring is crystallographically planar, and only slightly distorted from a perfect square ?e-Se-Fe angle 96.5(1)° versus a Se-Fe-Se angle 83.5(1)°). The iron centers are in a slightly istorted octahedral coordination environment with the Fe-Se distances orthogonal to the ring are ightly longer (2.454(3)Å) than the bridging ring distances (2.435(3)Å). The iron-iron distance is .633Å indicating that there is no metal metal interaction. The Fe-CO distances and angles are ?pical and deserve no further comment.

ISCUSSION

is well known that anionic main group clusters can be prepared by reacting various reducing ;ents with binary 15/16 solids. We have found that a number of unusual new compounds could ? prepared by careful variation of the nature of the reducing agent. In the case of antimony :lenides the chemistry seems particularly rich. Thus reduction of binary glasses with alkali metals ads to formation of the unusual $Sb_{12}Se_{20}^{4-}$, whereas other reducing agents lead to a number of ifferent antimony selenide anions not all of which have been fully characterized yet. It has been ›und that metal carbonyl anions are also suitable reducing agents, leading either to isolated binary ıions or new hybrid metal-main group cage structures. Here we report the reactions of HFe(CO)$_4$]$^-$ with Sb_xSe_y in DMF to provide an example of each type.

HFe(CO)$_4$]$^-$ + Sb_2Se_3 --------> $[Sb_4Se_6]^{2-}$

HFe(CO)$_4$]$^-$ + Sb_2Se_5 --------> $[Fe_2(CO)_4(SbSe_4)_2]^{2-}$

oth clusters could be isolated in reasonable yield using the $[PPh_4]^+$ cation. Each compound was ıaracterized by elemental analysis, IR and NMR in addition to x-ray diffraction. The far IR of ıch compound has a distinctive pattern between 150-300 cm-1. These stretches are probably all ;avily mixed modes and cannot be assigned with any confidence, but they provide a reliable ngerprint pattern for identifying each cluster. The ^{77}Se NMR of I has two resonances in a ratio of

Table IV. Selected Bond Distances and Angles for $Sb_4Se_6^{2-}$

Distances (Å)

Sb(1)-Se(1)	2.470 (2)	Sb(3)-Se(3)	2.606 (1)
Sb(1)-Se(2)	2.590 (2)	Sb(3)-Se(5)	2.601 (2)
Sb(1)-Se(3)	2.581 (2)	Sb(4)-Se(4)	2.585 (2)
Sb(2)-Sb(3)	2.858 (1)	Sb(4)-Se(5)	2.572 (1)
Sb(2)-Se(2)	2.617 (2)	Sb(4)-Se(6)	2.482 (2)
Sb(2)-Se(4)	2.591 (2)		

Angles (Deg)

Se(1)-Sb(1)-Se(2)	100.8(1)	Se(3)-Sb(3)-Se(5)	91.2(1)
Se(1)-Sb(1)-Se(3)	99.6(1)	Se(4)-Sb(4)-Se(5)	93.9(1)
Se(2)-Sb(1)-Se(3)	93.3(1)	Se(4)-Sb(4)-Se(6)	97.9(1)
Sb(3)-Sb(2)-Se(2)	100.2(1)	Se(5)-Sb(4)-Se(6)	99.6(1)
Sb(3)-Sb(2)-Se(4)	99.5(1)	Sb(1)-Se(2)-Sb(2)	93.5(1)
Se(2)-Sb(2)-Se(4)	92.4(1)	Sb(1)-Se(3)-Sb(3)	91.7(1)
Sb(2)-Sb(3)-Se(3)	99.6(1)	Sb(2)-Se(4)-Sb(4)	92.0(1)
Sb(2)-Sb(3)-Se(5)	100.5(1)	Sb(3)-Se(5)-Sb(4)	93.2(1)

Table V. Selected bond distances and angles for $[Fe_2(CO)_4(SbSe_4)_2]^{2-}$

Distances (Å)

Sb(1)-Se(1)	2.549(2)	Se(4)-Fe(1)	2.433(3)
Sb(1)-Se(2)	2.520(2)	Se(4)-Fe(1A)	2.437(3)
Sb(1)-Se(3)	2.546(2)	Fe(1)-C(1)	1.787(18)
Se(1)-Se(4)	2.402(3)	Fe(1)-C(2)	1.775(16)
Se(2)-Fe(1A)	2.452(3)	Fe(1)-Fe(1A)	3.633(2)
Se(3)-Fe(1)	2.455(3)	Se(4)-Se(4A)	3.243(3)

Angles (Deg.)

Se(1)-Sb(1)-Se(2)	95.1(1)	Se(3)-Fe(1)-C(2)	85.8(6)
Se(1)-Sb(1)-Se(3)	94.7(1)	Se(4)-Fe(1)-C(2)	171.4(6)
Se(2)-Sb(1)-Se(3)	104.6(1)	C(1)-Fe(1)-C(2)	98.2(8)
Sb(1)-Se(1)-Se(4)	97.0(1)	Se(3)-Fe(1)-Se(2A)	171.2(1)
Sb(1)-Se(2)-Fe(1A)	108.2(1)	Se(4)-Fe(1)-Se(2A)	86.7(1)
Sb(1)-Se(3)-Fe(1)	108.2(1)	C(1)-Fe(1)-Se(2A)	86.9(5)
Se(1)-Se(4)-Fe(1)	107.5(1)	C(2)-Fe(1)-Se(2A)	87.9(6)
Se(1)-Se(4)-Fe(1A)	107.3(1)	Se(3)-Fe(1)-Se(4A)	85.8(1)
Fe(1)-Se(4)-Fe(1A)	96.5(1)	Se(4)-Fe(1)-Se(4A)	83.5(1)
Se(3)-Fe(1)-Se(4)	100.2(1)	C(1)-Fe(1)-Se(4A)	168.7(5)
Se(3)-Fe(1)-C(1)	88.0(5)	C(2)-Fe(1)-Se(4A)	90.8(5)
Se(4)-Fe(1)-C(1)	88.3(6)	Se(2A)-Fe(1)-Se(4A)	100.4(1)

l, with the downfield peak assigned as the four cage selenides, and the higher field peak ributed to the more electron rich terminal selenides.

Thus we have shown that metal carbonyl anions react with heavy 15/16 binary compounds. ıe organometallic anions can act both as reducing agents to form new molecular main group ions, and as reagents incorporating new main group fragments into the framework, leading to w heavy main group-metal clusters. Preliminary indications are that other metal carbonyl anions ll also react with arsenic and antimony chalcogenides, leading to both new main group anions d transition metal-main group clusters.

(PERIMENTAL

;neral Considerations.

l group 15/16 anions are moderately air sensitive, and solutions were handled under purified ;on using standard Schlenk techniques. Solids were handled in a Vacuum Atmospheres)vebox under argon. All solvents were distilled using standard drying techniques, stored over ıivated seives and bubbled with argon before use. Reagents were purchased from Aldrich or ·em and used as received. Elemental analyses were performed by Atlantic Microlabs, Atlanta, ۸. IR spectra were taken on a Nicolet near-IR instrument as DMF solutions between CaF_2 ıtes, and far-IR spectra were obtained on a Nicolet 20F, as Nujol mulls in sealed polyethylene gs. The ^{77}Se NMR spectra were obtained from samples dissolved in 2.5mL of DMF, with ;mL of CD_3CN added to obtain lock, and sealed in 10mL tubes under vacuum. The compounds nominal composition Sb_2Se_3 and Sb_2Se_5 were prepared by reacting stoichiometric amounts of : elemental powders in sealed quartz tubes at 650°C for 10 h, while [PPN][$HFe(CO)_4$] was :pared according to a standard literature procedure.[13]

:paration of $[(C_6H_5)_4P]_2[Sb_4Se_6]$ (I):

Schlenk flask was charged with 0.30g (0.63 mmol) of Sb_2Se_3 and 0.22g (0.31 mmol) of ²N][$Fe(CO)_4H$]. To the dry solids, 15mL of dry DMF was added and the reaction mixture was ıted at 100°C for 12 h. To the resulting brown solution, 0.52g (1.3 mmol) of Ph_4PBr was ıed and the reaction was stirred for 1 h. The reaction mixture was filtered and the filtrate was ered with 10mL of diethyl ether. Storage of the reaction mixture at 4°C produced red-orange, l-shaped crystals in 39% yield (based on Se).Semiquantitative EDAX confirmed the presence of ıvy elements in approximately correct stoichiometries. Anal. Calcd. for $C_{48}H_{40}P_2Sb_4Se_6$: 35.16; H,2.46; Found: C,35.73; H,2.56.IR (cm^{-1},Nujol mull): 252(m), 212(sh), 203(sh), 5(m). ^{77}Se NMR ($\partial(Me_2Se) = 0$ ppm): 778 (1s), 804 (2s).

Preparation of $[(C_6H_5)_4P]_2[Fe(SbSe_4)(CO)_2]_2$ (II):

In a typical reaction, 0.30g (0.47 mmol) of Sb_2Se_5 and 0.335g (0.470 mmol) of [PPN][Fe(CO)$_4$H] were reacted at ambient temperature in 15mL of DMF for 12 h. To the resulting brown-orange solution, 0.40g (0.94 mmol) of Ph_4PBr were added and the reaction was stirred for 1 h. The mixture was filtered and layered with 10 mL of diethyl ether. Storage at 4°C overnight produced brown-red cubes in 52% yield (based on Se). IR (cm^{-1}): 1983(s), 1934(m), 551(s), 525(s), 238(m), 229(m), 221(m), 212(m).

X-Ray Crystallography

Intensity measurements were made at room temperature (21°C) on either a refurbished (Crystal Logic, Inc.) Syntex $P2_1$ diffractometer (I) or a Nicolet R3mV diffractometer (II) with graphite monochromated MoKα radiation (λ = 0.71073Å). Relevant crystallographic data are given in Table I. Data were measured to 2Θ=45° (in ω) of 2-15°/min. Periodic measurement of three standard reflections indicated crystal and electronic stability (± 2%) for both compounds. Lorentz and polarization corrections, and an empirical absorption correction was applied to the data for each compound.The structures were solved by direct methods and refined by full matrix least squares techniques using the SHELXTL-Plus package of programs. All non-hydrogen atoms in **I** were refined anisotropically, while in **II**, all atoms of the anion and the phosphorus were refined anisotropically, while the carbons of the phenyl ring were refined isotropically. Hydrogen atoms were included in the structure factor calculation for each compound at optimized positions (d_{C-H} = 0.96Å) with a refined group thermal parameter (U_H: 0.061(6)Å for **I** and U_H: 0.12(5)Å for **II**). Positional parameters of the anions are given in Tables II and III. Selected distances and angles are listed in Tables IV and V for the two compounds. Complete crystallographic information, full tables of distances and angles, anisotropic thermal parameters and hydrogen atoms positions have been deposited at the Cambridge Crystallographic Data Centre (CCDC) U.K.

ACKNOWLEDGMENTS We are indebted to the National Science Foundation (CHE-9102548) for support of this work.

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