Preparation of Salts of some Iodoselenium(IV) Cations

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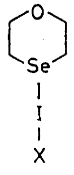
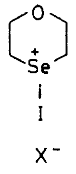
Bis(perfluoroethyl) diselenide reacts quantitatively with $[I_2][Sb_2F_{11}]$ and $[I_3][AsF_6]$ to give corresponding salts of the $[Se(C_2F_5)I_2]^+$ cation. Bis(perfluoroethyl) monoselenide reacts with $[I_2][Sb_2F_{11}]$, in the presence of excess of SbF_5, probably yielding $[Se(C_2F_5)_2I][Sb_2F_{11}]$. The reaction of AsF_5 with elemental iodine and selenium in a 3 : 1 atomic ratio yields $[SeI_3][AsF_6]$. Preliminary single-crystal *X*-ray diffraction results show $[SeI_3][AsF_6]$ to be monoclinic, space group $P2_1/c$, $a = 8.24(2)$, $b = 10.24(2)$, $c = 12.35(2)$ Å, $\beta = 99.3(3)°$, $U = 1\,028.4$ Å^3, and $Z = 4$.

VERY few compounds containing Se–I bonds are known. No neutral binary selenium iodides have been isolated, although pyridinium hexaiodoselenate(IV) has been reported.[1] Compounds with the general formula MR_2X_2 ($M = S$, Se, or Te; $X =$ halogen, $R =$ organo-substituent) have been the focus of a great deal of research effort.[2] Diorganotellurium di-iodides are iodotellurium(IV) compounds; for example the dimethyl compound exists in two forms,[3,4] $TeMe_2I_2$ and $[TeMe_3][TeMeI_4]$. The sulphur and selenium compounds are molecular adducts, $MR_2 \cdots I–I$, with M–I bonds appreciably longer than the sum of the covalent radii, while the I–I bonds are longer than in the free iodine molecule.[5] *X*-Ray crystallographic studies of the adducts (I; $X = I$ or Cl) show the ICl adduct[6] to have a greater contribution from the ionic formulation (II) than the I_2 adduct which is more covalent.[7] The compounds (III) are completely ionic.[2] The tendency towards increasing ionic character, with a full single M–I bond, $MR_2{}^+–I\ X^-$, thus follows the order of decreasing basicity of the anion, $I^- > Cl^- > [BF_4]^-$. In the present work, we have prepared some iodoselenium cations as salts of the very weakly basic anions $[AsF_6]^-$ and $[Sb_2F_{11}]^-$.



(I)



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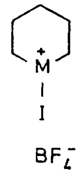

(III)

We have found[8] that bis(perfluoroethyl) diselenide,

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$[Se(C_2F_5)]_2$, is oxidized by SbF_5 to give salts of the cations $[\{Se(C_2F_5)\}_3]^+$ and $[\{Se(C_2F_5)\}_{4n}]^{2+}$. We initially became interested in reacting the diselenide with iodine cations as a potential alternative route to these species, *e.g.* as in (1).

$$3[Se(C_2F_5)]_2 + 2[I_2][Sb_2F_{11}] \longrightarrow 2[\{Se(C_2F_5)\}_3][Sb_2F_{11}] + 2I_2 \quad (1)$$

Instead, reaction proceeded smoothly in AsF_3 solution to give $[Se(C_2F_5)I_2][Sb_2F_{11}]$. This result led to a search for other iodoselenium(IV) cations.

RESULTS AND DISCUSSION

The $[Se(C_2F_5)I_2]^+$ *Cation.*—Bis(perfluoroethyl) diselenide reacted quantitatively with $[I_2][Sb_2F_{11}]$ in AsF_3 solution, according to equation (2). No elemental iodine

$$[Se(C_2F_5)]_2 + 2[I_2][Sb_2F_{11}] \longrightarrow 2[Se(C_2F_5)I_2][Sb_2F_{11}] \quad (2)$$

was formed, indicating that the reaction proceeds very cleanly. The product is an orange solid, stable for several months under normal lighting conditions, at room temperature, in the absence of moisture. Decomposition occurs rapidly on contact with moist air; this is the case with all the other new salts described here. The chemical analysis (Table) is in excellent agreement with the formulation. A ^{19}F n.m.r. spectrum of the salt in AsF_3 solution had three peaks in the ratio *ca.* 2 : 3 : 10, attributable to CF_2 (81.2), CF_3 (75.6), and $[Sb_2F_{11}]^-$ (very broad, 109 p.p.m.; CCl_3F external reference) in addition to the solvent peak at 48 p.p.m. A high-resolution spectrum could not be obtained at room temperature. The i.r. spectrum showed peaks typical[9,10] of C_2F_5 on Se, and $[Sb_2F_{11}]^-$. As spectra were obtained only above 400 cm^{-1}, no Se–I stretches were observed; these would be expected to appear in the 200—250 cm^{-1} region. Attempts to obtain Raman spectra were unsuccessful, both with solid and AsF_3 solution samples.

Elemental analyses (%)[a]

Compound	C	F	Se	I	As	Sb	H
$[I_3][AsF_6]$		20.1 (20.0)		66.7 (66.85)	13.0 (13.15)		
$[Se(C_2F_5)I_2][Sb_2F_{11}]$	2.75 (2.65)	33.25 (33.6)	8.50 (8.75)	27.8 (28.05)		27.35 (26.95)	
$[Se(C_2F_5)I_2][AsF_6]$	3.60 (3.75)	32.45 (32.6)	12.5 (12.3)	39.7 (39.6)	11.6 (11.7)		
$[SeMeI_2]_2[AsF_6]$	3.20 (2.25)	24.5 (21.25)	20.1 (14.7)	*b* *b*	18.9 (13.95)		0.90 (0.55)
$[SeI_3][AsF_6]$ (A)		17.45 (17.6)	12.3 (12.15)	58.4 (58.7)	11.25 (11.55)		
$[SeI_3][AsF_6]$ (B)		17.7 (17.6)	11.9 (12.15)	58.5 (58.7)	11.85 (11.55)		

[a] Calculated values are given in parentheses. [b] Not determined.

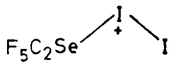
The $[AsF_6]^-$ salt of the $[Se(C_2F_5)I_2]^+$ cation was prepared by the reaction of the diselenide with $[I_3][AsF_6]$ in AsF_3. Although the $[I_3]^+$ cation has been identified in a number of systems,[11] the $[AsF_6]^-$ salt does not seem to have been isolated before. Iodine cations were observed by Kemmitt *et al.*[12] in the I_2–IF_5–AsF_5 system, and were presumably present as $[AsF_6]^-$ salts, but pure solid material was not isolated. In the present work, reaction of iodine with AsF_5 in AsF_3, according to equation (3), produced an intense brown solution, which yielded a brown-black solid on removal of solvent. The weight, elemental analysis (Table), and appearance of the solid are all consistent with the formulation $[I_3][AsF_6]$. The solid decomposes slowly on storage under anhydrous conditions. Bis(perfluoroethyl) diselenide reacted smoothly with $[I_3][AsF_6]$ in AsF_3, liberating iodine and forming orange $[Se(C_2F_5)I_2][AsF_6]$ according to equation (4). The elemental analysis (Table) and i.r. spectrum of

$$3I_2 + 3AsF_5 \longrightarrow 2[I_3][AsF_6] + AsF_3 \quad (3)$$

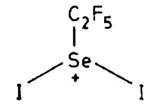
$$[Se(C_2F_5)]_2 + 2[I_3][AsF_6] \longrightarrow I_2 + 2[Se(C_2F_5)I_2][AsF_6] \quad (4)$$

this salt are consistent with the given formulation. It is rather less stable than the $[Sb_2F_{11}]^-$ salt.

There are two possible structures for the $[Se(C_2F_5)I_2]^+$ cation, (A) and (B). We are unable to distinguish between them. The favoured structure should depend on the relative electronegativities of the $Se(C_2F_5)$ group and the iodine atom, the more electropositive group occupying the central position. The electronegativity of $Se(C_2F_5)$ is not known, but is likely to be similar to that of iodine. By comparison with the general halogen chemistry of selenium, and particularly in view of the existence of the $[SeI_3]^+$ and, probably, $[Se(C_2F_5)_2I]^+$ cations (see below), structure (B) is preferred. It is possible that (A) is formed in the initial reaction between $[I_2]^+$ and the diselenide, and that it subsequently rearranges to (B).



(A)



(B)

The $[Se(C_2F_5)_2I]^+$ *Cation.*—The reactions of bis(perfluoroethyl) monoselenide, $Se(C_2F_5)_2$, with $[I_3][AsF_6]$ and $[I_2][Sb_2F_{11}]$ were also investigated, with the intention of preparing salts of the $[Se(C_2F_5)_2I]^+$ cation. No reaction occurred with $[I_3][AsF_6]$. However, $Se(C_2F_5)$ did react with $[I_2][Sb_2F_{11}]$, giving a dark yellow-brown solution, probably by reaction (5). The $[I_3]^+$ salt could not be

$$Se(C_2F_5)_2 + 2[I_2]^+ \longrightarrow [Se(C_2F_5)_2I]^+ + [I_3]^+ \quad (5)$$

removed, but when excess of SbF_5 was present this can oxidize the $[I_3]^+$ back to $[I_2]^+$, which can then react

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further with $Se(C_2F_5)_2$. This reaction was carried out and gave an orange solution. The salt was not isolated, as it decomposed on pumping and rapidly on warming, liberating $Se(C_2F_5)_2$. This shows that the $Se(C_2F_5)_2$ unit remains intact throughout the reaction sequence. The fact that the reaction only proceeded to completion in the presence of excess of SbF_5 confirms that $Se(C_2F_5)_2$ is oxidized by $[I_2]^+$, and does not simply form a weak adduct.

A Raman spectrum was obtained from an AsF_3 solution of the $[Se(C_2F_5)_2I]^+$ salt, prepared *in situ*, but it was of poor quality. However, a strong peak appeared at 211 cm^{-1} which we assign to $\nu(Se\text{–}I)$. The greater difficulty of preparation of $[Se(C_2F_5)_2I]^+$ compared with $[Se(C_2F_5)I_2]^+$ is consistent with the greater resistance to oxidation of $Se(C_2F_5)_2$ relative to $[Se(C_2F_5)]_2$. For example, $[Se(C_2F_5)]_2$ is easily chlorinated to $Se(C_2F_5)Cl$ and $Se(C_2F_5)Cl_3$, whereas $Se(C_2F_5)_2$ only reacts with chlorine under very vigorous conditions with cleavage of the C–Se bonds.[9]

The $[SeMeI_2]^+$ *Cation*.—An attempt was made to prepare $[SeMeI_2]^+$ by reaction (6) in AsF_3. The orange

$$(SeMe)_2 + 2[I_3][AsF_6] \longrightarrow 2[SeMeI_2][AsF_6] + I_2 \quad (6)$$

solid product was unstable, and did not give a satisfactory analysis. The ^1H n.m.r. spectrum in AsF_3 showed a sharp singlet at δ 3.67 p.p.m., together with a broad resonance centred at δ *ca.* 4.7 p.p.m. The singlet may be due to $[SeMeI_2]^+$, but the reaction is evidently not clean.

The $[SeI_3]^+$ *Cation*.—The stability of salts of the $[Se(C_2F_5)I_2]^+$ cation suggested that the simple binary iodoselenium species, $[SeI_3]^+$, could be made. Several different routes to this cation have been investigated. Attempts to prepare $[SeI_3]^+$ salts according to equations (7) and (8) in AsF_3 solution were inconclusive. How-

$$2Se + I_2 + 2[I_2][Sb_2F_{11}] \longrightarrow 2[SeI_3][Sb_2F_{11}] \quad (7)$$

$$Se + [I_3][AsF_6] \longrightarrow [SeI_3][AsF_6] \quad (8)$$

ever, the reaction of AsF_5 with selenium and iodine, in AsF_3, proceeded quantitatively according to equation (9)

$$2Se + 3I_2 + 3AsF_5 \longrightarrow 2[SeI_3][AsF_6] + AsF_3 \quad (9)$$

yielding crystalline material after filtration and removal of solvent. The elemental analysis of the recrystallized solid product (Table) is in excellent agreement with the given formulation.

We made a preliminary single-crystal *X*-ray diffraction study of $[SeI_3][AsF_6]$. Precession photographs (Mo-K_α radiation, $hk0$—1, $h0$—$1l$) show the unit cell to be monoclinic, space group $P2_1/c$, with dimensions $a = 8.24(2)$, $b = 10.24(2)$, $c = 12.35(2)$Å, $\beta = 99.3(3)°$, $U = 1\,028.4$ Å^3. Assuming $Z = 4$, this gives a volume per formula unit of 257.1 Å^3. This compares very well with the sum of the crystallographic volumes of arsenic tri-iodide,[13] which is isoelectronic with $[SeI_3]^+$ (161 Å^3) and $[AsF_6]^-$ (*ca.* 100 Å^3).[14] The salt is stable in the dark in the absence of moisture for several weeks, but appears to be rather unstable towards light and *X*-rays. The i.r. spectrum confirms the presence [10] of $[AsF_6]^-$, but we have been unable, so far, to obtain spectra in the Se–I stretching region. We could not obtain reproducible Raman spectra.

Conclusion.—We have established that cations containing Se–I bonds can be prepared as stable salts of very weakly basic anions. The existence of stable cationic derivatives of unstable neutral molecules has been observed in a number of systems. For example, $[SCl_3]$-$[AsF_6]$ is considerably more stable [15] than SCl_4. There are a number of unknown iodides, particularly of elements in high formal oxidation states, cationic derivatives of which could possibly be prepared by analogous routes to those described here.

EXPERIMENTAL

Materials.—Reactions were carried out in vigorously dried Pyrex vessels fitted with Whitey valves (1KS4). Volatile materials were transferred on a Monel high-vacuum line. Moisture-sensitive solids were transferred in a Vacuum Atmospheres Dri-Lab fitted with a Dri-train (HE493). I.r. spectra were recorded with a Perkin-Elmer 457 grating spectrometer using AgCl plates. Raman spectra were obtained using a Spex Ramalab spectrometer and a Spectra Physics model 164 2 W krypton–argon ion laser. Hydrogen-1 n.m.r. spectra were recorded on a Varian T-60 spectrometer, and ^{19}F n.m.r. spectra on a Varian HA60 spectrometer operating at 56.4 MHz. Elemental analyses were by Alfred Bernhardt, West Germany.

Antimony pentafluoride (Ozark Mahoning) was distilled *in vacuo* two to four times before use. Arsenic trifluoride (Ozark Mahoning) was distilled *in vacuo* over NaF, and stored over NaF. Arsenic pentafluoride was prepared by the reaction of fluorine (Matheson) with the trifluoride in a steel bomb. Bis(perfluoroethyl) mono-[9] and diselenides [16] were prepared by literature methods. Dimethyl diselenide (Ventron, Alfa Products) was distilled *in vacuo* once before use, and its purity checked by its ^1H n.m.r. spectrum. Selenium (B.D.H.) and iodine (Shawinigan) were used without further purification.

Preparations.—The preparation of $[I_2][Sb_2F_{11}]$ has been described elsewhere.[8]

Tri-iodine hexafluoroarsenate(V). Typically, I_2 (1.40 g, 5.5 mmol) reacted with AsF_5 (1.15 g, 6.8 mmol) in AsF_3 (2.34 g, 17.8 mmol), giving an intense brown solution. After 30 min, arsenic fluorides were pumped away leaving a brown-black solid (2.11 g), analysing as $[I_3][AsF_6]$. The expected yield of $[I_3][AsF_6]$, based on iodine, is 2.09 g. In a larger scale reaction, iodine (6.76 g) and AsF_5 (5.60 g; added in several aliquot portions, with thermal cycling from −196 °C to ambient temperature between additions) yielded 10.68 g of solid, rather more than the predicted yield of 10.11 g. This may have been due to incomplete removal of AsF_3, or to some further oxidation by the excess of AsF_5.

Reactions.—*Bis(perfluoroethyl) diselenide with* $[I_2][Sb_2F_{11}]$. In a typical reaction, $[I_2][Sb_2F_{11}]$ (3.98 g, 5.63 mmol) was allowed to react with excess of $[Se(C_2F_5)]_2$ (2.08 g, 5.25 mmol) in the presence of AsF_3 (6.20 g, 47.0 mmol). On shaking, the reaction proceeded rapidly to give an orange solution, topped by a layer of unchanged diselenide. This

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[14] W. H. Zachariason, *Acta Cryst.*, 1949, **2**, 388.

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[16] C. D. Desjardins and J. Passmore, *J.C.S. Dalton*, 1973, 2314.

was distilled out, together with most of the AsF_3, giving an orange syrup, which solidified on standing overnight at room temperature. Pumping to constant weight yielded 5.13 g of dry orange solid, corresponding to uptake of 1.15 g of the diselenide. This compares favourably with a predicted figure of 1.115 g, based on $[I_2][Sb_2F_{11}]$ according to equation (2).

Bis(perfluoroethyl) diselenide with $[I_3][AsF_6]$. Excess of $[Se(C_2F_5)]_2$ (0.88 g, 2.2 mmol) was shaken with $[I_3][AsF_6]$ (0.56 g, 0.98 mmol) in AsF_3 (2.10 g, 15.9 mmol). The solution, initially intense brown, turned orange and elemental iodine appeared. Removal of volatiles yielded 0.62 g of orange solid, analysing as $[Se(C_2F_5)I_2][AsF_6]$ (Table). The iodine was separated from the diselenide and AsF_3 by trap-to-trap distillation, and weighed 0.15 g. The predicted yields, based on $[I_3][AsF_6]$, according to equation (4), are 0.63 g of $[Se(C_2F_5)I_2][AsF_6]$ and 0.125 g of iodine. The salt decomposes slowly on prolonged pumping.

Dimethyl diselenide with $[I_3][AsF_6]$. A solution of $[I_3]$-$[AsF_6]$ was prepared *in situ* by reaction of iodine (0.79 g, 3.1 mmol) with AsF_5 (0.64 g, 3.8 mmol) in AsF_3 (3.0 g, 22.7 mmol). Excess of AsF_5 was removed and $(SeMe)_2$ (0.2 g, 1.5 mmol) was added. On shaking, the solution turned orange and iodine was liberated. Removal of volatiles by pumping yielded 1.12 g of an unstable flaky orange solid.

Bis(perfluoroethyl) monoselenide with $[I_2][Sb_2F_{11}]$. Bis(perfluoroethyl) monoselenide (0.364 g, 1.15 mmol) reacted with $[I_2][Sb_2F_{11}]$ (0.832 g, 1.18 mmol) in AsF_3 (1.154 g, 8.74 mmol) to give a yellow-brown solution, topped by a colourless layer of excess of the monoselenide. In another reaction, iodine (0.386 g, 1.52 mmol) was reacted with excess of SbF_5 (2.03 g, 9.35 mmol) in AsF_3 (4.1 g, 31.0 mmol), to give a solution containing $[I_2]^+$ cation and excess of SbF_5. Excess of $Se(C_2F_5)_2$ (1.39 g, 4.4 mmol) was added, and reaction proceeded on shaking to give an orange solution. More SbF_5 (0.74 g, 3.4 mmol) was added, without change in the appearance of the mixture.

Preparation of Tri-iodoselenium(IV) *Hexafluoroarsenate*(V).—Selenium (0.157 g) and iodine (0.754 g) reacted with excess of AsF_5 (0.89 g, 5.2 mmol) in AsF_3 (4.15 g, 31.4 mmol) to give a deep maroon solution; the appearance of the solution did not change on standing for 2 d. Removal of volatiles left an intense red-black solid (1.30 g). The predicted yield of $[SeI_3][AsF_6]$ is 1.29 g. Recrystallization from AsF_3 solution yielded a highly crystalline product, which analysed as $[SeI_3][AsF_6]$. In a second reaction, selenium (0.55 g), iodine (2.77 g, slight excess), and AsF_5 (2.05 g, 10% excess) yielded 4.64 g of solid (predicted, based on Se, 4.52 g). As a slight excess of iodine was used, the product may have contained a little $[I_3][AsF_6]$.

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