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Sulfur and Selenium Iodine Compounds: From Nonexistence to Significance

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It has been our goal to prepare quantitatively in one-step reactions simple compounds that are novel in terms of their stereochemistry and bonding, are first examples of new classes of compounds, and open up new areas of chemistry. Such achievements are often discoveries rather than planned syntheses, and the sulfur and selenium iodine cations (Table I) described here were prepared as a result of an unsuccessful search for SI_3AsF_6.[1]

Binary sulfur iodides are unstable under ambient conditions,[2-4] and selenium iodides[5] are unknown. Before our work, there were no examples of stable species at room temperature containing covalent S–I or Se–I bonds[2-5] except SeI_6^{2-}.[6] We have now prepared, usually quantitatively, a number of salts of the sulfur and selenium iodine (and bromine) cations shown in Table I, all of which contain covalent S–I and Se–I bonds. In addition, these cations provide examples of stable derivatives of S_7, Se_6, thermodynamically stable $np\pi-np\pi$ bonds ($n \geq 3$), and $\pi^*-\pi^*$ bonds. Many of the cations maximize intercationic halogen–chalcogen contacts and thus have cluster-like characteristics, e.g., the cube-like $Se_6I_2^{2+}$ (Figure 10) and the distorted right-triangular prismatic $S_2I_4^{2+}$ (Figure 4). The bonding encountered in these cations has been helpful in understanding the puzzling geometries of more complex related species, e.g., S_8^{2+}, Se_8^{2+}, S_4N_4, and $S_2O_4^{2-}$, a fuller account of which is given in ref 7.

Instability of Neutral Sulfur and Selenium Binary Iodides

Solid S_2I_2 has been characterized at −90 °C,[2] and SI_2 at 9 K,[3-4] but no structural evidence has been presented for the corresponding binary selenium iodides.[5] The instability of the S–I and Se–I bonds can be attributed to their very low ionic resonance stabilization energies as the electronegativity of iodine is about the same as that of sulfur and selenium. Thus ΔH (eq 1) and ΔH (eq 2) are −18.0 and −1.3 kJ mol^{-1}, respectively.[8] They

$$2\,\text{-S-I(g)} \rightarrow \text{-S-S-(g)} + I_2(g) \qquad (1)$$

$$2\,\text{-Se-I(g)} \rightarrow \text{-Se-Se-(g)} + I_2(g) \qquad (2)$$

are even more unstable in the solid state due (in part) to the large sublimation energy of solid I_2 (62.3 kJ mol^{-1}). For example, CF_3SI is detected as a gas, but readily disproportionates in the solid state above −100 °C according to eq 3.[9a] CH_3SI behaves similarly and is also only stable in the solid state at very low temperatures, decomposing to CH_3SSCH_3 and I_2.[9b]

$$2CF_3SI(s) \rightarrow CF_3SSCF_3(s) + I_2(s) \qquad (3)$$

The structure of Ph_3CSI, which is stable[10c] in the solid state at −78 °C and in solution in the dark, has been determined.[10b] Evidence for RCOSI (R = aryl) has been presented,[10a] but the material has not been structurally characterized. No neutral compound containing a room

Table I
Characterized[a] Binary Sulfur and Selenium Halogen Cations

	F	Cl	Br	I
S	SF_3^+	SCl_3^+	SBr_3^+	$S_2I_4^{2+}$
			S_7Br^+	S_7I^+
			Br_2S^+SSBr	$[(S_7I)_2I]^{3+}$
Se	SeF_3^+	$SeCl_3^+$	$SeBr_3^+$	SeI_3^+
		$Se_7^+SeSeCl$	$Se_2Br_5^+$	$Se_2I_4^{2+}$
			$Br_2Se^+SeSeBr$	$I_2Se^+SeSeSe^+I_2$[b]
				$(Se_6I^+)_n$
				$Se_6I_2^{2+}$

[a] Structure of cations determined by X-ray crystallography. [b] Identified in solution by ^{77}Se NMR.

Thomas Klapötke was born in Göttingen in 1961. He studied chemistry at the Technical University of Berlin under the supervision of Prof. Köpf and obtained his Ph.D. in 1986. In 1987 he won a Feodor-Lynen-Scholarship of the Alexander von Humboldt Foundation and spent a year as a visiting scholar with Prof. Jack Passmore at the University of New Brunswick in Canada. Since 1988 he has been at the Technical University of Berlin working on fluoro organometallic chemistry.

Jack Passmore was born in Barnstaple, Devon, England, and received his B.Sc. and D.Sc. from the University of Bristol, England, and his Ph.D. degree (with Dr. Neil Bartlett) from the University of British Columbia in Vancouver. He did postdoctoral work during the year 1968–1969 at MacMaster University, Hamilton, Ontario, Canada (with Dr. Ronald J. Gillespie). He then joined the faculty at the University of New Brunswick in 1969, where he is presently Professor of Chemistry.

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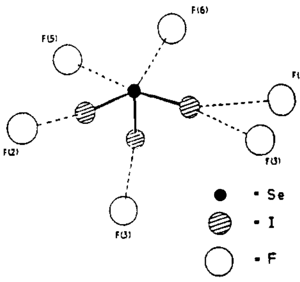

Figure 1. SeI_3^+ cation in SeI_3MF_6 (M = As, Sb). Weak contacts are indicated as ···· here and in other figures.

temperature stable covalent S–I bond has so far been characterized,[2] although the human thyroid is thought to contain such a compound.[10d] It is likely part of a protein, isolated from other S–I bonds, and thus kinetically stabilized. The first synthesis and structure of a stable neutral iodo selenide RSeI (R = 2,4,6-$^tBu_3C_6H_2$) has recently been reported;[11] is it likely kinetically stabilized by the bulky substituent (cf. kinetically stable RP═PR and $R_2Si═SiR_2$; R bulky groups).[12]

Sulfur and Selenium Iodine Cations

Preparation and Characterization of SeI_3MF_6 (M = As, Sb). Although neutral binary selenium iodides are unstable, salts of SeI_6^{2-} [6] have been known for some time. More recently we prepared SeI_3MF_6 according to eq 4 and 5 as well as various other routes.[13]

$$2Se + 3I_2 + 3AsF_5 \xrightarrow{SO_2(l)} 2SeI_3AsF_6 + AsF_3 \quad (4)$$

$$6Se + 9I_2 + 10SbF_5 \xrightarrow{SO_2(l)} 6SeI_3SbF_6 + (SbF_3)_3{\cdot}SbF_5 \quad (5)$$

The heat of reaction 4 was estimated to be −100 kJ mol^{-1}.[8a] The Se–I bonds in SeI_3^+ are probably only slightly stronger than those in SeI_2. The crystal lattice energy stabilizes SeI_3AsF_6 substantially.[8a] Presumably SeI_6^{2-} salts are also stabilized by their crystal lattice energies. The X-ray crystal structures of SeI_3MF_6 confirmed the identity of the pyramidal SeI_3^+ cation[8a] (Figure 1). The average selenium–iodine bond distance is 2.510 Å and is similar to the sum of the covalent radii of Se and I (2.493 Å). SBr_3MF_6[14] (N.B. SBr_4 is not known) and TeI_3MF_6[8a,15] have also been prepared.

Preparation of S_7IMF_6, $(S_7I)_4S_4(AsF_6)_6$, and $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$. The successful preparations of salts of SeI_3^+ led naturally to the attempted synthesis of the analogous SI_3^+ compounds.[1] Initial reactions were carried out with an excess of sulfur relative to the stoichiometric amounts indicated in eq 4 and 5. The chemical analyses of these products corresponded to S_7IMF_6 (M = As, Sb), vastly different from those calculated for SI_3MF_6. Subsequently S_7IMF_6 were prepared quantitatively, in liquid SO_2 or AsF_3 solution[16] according to eq 6–8.

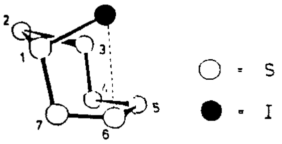

Figure 2. S_7I^+ cation in S_7ISbF_6.

$$^{14}/_{8}S_8 + I_2 + 3AsF_5 \rightarrow 2S_7IAsF_6 + AsF_3 \quad (6)$$

$$^{42}/_{8}S_8 + 3I_2 + 10SbF_5 \rightarrow 6S_7ISbF_6 + (SbF_3)_3{\cdot}SbF_5 \quad (7)$$

$$S_x(AsF_6)_2\ (x = \text{ca. } 19) + I_2 \rightarrow 2S_7IAsF_6 + [(x - 14)/8]S_8 \quad (8)$$

Attempts were made to prepare S_8I^+ according to eq 9 and 10, but S_7IAsF_6 was formed in both reactions; I_2 and S_8 (for eq 9), and $KAsF_6$ and S_8 (for eq 10), were also quantitatively produced. Presumably S_8I^+ is formed initially but it disproportionates to the more thermodynamically stable (estimated at ca. 26 kJ mol^{-1}) S_7IMF_6 and sulfur.[16] An important factor in the stability of S_7I^+, relative to S_8I^+, is the lower ionization energy of S_7 (836.4 kJ mol^{-1}) relative to that of S_8 (872.4 kJ mol^{-1}).[17] The ionization energy of S_5 (830 kJ mol^{-1}) is less than that of S_6 (868 kJ mol^{-1}) or S_4 (1000 kJ mol^{-1}),[17] and consistently the radical cation S_5^+ has been detected in solution but not S_4^+ or S_6^+.[18] Other S_7^+ derivatives to have been characterized are S_7I^+,[1,16] S_7Br^+,[19] $(S_7I)_2I^{3+}$,[20] and $S_7^+–S_5–S_7^+$ (S_{19}^{2+}).[21] This suggests that the odd unipositively charged rings S_7^+ and S_5^+ (with or without substituents) are most stable than the even-membered rings S_8^+ or S_6^+. This is in contrast to the situation for neutral rings, where even-membered rings are the most stable, with the stability sequence $S_8 > S_6 > S_7 >>> S_5$ (not isolated).[22] We have been unable to synthesize S_8I^+ (and S_8Br^+)[1,16,19] or S_6I^+ (and S_6Br^+),[19,20] and our attempts to make S_5I^+ (and S_5Br^+) led to the isolation of $(S_7I)_4S_4(AsF_6)_6$,[20,23] $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$,[20] and $(S_7Br)_4S_4(AsF_6)_6$.[19] These compounds were prepared quantitatively according to eq 11 and 12 from sulfur, iodine, and the corresponding pentafluoride.

$$I_3AsF_6 + nS_8 \rightarrow S_7IAsF_6 + I_2 + (n - 7/8)S_8 \quad (9)$$

$$S_8(AsF_6)_2 + KI \rightarrow S_7IAsF_6 + KAsF_6 + {}^{1}/_{8}S_8 \quad (10)$$

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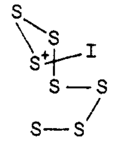
$$4S_8 + 2I_2 + 9AsF_5 \xrightarrow{SO_2(l)} (S_7I)_4S_4(AsF_6)_6 + 3AsF_3 \tag{11}$$

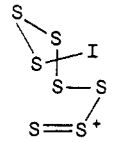
$$\tfrac{28}{8}S_8 + 3I_2 + 10SbF_5 \xrightarrow{AsF_3(l)} 2((S_7I)_2I)(SbF_6)_3{\cdot}2AsF_3 + (SbF_3)_3SbF_5 \tag{12}$$

We were surprised to find that S_4^{2+} had been formed in reaction 11, as a large excess of AsF_5 in SO_2 or AsF_3 oxidizes sulfur only to S_8^{2+}. In fact S_4^{2+} was only prepared by heating S_8 and liquid SbF_5 at 120 °C for several days![24-26] It was postulated that iodine facilitates the oxidation to S_4^{2+} and subsequently S_8 was quantitatively oxidized to $S_4(AsF_6)_2$ by AsF_5 in liquid SO_2 in the presence of trace halogen (I_2, Br_2, Cl_2) within minutes of the reaction mixture warming up to room temperature.[23-24]

Structures of S_7IMF_6, $(S_7I)_4S_4(AsF_6)_6$, and $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$. The structures of all four salts were determined by X-ray crystallography. The S_7I^+ cations in both S_7IMF_6[1,16] salts and in $(S_7I)_4S_4(AsF_6)_6$[20] are essentially identical; S_7I^+ (Figure 2) consists of a seven-membered homoatomic sulfur ring in a slightly distorted chain configuration similar to those in γ- and δ-S_7,[27] S_7O,[28] and S_{19}^{2+},[21] but with an exocyclic iodine. The geometries of S_7O and S_7I^+ are similar, with similar bond-length alternations.[1,16,27,29] These alternations may be viewed as arising from the alternations present in S_7 and the presence of a positively charged tricoordinate sulfur atom (connected to the iodine).[1,16] The extent of the lengthening and shortening is greatest near the source of the perturbation: S(1)–S(7) is very long (2.389 (4) Å, bond order of 0.37)[31] and S(7)–S(6) very short (1.900 (5) Å, bond order of 1.76) (Figure 2). In valence-bond terms, the structure can be viewed as consisting of structure A and a number of other resonance structures that delocalize the charge into the ring, the most important of which is B.



A



B

The S^+–I distances (2.30–2.37 Å)[16] in all S_7I^+ salts (including $(S_7I)_4S_4(AsF_6)_6$) correspond to a bond order of 1 (sum of covalent radii: 2.37 Å) and are all shorter than the S–I bond length (2.406 (4) Å) in $(C_6H_5)_3CSI$.[10c] These are the only examples of structural determinations of covalent S–I bonds. $(CH_3)_2SISbF_6$, $(CH_3)_2SISbCl_6$,[32a] and $(CH_3)(CF_3)SIMF_6$[32b] have recently been reported to be stable up to −20 °C or −35 °C, respectively, and were characterized by Raman and NMR spectroscopy.

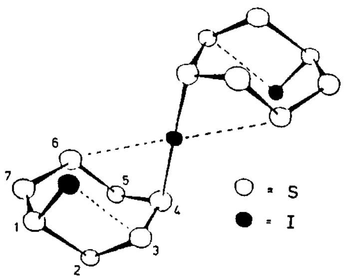


Figure 3. $(S_7I)_2^{3+}$ cation in $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$.

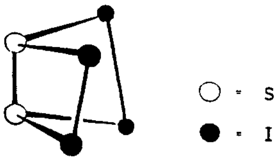


Figure 4. The $S_2I_4^{2+}$ cation in $S_4I_4(AsF_6)_2$.

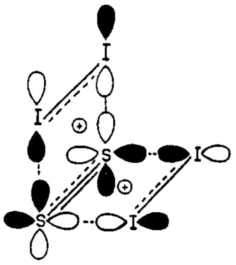


Figure 5. The S_2 and $2I_2$ dimers joined via π*–π* interactions to give $S_2I_4^{2+}$.

$(S_7I)_4S_4(AsF_6)_6$ contains discrete S_7I^+ and S_4^{2+} cations and AsF_6^- anions.[20] The S_4^{2+} cation has a square-planar geometry similar to those in $S_4(AsF_6)_2{\cdot}0.6SO_2$[23] and $(S_7Br)_4S_4(AsF_6)_2$.[19] The structure of the $(S_7I)_2I^{3+}$ cation consists of two equivalent S_7I^+ units that have geometries similar to those observed in S_7IMF_6[16] and $(S_7I)_4S_4(AsF_6)_6$[20,23] (Figure 3), joined by a bridging iodine atom. The structure is approximately described in terms of two resonance structures $S_7I_2^{2+}$ and S_7I^+, and thus the bridging sulfur–iodine bond (2.674 (7) Å) has a formal bond order of 0.5. The I(1)–S(6) intercationic distance (3.394 (3) Å) in S_7I^+ itself and the corresponding I(1)–S(3) interaction in $(S_7I)_2I^{3+}$ (3.381 (9) Å) are significantly less than the corresponding sum of the van der Waals radii of 4.0 Å. In addition, the bridging iodine atom also has a very weak contact with each of the S_7I^+ units (I(2)–S(6), 3.777 (8) Å). Thus both S_7I^+ and $(S_7I)_2I^{3+}$ have cluster-like characteristics.

Preparation and Structure of $S_2I_4(AsF_6)_2$. In an attempt to prepare other salts of novel sulfur–iodine cations (e.g., $S_2I(AsF_6)$, cf. S_2FAsF_6), we reacted $S_4(AsF_6)_2$ with an excess of iodine. One product was characterized as $S_2I_4(AsF_6)_2$ and was subsequently synthesized quantitatively in liquid sulfur dioxide according to eq 13.[33] Systematic attempts to prepare

$$\tfrac{1}{4}S_8 + 2I_2 + 3AsF_5 \rightarrow S_2I_4(AsF_6)_2 + AsF_3 \tag{13}$$

SI_3AsF_6 were unsuccessful. All reactions lead to $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$ although SI_3AsF_6 formation was

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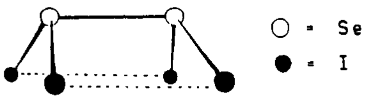

Figure 6. The $Se_2I_4^{2+}$ cation in $Se_2I_4(Sb_2F_{11})_2$.

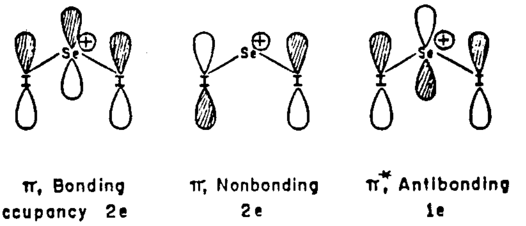

Figure 7. The SeI_2^+ radical cation π MOs derived from p_z selenium and iodine AOs.

shown to be thermodynamically feasible; the disproportionation to solid $S_2I_4(AsF_6)_2$ and $I_2(s)$ was shown to be even more thermodynamically favorable.[24,33]

The structure of $S_2I_4(AsF_6)_2$ consists of discrete $S_2I_4^{2+}$ and AsF_6^- ions with weak anion–cation contacts.[24,33] The $S_2I_4^{2+}$ cation has a unique distorted right triangular prismatic structure (C_2 symmetry) (Figure 4)[33] and, unexpectedly, does not have the structure as the isoelectronic P_2I_4.[34]

The S–S (1.828 (1) Å, cf. S_2, $S_2(X^3\Sigma g)$ 1.8894 Å[35]) and I–I bond lengths (2.597 (2) Å, cf. $I_2(g)$, 2.662 Å[36] and I_2^+, 2.557 (4) Å[37]) in $S_2I_4^{2+}$ indicate bond orders of 2.33 and 1.33, respectively. The S–S bond distance in this cation is the shortest reported. The S–I distances of 2.858 (6) Å and 3.195 (6) Å are comparable to sulfur–iodine distances in sulfur–iodine charge-transfer complexes[2c] and are longer than that in $[(H_2N)_2CS]_2I^+$ (2.629 Å),[38] which has a formal S–I bond order of 0.5, but they are less than the sum of the van der Waals radii (4.00 Å).[39] The $S_2I_4^{2+}$ cation may be regarded as consisting of $S_2^{0.66+}$ and $2I_2^{0.66+}$ units, weakly bonded together via two mutually perpendicular sets of $\pi^*-\pi^*$ orbitals (Figure 5) by electrons in π^* orbitals. Thus, π bonding in the cation is maximized. The equidistributions of charge over all three dimer units ($S_2^{0.66+}$, $2I_2^{0.66+}$) and the resulting bonding situation may arise from the near equality of the ionization energies of S_2 (9.36 eV) and I_2 (9.3995 eV).[40] Therefore, $S_2I_4^{2+}$ is an example, par excellence, of a thermodynamically stable species that contains a $np\pi-np\pi$ ($n \geq 3$) bond.[7]

Preparation and Structure of $Se_2I_4(Sb_2F_{11})_2$. It was postulated that the structure and bonding in $S_2I_4^{2+}$ were a consequence of the near equality of the ionization energies (IEs) of S_2 and I_2. To test this hypothesis, we attempted the synthesis of $Se_2I_4^{2+}$ (IE of Se_2 = 8.33 eV),[40] and subsequently $Se_2I_4(Sb_2F_{11})_2$ was prepared according to eq 14 and its structure determined.[41] The $Se_2I_4^{2+}$ cation has an eclipsed structure (Figure 6) similar to that of $S_2O_4^{2-}$[42] with two SeI_2 units joined by a weak selenium–selenium bond (2.841 (2) Å) and very weak iodine–iodine interactions (3.756 (2), 3.661 (2) Å) (Figures 6 and 8)[41] (i.e., the structure of $Se_2I_4^{2+}$ only superficially resembles that of $S_2I_4^{2+}$).

$$2I_2Sb_2F_{11} + 2Se \xrightarrow[\text{room temperature}]{SO_2} Se_2I_4(Sb_2F_{11})_2 \qquad (14)$$

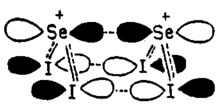

Figure 8. Two SeI_2^+ radical cations joined via weak $\pi^*-\pi^*$ interactions to give $Se_2I_4^{2+}$.

The $Se_2I_4^{2+}$ cation may be regarded as two SeI_2^+ radical cations, joined, in part, by overlap of the odd electron in each of the π^* SeI_2^+ molecular orbitals (Figure 7) resulting in some bonding between all six atoms and a formal selenium–iodine bond order of 1.25[41] (Figure 8). Consistently, the selenium–iodine bond distances in $Se_2I_4^{2+}$ (2.436 (2)–2.450 (2) Å) are significantly shorter than those in SeI_3^+ (2.510 (2)–2.513 (2) Å).[8a] Thus $S_2I_4^{2+}$ and $Se_2I_4^{2+}$ are different from one another, and from their isoelectronic counterparts P_2I_4[34] and As_2I_4,[43] which have classical all σ eclipsed geometries. However, they both are cluster-like, and both contain $np\pi-np\pi$ ($n > 2$) and $\pi^*-\pi^*$ bonds. That the structure of $Se_2I_4^{2+}$ is different from $S_2I_4^{2+}$ supports our contention that the geometry and bonding in the sulfur cation are dependent on the equality of the IEs of S_2 and I_2.

Preparation of $(Se_6I)_n(AsF_6)_n$ and $Se_6I_2(AsF_6)_2$. Several allotopes of sulfur and their derivatives have been isolated and characterized, including S_n (n = 6–13, 18, 20, and ∞),[44] S_nO (n = 6–10),[28] S_7O_2,[45] and $S_{12}O_2$ in $S_{12}O_2\cdot 2\ SbCl_5$,[46] and in various cations, for example, S_7I^+,[16] S_7Br^+,[19] $(S_7I)_2I^{3+}$,[20] and $(S_8)_2Ag^+$.[47] Selenium forms[48a] only the unstable rings Se_8,[48b] Se_6,[48c] and Se_7,[48d,e,49] in addition to polymeric gray selenium. Derivatives of selenium rings had not been reported prior to our work. $(S_7I)_4(S_4)(AsF_6)_6$[20,23] has the greatest thermal stability, of the salts containing sulfur–iodine cations, and therefore we attempted to prepare $(Se_7I)_4Se_4(AsF_6)_6$.[50] Selenium and iodine were reacted with AsF_5 in liquid AsF_3 as indicated in eq 11 but by using selenium instead of sulfur. However, the reaction proceeded according to eq 15, and subsequently Se_6I-

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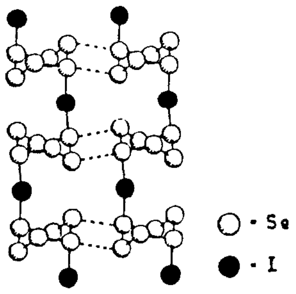

Figure 9. View of the polymeric cations $(Se_6I^+)_n$ in $(Se_6I)_n{\cdot}n(AsF_6)$, ···· representing weak intercationic selenium–selenium contacts (3.591 (3) Å).

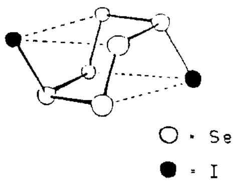

Figure 10. $Se_6I_2^{2+}$ cation in $Se_6I_2(AsF_6)_2{\cdot}2SO_2$.

AsF_6 was prepared quantitatively according to eq 16 in liquid SO_2 solution.[50] Large crystals of Se_6IAsF_6 can

$$32Se + 2I_2 + 9AsF_5 \xrightarrow{\text{3 months}} 4Se_6IAsF_6 + Se_8(AsF_6)_2 + 3AsF_3 \quad (15)$$

$$12Se + I_2 + 3AsF_5 \xrightarrow{\text{1 week}} 2Se_6IAsF_6 + AsF_3 \quad (16)$$

be prepared by thermally cycling the reaction mixture. The crystals appeared ruby red in transmitted light and have a golden appearance in reflected light.

The successful synthesis of the polymeric $(Se_6I)_nn(AsF_6)$ suggested that $Se_6I_2(AsF_6)_2$ might be preparable. Subsequently, selenium and iodine were reacted with AsF_5 in liquid SO_2 according to eq 17.[51]

$$6Se + I_2 + 3AsF_5 \xrightarrow{SO_2(l)} Se_6I_2(AsF_6)_2{\cdot}2SO_2 + AsF_3 \quad (17)$$

The ^{77}Se NMR of this solution showed the presence of about 11 different selenium cations (see below), and many attempts to produce crystals at room temperature were unsuccessful. However, when the solution was cooled to −70 °C for 1 h and left at room temperature, then 80% of the selenium crystallized out as highly crystalline $Se_6I_2(AsF_6)_2{\cdot}2SO_2$.[51-52]

Structure of $(Se_6I)_n{\cdot}n(AsF_6)$ and $Se_6I_2(AsF_6)_2{\cdot}2SO_2$. The structure of $(Se_6I)_n{\cdot}n(AsF_6)$ consists of AsF_6^- anions and polymeric strands of $[Se_6I^+]_n$ cations with some cation–cation and cation–anion interactions[50] (Figure 9). The cation contains hexaselenium rings in a chair conformation similar to that of cyclohexaselenium.[48c] The rings are joined to two neighboring hexaselenium rings by two weak (2.736 (3) Å) exocyclic 1,4 diaxial Se–I bonds (Figure 9) of bond order ca. 0.5; each tricoordinate Se atom carries a charge of 0.5. The $[Se_6I^+]_n$ cation was the first example of a derivative of a selenium ring; and it is also polymeric, unlike the known sulfur–iodine cations.

The discrete centrosymmetric $Se_6I_2^{2+}$ cation contains hexaselenium rings of chair conformation (Figure 10) similar to those in Se_6[48b] and $[Se_6I^+]_n$,[50] but in contrast to that in $[Ph_2Se_6^{2+}]$,[53] which has an Se_6 ring with a boat conformation. The iodine substituents are in the 1,4 axial positions.

The tricoordinate selenium atoms in the $Se_6I_2^{2+}$ cation are positively charged, but there is delocalization of charge into the ring, resulting in bond alternation[51] (2.482 (2) Å, 2.227 (2) Å) and the formation of 4pπ–4pπ bonds. Each of the two iodine atoms makes two intraionic contacts with both the dicoordinate, but partially charged, selenium atoms within the ring and the contacts (3.719 (2) Å and 3.709 (2) Å) that are substantially shorter than the sum of the van der Waals radii of Se and I (4.15 Å). Thus the $Se_6I_2^{2+}$ has a definite distorted cube cluster-like geometry, which it probably retains in solution (see below).

Identification of $Se_4I_4^{2+}$ and $Se_6I_2^{2+}$ by ^{77}Se NMR Spectroscopy in Solution. The characterization of the sulfur–iodine cations is seriously hindered by the lack of a suitable spectroscopic technique, but ^{77}Se NMR can be used in the selenium system. We therefore systematically searched for selenium–iodine cations in SO_2 solution, by natural abundance ^{77}Se NMR. As part of this investigation, we followed the reaction of Se_4^{2+} with varying amounts of I_2 and found that the equation proceeded according to eq 18.[55]

$$Se_4(AsF_6)_2 + 2I_2 \rightarrow Se_4I_4(AsF_6)_2 \quad (18)$$

The major features of the spectrum were two peaks of equal intensity and satellite peaks showing ^{77}Se–^{77}Se couplings consistent with an AXX′A′ spectrum. These data are consistent with an $I_2Se^+SeSeSe^+I_2$ formulation for the cation. In addition to the two major peaks attributable to $Se_4I_4^{2+}$, there were three other less intense peaks present, one attributable to SeI_3^+ and the other two due to $Se_6I_2^{2+}$, whose integrated areas were in a ratio of 1:2. The latter two peaks have satellites due to ^{77}Se–^{77}Se couplings consistent with an $AX_2X_2'A'$ spectrum and therefore attributable to a symmetric $Se_6I_2^{2+}$. $Se_4I_4^{2+}$ was shown to be in equilibrium with SeI_3^+ and $Se_6I_2^{2+}$ according to eq 19, and $\Delta H°$ and $\Delta S°$ have been estimated to be 20 kJ mol^{-1} and 60 J K^{-1} mol^{-1}.[55]

$$2Se_4I_4^{2+} \rightleftharpoons 2SeI_3^+ + Se_6I_2^{2+} \quad (19)$$

The ^{77}Se NMR spectra of solutions of $Se_6I_2(AsF_6)_2$ at various temperatures show that $Se_6I_2^{2+}$ itself is in equilibrium with Se_8^{2+} and $Se_4I_4^{2+}$ according to eq 20.[52]

$$2Se_6I_2^{2+} \rightleftharpoons Se_8^{2+} + Se_4I_4^{2+} \quad (20)$$

It is also in equilibrium with several other species, which are presently under investigation. $Se_4I_4^{2+}$ and $Se_6I_2^{2+}$ undergo Se^+–I and Se–Se bond redistribution reactions, and since the various combinations do not differ greatly in enthalpy, the formation of the large number of species is probably entropy driven. It is likely that the sulfur–iodine cations also give complex equilibrium mixtures in solution.

Chloro and Bromo Cations of Sulfur and Selenium. All binary chalcogen–chlorine cations of the type XCl_3^+ (X = S, Se, Te) have been prepared, and the

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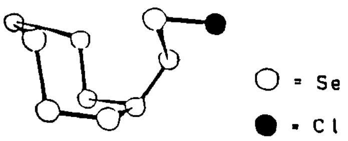


Figure 11. Se_9Cl^+ cation in $Se_9ClSbCl_6$.

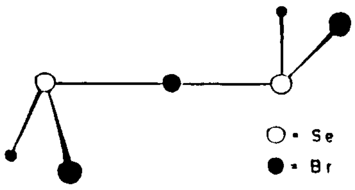


Figure 12. $Se_2Br_5^+$ cation in $Se_2Br_5AsF_6$.

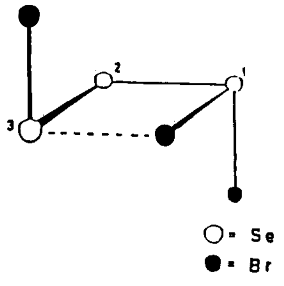


Figure 13. $Se_3Br_3^+$ cation in $Se_3Br_3AsF_6$.

structures of the SCl_3^+ [56] and $SeCl_3^+$ [57] cations are similar to that of SeI_3^+ (Figure 1). Gillespie et al. prepared and characterized by X-ray crystallography the Se_7^+-Se_2Cl cation in $Se_9ClSbCl_6$.[58] This compound contains the first example of a structurally characterized seven-membered selenium ring. The chair conformation of the Se_7 ring with the Se_2Cl in the endo position is shown in Figure 11. The geometry of the $Se_7^+SeSeCl$ is similar to that of $Br_2Se^+SeSeBr$ (see below) with the Se_7^+ replacing the Br_2Se^+ in $Br_2Se^+SeSeBr$.

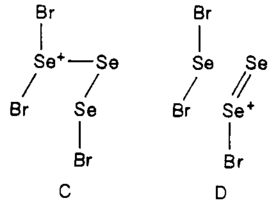
The bromine cations SBr_3^+ [8a,14a,b] and $SeBr_3^+$ [14c,d] are also of interest as these are the simplest binary bromine cations which contain the $X(IV)^+$–Br (X = S, Se) bond. The X-ray crystal structures of SBr_3MF_6 and $SeBr_3MF_6$ confirm the identity of the pyramidal cations[8a] (Figure 1). S_7BrMF_6 and $(S_7Br)_4S_4(AsF_6)_6$ were prepared quantitatively by routes similar to those of the iodine counterparts[19] (see above). The structure of S_7Br^+ in $(S_7Br)_4S_4(AsF_6)_6$ is very similar to that of S_7I^+ (Figure 2).

The first example of an $X_2Hal_5^+$ species (X = chalcogen) is the cation $Se_2Br_5^+$, which was prepared quantitatively according to eq 21 and 22.[59] The $Se_2Br_5^+$ cation (C_{2h} symmetry) contains two trans $SeBr_2$ units, linked by a bridging bromine atom at an inversion center (Figure 12). Recently $Br_2X^+XXBr(AsF_6^-)$ [X = S, Se] have been prepared quantitatively according to eq 23,[60] containing the Br_2X^+XXBr cation (Figure 13). The Se–Se bond orders vary from substantially less than 1 (Se(1)–Se(2), 2.554 (6) Å) to ca. 1.5 (Se(2)–Se(3), 2.211 (6) Å). This implies substantial 4pπ–4pπ bonding between Se(2) and Se(3) and, in valence-bond terms, suggests that the bonding may be represented by valence-bond structures C and D.

$$4Se + 5Br_2 + 3AsF_5 \rightarrow 2Se_2Br_5AsF_6 + AsF_3 \qquad (21)$$

$$Se_4(AsF_6)_2 + 5Br_2 \rightarrow 2Se_2Br_5AsF_6 \qquad (22)$$

$$3Br_2 + {}^6\!/_8S_8 \text{ (or 6Se)} + 3AsF_5 \rightarrow Br_2XXXBr(AsF_6) + AsF_3 \qquad (23)$$



The cluster-like geometry of this cation maximizes intracationic contacts, charge delocalization, the number of Se^+–Br bonds (cf. $MeSeSe^+(Me)SeMe$)[61], Se–Se bond alternation, and π bonding.

Conclusions

A New Class of Compounds Discovered: The Chalcogen Iodine (and Bromine) Cations. As a result of our unsuccessful attempts to prepare $SI_3(MF_6)$, a large number of novel, stable sulfur and selenium iodine and bromine cations have been prepared quantitatively and their structures have been determined (Table I). Thus, whereas stable neutral sulfur iodides and selenium iodides either are not known (selenium) or can only be prepared at low temperatures (sulfur), sulfur–iodine and selenium–iodine cations have been shown to be unexpectedly numerous. These simple cations have novel structures and bonding arrangements, and it may be argued that the goals outlined at the beginning of this Account have been achieved.

The Stable >X⁺–I (X = S, Se) Bond. The crystal lattice component is likely not the only factor responsible for the stability of the X^+–I bonds in the salts described in this Account, as $(CH_3)_2SISbF_6$, $(CH_3)_2SISbCl_6$, and $(CH_3)(CF_3)SIMF_6$[32] are stable only at low temperatures. The S^+–I (Br) and Se^+–I (Br) bond distances in the more complex chalcogen halide cations are all slightly shorter than the sums of the corresponding covalent radii and the corresponding bond lengths in neutral S(II)–I (Br) and Se(II)–I (Br) containing compounds.[10c,11] They are also shorter than the observed or predicted[8a] X–Hal bond lengths in $XHal_3^+$ (X = S, Se; Hal = I, Br).[8a] The S^+–I (Br) and Se^+–I (Br) bonds in the chalogen halide cations are therefore presumably stronger than those in corresponding neutral compounds, or simple $MHal_3^+$ salts and their simple derivatives. In addition, the more complex chalcogen halide cations, as a whole, are probably stabilized by charge delocalization, bond alternation, and halogen–chalcogen intercationic contacts, as a consequence of the presence of X^+–I (Br) bonds (much less extensive, or not possible, in SeI_3MF_6, $(CH_3)_2SISbF_6$, $(CH_3)_2SISbCl_6$, and $(CH_3)(CF_3)SIMF_6$[32]). Neutral sulfur and selenium bromides and chlorides are stable, consistently; $X_hHal_y^{n+}$ cations containing an Se–Cl bond (in $Se_7^+SeSeCl$)[58] and X–Br bond (in Br_2X^+XXBr, X = S, Se)[60] are observed whereas iodine-containing analogues are not.

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Table II
M-M Bond Distances and Bond Orders

cation	M-M shortest bond distance, Å	bond order (ref 31)
S_7Br^+	1.92 (2)	1.7
$S_2I_4^{2+}$	1.828 (1)	2.3
S_7I^+	1.906 (5)	1.8
$(S_7I)_2I^{3+}$	1.897 (10)	1.8
Se_9Cl^+	2.223 (5)	1.5
$Se_3Br_3^+$	2.211 (6)	1.6
$Se_2I_4^{2+}$	2.841 (2)	0.2
Se_6I^+	2.292 (4)	1.2
$Se_6I_2^{2+}$	2.227 (2)	1.5

Examples of Thermodynamically Stable *n*pπ–*n*pπ (*n* ≥ 3) Bonds. Charge delocalization and bond alternation lead to the presence of particularly short Se–Se and S–S bonds in the homopolyatomic sulfur and selenium halogen cations (Table II) except for $Se_2I_4^{2+}$. Thus these cations can be regarded as containing examples of thermodynamically stable 3pπ–3pπ bonds and 4pπ–4pπ bonds. $S_2I_4^{2+}$ is particularly remarkable in that it maximizes π bonding and contains 3σ and 3*n*pπ–*n*pπ bonds (*n* ≥ 3) (Figure 5). The bond order of the S_2 unit corresponds to 2.33, the highest observed for any isolated non second row element containing compound. It is thermodynamically stable with respect to an all σ bonded isomer and also with respect to addition of $I_2(s)$ (eq 24).[24] $Se_2I_4^{2+}$ is also thermodynamically stable with respect to an all σ bonded isomer. It consists of two SeI_2^+ units, joined by a weak π*–π* interaction (Figures 6–8), and the dimer contains one 4pπ–5pπ bond delocalized over the four Se–I bonds. A similar situation is found for many homopolyatomic chalcogen and halogen cations (e.g., X_4^{2+}, X = S, Se, Te; Hal_2^+, Hal = Br, I, I_4^{2+})[7] which also contain thermodynamically stable *n*pπ–*n*pπ (*n* ≥ 3) bonds. This is in contrast with the neutral group 14 and 15 compounds containing *n*pπ–*n*pπ (*n* ≥ 3) bonds which are kinetically, but not thermodynamically, stable.[12] This is in part because there is charge localization on adjacent positively charged atoms in the alternative σ-bonded isomer $[I_2X^+X^+I_2]$ (X = S, Se). The S^+–S^+ σ bond dissociation energy will be significantly less than that in a normal sulfur–sulfur bond, and in addition, there will be an energy loss accompanying charge localization. Thus the energetics of the σ versus π bonds in the cations are very different from those in neutral molecules.[62]

$$S_2I_4(AsF_6)_2(s) + I_2(s) \rightarrow 2SI_3AsF_6(s) \qquad (24)$$

Presence of π*–π* Bonds in $S_2I_4^{2+}$ and $Se_2I_4^{2+}$ and Its Implications for Bonding in Related Species. The dimers in $S_2I_4^{2+}$ are joined by two weak naturally perpendicular sets of π*–π* bonds (Figure 5). This situation is similar to that found in I_4^{2+} and in $(NO)_2$ dimers in the solid state, and in a variety of other sulfur-containing dimers.[7,63] Similarly, the two SeI_2^+ units are joined via a six-center two-electron π*–π* bond (Figure 8), similar to the bonding in $S_2O_4^{2-}$.[42]

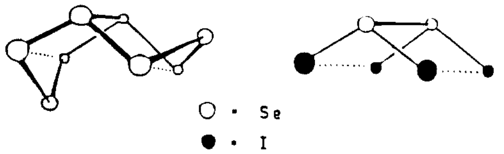

Figure 14. The structure of Se_8^{2+} compared with that of $Se_2I_4^{2+}$.

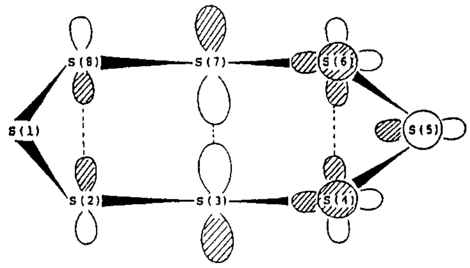

Figure 15. The HOMO-1 of S_8^{2+}.

The long Se–Se bonds in $Se_2I_4^{2+}$ (2.841 Å) and Se_8^{2+} (2.83 Å)[7] are similar in length. In addition, both $Se_2I_4^{2+}$ and, in Se_8^{2+}, the two tricoordinate formally positively charged selenium atoms and the four selenium atoms to which they are joined have the same eclipsed geometries (Figure 14). Thus the six selenium atoms in Se_8^{2+} are also joined by a six-center two-electron π*–π* bond. The geometry of S_8^{2+} is also similar, and the HOMO-1 has been shown[64] to have π*–π* characteristics (Figure 15). Therefore, the presence of π*–π* bonds of both the four-center two-electron type and the six-center two-electron type are likely to be found in a variety of compounds of the electron-rich elements (e.g., in S_4N_4, which may be viewed as containing a six-center two-electron bond about each of the two S–S interactions). Where they have been measured, the strengths of the π*–π* bonds are weak (less than 40 kJ mol^{-1}).[7] In contrast, a high bond energy is associated with π bonding within the monomer. Thus the π*–π* bond formation follows that of the π-bonded fragments.

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