Halogen-facilitated Preparation of $S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leqslant 1$) and $S_4(Sb_2F_{11})_2$, and a Convenient Synthesis of $Se_4(AsF_6)_2$ and $Se_4(Sb_2F_{11})_2$†

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Sulfur reacted with an excess of AsF_5 at room temperature in the presence of a trace amount of halogen (X_2 = Cl_2, Br_2 or I_2) or $AsCl_4AsF_6$ in SO_2 to give $S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leqslant 1$) quantitatively in a few minutes. A similar, but slower, reaction with SbF_5 in SO_2 or AsF_3 at room temperature gave quantitative yields of $S_4(Sb_2F_{11})_2$. The vibrational spectra of these salts with tentative assignments are reported. The corresponding preparations of $Se_4(AsF_6)_2$ and $Se_4(Sb_2F_{11})_2$ are also greatly facilitated by the presence of traces of halogen. Reactions of sulfur (or selenium) with SbF_5 with and without traces of X_2 in SO_2 designed to give $M_4(SbF_6)_2$ (M = S or Se) gave products that contained $M_4{}^{2+}$, an unidentified Sb^V fluoroanion and some Sb^{III}-containing species. A comparative study was made on the effect of solvent, oxidising agent and facilitating reagent on the course of reaction. Possible reaction pathways for oxidation of sulfur (or selenium) by AsF_5 (or SbF_5) with and without the addition of traces of X_2 or $AsCl_4AsF_6$ have been proposed.

Sulfur is oxidised quantitatively [1,2a,b] by arsenic pentafluoride to $S_8(AsF_6)_2$ according to equation (1). Further oxidation does

$$S_8 + 3AsF_5 \xrightarrow[\text{or } AsF_3]{HF, SO_2} S_8(AsF_6)_2 + AsF_3 \qquad (1)$$

not occur even with a large excess [1,2a,b] of AsF_5. However, in a preliminary communication we reported [3] that in the presence of a trace of bromine or iodine further oxidation occurs within minutes yielding crystalline $S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leqslant 1$) according to equation (2) (r.t. = room temperature).

$$\tfrac{1}{2}S_8 + 3AsF_5 \xrightarrow[\text{traces of } X_2 \text{ (X = Br or I)}]{SO_2,\text{ r.t.}} S_4(AsF_6)_2{\cdot}xSO_2 + AsF_3 \qquad (2)$$

Selenium is oxidised to $Se_4(AsF_6)_2$ by heating the reactants for several days.[2c] However, we discovered [3] that with a trace of halogen the reaction proceeded quantitatively in minutes. In this paper we give a full report of the oxidation of sulfur and selenium by AsF_5 and SbF_5 in a number of solvents with traces of halogen (X_2 = Cl_2, Br_2 or I_2) or $AsCl_4AsF_6$ to give $M_4(AsF_6)_2$ or $M_4(Sb_2F_{11})_2$ (M = S or Se) in quantitative yields. We propose possible reaction pathways for the oxidation process with and without traces of facilitating agent. The preparation, structure bonding and energetics of formation of the homopolyatomic cations of Group 16 have been the subject of a recent review.[4]

Experimental

All 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) which was attached to a Monel vacuum line. Sulfur dioxide (Canadian Liquid Air) and SO_2ClF (Aldrich) were distilled onto and stored over CaH_2. Chlorine (Canadian Liquid Air) and bromine (Fisher Scientific) were kept over P_4O_{10} in a flask equipped with a Rotoflo valve. Iodine (BDH) was taken in slight excess in a reaction vessel and evacuated under dynamic vacuum until the desired weight was obtained. Sulfur (Fisher Scientific), selenium (BDH, 99.9%) and AsF_5 (Ozark-Mahoning) were used without further purification. Antimony pentafluoride (Ozark-Mahoning) was purified by double or triple distillation in an all-glass apparatus and stored in a Pyrex glass vessel fitted with a Rotoflo valve.

The IR spectra were recorded on Perkin-Elmer model 457 and 683 spectrometers. Spectra of solids were obtained as finely ground powders between AgCl and KBr plates and frequencies corrected using a polyethylene film. Raman spectra were recorded using a Ramalab spectrometer and a Spectra Physics 164 2 W argon-ion laser (5145 Å) with samples either in sealed glass melting-point tubes or *in situ* in the reaction vessels at r.t. using a slit width of 4 cm^{-1}. The ^{19}F and ^{77}Se NMR spectra were recorded as in ref. 5, with high-frequency direction positive. Other techniques and general procedures have been described.[5,6]

Preparations of $S_4{}^{2+}$ *Compounds.—Reaction of sulfur with* AsF_5 *in the presence of traces of halogen* (X_2 = Cl_2, Br_2 *or* I_2) *or* $AsCl_4AsF_6$. (*i*) Arsenic pentafluoride (2.45 g, 14.41 mmol) was condensed onto a mixture of sulfur (0.51 g, 16.08 mmol) and liquid SO_2 (6.38 g). A dark blue solution was obtained on warming the contents to r.t. A trace quantity of Cl_2 (0.1 mmol) was condensed onto the solution, and a colourless crystalline precipitate under a light blue solution formed in less than 10 min after the solution had warmed to r.t. The solution was filtered and the precipitate washed twice with solvent (1–2 cm^3). The volatile materials [SO_2, AsF_3, SiF_4 (trace) (IR spectroscopy)] were removed under a dynamic vacuum leaving a white solid (2.10 g, see Table 1). The vibrational frequencies are listed in Table 2. The crystals collapsed to a powder when subjected to a dynamic vacuum for less than 10 min {Found [Calc. for $S_4(AsF_6)_2{\cdot}0.6SO_2$]: As, 28.35 (27.50); F, 41.50 (41.90); S, 27.20 (27.10%)} The X-ray crystal structure was reported in a preliminary communication.[3]

The results from similar experiments [(b)–(f)] with different halogens (X_2; X = Cl, Br or I) and containing varying amounts of X_2 are included in Table 1.

(*ii*) A similar experiment but using trace amounts of $AsCl_4AsF_6$ [12] as a catalyst (instead of X_2) gave white crystals of $S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leqslant 1$) in quantitative yield in 2 d.

Reaction of sulfur with an excess of SbF_5 *in the presence of traces of* X_2. Arsenic trifluoride (12.19 g), SbF_5 (6.92 g, 31.89

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

Table 1 Preparation of $S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leqslant 1$) and the attempted bromine-facilitated preparation of $S_4(SbF_6)_2$

Reaction		S		AsF_5		SO_2	X_2	Weight (g) of $S_4(AsF_6)_2{\cdot}xSO_2$		
		g	mmol	g	mmol	(g)	(mmol)	observed	calc. ($x = 1$)	calc. ($x = 0$)
$S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leqslant 1$)	(a)	0.51	16.08	2.45	14.41	6.38	Cl_2 (0.10)	2.10	2.27	2.01
	(b)	0.34	10.74	4.53	26.65	2.10	Br_2 (0.03)	1.54	1.53	1.36
	(c)	0.52	16.24	2.85	16.76	3.80	I_2 (0.04)	1.96	2.34	2.06
	(d)	0.27	8.37	2.45	14.41	1.46	Cl_2 (0.44)	1.32	1.20	1.06
	(e)	0.49	15.28	3.32	19.53	2.49	Br_2 (<0.01)	1.93	2.18	1.93
	(f)	0.72	22.64	2.05	12.06	4.91	I_2 (0.01)	2.25[a]		
		S		SbF_5		SO_2 or AsF_3* (g)	Br_2 (mmol)	$S_4(Sb_yF_z)$ (g)		Soluble product (g)
		g	mmol	g	mmol					
$S_4(SbF_6)_2$	(g)	0.71	22.00	5.54	25.53	9.41	0.03	3.65		2.87[b]
	(h)	0.50	15.52	3.43	15.81	4.26*	0.02	3.96 (total)		
	(i)	0.46	14.48	3.18	14.65	5.78*	0.05	2.43		1.29[c]
	(j)	0.50	15.76	2.84	13.09	3.60	0.08	3.36 (total)		

[a] The product was a mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$. [b] The solution was transparent red-brown. The beige $S_4(Sb_2F_{11})_2$ was identified by IR and Raman spectroscopy (Table 2). [c] The solution was dark blue. The IR spectrum indicated the presence of $Sb_2F_{11}^-$.

Table 2 Vibrational spectra (cm^{-1}) with tentative assignments of $S_4(AsF_6)_2{\cdot}xSO_2$ where $x \leqslant 1$[a]

IR[b]	Raman	Tentative assignment[c]
1330w		
1305w		$\nu_3(SO_2)$
1270vw		AsF_6^-
1148w	1146 (0.5)	$\nu_1(SO_2)$
1020w		
810vw		
	728 (0.5)	
	707 (0.5)	AsF_6^-
699vs		$\nu_3(AsF_6^-)$
	673 (2.0)	$\nu_1(AsF_6^-)$
668 (sh)		
	605 (5.5)	$\nu_3(S_4^{2+})$
	585 (10.0)	$\nu_1(S_4^{2+})$
575m	572(sh)	
552ms		$\nu_2(AsF_6^-)$
	545 (2.0)	$\nu_5(S_4^{2+})$
539m (sh)		
522vw	520 (0.5)	$\nu_2(SO_2)$
	396 (0.5)	$\nu_2(S_4^{2+})$
390s		$\nu_4(AsF_6^-)$
	368 (1.5)	$\nu_5(AsF_6^-)$

[a] Wavenumbers accurate to *ca.* ±3 cm^{-1}. All data reported for spectra recorded at room temperature. [b] Key: s = strong, m = medium, w = weak, v = very, sh = shoulder and br = broad. Intensities in parentheses. [c] Assigned by comparison with the vibrational spectrum of solid SO_2,[7,8] the AsF_6^- anion in $Cs[AsF_6]$[9] and IF_6AsF_6,[10] and the S_4^{2+} cation in $S_4(SO_3F)_2$ and $S_4(S_2O_6F)_2$.[11] The AsF_6^- sites in the crystal structure of $S_4(AsF_6)_2{\cdot}xSO_2$ are C_1,[3] *i.e.* no symmetry, therefore considerable splitting is expected.

mmol) and Br_2 (0.11 mmol) were successively condensed onto sulfur (0.54 g, 17.04 mmol), giving a precipitate under a dark blue solution within 24 h. The solution changed from dark blue to transparent pink-red on standing at r.t. for 2 weeks. The solution was filtered through the frit and the insoluble solid was washed three times with solvent (*ca.* 2 cm^3). The volatile materials were removed leaving 4.41 g of a beige-white soluble solid [calc. weight of $S_4(Sb_2F_{11})_2$: 4.40 g, based on sulfur] and 2.24 g of a white insoluble solid [calc. weight of $SbF_3{\cdot}SbF_5$ (Raman spectroscopy[13]) 1.68 g]. {Found [Calc. for $S_4(Sb_2F_{11})_2$]: F, 39.90 (40.45); S, 11.70 (12.40); Sb, 48.45 (47.20%)}. The Raman and IR vibrational frequencies with tentative assignments are given in Table 3. The ^{19}F NMR chemical shifts of the solid in SO_2 at −70 °C relative to CCl_3F are δ −90.0(1), −108.9(8) and −130.9(2) (relative intensities in parentheses) and indicate the presence of $Sb_2F_{11}^-$.[16] A similar reaction carried out in liquid SO_2 was complete after 1 week.

Attempted preparation of $S_4(SbF_6)_2$. (*i*) In the presence of traces of X_2. The Br_2-facilitated preparation of $S_4(SbF_6)_2$ was attempted by allowing sulfur and SbF_5 to react at mole ratios in the range 1:1.2 to 1:0.8 according to equations (3) and (4)

$$\tfrac{1}{2}S_8 + 4SbF_5 \xrightarrow[SO_2\ \text{or}\ AsF_3,\ \text{r.t.}]{\text{traces of } Br_2} S_4(SbF_6)_2 + SbF_3SbF_5 \quad (3)$$

$$\tfrac{3}{2}S_8 + 10SbF_5 \xrightarrow[SO_2\ \text{or}\ AsF_3,\ \text{r.t.}]{\text{traces of } Br_2} 3S_4(SbF_6)_2 + (SbF_3)_3SbF_5 \quad (4)$$

[Table 1, (g)–(j)]. All reactions gave a white precipitate under a dark blue solution which remained unchanged after 1 week, except for reaction (g) Table 1 (mole ratio S:SbF_5 = 1:1.2) which changed to a transparent red-brown solution over a white precipitate. The solutions for all reactions were filtered, the insoluble solids were washed until white, and the volatiles removed. The Raman and IR spectra of the white insoluble solids were essentially identical for all reactions [Table 1, (g)–(j)]. Raman: 658 (4.0), 652 (4.5), 635 (0.5), 605 (8.0), 594 (sh), 581 (sh), 578 (6.0), 549 (0.5), 516 (10.0), 376 (0.5) and 288 (0.5) cm^{-1} (relative intensities in parentheses). IR: 662vs, 628*, 601*, 560*, 543* and 514 cm^{-1} (asterisk indicates feature of a broad shoulder). The soluble beige powder from reaction (g) in Table 1 was identified as $S_4(Sb_2F_{11})_2$ (Raman spectroscopy). The soluble blue solids [reactions (h)–(j) in Table 1] contained $Sb_2F_{11}^-$ (IR spectroscopy).

(*ii*) *In the absence of* X_2. Antimony pentafluoride (10.67 g, 49.18 mmol) was condensed onto sulfur (0.23 g, 7.27 mmol) in a one-bulbed glass vessel. A dark blue solid under the colourless SbF_5 was formed on warming the mixture to r.t. The reactants were heated at 150 °C for 5 d during which time the solid and solution changed from dark to light blue to colourless. The volatiles were removed and the white solid was subjected to a dynamic vacuum for 3 d at 100 °C. The expected weight for $S_4(SbF_6)_2$ was only 1.08 g, *i.e.* 21% of the actual recovered solid (5.08 g). The powdered product contained a few irregular solid pieces of β-$6SbF_3{\cdot}5SbF_5$ (Raman spectroscopy[13]). Raman: 705 (0.5), 678 (4.5), 654 (10.0), 643 (6.0), 632 (5.5), 606 (3.5), 582 (10.0), 539 (0.5), 370 (1.0) and 283 (br) cm^{-1}

Table 3 Vibrational spectra (cm^{-1}) with tentative assignments for $S_4(Sb_2F_{11})_2$[a]

$S_4(Sb_2F_{11})_2$		
IR	Raman	Tentative assignment[b]
697[c]	697w	
	682 (1.0)	Sb–F stretching modes ($Sb_2F_{11}^-$)
666[c]	669 (2)5)	
654[c]		
630[c]	648 (1.0)	
	603 (3.0)	$\nu_3(S_4^{2+})$, Sb–F stretching modes ($Sb_2F_{11}^-$)
583m	580 (10.0)	$\nu_1(S_4^{2+})$, Sb–F stretching modes ($Sb_2F_{11}^-$)
490ms		Sb–F–Sb bridging modes ($Sb_2F_{11}^-$)
	367 (0.5)	$\nu_2(S_4^{2+})$

[a] Refer to footnotes in Table 2. [b] Assigned by comparison with the $Sb_2F_{11}^-$ anion in $NF_4Sb_2F_{11}$[14] and $CsSb_2F_{11}$,[15] and S_4^{2+} in $S_4(SO_3F)_2$ and $S_4(S_2O_6F)_2$.[11] [c] Definite peaks superimposed on a broad strong band.

(relative intensities in parentheses). IR: 661s, 525w (br) and 460w (br) cm^{-1}.

Preparation of Se_4^{2+} *Compounds.—Reaction of selenium with* AsF_5 *in the presence of traces of* X_2. (*i*) Arsenic pentafluoride (2.91 g, 17.12 mmol) was condensed onto a mixture of Se (1.27 g, 16.08 mmol) and SO_2 (5.12 g) followed by traces of Br_2 (0.04 mmol). On warming to r.t. a bright yellow precipitate appeared under an intense yellow-brown solution in about 5 min. The large amount of the yellow solid, which formed within 2 h, was filtered off and washed with SO_2. The volatiles were removed leaving 0.33 g of a more soluble yellow-green solid [mainly $Se_4(AsF_6)_2$ with a trace of green $Se_8(AsF_6)_2$] and 2.50 g of the bright yellow solid identified as $Se_4(AsF_6)_2$ by Raman and IR spectra[9,11] (calc. yield based on Se: 2.79 g).

(*ii*) In another experiment, a large excess of AsF_5 (5.74 g, 33.76 mmol) was added to Se (0.64 g, 8.15 mmol) in liquid AsF_3 (8.74 g) in the presence of a trace quantity of Cl_2 (0.25 mmol), and refluxed at 135 °C for 2 weeks. A quantitative amount of $Se_4(AsF_6)_2$ (Raman and IR spectroscopy[9,11]) was recovered.

(*iii*) Selenium and AsF_5 were allowed to react in a 10 mm NMR tube in mole ratios in the range 21 : 3 to 1 : 3, according to equation (5). The products were identified *in situ* by ^{77}Se NMR

$$x\text{Se} + 3\text{AsF}_5 \xrightarrow[\text{SO}_2,\ \text{r.t.}]{\text{traces of Br}_2} \text{Se}_x(\text{AsF}_6)_2 + \text{AsF}_3 \quad (5)$$

spectroscopy as Se_n^{2+} (n = 4, 8 or 10).[17,18] The reactions proceeded quantitatively, up to the formation of $Se_4(AsF_6)_2$.

Reaction of selenium with SbF_5 *in the presence of* X_2. (*i*) Antimony pentafluoride (3.59 g, 16.53 mmol) and a trace of Br_2 (0.02 mmol) were condensed onto a mixture of Se (0.73 g, 9.18 mmol) and SO_2 (10.68 g) as per equation (6). A yellow-green

$$24\text{Se} + 35\text{SbF}_5 \xrightarrow[\text{SO}_2,\ \text{r.t.}]{\text{traces of Br}_2} 6\text{Se}_4(\text{Sb}_2\text{F}_{11})_2 + 6\text{SbF}_3\cdot5\text{SbF}_5 \quad (6)$$

solution over a white precipitate was obtained after 4 d of stirring at r.t. The solution was transferred and the insoluble white solid was washed with SO_2. The volatiles were removed leaving 2.96 g of a bright yellow solid [calc. yield for $Se_4(Sb_2F_{11})_2$: 2.81 g] and 0.74 g of an insoluble white solid β-$6SbF_3\cdot5SbF_5$ (Raman spectroscopy[13]) (calc. yield for $6SbF_3\cdot5SbF_5$: 0.83 g). The yellow solid was identified as $Se_4(Sb_2F_{11})_2$ [Raman,[11] IR,[15] ^{19}F[16] and ^{77}Se NMR[17,18] spectroscopy; $\delta_{(CH_3)_2Se}$ 1941.2 at r.t. for 0.64 g in 3.07 g SO_2].

(*ii*) In another experiment designed to yield a selenium cation more highly oxidised than Se_4^{2+}, Se (0.53 g, 6.67 mmol) was treated with a large excess of SbF_5 (4.95 g, 22.81 mmol) with traces of Br_2 (0.05 mmol) in AsF_3 (7.59 g) at 63 °C for 2 weeks. The solution was filtered and the precipitate was washed about 15 times with AsF_3 (*ca.* 1–2 cm^3), leaving the white insoluble $SbF_3\cdot SbF_5$ (Raman spectroscopy[13]) (0.66 g) and a quantitative yield of a yellow solid, $Se_4(Sb_2F_{11})_2$ (Raman,[11] IR spectroscopy[15]).

Attempted preparation of $Se_4(SbF_6)_2$. Selenium (0.74 g, 9.41 mmol) and SbF_5 (2.11 g, 9.79 mmol) were allowed to react as per equation (4) (but Se instead of S) in liquid SO_2 (3.61 g) in the presence of Br_2 (0.06 mmol). A yellow precipitate under a yellow-orange solution was observed on stirring at r.t. for about 1 week. The volatiles were removed leaving 2.88 g of a solid product, which was extracted[19] with SO_2, to give a bright yellow soluble product (2–3 g), and a white insoluble solid [≈0.5 g $(SbF_3)_3SbF_5$ (Raman spectroscopy[20]) with a weak peak attributable to Se_4^{2+} (Raman spectroscopy[11])]. The soluble yellow solid was shown to contain Se_4^{2+} and a complex Sb^{V}–Sb^{III} fluoroanion by Raman [672vw, 653m, 647m, 631vw, 600vw, 586vw, 549vw (br), 534vw and 324vvs (Se_4^{2+}) cm^{-1}] and IR spectroscopy [673vs, 667vs, 651 (sh), 630mv, 537m and 491w cm^{-1}].

Reaction of CsCl *with* AsF_5.—Caesium chloride (0.52 g, 3.07 mmol) and AsF_5 (2.22 g, 13.09 mmol) were allowed to react at a 1 : 4.3 mole ratio in liquid SO_2 (4.91 g). A white precipitate under a light yellow solution was observed after several days. The solution was transferred to a second bulb through a frit and the white solid was washed two or three times with solvent (1–2 cm^3). The volatiles were removed giving 0.83 g insoluble, solid $Cs[AsF_6]$[9] and 0.37 g of soluble, beige-white $AsCl_4AsF_6$ (Raman spectroscopy[12]).

Reaction of KBr *with* AsF_5.—Potassium bromide (0.46 g, 3.88 mmol) and AsF_5 (2.58 g, 15.19 mmol) were allowed to react in 1 : 3.9 mole ratio in liquid SO_2 (5.37 g). A vigorous reaction with evolution of a red-brown vapour took place on warming to r.t. A red-brown vapour (Br_2) and a transparent brown solution over a white precipitate were noted after 16 h. The volatiles [SO_2,[7] AsF_5,[21] SO_2BrF (trace),[22] AsF_3,[23] SiF_4[24] (trace) and SO_2F_2 (trace)[22a,25] (IR spectroscopy)] were removed leaving 0.81 g of insoluble white powder $K[AsF_6]$ (IR spectroscopy[9]) and 0.13 g of a soluble unidentified beige tar.

Results and Discussion

Preparation of $S_4(AsF_6)_2\cdot xSO_2$ *and* $S_4(Sb_2F_{11})_2$.—$S_4(AsF_6)_2\cdot xSO_2$ ($x \leqslant 1$). Reaction between sulfur and AsF_5 in SO_2, in the presence of traces of Cl_2, Br, I_2 or $AsCl_4AsF_6$ according to equation (2) gave white crystals of $S_4(AsF_6)_2\cdot xSO_2$ ($x \leqslant 1$) quantitatively. Reactions carried out with different halogens in varying amounts [Table 1, (a)–(e)] all produced this compound in quantitative yield within minutes at r.t. Using AsF_3 as a solvent the reaction took 1 d.[26] The salt was identified by product weights, elemental analyses, vibrational spectroscopy (Table 2) and its X-ray crystal structure.[3]

$S_4(Sb_2F_{11})_2$. Reaction between sulfur and excess of SbF_5 in the presence of traces of Br_2 [equation (7)] yielded $S_4(Sb_2F_{11})_2$ quantitatively in SO_2 within 1 week and 2 weeks in AsF_3. The salt was identified by product weight, elemental analysis, vibrational spectroscopy (Table 3) and ^{19}F NMR spectroscopy in SO_2. Pure $S_4(Sb_2F_{11})_2$ was not obtained (Table 1) in the absence of excess of SbF_5.

$$\tfrac{1}{2}\text{S}_8 + 6\text{SbF}_5 \xrightarrow[\text{traces of X}_2]{\text{SO}_2\text{ or AsF}_3} \text{S}_4(\text{Sb}_2\text{F}_{11})_2 + \text{SbF}_3\cdot\text{SbF}_5 \quad (7)$$

Other characterised S_4^{2+}-containing salts, $S_4(SO_3F)_2$[27] and

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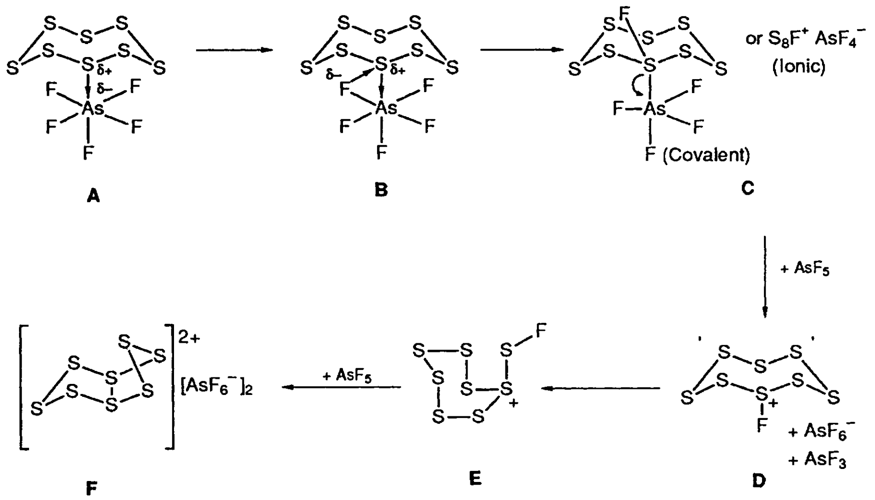
* We have also observed that sulfur is oxidised by AsF_5 in the presence of traces of bromine in HF or AsF_3 to give $S_4(AsF_6)_2\cdot AsF_3$.[26]



Scheme 1 A possible reaction pathway to the formation of $S_8(AsF_6)_2$ from S_8 and AsF_5

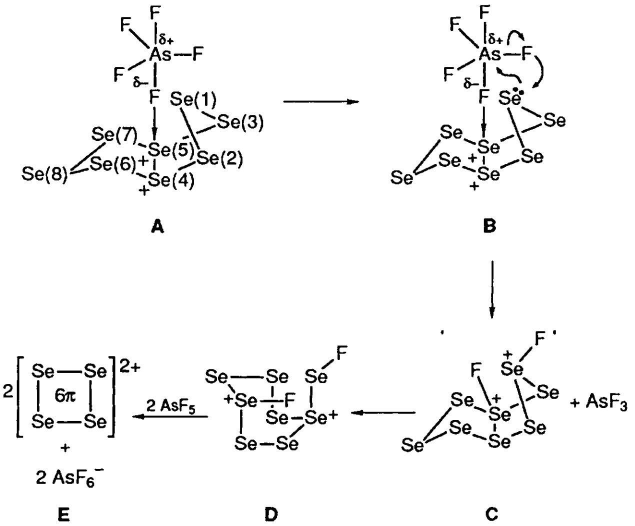
$S_4(S_2O_6F)_2$,[11] have been prepared by the reaction of sulfur with $S_2O_6F_2$ (which is not commercially available) for several days. Thus, $S_4(AsF_6)_2{\cdot}xSO_2$ ($x \leq 1$) and $S_4(Sb_2F_{11})_2$ are the only* conveniently preparable salts of S_4^{2+}. Gillespie and co-workers[27] reported the preparation of $S_4(SbF_6)_2$ by the reaction of SbF_5 and sulfur on refluxing at 140 °C. However, our attempts to prepare $S_4(SbF_6)_2$ with or without halogen led to white solids that contained S_4^{2+}, an unidentified Sb^V fluoroanion, and some Sb^{III}–F-containing species, according to their Raman spectra. These compounds may be related to $(SeS_3)_2(Sb_4F_{17})(SbF_6)_3$,[28] $Te_2Se_2(Sb_3F_{14})(SbF_6)$, $Te_3Se(Sb_3F_{14})(SbF_6)$[29] or $Se_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$.[30] It is possible that $M_4(SbF_6)_2$ (M = S or Se) could be prepared by reaction of $M_4(AsF_6)_2$ with an exact equivalent of SbF_5 in SO_2 solution.

Preparation of $Se_4(AsF_6)_2$ *and* $Se_4(Sb_2F_{11})_2$.—The syntheses of the previously known[2,4] $Se_4(AsF_6)_2$ [by equation (2), but with Se] and $Se_4(Sb_2F_{11})_2$ [equation (7)] are greatly facilitated by the presence of traces of X_2. In the present work the reduced product of the reaction with SbF_5 was identified as β-$6SbF_3{\cdot}5SbF_5$[13] and with a large excess of SbF_5, $SbF_3{\cdot}SbF_5$,[13,31] whereas SbF_3 was reported in the earlier investigation.[2c] Attempts to prepare $Se_4(SbF_6)_2$ led to a yellow, soluble material containing Se_4^{2+}, an unidentified Sb^V fluoroanion and some Sb^{III}-containing species (Raman).

Some Comments on the Choice of Solvents, Oxidising Agents and Facilitating Agents.—Reactions proceed faster in SO_2 than AsF_3 because SO_2 is a weaker base ($SbF_5{\cdot}AsF_3$[32,33] is more stable to dissociation than is $SbF_5{\cdot}SO_2$).[34,35] Similarly, reactions also proceed faster with AsF_5 than SbF_5, because AsF_5 is a weaker Lewis acid. Arsenic pentafluoride is easier to manipulate because it is more volatile. Its reduced product is the simple, volatile AsF_3, and not an insoluble, complex fluoride, *cf.* $SbF_3{\cdot}SbF_5$,[31] $(SbF_3)_3SbF_5$,[20] $(SbF_3)_6(SbF_5)_5$[13] and $(SbF_3)_5(SbF_5)_3$.[36] Also the counter anion is simple AsF_6^-, and not the more complex $Sb_2F_{11}^-$, $Sb_3F_{16}^-$ or $Sb_4F_{17}^-$.[29]

Reactions using Cl_2 or Br_2 as facilitators are faster than those with I_2 or $AsCl_4AsF_6$, probably because of the lower solubility of the latter. In addition $AsCl_4AsF_6$ only slowly loses Cl_2 in SO_2[26] (slow increase in AsF_3 concentration in a solution of $AsCl_4AsF_6$ monitored by ^{19}F NMR spectroscopy). Thus the combination SO_2–AsF_5–X_2 (Cl_2 or Br_2) is the most ideal for preparing salts of polyatomic chalcogen cations and AsF_3–SbF_5–I_2 the least preferred.

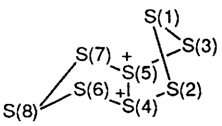
Our attempts to prepare $S_6(AsF_6)_2$ and more highly oxidised homopolyatomic cations of sulfur and selenium, *e.g.* M_6^{4+} (M = S or Se), *cf.* Te_6^{4+},[37] using traces of halogen were unsuccessful.



Scheme 2 A possible reaction pathway for the oxidation of Se_8^{2+} to Se_4^{2+} by AsF_5

Possible Reaction Pathways for the Oxidation of Sulfur and Selenium by AsF_5.—(*i*) *Without the facilitating agent* (X_2). Sulfur and selenium are oxidised by AsF_5 to give cations of the type S_{19}^{2+}, Se_{10}^{2+}, M_8^{2+} (M = S or Se) and Se_4^{2+} (on heating).[1,2,4] Initially the weak donor S_8 and AsF_5 may form a 1:1 adduct (Scheme 1, **A**) similar to the weak adducts $PF_3{\cdot}AsF_5$,[38] $SO_2F_2{\cdot}AsF_5$,[39] $SO_2{\cdot}AsF_5$.[39,40] The first ionisation energy of S_8 is 9.04 eV and that of SO_2 is 12.34 eV, and so sulfur (S_8) may be expected to form an adduct with AsF_5, even in the presence of excess of SO_2. The 1:1 adduct **A** may rearrange and donate F^- to another AsF_5 to give $S_8F^+AsF_6^-$ **D** (Scheme 1); S_8F^+ may rearrange to the structure S_7SF^+ **E** (analogous structural features are observed in S_{19}^{2+}[41] and $Se_7SeSeCl^+$[42]) from which the fluorine atom is more easily abstracted. It is more difficult to envisage the abstraction of fluorine from the electrophilic, positively charged S atom in S_8F^+ **D**. Attempts to prepare S_8X^+ (X = I, Br, Cl or F) led to the isolation of the crystalline salts of S_7I^+[43] and S_7Br^+,[44] and in more recent work to S_7X^+ (X = Cl or F).[45] It is possible that S_7SX^+ (**E**, Scheme 1) is also an intermediate in these reactions.

The S_8^{2+} cation is not further oxidised by AsF_5 in the absence of halogen. However, Se_8^{2+} (which may be formed in a manner described for S_8^{2+}) is slowly oxidised by AsF_5 and SbF_5 to Se_4^{2+} on heating. The first step in the oxidation of



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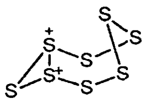

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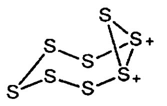


3

Se_8^{2+} to Se_4^{2+} may be the formation of an $Se_8^{2+}\cdot AsF_5$ intermediate (**A** in Scheme 2) formed by the donation of an electron pair from the slightly negative charged axial fluorine in AsF_5 to the more acidic positive charged three-co-ordinate selenium atoms in Se_8^{2+} [*i.e.* Se(4) and Se(5) in **A**].[46] The selenium atom Se(1) is the most basic atom in Se_8^{2+},[46] and may donate a pair of electrons to the partially positive arsenic in the AsF_5 molecule. Rearrangement may follow, resulting in the formation of $Se_8F_2^{2+}$ and the reduction of AsF_5 to AsF_3 (Scheme 2, **A** to **C**). Attempts to prepare solutions of the analogous $Se_8I_2^{2+}$ cation led to crystalline $(Se_6I)_n(AsF_6)_n$[47] over a solution of Se_8^{2+}, $Se_6I_2^{2+}$ and its equilibrium products (SeI_3^+, $Se_4I_4^{2+}$, and five unidentified selenium species at lower concentration) and Se_{10}^{2+} (2%, ^{77}Se NMR spectroscopy).[48] Therefore, the postulated species $Se_8F_2^{2+}$ **C** may rearrange to **D** [*cf.* $(S_7I)_2I^{3+}$ [49]] containing an abstractable fluorine, and/or to other equilibrium products, which may disproportionate, or lose F^- by abstraction with AsF_5, finally to give $2Se_4^{2+}$.

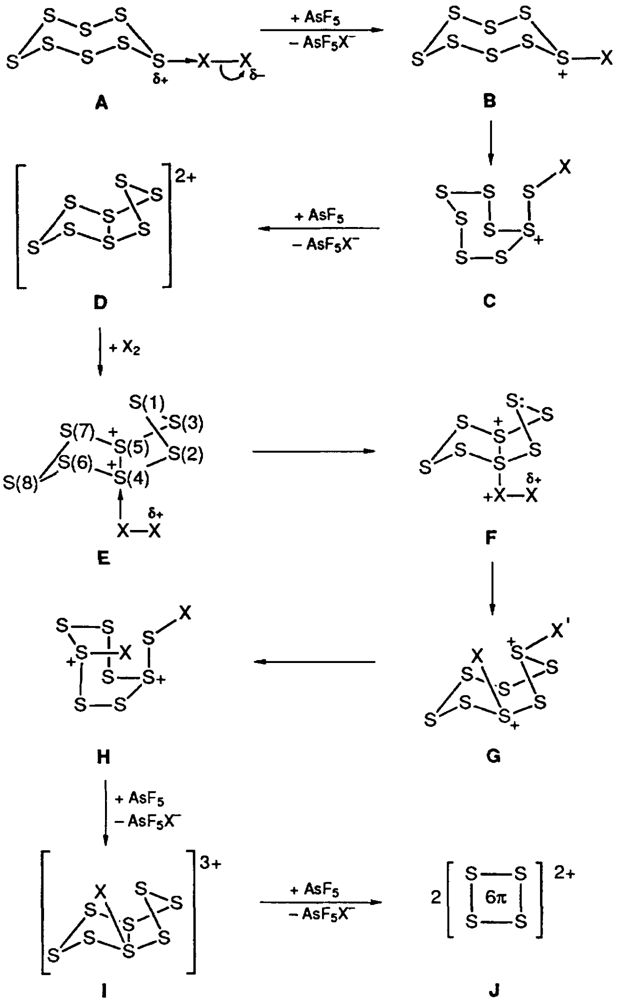
The absence of an analogous ($S_8^{2+} \longrightarrow S_4^{2+}$) oxidation step in the sulfur system may relate to the Se(4)–Se(5) distance being relatively longer in Se_8^{2+} than the S(4)–S(5) transannular bond in S_8^{2+}. In the valence bond terms this implies that resonance structure **1** is more important for Se_8^{2+} than S_8^{2+}, and other resonance structures **2** and **3** are relatively more important for S_8^{2+}. Consistently, the charges on Se(4)–Se(5) (+0.42) were calculated to be higher than those on S(4)–S(5) (+0.38).[46] It is possible, therefore, that the more negative axial fluorine on AsF_5 may act as a base to Se_8^{2+}, but not to S_8^{2+}.

(*ii*) *In the presence of halogen.* In the presence of a trace amount of halogen (Cl_2, Br_2, I_2) and an excess of AsF_5 the oxidation of S_8 to $S_8(AsF_6)_2$ may proceed through an S_8X^+-AsF_5X^- intermediate (Scheme 3). The neutral S_8 species may initially form a donor–acceptor adduct with X_2 [*cf.* $S_8\cdot I_2$[50a] and $=M\cdot X_2$ (M = S, Se or Te; X = Cl, Br or I)[50b]] by donating a lone pair of electrons into the σ* lowest occupied molecular orbital of X_2.[50] This would weaken the X–X bond and AsF_5 may then abstract X^- to give AsF_5X^- [51] and S_8X^+ which may rearrange to $(S_7)SX^+$ (**C**, Scheme 3) [*cf.* S_7X^+ (X = Br or I),[43,44] $Se_7SeSeCl$].[42] Further halide abstraction by AsF_5, and rearrangement of the cation, leads to S_8^{2+} (**C** ⟶ **D**, Scheme 3). The compound $S_8(AsF_6)_2$, in the presence of a trace quantity of X_2 and an excess of AsF_5, is rapidly oxidised to $S_4(AsF_6)_2$, possibly *via* $S_8X_2^{2+}$ which may isomerise to the more stable $[(S_7X)SX]^{2+}$ (**H**, Scheme 3). This cationic species may undergo X^- abstraction to form S_8X^{3+} which may rearrange, or disproportionate, and/or loose another X^- ion by abstraction with AsF_5 to give two S_4^{2+} cations. Alternatively disproportionation or rearrangement products may themselves be oxidised by fluoride-ion abstraction to give S_4^{2+}.

The S_4^{2+} and Se_4^{2+} cations are not further oxidised by AsF_5 to other homopolyatomic cations, even in the presence of a trace quantity of halogen. However, Se_4^{2+} has been shown to react with a stoichiometric amount of bromine, in the presence of an excess of AsF_5, to form $SeBr_3^+$.[52] Thus, it is reasonable that Se_4^{2+} and S_4^{2+} react with trace quantities of halogen in excess of AsF_5 to form MX_3^+ cations (M = S or Se; X = Cl, Br or I)[53] or $S_2I_4^{2+}$[54] as intermediates. The compound $Se_8(AsF_6)_2$ reacts with SeI_3AsF_6[47,48] in a 1:1 mole ratio to form $Se_6I_2(AsF_6)_2$ according to equation (8). Therefore, the MX_3^+ (X = I, Br or

$$2SeI_3AsF_6 + 2Se_8(AsF_6)_2 \longrightarrow 3Se_6I_2(AsF_6)_2 \tag{8}$$

Cl) species and $S_2I_4^{2+}$ may act as oxidising agents themselves and also recycle the halogen providing an alternative reaction pathway to that proposed above. However, SF_3AsF_6 does not react with $S_8(AsF_6)_2$ (^{19}F NMR spectroscopy) under similar conditions,[26] and so if MF_3^+ is formed at all in reactions without a halogen facilitator it cannot recycle the fluorine and thus does not act as a 'catalyst'. It is only when there is no low-oxidation-state species (*e.g.* S_8^{2+}, Se_8^{2+} and Se_{10}^{2+}) left that MX_3^+ (X = Cl, Br or I) species and $S_2I_4^{2+}$ will exist (in trace quantities) and represent the final fate of the halogen in these reactions In this sense the halogens are not true catalysts as they are not regenerated at the end of the reaction.



Scheme 3 A possible pathway to the formation of $S_4(AsF_6)_2$ by the reaction of S_8 and AsF_5 in the presence of a trace amount of halogen

The Reaction of AsF_5X^- *with Excess of* AsF_5.—The ion AsF_5X^- has been proposed as an intermediate in the various reaction pathways given above which we presumed reacts with AsF_5 to give AsF_6^-. To test this proposal we investigated the reactions of CsCl and KBr with an excess of AsF_5.

The reaction CsCl with AsF_5 gave $Cs[AsF_6]$ and $AsCl_4AsF_6$ according to equation (9). The initial product reasonably

$$4CsCl + 6AsF_5 \longrightarrow 4Cs[AsF_6] + AsCl_4AsF_6 \tag{9}$$

contains AsF_5Cl^- [51] which may exchange with AsF_5 to form $Cs[AsF_6]$ and AsF_4Cl. The latter may rearrange to give AsF_3Cl_2 and/or $AsCl_4AsF_6$ [equation (10] and the various complex equilibria given in equation (12), or AsF_3 and Cl_2 *via* equations (10) and (11).

$$2AsF_4Cl \longrightarrow AsF_3Cl_2 + AsF_5 \tag{10}$$

$$AsF_3Cl_2 \longrightarrow AsF_3 + Cl_2 \tag{11}$$

$$\begin{tikzcd}
2AsF_3Cl_3 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & {[AsF_2Cl_2^+][AsF_4Cl_2^-]} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & AsCl_3F_2 + AsF_4Cl \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\
{[AsCl_4^+][AsF_6^-]} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & AsCl_4F + AsF_5 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & {[AsCl_3F^+][AsF_5Cl^-]}
\end{tikzcd} \qquad (12)$$

We have also shown that $AsCl_4AsF_6$ is a halogen-facilitating agent. One of the disproportionation products (*e.g.* $AsCl_3F_2$ or Cl_2) may act as a chlorinating agent toward chalcogen homopolyatomic cations. The analogous $AsBr_4AsF_6$[55] and AsI_4AsF_6[55,56] are unstable at r.t. and readily revert to AsF_3 and X_2 (X = Br or I). Consistently the reaction of KBr gave $KAsF_5$, Br_2 and AsF_3 as the major identified products.

Very recently a paper on vibrational and normal coordinates analysis of isotopically substituted $S_4(AsF_6)\cdot 0.62\ SO_2$ and $S_4(SbF_6)_2\cdot SO_2$ has appeared.[57] However, no mention of how the $S_4(SbF_6)_2\cdot SO_2$ was prepared was included.

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