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Preparation and X-ray Crystal Structure of 1,4-Diiodo-*cyclo*-hexaselenium Bis(hexafluoroarsenate)-Bis(sulfur dioxide), $Se_6I_2(AsF_6)_2 \cdot 2SO_2$, and $(Se_6I)_n \cdot nMF_6$ (M = As, Sb) Containing the *catena*-Poly[cyclohexaselenium(1+)-4:1-μ-iodo] Cation

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Highly crystalline $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ was obtained in 80% yield, from an SO_2 solution of a very complex equilibrium mixture of average composition $Se_6I_2(AsF_6)_2$. $(Se_6I)_n \cdot nAsF_6$ was prepared quantitatively by reacting stoichiometric amounts of Se, I_2, and AsF_5 in SO_2. Attempts to prepare related selenium-iodine cations led to mixtures of $(Se_6I)_n \cdot nAsF_6$ and $Se_6I_2(AsF_6)_2 \cdot 2SO_2$. Single crystals of $(Se_6I)_n \cdot nSbF_6$ were obtained from a reaction of elemental selenium and $I_2Sb_2F_{11}$ in liquid SO_2. Crystal data for $Se_6I_2(AsF_6)_2 \cdot 2SO_2$: monoclinic, space group $P2_1/n$, with $a = 10.6421$ (9) Å, $b = 13.076$ (3) Å, $c = 8.631$ (1) Å, $\beta = 103.66$ (1)°, $Z = 2$, and $R = 0.048$ for 1011 significant reflections. Crystal data for $(Se_6I)_n \cdot nAsF_6$: monoclinic, space group $P2/n$, with $a = 9.085$ (6) Å, $b = 6.948$ (2) Å, $c = 10.470$ (5) Å, $\beta = 107.27$ (2)°, $Z = 2$, and $R = 0.082$ for 761 significant reflections. Crystal data for $(Se_6I)_n \cdot nSbF_6$: monoclinic, space group $P2/n$, with $a = 9.232$ (5) Å, $b = 7.025$ (3) Å, $c = 10.638$ (5) Å, $\beta = 108.21$ (4)°, $Z = 2$, and $R = 0.073$ for 790 significant reflections. The $Se_6I_2^{2+}$ cation in $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ contains a six-membered ring of chair conformation and the two iodine atoms joined to the ring in the 1,4-positions with an endo conformation. There are four intracationic I-Se contacts (average 3.714 (2) Å), which gives the cation a distorted cubelike shape. The Se(tricoordinate)-Se(dicoordinate) distances (2.468 (2) and 2.482 (2) Å) are longer than the Se(dicoordinate)-Se(dicoordinate) distance (2.227 (2) Å), and the Se-I bond (2.454 (2) Å) is shorter than that in SeI_3^+ (2.510 (2) Å), implying $4p\pi$-$4p\pi$ and $4p\pi$-$5p\pi$ bonding. The structures of $Se_6I_2^{2+}$ and related species are compared. The $(Se_6I)_n \cdot nMF_6$ (M = As, Sb) complexes are isostructural, and the structures of polymeric $(Se_6I^+)_n$ cations are essentially identical. The geometry of the Se_6I_2 unit in $(Se_6I^+)_n$ is similar to that in $Se_6I_2^{2+}$, but the iodine atoms bridge Se_6 rings, giving rise to $(Se_6I^+)_n$ strands. The mean bond alternation within the Se_6 ring, Se(tricoordinate)-Se(dicoordinate) = 2.366 (3) Å and Se(dicoordinate)-Se(dicoordinate) = 2.294 (4) Å, is less than that in $Se_6I_2^{2+}$, consistent with the lower charge per Se_6 ring. The Se-I distances (2.736 (3) Å (AsF_6^-), 2.742 (3) Å (SbF_6^-)) correspond to a bond order of about 0.5. There are weak but definite selenium-selenium interactions (average 3.619 (5) Å) between the $(Se_6I^+)_n$ strands, giving the cation an infinite two-dimensional polymeric structure.

Introduction

Sulfur iodides were once thought to be nonexistent.[1] However, S_2I_2[2,3] and SI_2[4] have been prepared and characterized at -90 and -246 °C, respectively. The chemistry of sulfur-iodine cations has proven to be extensive,[5] and S_7IMF_6 (M = As, Sb),[6] $(S_7I)_2I$-$(SbF_6)_3 \cdot 2AsF_3$,[7] $(S_7I)_4S_4(AsF_6)_6$,[7] and $S_2I_4(MF_6)_2$[8] have all been prepared and their X-ray crystal structures determined. This paper focuses on our attempts to prepare the selenium analogues of the more sulfur rich sulfur-iodine cations. Neutral selenium iodides are nonexistent,[9] although salts of SeI_6^{2-} have been known for some time.[10] More recently we have prepared and characterized various salts of SeI_3^+[11] and the $Se_2I_4^{2+}$ cation in $Se_2I_4(Sb_2F_{11})_2$[12] and $Se_2I_4(AsF_6)_2 \cdot SO_2$.[13] However, the sulfur analogue SI_3^+ has not been prepared despite many attempts.[8c,11] This area of chemistry has recently been reviewed.[5]

The $(S_7I)_4S_4(AsF_6)_6$[7] and $(S_7Br)_4S_4(AsF_6)_6$[14] salts are the most thermally stable of the $(S_7\text{-halogen})^+$-containing salts. In attempting to prepare a selenium-iodine analogue, we obtained $(Se_6I)_n \cdot nAsF_6$.[15] The polymeric $(Se_6I^+)_n$ cation contained the first reported simple derivative of a selenium ring, paradoxically, as an iodine derivative. Subsequently $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ was prepared.[16] Both $(Se_6I^+)_n$ and $Se_6I_2^{2+}$ are derivatives of the chair form of Se_6, which exists as such as an unstable allotrope of selenium.[17] Thus, Se_6 is stabilized in these cations. This parallels the stabilization of the S_7 ring, in S_7I^+ salts.[6,7] The Se_6 ring, in the boat conformation, is observed in Se_{10}^{2+}[18,19] and in $Se_6(C_6H_5)_2 \cdot 2AsF_6$.[20] The geometry of and bonding in the cubelike $Se_6I_2^{2+}$ (and $(Se_6I^+)_n$) are fully discussed in this paper and compared with those of related species, including the isovalent $As_2Se_6^{2-}$.[21]

We envisaged many $Se_xI_y^{n+}$ cations that could contain both tricoordinate Se^+ and neutral dicoordinate Se atoms (e.g. the iodine analogue of $Se_7^+Se_2Cl$ in $Se_9ClSbCl_6$).[22] We systematically attempted to prepare crystalline salts of such cations with high selenium content, and our results are given below. Preliminary accounts[15,16] of part of this work have been reported.

Experimental Section

Apparatus, techniques, and chemicals used in this work have been described elsewhere,[23-25] except where stated. Reactions were carried out in a two-bulb Pyrex glass vessel equipped with a J. Young Teflon-stemmed glass valve and a coarse sintered-glass frit[23] (vessel A). SeI_3AsF_6 and $I_2Sb_2F_{11}$ were prepared as described.[24,25]

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$Se_8(AsF_6)_2$ was prepared by a modification of the reported method[26] but with SO_2 as a solvent. A stoichiometric amount of AsF_5 (5.26 g, 31.0 mmol) was condensed onto frozen SO_2 (15.3 g) and selenium (6.445 g, 81.6 mmol) in vessel A, containing a Teflon-coated stirring bar. A dark blue-green solution and copious insoluble materials were formed. The mixture was stirred for 1 week, and the volatile products were removed by subjecting them to a dynamic vacuum for 12 h. A dark solid product (10.39 g) corresponded to a 101% yield of $Se_8(AsF_6)_2$ (cf. expected yield of $Se_8(AsF_6)_2$, 10.30 g, or crystalline $Se_8(AsF_6)_2\cdot {}^1/_3SO_2$, 10.52 g, assuming selenium is the limiting reagent). Thus, it is reasonable to assume the bulk product is $Se_8(AsF_6)_2$. Crystals of $Se_8(AsF_6)_2\cdot {}^1/_3SO_2$ were obtained from a similar preparation mixture that was not stirred, with very minimal evacuation of volatile products. Single crystals were mounted in glass capillaries in the Vacuum Atmospheres "Dri-Lab" as previously described[27] and identified as $Se_8(AsF_6)_2\cdot {}^1/_3SO_2$ by a subsequent X-ray crystal structure determination.[28]

1. Preparation of $Se_6I_2(AsF_6)_2\cdot 2SO_2$ by Reaction of AsF_5, I_2, and Selenium. In a typical reaction, AsF_5 (2.368 g, 13.94 mol) was condensed onto a mixture of Se (2.179 g, 27.60 mmol) and I_2 (1.17 g, 4.61 mmol) in SO_2 (8.66 g) in vessel A. An immediate reaction took place, resulting in a brown-green solution. After 3 h, with occasional agitation, no insoluble material was observed. The solution was cooled to −80 °C for 10 min and then warmed to room temperature. A dark homogeneous crystalline precipitate was observed after 15 h. The crystals did not redissolve into the supernatant solution when left for 2 days at room temperature. They were separated from the supernatant solution by filtration and were washed twice with ca. 1 mL of solvent. The volatile materials were removed, giving 4.49 g of crystalline product, small fragments of which appeared ruby red in transmitted light. Several crystals were identified as $Se_6I_2(AsF_6)_2\cdot 2SO_2$ by X-ray crystallography. Anal. Calcd for $Se_6I_2(AsF_6)_2\cdot 2SO_2$: Se, 38.41; I, 20.58; As, 12.15; F, 18.48; S, 5.20; O, 5.19. Found: Se, 37.16; I, 19.90; As, 11.98; F, 18.1; S, 4.63.

2. Preparation of $Se_6I_2(AsF_6)_2\cdot 2SO_2$ by Reaction of $Se_8(AsF_6)_2$ and SeI_3AsF_6. In a typical reaction $Se_8(AsF_6)_2$ (0.710 g, 0.703 mmol) and SeI_3AsF_6 (0.459 g, 0.708 mmol) were placed into the first and second bulbs of vessel A. SO_2 (10.4 g) was condensed onto $Se_8(AsF_6)_2$, which was washed onto SeI_3AsF_6 by repeatedly (ca. 20 times) condensing ca. 3 mL of SO_2 back onto $Se_8(AsF_6)_2$ and refiltering, resulting in a brown-green solution containing no insoluble material. Three-fourths of the solvent (SO_2, 7.87 g) was removed, and the more concentrated solution which contained no precipitate was cooled to −80 °C for ca. 10 min and warmed to room temperature. A dark crystalline precipitate was observed after 15 h, which did not redissolve into the supernatant solution when left for 1 week. The crystalline precipitate was filtered and washed twice with ca. 1 mL of solvent and the volatile material removed, giving 1.09 g of crystalline product. Several crystals were identified as $Se_6I_2(AsF_6)_2\cdot 2SO_2$ by single-crystal X-ray crystallography.

Properties of $Se_6I_2(AsF_6)_2\cdot 2SO_2$. When it was ground, the dark red crystalline $Se_6I_2(AsF_6)_2\cdot 2SO_2$ became a reddish brown powder. The IR spectrum (powder AgCl plates) showed peaks at 1322 m (SO_2), 1144 w (SO_2), 694 vs (AsF_6^-), 576 w (AsF_6^-), and 528 w (SO_2) cm^{-1} indicative of SO_2[29] and AsF_6^-.[30] A sample was sealed in a glass tube under dry nitrogen and stored at −20 °C without noticeable decomposition (IR spectrum, appearance) or loss of crystallinity for >1.5 years.

A sample of freshly ground crystalline $Se_6I_2(AsF_6)_2\cdot 2SO_2$ (0.244 g, 0.199 mmol) was subjected to a dynamic vacuum for 10 h. The weight of the remaining black solid (0.205 g) was lower than that expected (0.231 g based on complete removal of SO_2 only), according to eq 1. A

$$\begin{array}{llll} & Se_6(AsF_6)_2\cdot 2SO_2(cr) \rightarrow & Se_6I_2(AsF_6)_2(s) + & 2SO_2(g)\uparrow \quad (1) \\ \text{obsd wt, g} & 0.244 & 0.205 & \\ \text{calcd wt, g} & 0.244 & 0.231 & 0.013 \end{array}$$

dark solid, presumably elemental iodine, was found in the cold trap (−196 °C). This suggests that the crystalline $Se_6I_2(AsF_6)_2\cdot 2SO_2$ decomposes under a dynamic vacuum at room temperature.

Crystalline $Se_6I_2(AsF_6)_2\cdot 2SO_2$ did not redissolve into the supernatant solution at room temperature. It was redissolved by agitating the mixture in a sonic bath at 30–35 °C[31] and recrystallized by cooling the solution to −80 °C for ~10 min and then leaving it at room temperature for 1 day.

3. Attempted Preparation of $(Se_7I)_4Se_4(AsF_6)_6$ Leading to Single Crystals of $(Se_6I)_n\cdot nAsF_6$. AsF_5 (1.477 g, 8.69 mmol) was condensed onto a mixture of Se (2.441 g, 30.91 mmol) and I_2 (0.472 g, 1.86 mmol) in AsF_3 (10.28 g) in vessel A. An immediate reaction took place, resulting in a dark green solution over a solid mass. The system was stored at room temperature for 3 months, during which time a crystalline material grew on top of the insoluble material. The solids were separated from the supernatant solution by filtration and the volatile materials removed, giving 0.933 g of soluble (from the green supernatant solution) and 2.936 g of insoluble (crystalline material and solid lump) materials. The crystals appeared to be about 10% of the solid mass, several of which were characterized as $(Se_6I)_n\cdot nAsF_6$ by X-ray crystallography.

Properties of Crystalline $(Se_6I)_n\cdot nAsF_6$. Some of the crystals were relatively large, ca. 1.50 × 0.75 × 0.25 mm, and were gray-black, with a metallic luster, in normal light. Viewed through a microscope with a bright source of light, they were golden in reflected light and deep ruby red in transmitted light. IR bands (powder Nujol mull, KBr plates) at 682 s, 382 m, and 388 sh cm^{-1} were indicative of AsF_6^-.[30]

The crystals were kept at room temperature under dry nitrogen for 7 weeks without decomposition. A large crystal was exposed to normal atmospheric conditions; the surface appeared wet after 4–5 h, but the basic shape of the crystal was retained; mp 140–150 °C dec.

4. Quantitative Preparation of $(Se_6I)_n\cdot nAsF_6$. In a typical reaction AsF_5 (2.344 g, 13.90 mmol) was condensed onto a mixture of Se (4.359 g, 55.21 mmol) and I_2 (1.62 g, 4.58 mmol) in SO_2 (10.7 g) in vessel A, containing a Teflon-coated stirring bar. Immediately a green solution and a gray-black solid were formed. After 5 days the stirred solution started to turn brown and became completely red-brown in 12 days. The solution was filtered into the other bulb and the solvent repeatedly condensed (25 times, 4 days) back onto the solid mass. A small amount of crystalline material accumulated in the bulb containing the soluble products. The volatile materials were removed, giving 7.229 g of product. The physical appearance of the crystalline material was very similar to that of $(Se_6I)_n\cdot nAsF_6$ when viewed under a microscope, but the crystals diffracted X-rays poorly. Anal. Calcd for Se_6IAsF_6: Se, 60.00; I, 16.07; As, 9.49; F, 14.4. Found: Se, 59.88; I, 16.07; As, 9.60; F, 14.1. The solubility of $(Se_6I)_n\cdot nAsF_6$ in pure liquid SO_2 at room temperature is ca. 4×10^{-3} M.

5. Preparation of Crystalline $(Se_6I)_n\cdot nSbF_6$ by the Reaction of Selenium with $I_2Sb_2F_{11}$. $I_2Sb_2F_{11}$ (3.847 g, 5.45 mmol) and Se (3.441 g, 43.57 mmol) were placed into two separate bulbs of vessel A, which were separated by a second Rotoflo valve. SO_2 (10.8 g) was condensed onto the $I_2Sb_2F_{11}$ and washed onto the selenium. An immediate reaction took place, resulting in a brown solution over an insoluble brown mass. After 7 weeks some crystalline material was observed on the solid mass. The brown supernatant solution was filtered into the other bulb. SO_2ClF (4.0 g) was condensed onto the solution, and a solid material separated out slowly over 1 week, leaving a purple-red solution over a brown solid. The volatile materials were removed, and crystals on the solid mass were characterized as $(Se_6I)_n\cdot nSbF_6$ by single-crystal X-ray crystallography. The infrared spectrum of the ground crystalline material as a Nujol mull between KBr plates between 4000 and 400 cm^{-1} showed peaks at 640 s, br (SbF_6^-) and 460 vw cm^{-1} (possibly due to a reduced product of SbF_5). Although small in size, the physical appearance of these crystals was very similar to that of $(Se_6I)_n\cdot nAsF_6$, in both reflected light (golden) and transmitted light (ruby red). The solid that precipitated, on addition of the SO_2ClF, was poorly crystalline (X-ray diffraction).

6. Attempted Preparations. (A) $Se_8I_2(AsF_6)_2$. (i) AsF_5 (0.431 g, 2.54 mmol) was condensed onto a mixture of Se (0.520 g, 6.59 mmol) and I_2 (0.204 g, 0.804 mmol) in liquid SO_2 (4.64 g) in a 10 mm o.d. thick-walled (1 mm) NMR tube with a Teflon-in-glass valve (J. Young, O-ringette PTFE stopcock; Model BST/2). After 12 h a brown-green solution formed on top of some insoluble solid. The ^{77}Se NMR spectrum, obtained at −80 °C, indicated the presence of Se_8^{2+},[32] $Se_6I_2^{2+}$,[33] a small amount of Se_{10}^{2+},[32] and species in equilibrium with $Se_6I_2^{2+}$.[33] A highly crystalline material grew on top of a solid mass after 2 years. The crystals (0.333 g) were homogeneous, were gold in reflected light and ruby red in transmitted light and were identified as $(Se_6I)_n\cdot nAsF_6$ by

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Table I. Attempted Preparations of Se_xIAsF_6 (x = 4, 5, 8, 10)[a]

$$2x\text{Se} + \text{I}_2 + 3\text{AsF}_5 \xrightarrow[60\ ^\circ\text{C}]{\text{AsF}_3} 2\text{Se}_x\text{IAsF}_6 + \text{AsF}_3$$

	amt, g (mmol)				total obsd[b] (calcd[c])
	Se	I_2	AsF_5	AsF_3	wt of the solid products, g
(i) x = 4	1.913 (24.22)	0.774 (3.05)	1.881 (11.07)	4.28	4.032 (3.825)
(ii) x = 5	2.1866 (27.69)	0.700 (2.76)	1.417 (8.34)	4.18	4.171 (3.935)
(iii) x = 8	2.034 (25.76)	0.406 (1.60)	0.811 (10.3)	7.39	3.109 (2.541)
(iv) x = 10	2.098 (26.57)	0.345 (1.36)	0.671 (3.95)	5.46	2.916 (2.307)

[a] The reaction mixtures were stored at room temperature for 25 days. Then they were heated to 60 °C for 12 and cooled to room temperature over 12 h, and the procedure was repeated for 10 days. [b] The total weight of soluble and insoluble material; separate weights were not recorded. [c] The calculated total weight of product with Se as the limiting reagent assuming all reagents had reacted and gave the products as indicated by the corresponding equation.

single-crystal X-ray crystallography.

(ii) $Se_8(AsF_6)_2$ (0.642 g, 0.636 mmol) in SO_2/AsF_3 (11.40/2.53 g) in one of the bulbs of vessel A was washed onto I_2 (0.160 g, 0.630 mmol), in the second bulb, by repeatedly (ca. 10 times) condensing 5 mL of the solvent back onto the $Se_8(AsF_6)_2$ and refiltering. After the mixture was stirred overnight, a brown-green solution, with some insoluble precipitate, was formed. The solvent was slowly condensed (~5 h) into the empty bulb and poured back onto the solid repeatedly (15 times). Some small crystals were formed, which were separated by filtration. The crystals were hexagonal-shaped, with a thickness of less than 0.1 mm, and were golden in reflected light and deep ruby red in transmitted light. One of the crystals was characterized as $(Se_6I)_n{\cdot}nAsF_6$ by single-crystal X-ray crystallography.

(B) $Se_3I_3AsF_6$. AsF_5 (0.560 g, 3.30 mmol) was condensed onto a mixture of Se (0.510 g, 6.46 mmol) and I_2 (0.827 g, 3.26 mmol) in SO_2 (4.45 g). An immediate reaction took place, resulting in a dark reddish brown solution on top of some black insoluble material, which appeared to be unreacted iodine. After the mixture was cooled to −80 °C for 1 h and warmed to room temperature, more solid appeared, which consisted of crystals sandwiched between layers of black amorphous solid. Several fragments of large single crystals were identified as $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ by X-ray crystallography, and the black solid was found to be unreacted iodine (melting point).

(C) Se_xIAsF_6 (x = 4, 5, 8, 10). Weighted amounts of AsF_5 were condensed onto mixtures of Se and I_2 in AsF_3 in 14-mm Pyrex tubes equipped with J. Young Teflon-stemmed glass valves (data given in Table I). A dark solution, over a dark solid mass, was observed in all cases; no apparent change occurred after 3 weeks. The bottom halves of the four vessels were heated to 60 °C for 12 h and then cooled to room temperature over 12 h, and the process was repeated for 10 days. A small amount of iodine sublimed to the top half of each of the four vessels, which was washed back into the solution. Some crystals formed on top of the mass of solid in all four reactions after 10 days. One of the crystals from each reaction was characterized as $(Se_6I)_n{\cdot}nAsF_6$ by single-crystal X-ray crystallography.

7. X-ray Crystal Structures of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$, $(Se_6I)_n{\cdot}nAsF_6$, and $(Se_6I)_n{\cdot}nSbF_6$. Suitable crystals, sealed under N_2, were subjected to a preliminary photographic investigation. Intensity data from ω–2θ scans and final unit cell parameters were then obtained with use of a Picker FACS-I diffractometer equipped with graphite-monochromated Mo Kα radiation. Crystal data are summarized in Table II. The structures were solved by using the MULTAN-80 direct methods package.[34] All other computations were performed by using the NRCVAX[35] and SHELX-76[36] program packages. The data were corrected for absorption and refined by least squares with use of weights derived from counter statistics. Scattering factors were taken from ref 37 and corrected for anomalous dispersion.

Table II. Crystallographic Data for $(Se_6I)_n{\cdot}nAsF_6$, $(Se_6I)_n{\cdot}nSbF_6$, and $Se_6I_2(AsF_6)_2{\cdot}2SO_2$

	$(Se_6I)_n{\cdot}nAsF_6$	$(Se_6I)_n{\cdot}nSbF_6$	$Se_6I_2(AsF_6)_2{\cdot}2SO_2$
chem formula	Se_6IAsF_6	Se_6ISbF_6	$Se_6I_2(AsF_6)_2{\cdot}2SO_2$
fw	789.58	836.41	1233.5
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2/n$ (No. 13)	$P2/n$ (No. 13)	$P2_1/n$ (No. 14)
a, Å	9.085 (6)	9.232 (5)	10.6421 (9)
b, Å	6.948 (2)	7.025 (3)	13.076 (3)
c, Å	10.470 (5)	10.638 (5)	8.631 (1)
β, Å	107.27 (2)	108.21 (4)	103.66 (1)
V, Å^3	631 (1)	655 (1)	1167.1 (5)
Z	2	2	2
T, °C	20	20	20
calcd density, g cm^{-1}	4.15	4.24	3.51
μ, cm^{-1}	222.8	209.9	150.0
transmission coeff	0.014–0.029	0.015–0.099	0.026–0.045
R (including unobsd rflns)	0.082 (0.115)	0.073 (0.107)	0.048 (0.060)
R_w (including unobsd rflns)	0.103 (0.116)	0.088 (0.097)	0.049 (0.060)

Table III. Atomic Positional Parameters (Fractional) for $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ (Estimated Standard Deviations in Parentheses)[a]

atom	x/a	y/b	z/c
I(1)	0.2800 (1)	0.1620 (1)	0.9469 (1)
Se(1)	0.6209 (1)	0.0904 (1)	1.1835 (2)
Se(2)	0.5061 (1)	0.1686 (1)	0.9271 (2)
Se(3)	0.5238 (1)	0.0180 (1)	0.7612 (2)
S(1)	0.1419 (6)	0.0344 (4)	0.3831 (6)
O(1)	0.233 (2)	−0.032 (1)	0.474 (2)
O(2)	0.072 (2)	0.098 (1)	0.462 (3)
As(1)	0.1022 (1)	−0.2046 (1)	1.0456 (2)
F(1)	0.247 (1)	−0.173 (1)	1.165 (2)
F(2)	0.121 (2)	−0.325 (1)	1.112 (2)
F(3)	−0.040 (1)	−0.236 (2)	0.924 (2)
F(4)	0.091 (2)	−0.083 (1)	0.980 (3)
F(5)	0.022 (1)	−0.175 (1)	1.191 (2)
F(6)	0.183 (1)	−0.239 (1)	0.905 (2)
F(1a)	−0.0370	−0.1546	0.9390
F(2a)	0.1685	−0.0873	1.0680
F(3a)	0.2413	−0.2545	1.1521
F(4a)	0.0508	−0.1886	1.2137
F(5a)	0.0359	−0.3218	1.0231
F(6a)	0.1535	−0.2205	0.8774

[a] F(1a)–F(6a) represent a second orientation of the anion, which was refined as a rigid group with 15% occupancy.

$Se_6I_2(AsF_6)_2{\cdot}2SO_2$. After the initial cycles of refinement a number of peaks appeared in a difference synthesis, indicating disorder of the anion. This disorder was modeled by superimposing two octahedra of fluorine atoms both centered at the arsenic position. The primary and secondary octahedra were assigned occupancies of 0.85 and 0.15, respectively. In the final refinement the primary fluorines were assigned anisotropic thermal parameters and refined freely whereas the secondary ones were constrained to an idealized octahedron with an overall isotropic thermal parameter. Final atomic coordinates are given in Table III.

$(Se_6I)_n{\cdot}nAsF_6$ and $(Se_6I)_n{\cdot}nSbF_6$. These isostructural compounds were originally refined and reported[12] in space group $P2/c$. However, because of the large value of β (>130°) the data were transformed to the setting

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Table IV. Atomic Positional Parameters (Fractional) for $(Se_6I)_n{\cdot}nAsF_6$ and $(Se_6I)_n{\cdot}nSbF_6$ (Estimated Standard Deviations in Parentheses)[a]

	x/a	y/b	z/c	B_{iso}, Å^2
		(a) $(SeI_6)_n{\cdot}nAsF_6$		
I	$-^1/_4$	0.2775 (3)	$^1/_4$	2.78 (9)
Se(1)	0.1479 (3)	0.5738 (3)	0.3808 (3)	3.27 (10)
Se(2)	0.0572 (3)	0.2558 (3)	0.38649 (24)	2.83 (10)
Se(3)	0.0573 (3)	0.2387 (3)	0.61255 (25)	3.30 (12)
As	0	0	0	2.83 (13)
F(1)	−0.0398 (19)	−0.2142 (24)	−0.0850 (17)	4.7 (7)
F(2)	−0.095 (3)	−0.081 (4)	0.103 (3)	8.9 (15)
F(3)	−0.1670 (22)	0.090 (3)	−0.096 (3)	7.8 (12)
		(b) $(Se_6I)_n{\cdot}nSbF_6$		
I(1)	$-^1/_4$	0.2754 (3)	$^1/_4$	2.92 (9)
Se(1)	0.1449 (3)	0.5686 (4)	0.38221 (24)	3.44 (10)
Se(2)	0.05434 (24)	0.2558 (3)	0.39018 (25)	3.07 (9)
Se(3)	0.0564 (3)	0.2430 (3)	0.61292 (25)	3.37 (10)
Sb(1)	0	0	0	2.95 (9)
F(1)	0.0456 (21)	0.2224 (21)	0.1024 (18)	5.6 (9)
F(2)	0.0953	0.102 (3)	−0.1153 (16)	6.7 (10)
F(3)	0.1836 (18)	−0.1036 (24)	0.1045 (19)	6.3 (9)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

*P*2/*n* before final refinement. Atomic coordinates for both structures are given in Table IV.

Results and Discussion

Preparative Chemistry. Preparation of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$. Solutions of average stoichiometry $Se_6I_2(AsF_6)_2$ were prepared by reactions 2 and 3. The ^{77}Se NMR spectra of these solutions

$$6Se + I_2 + 3AsF_5 \xrightarrow{SO_2} Se_6I_2(AsF_6)_2 + AsF_6 \qquad (2)$$

$$2Se_8(AsF_6)_2 + 2SeI_3AsF_6 \xrightarrow{SO_2} 3Se_6I_2(AsF_6)_2 \qquad (3)$$

are identical and consist of $Se_6I_2^{2+}$ and its equilibrium products,[33] which include $Se_4I_4^{2+}$, SeI_3^+, Se_8^{2+}, Se_4^{2+}, and probably five other unidentified selenium-containing species.[38]

About 80% recovered yield of highly crystalline $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ was achieved by cooling the solution to −80 °C for 1 h and then leaving it at room temperature for 15 h, prior to filtration. The product was identified as $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ by elemental analysis and single-crystal X-ray structure determination. Both products had a homogeneous appearance, and several single crystals from both reactions were identified as $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ by X-ray diffraction. The infrared spectrum of the ground product showed the presence of both AsF_6^- and SO_2, indicating that the SO_2 is not very labile. Many attempts to prepare crystalline $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ by slow removal of the solvent and addition of SO_2ClF led to heavy pastelike products. At −70 °C ca. 20% of the total selenium in solution is present as $Se_6I_2^{2+}$. This concentration decreases as the temperature increases. It is estimated that, from the data obtained at lower temperatures,[33,38] 8% of the total selenium is present at room temperature as $Se_6I_2^{2+}$. It is therefore not surprising that at room temperature removal of the solvent leads to a mixture of solid products. At −70 °C, it is possible that the concentration of $Se_6I_2(AsF_6)_2$ is high enough for it to crystallize out as seed crystals. Presumably the solubility of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ is sufficiently low at room temperature that it crystallizes out onto the seed crystals, displacing the various equilibria to $Se_6I_2(AsF_6)_2{\cdot}2SO_2$.

Preparation of $(Se_6I)_n{\cdot}nAsF_6$. The attempted preparation of $(Se_7I)_4Se_4(AsF_6)_6$, the selenium analogue of $(S_7I)_4S_4(AsF_6)_6$, according to eq 4, led to the formation of solid $(Se_6I)_n{\cdot}nAsF_6$.

$$32Se + 2I_2 + 9AsF_5 \xrightarrow{AsF_3} (Se_7I)_4Se_4(AsF_6)_6 + 3AsF_3 \qquad (4)$$

$$32Se + 2I_2 + 9AsF_5 \xrightarrow[3\ months]{AsF_3} (4/n)(Se_6I)_n{\cdot}nAsF_6 + Se_8(AsF_6)_2 + 3AsF_3 \qquad (5)$$

The actual reaction might proceed as indicated by eq 5. The formation of $(Se_6I)_n{\cdot}nAsF_6$ and the green supernatant solution (characteristic of Se_8^{2+}) supports this hypothesis.

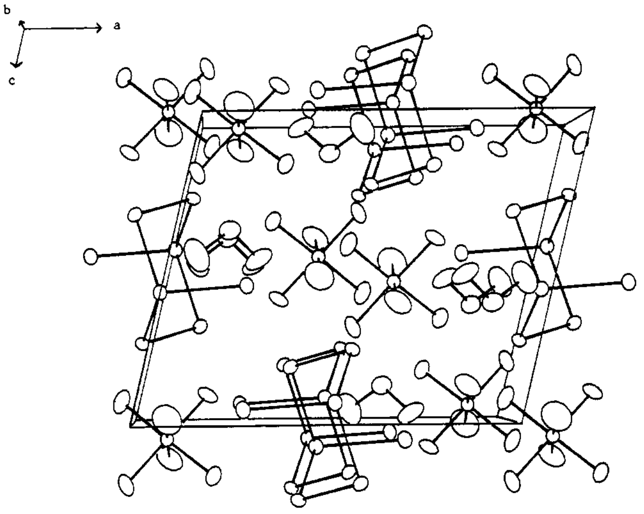

Figure 1. Crystal packing of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$.

The stoichiometric preparation of $(Se_6I)_n{\cdot}nAsF_6$ was carried out quantitatively according to eq 6.

$$12Se + I_2 + 3AsF_5 \xrightarrow[11\ days]{SO_2,\ room\ temp} (2/n)(Se_6I)_n{\cdot}nAsF_6 + AsF_3 \qquad (6)$$

The weight of the bulk microcrystalline product (7.239 g) corresponded to a 100% yield of $(Se_6I)_n{\cdot}nAsF_6$ according to eq 6, and the elemental analyses were in excellent agreement with the given formulation.

The formation of $(Se_6I)_n{\cdot}nAsF_6$ single crystals, which were suitable for X-ray diffraction analyses, were obtained within 10 days in related reactions designed to give Se_xIAsF_6 (x = 4, 5, 8, 10; Table I). These reaction mixtures were thermally cycled between 60 °C and room temperature every 12 h, with AsF_3 as solvent.

Preparation of $(Se_6I)_n{\cdot}nSbF_6$. The reaction between Se and $I_2Sb_2F_{11}$ (mole ratio of 8:1) that yielded $(Se_6I)_n{\cdot}nSbF_6$ crystals is likely complex. This is not the best route to $(Se_6I)_n{\cdot}nSbF_6$, but it did yield single crystals. One of the products is possibly a mixed Sb(III), Sb(V) fluoride (possibly $(SbF_3)_3{\cdot}SbF_5$[39]) formed on reduction of $Sb_2F_{11}^-$. The difficulty of separating this insoluble material from the insoluble $(Se_6I)_n{\cdot}nSbF_6$ discouraged us from attempting its preparation by a reaction analogous to that given by eq 6, but with SbF_5.

Attempted Preparations of Se_xIAsF_6 (x = 4, 5, 8, 10) and $Se_3I_3(AsF_6)_2$. Attempts to prepare crystals of Se_xIAsF_6 (x = 4, 5, 8, 10) in liquid AsF_3 at 60 °C according to eq 7 led to single crystals of $(Se_6I)_n{\cdot}nAsF_6$ in every case.

$$2xSe + I_2 + 3AsF_5 \xrightarrow[room\ temp-60\,°C]{AsF_3} 2Se_xIAsF_6 + AsF_3 \qquad (7)$$

A similar result was obtained in SO_2 solution at room temperature in an attempted synthesis of $Se_8I_2(AsF_6)_2$ ($2xSe_4IAsF_6$), in addition Se_8^{2+}, Se_{10}^{2+},[32] $Se_6I_2^{2+}$,[33] and equilibrium products[38] were identified by ^{77}Se NMR spectroscopy in the solution. The attempted preparation of $Se_3I_3AsF_6$ ($I_2Se^+SeSeI(AsF_6^-)$), the iodine analogue of $Br_2Se^+SeSeBr(AsF_6)$,[40] led to solid $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ and elemental iodine. In fact stable compounds containing an Se^{II}–I bond have not been prepared, except RSeI (R = 2,4,6-$^tBu_3(C_6H_2)$[41]), which likely owes its stability to the bulkly substituent. Thus, all attempts to prepare selenium–iodine

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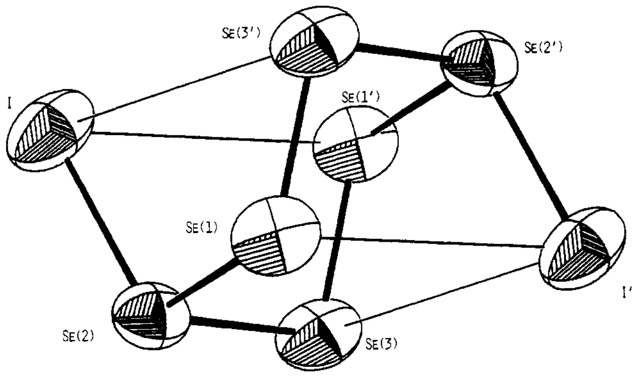


Figure 2. The $Se_6I_2^{2+}$ cation in $Se_6I_2(AsF_6)_2{\cdot}SO_2$.

Table V. Bond Distances (Å) in $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ (Estimated Standard Deviations in Parentheses)

	$Se_6I_2^{2+}$		
Se(2)–I	2.454 (2)	Se(1)–Se(3′)	2.227 (2)
Se(1)–Se(2)	2.482 (2)	Se(2)–Se(3)	2.468 (2)
	AsF_6^-[a]		
As–F(1)	1.68 (1)	As–F(1a)	1.68 (2)
As–F(2)	1.67 (1)	As–F(2a)	1.68
As–F(3)	1.68 (1)	As–F(3a)	1.68
As–F(4)	1.69 (2)	As–F(4a)	1.68
As–F(5)	1.72 (2)	As–F(5a)	1.68
As–F(6)	1.70 (2)	As–F(6a)	1.68
	SO_2		
S–O(1)	1.40 (2)	S–O(2)	1.40 (2)
	Intraionic Contacts[b]		
I–Se(1′)	3.719 (2)	I–Se(3′)	3.709 (2)
	Interionic Contacts[b]		
I–F(3)	3.17 (2)	Se(2)–F(1)	2.92 (1)
I–F(5)	3.16 (1)	Se(2)–F(6)	3.32 (1)
I–F(6)	3.42 (2)	Se(2)–O(2)	3.13 (2)
I–Se(1′)	4.086 (2)		
Se(1)–F(6)	3.08 (2)	Se(3)–F(1)	3.12 (2)
Se(1)–O(1)	3.09 (1)	Se(3)–F(2)	3.11 (2)
Se(1)–I″	4.086 (2)		

[a] F(1)–F(6) were assigned an occupancy of 0.85 and were refined freely. F(1a)–F(6a) were given an occupancy of 0.15 and were refined as a rigid group with an idealized octahedral environment around the As atom. [b] Includes all contacts less than the sum of van der Waals radii (Se–Se = 4.00, Se–I = 4.15, Se–F = 3.35, Se–O = 3.50, I–F = 3.50, I–O = 3.55 Å).[43]

cations with high selenium content led to either $Se_6I_n{\cdot}nAsF_6$ or $Se_6I_2(AsF_6){\cdot}2SO_2$ in the solid state.

X-ray Crystal Structure of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$. The structure of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ consists of the discrete entities $Se_6I_2^{2+}$, SO_2, and disordered AsF_6^-,[42] joined by weak cation–anion and cation–oxygen interactions. The crystal packing of $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ is shown in Figure 1; the $Se_6I_2^{2+}$ cation is illustrated in Figure 2. Appropriate bond distances and angles are presented in Tables V and VI.

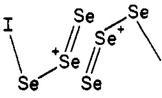
Structure and Bonding in the Cubelike $Se_6I_2^{2+}$ Cation. Evidence for Thermodynamically Stable 4pπ–4pπ and 5pπ–4pπ Bonds. The $Se_6I_2^{2+}$ cation has C_i symmetry and contains a hexaselenium ring in the chair conformation similar to that of Se_6.[17] The Se_6 ring is substituted in the 1,4-positions by two iodine atoms in the endo conformation. The selenium–iodine bond length (2.454 (2) Å) is significantly less than that in SeI_3MF_6 (M = As, Sb; average 2.510 (2) Å). The ISe(1′)Se(2′)Se(3′) and I′Se(1)Se(2)Se(3) atoms lie on two approximately parallel planes. There are four intracationic selenium–iodine contacts (2 × 3.709 (2), 2 × 3.719 (2) Å) that are significantly less than the sum of the van der Waals radii[43] of selenium and iodine (4.15 Å) that give the cation clusterlike characteristics (Figure 2).

Table VI. Bond Angles (deg) in $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ (Estimated Standard Deviations in Parentheses)

	Interatomic Angles		
I–Se(2)–Se(1)	101.99 (7)	I–Se(2)–Se(3)	102.87 (6)
Se(1)–Se(2)–Se(3)	95.72 (7)	Se(3)–Se(1′)–Se(2′)	103.52 (6)
Se(2)–Se(3)–Se(1′)	103.43 (8)		
Se(2)–I–Se(1′)	69.96 (5)	Se(2)–I–Se(3′)	70.47 (5)
F(1)–As–F(2)[a]	90.3 (9)	F(3)–As–F(4)	92.2 (11)
F(1)–As–F(3)	178.9 (8)	F(3)–As–F(5)	89.0 (8)
F(1)–As–F(4)	87.5 (9)	F(3)–As–F(6)	91.3 (8)
F(1)–As–F(5)	92.1 (7)	F(4)–As–F(5)	91.0 (10)
F(1)–As–F(6)	87.7 (7)	F(4)–As–F(6)	91.1 (10)
F(2)–As–F(3)	90.0 (11)	F(5)–As–F(6)	177.9 (7)
F(2)–As–F(4)	177.5 (11)		
F(2)–As–F(5)	90.2 (9)		
F(2)–As–F(6)	87.7 (9)		
O(1)–S–O(2)	118.5 (11)		
	Interionic Angles		
Se(2)–I–F(3)	154.0 (4)	Se(2)–I–F(6)	66.5 (2)
Se(2)–I–F(5)	154.2 (3)	Se(2)–I–Se(1″)	102.6 (1)
Se(2)–Se(1)–F(6)	74.9 (3)	Se(3)–Se(1)–I″	127.0 (1)
Se(2)–Se(1)–O(1)	169.8 (3)	Se(1)–Se(3)–F(1)	156.5 (3)
Se(2)–Se(1)–I″	102.8 (1)	Se(1)–Se(3)–F(2)	83.5 (4)
Se(3)–Se(1)–F(6)	178.0 (3)	Se(2)–Se(3)–F(1)	61.7 (3)
Se(3)–Se(1)–O(1)	81.6 (3)	Se(2)–Se(3)–F(2)	164.5 (4)
I–Se(2)–F(1)	168.6 (3)	Se(1)–Se(2)–O(2)	105.3 (4)
I–Se(2)–F(6)	70.8 (3)	Se(3)–Se(2)–F(1)	70.2 (3)
I–Se(2)–O(2)	103.2 (4)	Se(3)–Se(2)–F(6)	84.5 (3)
Se(1)–Se(2)–F(1)	88.0 (3)	Se(3)–Se(2)–O(2)	142.0 (5)
Se(1)–Se(2)–F(6)	60.6 (3)		

[a] See footnote *a* in Table V.

The two Se$^+$(*tricoordinate*)–Se(*dicoordinate*) bonds (Se(2)–Se(1) = 2.482 (2) Å; Se(2)–Se(3) = 2.468 (2) Å; bond order of ca. 0.7[44]) are considerably longer than the Se(*dicoordinate*)–Se(*dicoordinate*) adjacent cyclic bonds (Se(1)–Se(3′) = 2.227 (2) Å; bond order of ca. 1.5[44]). This suggests that the alternation arises from a contribution from valence bond structures **3** and **4**, which also delocalize the positive charge into the ring.



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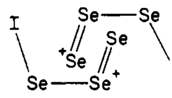

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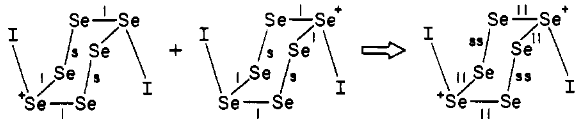
Alternatively the bond alternation can be viewed as arising from the superimposition of that arising separately from each positively charged tricoordinate selenium. Such positively charged atoms are known to produce bond lengthening in adjacent chalcogen–chalcogen bonds,[5,6,45] shortening in the next, and so on. The alternation resulting from one tricoordinate positively charged selenium atom is depicted in **5** and the other in **6**. The resultant is **7**. Thus, the 1,4-positions of iodine substitution of the Se_6 ring maximize bond alternation and charge delocalization within the



5 **6** **7**

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(42) The AsF_6^- anion is disordered and modeled by two cocentric AsF_6^- anions with occupancies of 85% and 15%, respectively. The cation–anion contacts quoted are to the fluorine atoms of 85% occupancy. The AsF_6^- anion illustrated in Figure 1 is that of 85% occupancy.

(43) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

(44) Selenium–selenium bond order, $n = 10^{(2.35-R)/0.71}$, where R is the Se–Se bond distance (Å), from ref 43.

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Table VII. Comparison of Selected Selenium–Selenium Bond Distances in Various Cations Containing a Tricoordinate Selenium[a]

	bond dist, Å[a]		bond alternation,	
	$d(Se_A-Se_B)$	$d(Se_B-Se_C)$	Δ, Å[g]	ref
$Se_6I_2^{2+}$	2.475 (2)[b]	2.227 (2)	0.25	
$(Se_6I^+)_n \cdot nAsF_6^-$	2.365 (3)	2.292 (4)	0.07	
$(Se_6I^+)_n \cdot nSbF_6^-$	2.362 (3)	2.295 (4)	0.07	
$Se_6(C_6H_5)_2^{2+}$	2.417 (4)	2.261 (2)	0.16	20
Se_{10}^{2+}	2.42 (1)[c]	2.25 (1)[c]	0.17	18
	2.43 (1)[d]	2.34 (1)[d]	0.09	18
$Br_2Se^+SeSeBr$	2.554 (6)	2.211 (6)	0.34	40
$Se_7^+SeSeCl$	2.308 (5)[e]	2.289 (7)[e]	0.02	22
	2.439 (5)[e]	2.202 (5)[e]	0.24	
	2.470 (5)[f]	2.234 (6)[f]	0.24	

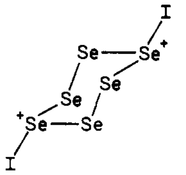
[a] Configuration $-Se_C-Se_B-Se_A(Y)-X$, where X = –Se–, Br, C_6H_5 and Y = –Se–, Br, I. [b] Average of Se(tricoordinate)–Se(dicoordinate) bond distances. [c] Bond distances within the six-membered ring of the Se_{10}^{2+} cation. [d] Bond distances of the exocyclic four-membered Se chain in the Se_{10}^{2+} cation. [e] Bond distances within the seven-membered ring. [f] Bond distances in the exocyclic >Se–Se–Se–Cl fragment. [g] $d(Se_A-Se_B) - d(Se_B-Se_C)$.

ring. All other combinations of iodine substitution lead to some bond alternation cancellation.

The interionic contacts between the dicoordinate selenium atoms (Se(1) and Se(3)) and fluorine atoms (Table V) are significant and consistent with the proposed partial positive charge delocalization onto Se(1) and Se(3). The short Se(1)–Se(3) bond length (2.227 (2) Å) corresponds to a bond order of ca. 1.5 and implies substantial 4pπ–4pπ bonding between these dicoordinate selenium atoms. This represents an example of an exception of the "double bond rule", that is, the thermodynamic preference for homoatomic σ-bonds over npπ–npπ bonds for the heavier main-group elements ($n > 3$).[46]

Similar maximization of bond alternation, and charge delocalization, and the presence of short chalcogen–chalcogen bonds implying some npπ–npπ ($n \geq 3$) bonding are observed in related cations and molecules[5,6,46,47] (see Table VII and S_7I^+,[6] S_7Br^+,[14] $(S_7I)_2I^{3+}$,[7] S_7O,[48] and S_8O[48]). Thermodynamically stable npπ–npπ ($n \geq 3$) bonds involving the more electron rich elements may be inferred from short bond distances in various homopolyatomic cations,[47] e.g. S_4^{2+},[49] in $S_2I_4^{2+}$,[8] as well as some neutral sulfur compounds (e.g., FSSF and S_2F_2)[50] and anionic compounds (e.g. S_2^- in solution).[51]

The exocyclic Se–I bond distance in the $Se_6I_2^{2+}$ cation (2.454 (2) Å) is slightly longer than that in $Se_2I_4^{2+}$ (average 2.447 (2) Å, formal bond order of 1.25),[12] SeI_3^+ (average 2.510 (2) Å, formal bond order of 1),[11] and RSe–I (R = 2,4,6-$^tBu_3C_6H_2$, 2.529 Å).[41] This implies that the Se–I bond in $Se_6I_2^{2+}$ has some π-bond character (4pπ–5pπ). This may arise from some delocalization of electron density in a π*-antibonding orbital, based on the exocyclic Se–I bond, to the partially positively charged dicoordinate Se(1′) and Se(3′) atoms through the I–Se(1′) and I–Se(3′) (3.719 (2) and 3.709 (2) Å, respectively) intracationic contacts (cf. the sum of iodine and sulfur van der Waals radii, 4.15 Å).[43] The bond angles between the exocyclic primary Se–I bond and intracationic contacts (Se(2)–I–Se(1′) = 69.96 (5)°; Se(2)–I–Se(3′) = 70.47 (5)°) are consistent with the iodine atom acting as an electron donor. Similar situations have been observed in S_7I^+,[7] $(S_7I)_2I^{3+}$,[6] S_7Br^+,[14] and $Br_2Se^+SeSeBr$.[40] The delocalization of the electron density from the π*-antibonding orbital of the Se–I bond into the ring would lead to a reduction of π*-electron density in the primary Se–I bond, a decrease in its bond length, and a partial positive charge on the iodine atom. This interaction is almost certainly positive; otherwise, the less sterically hindered isomer **8** would be formed with the two iodine atoms adopting the exo position.



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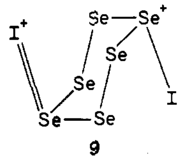

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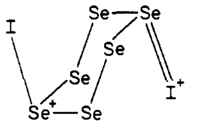

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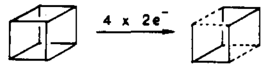
Charge delocalization and an increase in Se–I bond order could in addition arise from some contribution from resonance structures **9** and **10**. Consistently, the I–F interionic contacts (3.16 (2) and 3.17 (2) Å, Table V) are significant and approximately trans to the primary Se–I bond. It is therefore reasonable to conclude that the dipositive charge is delocalized to some extent over all eight atoms in $Se_6I_2^{2+}$. Thus, the clusterlike configuration of $Se_6I_2^{2+}$, the selenium–selenium bond alternation, and the presence of both 4pπ–5pπ Se–I and 4pπ–4pπ Se–Se bonds arise from positive charge delocalization.

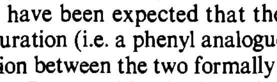
Gillespie[52] has shown that the structures of a large number of main-group cage and ring compounds can be related to a small number of basic cluster structures. $Se_6I_2^{2+}$ may be derived from the electron-precise cubic cluster **11** by adding four electron pairs,



11 **12**

with subsequent bond cleavage, to give the distorted cubic quasi-cluster **12**, with four of the bonds each replaced by two lone pairs. $Se_6I_2^{2+}$ can be regarded as having 16 electron pairs ([6 × 4](Se[53]) + [2 × 5](I[53]) − 2[54] = 32e), eight of which are involved in the Se–Se and Se–I bonds (cf. 12 bonds in the electron-precise cluster, structure **11**). Our analysis suggests that the clusterlike shapes in fact arise as a consequence of the intermolecular or interionic contacts, or weak bonding.

Comparison of, and a Possible Explanation for the Differences in Geometries of, $Se_6I_2^{2+}$, $Se_6Ph_2^{2+}$, and $As_2Se_6^{2-}$. The hexaselenium ring in the $Se_6(C_6H_5)_2^{2+}$ cation in $Se_6(C_6H_5)_2(AsF_6)_2 \cdot 2SO_2$[20] has the boatlike structure **13** similar to that of $Te_2Se_4^{2+}$.[55] Both $Se_6(C_6H_5)_2^{2+}$ and $Te_2Se_4^{2+}$ contain weak Se–Se intracationic contacts across the top of the boat (3.550 (3) and 3.41 Å, respectively; sum of van der Waals radii 4.00 Å). The phenyl groups in $Se_6(C_6H_6)_2^{2+}$ do not form intracationic contacts with the hexaselenium ring. Thus, the geometry of $Se_6(C_6H_5)_2^{2+}$ is solely determined by the bonding between selenium atoms. It might have been expected that the Se_6 ring would adopt a chair configuration (i.e. a phenyl analogue of **8**), which minimizes charge repulsion between the two formally charged tricoordinate selenium atoms. Presumably the boatlike geometry of the Se_6 ring in $Se_6(C_6H_5)_2^{2+}$ is a consequence of the weak Se–Se contact across



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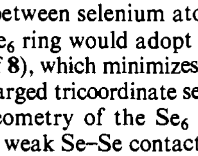

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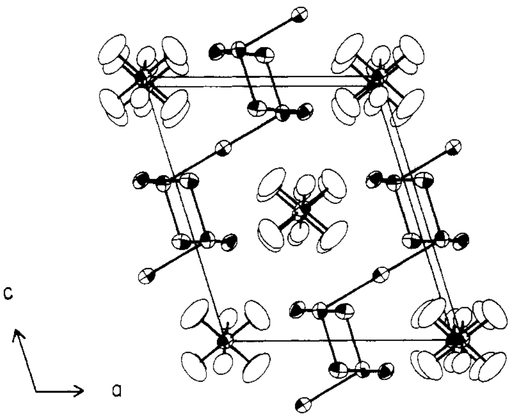

Figure 3. Crystal packing of $(Se_6I)_n \cdot nAsF_6$.

the top of the boat; the clusterlike geometry of $Se_6I_2^{2+}$, with the Se_6 in a chair configuration, results from the four weak Se–I intracationic contacts and the extensive positive charge delocalization.

The $As_2Se_6^{2-}$ anion **14** in $(2,2,2\text{-crypt-Na}^+)_2As_2Se_6^{2-}$[21] is isovalent with the $Se_6I_2^{2+}$ cation. To confirm that the observed solid-state structures of $Se_6I_2^{2+}$ and $As_2Se_6^{2-}$ do not result from complex solid-state effects but are intrinsic, minimum energy geometry, ab initio STO-3G (nonoptimized) total energy calculations were carried out on the exo and endo isomers of $S_6Cl_2^{2+}$[56] and $P_2S_6^{2-}$[56] as models for $Se_6I_2^{2+}$ and $As_2Se_6^{2-}$. The results showed that *exo*-$P_2S_6^{2-}$ is significantly lower in energy (ca. 260 kJ mol^{-1}) than *endo*-$P_2S_6^{2-}$, consistent with the observed endo structure of $As_2Se_6^{2-}$ (**14**). This is reasonable as it minimizes repulsion between the negatively charged exocyclic selenium atoms.

In contrast, the energies of *endo*-$S_6Cl_2^{2+}$ and *exo*-$S_6Cl_2^{2+}$ are almost the same. The energy of the intracationic contacts would be greater in $Se_6I_2^{2+}$ than in $S_6Cl_2^{2+}$, since all long-range interactions are more favorable for the heavier p-block elements. Thus, the observed endo structure is likely intrinsically stable for $Se_6I_2^{2+}$ and is not a consequence of solid-state effects. The $Se_6I_2^{2+}$ cation is therefore expected to retain its solid-state structure in solution.[33] Presumably, the electrostatic repulsion between the partially charged iodine and selenium atoms is offset by the energy involved in intracationic contact formation, and charge delocalization (see above).

Table VIII. Bond Distances (Å)[a] in $(Se_6I)_n \cdot nAsF_6$ and $(Se_6I)_n \cdot nSbF_6$

	$(Se_6I)_n \cdot nAsF_6$	$(Se_6I)_n \cdot nSbF_6$
Intraionic Distances and Contacts within the $(Se_6I^+)_n$ Cation and MF_6^- Anion (M = As, Sb)		
Se(2)–I	2.736 (3)	2.742 (3)
Se(1)–Se(2)	2.365 (3)	2.362 (3)
Se(1)–Se(3′)	2.292 (4)	2.295 (4)
Se(2)–Se(3)	2.370 (4)	2.365 (4)
I–Se(1′)	3.839 (3)	3.883 (3)
I–Se(3′)	3.865 (3)	3.891 (3)
I–Se(1)	4.030 (3)	4.038 (3)
I–Se(3)	3.998 (3)	4.017 (3)
M–F(1)[b]	1.72 (2)	1.87 (1)
M–F(2)	1.67 (2)	1.87 (2)
M–F(3)	1.67 (2)	1.86 (1)
Interionic Contacts between Strands of $(Se_6I^+)_n$ Cations		
Se(2)–Se(3″)	3.591 (3)	3.647 (3)
Se(1)–Se(1″)	3.736 (5)	3.884 (5)
Cation–Anion Contacts		
Se(1)–F(3)	2.85 (2)	2.77 (2)
Se(2)–F(1)	3.13 (2)	3.05 (2)
Se(3)–F(2)	3.10 (3)	2.97 (2)
I–F(2)	3.44 (2)	3.52 (2)

[a] Includes all contacts less than the sum of van der Waals radii (Se–Se = 4.00, Se–I = 4.15, Se–F = 3.35, Se–O = 3.50, I–F = 3.50, I–O = 3.55 Å).[43] [b] M = As, Sb.

Table IX. Bond Angles (deg) in $(Se_6I)_n \cdot nAsF_6$ and $(Se_6I)_n \cdot nSbF_6$

	$(Se_6I)_n \cdot nAsF_6$	$(Se_6I)_n \cdot nSbF_6$
Angles within the $(Se_6I^+)_n$ Cation and MF_6^- Anion		
Se(2)–Se(1)–Se(3′)	103.7 (1)	103.7 (1)
Se(1)Se(2)–Se(3)	100.1 (1)	100.3 (1)
Se(1′)–Se(3)–Se(2)	104.0 (1)	104.3 (1)
Se(1)–Se(2)–I	104.2 (1)	104.4 (1)
Se(3)–Se(2)–I	102.9 (1)	103.5 (1)
Se(2)–I–Se(2‴)	173.7 (1)	174.2 (1)
F(1)–M–F(2)	88.4 (9)	89.7 (8)
F(1)–M–F(3)	89.8 (9)	88.9 (8)
F(2)–M–F(3)	87.9 (2)	90.8 (9)
Angles Associated with Interionic Contacts		
Se(1)–Se(2)–Se(3″)	175.8 (1)	174.2 (1)
Se(2″)–Se(3)–Se(2)	97.9 (1)	96.5 (2)
Se(2″)–Se(3)–Se(1)	107.7 (1)	109.1 (2)
Se(2)–Se(1)–F(3)	165.1 (5)	166.8 (4)
Se(3)–Se(1)–F(3)	89.8 (1)	88.5 (6)
I–Se(2)–F(1)	74.9 (3)	75.9 (3)
Se(1)–Se(2)–F(1)	88.5 (3)	86.2 (3)
Se(2)–Se(3)–F(2)	161.1 (5)	161.6 (6)
Se(1)–Se(3)–F(2)	91.8 (6)	91.3 (6)

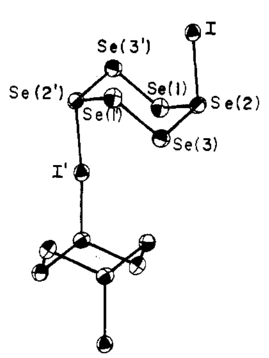

Figure 4. The $(Se_6I^+)_n$ polymeric cation in $(Se_6I)_n \cdot nMF_6$ (M = As, Sb).

Cation–Anion Contacts. There are significant interionic interactions between the atoms in the cation and the anionic fluorine atoms and the oxygen atoms (Table V). This is consistent with all the atoms in $Se_6I_2^{2+}$ having some positive charge. A description (with figures) of the complete coordination around the selenium

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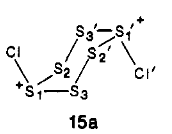
(56) The geometries chosen are estimated by comparison with the known structures of $Se_6I_2^{2+}$ and $As_2Se_6^{2-}$. The estimated bond distances (Å) and angles (deg) for the models



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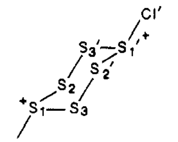
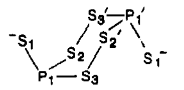


15b



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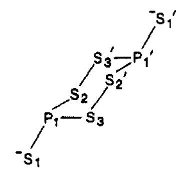


16b

are as follows: $S_6Cl_2^{2+}$ (**15a,b**), S_1–S_2 = 2.20, S_1–S_3 = 2.20, S_2–S_3' = 2.00, S_1–Cl_1 = 1.97, S_2–S_1–S_3 = 95.9, S_1–S_2'–S_3' = 103.5°, S_1–S_3–S_2' = 103.5°, S_2–S_1–Cl_1 = 104.6, S_3–S_1–Cl_1 = 104.6°, torsional angles S_1–S_2–S_3'–S_1' = 80.6, Cl_1–S_1–S_2–S_3' = 32.1 for *endo*-$S_6Cl_2^{2+}$ (**15a**) and Cl_1–S_1–S_2–S_3' = 178.7 for *exo*-$S_6Cl_2^{2+}$ (**15b**); $P_2S_6^{2-}$ (**16a,b**), P_1–S_1 = 2.06, P_1–S_2 = 2.18, P_1–S_3 = 2.18, S_2–S_3' = 2.05 Å, S_2–P_1–S_3 = 101, P_1–S_2–S_3' = 101, P_1–S_3–S_2' = 101, S_2–P_1–S_1 = 96, S_3–P_1–S_1 = 96, torsional angles P_1–S_2–S_3'–P_1' = 76.4, S_1–P_1–S_2–S_3' = 21 for *endo*-$P_2S_6^{2-}$ (**16a**) and S_1–P_1–S_2–S_3' = −173.7 for *exo*-$P_2S_6^{2-}$ (**16b**). The crystal structure of $P_2S_6^{2-}$, one of the anions in $Zn_4(P_2S_6)_3$, has been determined, and it is very different from structure **16a,b**: Bouchetiere, M.; Toffoli, P.; Khodadad, P.; Rodier, N. *Acta Crystallogr.* **1978**, *B34*, 384.

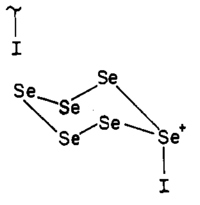
and iodine atoms is given in the supplementary material.

Geometries of SO_2 and AsF_6^-. The average bond distance and angle of the SO_2 unit in $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ (average 1.40 (2) Å and 118 (1)°) are similar to those in $Te_6(AsF_6)_4{\cdot}2SO_2$ (average 1.41 (7) Å and 117 (4)°)[57] and solid SO_2 (1.43 (2) Å, 119 (2)°).[58]

The AsF_6^- anion is disordered. The major component with 85% occupancy has an average AsF bond distance of 1.69 (2) Å (cf. 1.70 (1) Å in SeI_3AsF_6[11]) and a distorted-octahedral geometry with an average angle of 90 (1)°. The minor component was constrained to be octahedral with an As–F bond length of 1.68 Å.

X-ray Crystal Structures of $(Se_6I)_n{\cdot}nMF_6$ (M = As, Sb). $(Se_6I)_n{\cdot}nMF_6$ compounds are isomorphous and isostructural, and both contain polymeric strands of $(Se_6I^+)_n$, MF_6^- (M = As, Sb) anions with some cation–cation and cation–anion interactions. The packing is illustrated in Figure 3. The corresponding bond distances and angles in the two cations are essentially identical (Tables VIII and IX). Presumably the basicity difference of the two MF_6^- anions is not sufficiently large to affect the geometry of the cations. Similarly, the geometries of MF_6^- salts of the chalcogen trihalide cations MX_3^+ (M = Se, Te; X = Br, I) are also the same[11] within experimental error.

Geometry of the Se_6I_2 Unit within the $(Se_6I^+)_n$ Strand. The geometry of the ISe_6I unit in $(Se_6I^+)_n$ is similar to that in $Se_6I_2^{2+}$. The Se_6 rings, in the chair conformation, are linked to iodine atoms in the 1,4-positions in an endo configuration (see Figure 4). The Se–I bond lengths, 2.736 (3) Å (AsF_6^-) and 2.742 (3) Å (SbF_6^-), are very much longer than those in RSeI (R = 2,4,6-$^tBu_3(C_6H_2)$; 2.529 Å)[41] and SeI_3^+ (2.510 (2) Å)[11] but similar to that in $C_4H_8OSeI_2$ (2.755 (4) Å),[59] which contains a Se–I bond with a formal bond order of 0.5. The ratio of the bridging Se–I bond distance to that in $Se_6I_2^{2+}$ is 0.90, similar to the ratio (0.87) of the bridging S–I–S bond (2.674 (7) Å) in $(S_7I)_2I^{3+}$[7] to that of the terminal sulfur–iodine bond in the S_7I groups. The Se–I–Se bond angle (average 174.0 (2)°) is almost linear and is similar to the bridging S–I–S bond angle in $(S_7I)_2I^{3+}$ (180°). In valence bond terms the structure may be represented by a combination of resonance structures **17** and **18**, giving a Se–I bond order of 0.5. Alternatively the bridging Se–I–Se atom may be regarded as being joined by a three-center–four-electron bond. The Se–Se bond alternation within the Se_6 ring is less than that in $Se_6I_2^{2+}$ (Table VII), consistent with the lower formal charge (0.5+) on the tricoordinate Se(2) atoms and less positive charge delocalization into the ring.



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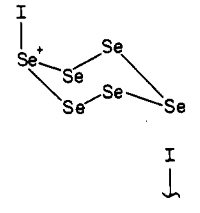

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There are definite but weak intraionic contacts between the bridging iodine atoms and the partially positively charged dicoordinate Se(1) and Se(3) atoms, of average length 3.852 (3) Å (AsF_6^-) and 3.887 (5) Å (SbF_6^-), respectively (Figure 5 and Table VIII). These contacts are weaker than those in $Se_6I_2^{2+}$ (3.714 (2) Å), in part a consequence of the lower positive charge on the dicoordinate cyclic selenium atoms. In addition, each iodine atom in $(Se_6I^+)_n$ makes four weak contacts (Figure 5, Table VIII), two to each Se_6 ring, rather than two in $Se_6I_2^{2+}$ (Figure 2). However, both $Se_6I_2^{2+}$ and the Se_6I_2 fragment in $(Se_6I^+)_n$ have similar geometries. This is further evidence that the clusterlike configurations of both $Se_6I_2^{2+}$ and the Se_6I_2 fragment in $(Se_6I^+)_n$ are intrinsic and not a consequence of solid-state effects.

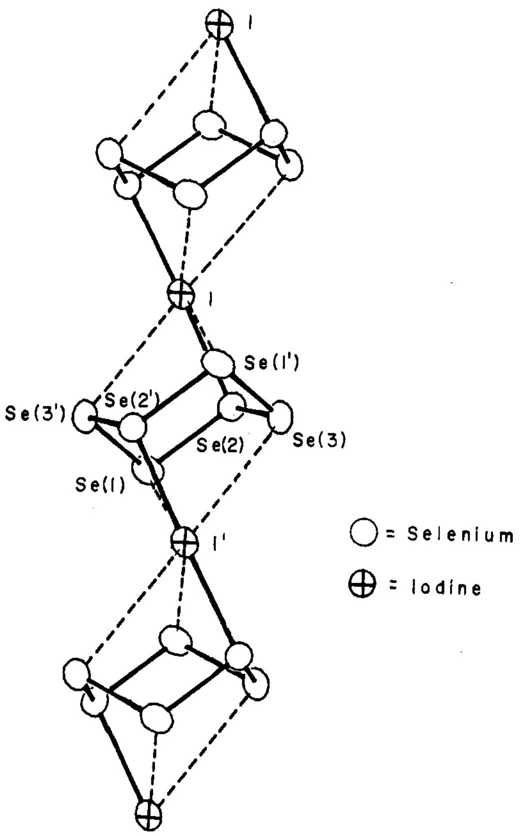

Figure 5. The $(Se_6I^+)_n$ polymeric cation in $(Se_6I)_n{\cdot}nMF_6$ (M = As, Sb) illustrating the interaction of the bridging iodine atom with the adjacent Se_6 rings.

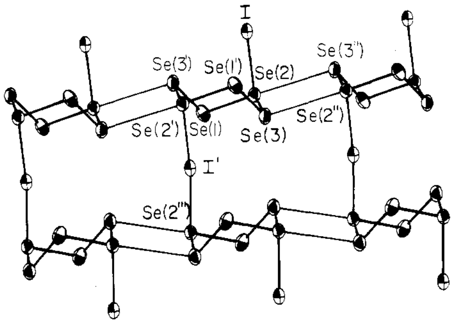

Figure 6. The $(Se_6I^+)_n$ polymeric cations in $(Se_6I)_n{\cdot}nMF_6$ (M = As, Sb) with intercationic interactions.

Overall Geometry of the $(Se_6I^+)_n$ Cation. Each strand of $(Se_6I^+)_n$ cations can be described as an infinite chain of distorted Se_6I_2-containing cubes joined at two opposite corners (i.e. at the bridging iodine atoms) as shown in Figure 5. The $(Se_6I^+)_n$ strands are joined together by weak intercationic interactions between Se(2) and Se(3″) (3.591 (3) Å (AsF_6^-), 3.647 (3) Å (SbF_6^-)), as illustrated in Figure 6. These intracationic contacts are likely of the charge-transfer type with the tricoordinate Se(2) of formal 0.5+ charge acting as an acceptor and the dicoordinate Se(3) as a donor. Consistently the Se(1)–Se(2)–Se(3″) angle is 175.8 (1)° (AsF_6^-) and 174.2 (1)° (SbF_6^-) (see Figure 6), Se(2″)–Se(3)–Se(2) is 97.9 (1)° (AsF_6^-) and 96.5 (2)° (SbF_6^-), and Se(2″)–Se(3)–Se(1) is 107.7 (1)° (AsF_6^-) and 109.1 (2)° (SbF_6^-), respectively. These contacts are reminiscent of the intermolecular and interchain interactions in allotropes of selenium containing Se_6[17] and Se_8[60–63] and gray selenium.[64] The selenium–selenium

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interstrand contacts join the $(Se_6I^+)_n$ strands into a two-dimensional sheet of $(Se_6I)_n^{n+}$ (Figure 6). The overall structure consists of these sheets separated by layers containing MF_6^- anions.

Cation-Anion Interactions. The number of cation-anion interactions in the $(Se_6I^+)_n$ cation (Table VIII) are fewer than those in the $Se_6I_2^{2+}$ cation (Table V). This is consistent with the lower charge in $(Se_6I^+)_n$. In addition, it is conceivable that some of the cation-anion interactions in the $Se_6I_2^{2+}$ cation are replaced by the Se(2)-Se(3″) intercationic contacts in $(Se_6I^+)_n$. The complete description (including figures) of the coordination around the selenium atoms in $(Se_6I)_n \cdot nMF_6$ (M = As, Sb) is given in the supplementary material.

Summary and Conclusion

Our attempts to prepare selenium-rich selenium-iodine cations, in the solid state, led to the discovery of $Se_6I_2(AsF_6)_2 \cdot 2SO_2$, $(Se_6I)_n \cdot nAsF_6$, and $(Se_6I)_n \cdot nSbF_6$. Both cations contain a hexaselenium ring in the chair configuration; i.e., they are iodine derivatives of the unstable allotrope of selenium, Se_6.[17] In the sulfur system the solid S_7IMF_6 (M = As, Sb)[6] and $(S_7I)_2I(SbF_6)_3 \cdot 2AsF_3$[7] have been prepared containing S_7I^+ and $(S_7I)_2I^{3+}$. These cations are both iodine derivatives of the S_7 ring in the chair configuration, which as a neutral species is unstable with respect to S_8.

The structure of $Se_6I_2^{2+}$ is endo and cubelike. Weak intracationic selenium-iodine contacts (2 × 3.709 (2), 2 × 3.719 (2) Å) complete the distorted cube. There is substantial selenium-selenium bond alternation within the Se_6 ring. The bonds between the dicoordinate selenium (2.227 (2) Å) correspond to a bond order of ca. 1.5,[44] which implies substantial $4p\pi$-$4p\pi$ bonding. The selenium-iodine bond distance (2.454 (2) Å) is also significantly shorter than that expected for bond order 1 (average 2.510 (2) Å in SeI_3^+)[11] and implies significant $4p\pi$-$5p\pi$ bonding. These thermodynamically stable $4p\pi$-$4p\pi$ and $4p\pi$-$5p\pi$ bonds arise as a consequence of charge delocalization within the Se_6 ring and onto the iodine atoms. The cluster-like structure adopted by $Se_6I_2^{2+}$ maximizes charge delocalization, π bonding, and intracationic selenium-iodine contacts.

The structure of the $(Se_6I^+)_n$ cation consists of Se_6I_2 units linked through common bridging iodine atoms. Each Se_6I_2 unit is similar to that of $Se_6I_2^{2+}$, except that the selenium-iodine bond length (average 2.739 (3) Å) corresponds to a bond order of 0.5; the selenium-selenium bond alternation within the Se_6 ring is much less substantial, corresponding to the lower charge per Se_6 ring. There are four (rather than two) weaker intracationic selenium-iodine contacts (average 3.870 (3) Å), two to each adjacent Se_6I_2 units. The $(Se_6I^+)_n$ cations are linked through weak selenium-selenium intercationic contacts, giving rise to sheets containing linked $(Se_6I^+)_n$ cations separated by sheets containing the MF_6^- anions.

Thus, whereas selenium-iodine neutral compounds have not been isolated, there is a rich chemistry of binary selenium-iodine cations. As well as the salts described in this paper, SeI_3MF_6 (M = As, Sb),[11] $Se_2I_4(Sb_2F_{11})_2$,[12] and $Se_2I_4(AsF_6)_2 \cdot SO_2$[13] have all been prepared and their X-ray crystal structures determined. In addition $Se_4I_4^{2+}$ and $Se_6I_2^{2+}$ [33,38] have been identified in solution by ^{77}Se NMR spectroscopy. The chemistry of these sulfur and selenium iodide cations has recently been reviewed.[5]

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Registry No. $Se_6I_2(AsF_6)_2 \cdot 2SO_2$, 100908-48-3; AsF_5, 7784-36-3; I_2, 7553-56-2; Se, 7782-49-2; $Se_8(AsF_6)_2$, 52374-78-4; SeI_3AsF_6, 59544-89-7; $(Se_6I)_n \cdot nAsF_6$, 87800-53-1; $(Se_6I)_n \cdot nSbF_6$, 121867-50-3; $I_2Sb_2F_{11}$, 53108-64-8.

Supplementary Material Available: A discussion of the complete coordination around the selenium and iodine atoms in $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ and $(Se_6I)_n \cdot nMF_6$ (M = As, Sb), Figures S1-S11, showing the coordination around various atoms in these compounds, and tables of crystallographic data (Table S1) and of the thermal parameters for $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ $(Se_6I)_n \cdot nAsF_6$, and $(Se_6I)_n \cdot nSbF_6$ (Tables S2, S4, and S6, respectively) (19 pages); tables of observed and calculated structure factors (Tables S3, S5, and S6) (22 pages). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of a Six-Coordinate 21-Thiaporphyrin Complex: $Rh^{III}(STPP)Cl_2$ (STPP = Tetraphenyl-21-thiaporphyrin Anion)

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Treatment of tetraphenyl-21-thiaporphyrin (STPPH) with rhodium(III) chloride in acetonitrile in the presence of metallic zinc yields diamagnetic $Rh^{III}(STPP)Cl_2$. The electronic and ^1H NMR spectra are reported. $Rh^{III}(STPP)Cl_2$ crystallizes in the monoclinic space group $P2_1$ with a = 10.522 (2) Å, b = 13.065 (2) Å, c = 12.898 (3) Å, and β = 108.06 (2)° at 130 K with Z = 2. Refinement of 2760 reflections and 344 parameters yielded R = 0.062. The rhodium is six-coordinate with bonds to the three pyrrole nitrogens (Rh-N = 2.00 (1), 2.033 (9), 2.080 (8) Å), the thiophene sulfur (Rh-S = 2.32 (3) Å), and the two axial chloride ligands (Rh-Cl = 2.333 (3), 2.346 (3) Å). The rhodium atom lies near the plane of the three pyrrole nitrogen atoms, while the thiophene ring is sharply tilted out of that plane. The thiophene group is bound to the rhodium through the pyramidal sulfur in the η^1 fashion. The thiophene ring is bent so that the dihedral angle between the $SC_\alpha C_\alpha$ and $C_\alpha C_\alpha C_\beta C_\beta$ planes is 26.4°. The structure is compared to those of the related high-spin, five-coordinate $M^{II}(STPP)Cl$ (M = Fe, Ni, Cu).

Introduction

The novel features of rhodium porphyrins, including their versatile redox behavior,[1] the formation of reactive Rh-H,[2,3] Rh-Rh,[3] and Rh-C[4] bonds, and their relation to naturally occurring porphyrins, have attracted considerable attention. Generally, the properties of a metal ion in a porphyrin can be modified by alterations in the axial ligands or chemical changes in the porphyrin periphery. In view of the versatile behavior of rhodium porphyrins, alteration of properties through core modification offers considerable promise. For example, polypyrroles (corroles), with a shrunken central binding site, have been examined as ligands for rhodium.[5]

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