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Polyatomic Cations of Sulfur. I. Preparation and Properties of S_{16}^{2+}, S_8^{2+}, and S_4^{2+}

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It is shown that sulfur can be oxidized with $S_2O_6F_2$, AsF_5, or SbF_5 to the cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+}. The compounds $S_{16}(AsF_6)_2$, $S_8(AsF_6)_2$, $S_{16}(SbF_6)_2$, $S_8(Sb_2F_{11})_2$, and $S_4(SO_3F)_2$ have been isolated and characterized. The Raman spectrum of $S_4(SO_3F)_2$ is reported and assigned.

Introduction

We have shown in recent papers that selenium and tellurium can be oxidized in solution in strong acids such as H_2SO_4 and HSO_3F to polyatomic cations containing the element in low valency states. The existence of the ions Se_8^{2+}, Se_4^{2+}, and Te_4^{2+} in solution has been established by a combination of cryoscopic, conductometric, and spectroscopic measurements.[1-3] X-Ray crystallographic investigations of the crystalline compounds $Se_4(HS_2O_7)_2$ and $Se_8(AlCl_4)_2$ have established that the Se_4^{2+} ion has a square-planar structure[4] and that the Se_8^{2+} ion has the bicyclic structure I in

I
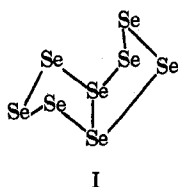
which opposite atoms in an Se_8 ring are bridged by a long bond.[5] Raman and infrared spectra demonstrate that the square-planar Se_4^{2+} structure is retained in solution.[6] Similarities in the vibrational spectra of Te_4^{2+} and Se_4^{2+} and in their magnetic circular dichroism strongly suggest that Te_4^{2+} also has a square-planar structure.[7,8]

As early as 1804 it was reported by Bucholz[9] that sulfur dissolves in oleum to give brown, green, or blue solutions. The blue solutions have subsequently been the subject of considerable investigation.[10-12] Weber[11] was the first to attribute the blue color of the oleum solutions to the compound "S_2O_3" which can be obtained as a deep blue solid material by the direct reaction of sulfur with sulfur trioxide in the presence of a trace of moisture. This compound was also studied later by Vogel and Partington,[12] who again obtained the composition S_2O_3. Auerbach[13] made cryoscopic measurements on solutions of sulfur in oleum and concluded that the sulfur was dissolved as S_2 molecules, but later Brayford and Wyatt,[14] who also attempted to make cryoscopic measurements, found that the solutions were not stable with time and they were unable to come to any certain conclusions. Symons, et al.,[15,16] reported that sulfur does not increase the conductivity of 65% oleum and hence they concluded that it is not protonated nor is it oxidized to a radical cation. However solutions of sulfur in antimony pentafluoride also have the same blue color as the oleum solutions[17-19] and in further experiments Symons, et al., showed that on electrolysis the blue color moved to the cathode,[19] indicating that, contrary to their earlier conclusions, the blue color is in fact due to a cationic species and that it is therefore unlikely to be S_2O_3. These authors also showed that these solutions contain a species in low concentration that has an esr spectrum and must therefore be a radical. They claimed that the esr spectrum is best interpreted by postulating that it arises from a species of the type $X_2S\text{–}SX_2^+$ where X is a univalent group derived from the solvent. Solutions of sulfur in

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(2) R. J. Gillespie, J. Barr, D. B. Crump, R. Kapoor, and P. K. Ummat, *Can. J. Chem.*, **46**, 3607 (1968).

(3) R. J. Gillespie, J. Barr, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).

(4) I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Commun.*, 853 (1968).

(5) R. K. McMullan, D. J. Prince, and J. D. Corbett, *ibid.*, 1438 (1969).

(6) R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, **8**, 1229 (1969).

(7) R. J. Gillespie, J. Barr, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).

(8) P. J. Stephens, *Chem. Commun.*, 1496 (1969).

(9) C. F. Bucholz, *Gehlen's Neues. J. Chem.*, **3**, 7 (1804).

(10) F. C. Vogel, *J. Chem. Phys. (Germany)*, **4**, 121 (1812).

(11) R. Weber, *Ann. Phys. (Leipzig)*, [2] **156**, 531 (1875).

(12) I. Vogel and J. R. Partington, *J. Chem. Soc.*, **127**, 1514 (1925).

(13) R. Auerbach, *Z. Phys. Chem. (Leipzig)*, **121**, 337 (1926).

(14) J. R. Brayford and P. A. H. Wyatt, *Trans. Faraday Soc.*, **52**, 642 (1956).

(15) M. C. R. Symons, *J. Chem. Soc.*, 2440 (1957).

(16) D. J. E. Ingram and M. C. R. Symons, *ibid.*, 2437 (1957).

(17) E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. Ind. (London)*, 1117 (1951).

(18) O. Ruff, H. Graf, W. Heller, and Knoch, *Ber.*, 4310 (1906).

(19) D. A. C. McNeil, M. Murry, and M. C. R. Symons, *J. Chem. Soc.*, 1019 (1967).

oleum have also been studied recently by Lux and Bohm,[20] who attributed the blue color to a species S_x that they were unable to identify with certainty. In view of our evidence for colored polyatomic cations of selenium and tellurium, it seems reasonable to suppose that the colored solutions of sulfur in oleum and antimony pentafluoride contain polyatomic cations of sulfur. The object of the work reported in this paper was to obtain evidence for such polyatomic cations of sulfur, to establish their identity, and, if possible, to prepare crystalline compounds of these cations. It was found that it was easier to identify the cations if they were prepared using other oxidizing agents than oleum and consequently this paper reports the results of an investigation of the oxidation of sulfur with AsF_5, SbF_5, and $S_2O_6F_2$. Preliminary reports of our results on the reactions of sulfur with AsF_5 and with $S_2O_6F_2$ have been published.[21,22] The results of our studies of solutions of sulfur in oleum will be reported in a later paper.[23]

Results and Discussion

Oxidation of Sulfur with Peroxydisulfuryl Difluoride. —When sulfur was oxidized with $S_2O_6F_2$ in solution in HSO_3F depending on the amount of $S_2O_6F_2$ added, orange, green, blue, and pale yellow solutions were obtained with increasing amounts of $S_2O_6F_2$. For ratios of sulfur to $S_2O_6F_2$ of greater than 16:1 some sulfur remained unreacted. At the 16:1 ratio complete solution of the sulfur occurred and the solution had the absorption spectrum shown in Figure 1 (curve A) with
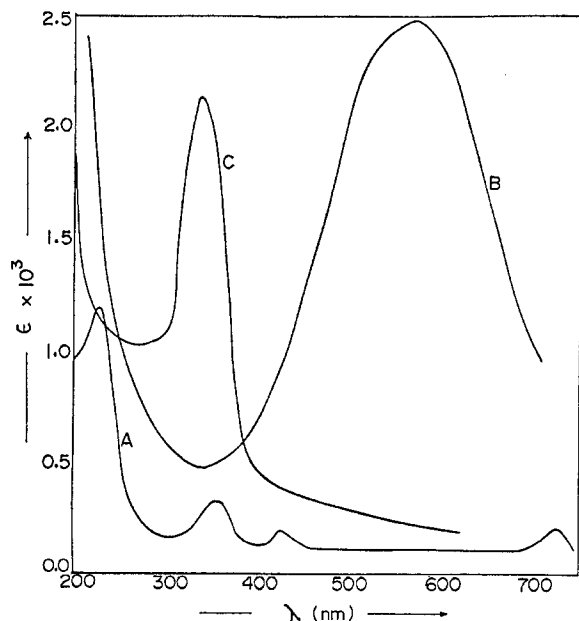

Figure 1.—Absorption spectra of HSO_3F solutions of $S_4{}^{2+}$, $S_8{}^{2+}$, and $S_{16}{}^{2+}$: A, $S_{16}{}^{2+}$; B, $S_8{}^{2+}$; C, $S_4{}^{2+}$.

maxima at 235, 350, 430, and 723 nm. Freezing point and conductivity measurements were made on these solutions and the results are given in Table I. The freezing point depressions obtained in two separate experiments gave a common linear plot against molality of S_8 that had a slope of 6.0 corresponding to a ν

(20) H. Lux and E. Bohm, *Chem. Ber.*, **98**, 3210 (1965).
(21) R. J. Gillespie and J. Passmore, *Chem. Commun.*, 1333 (1969).
(22) J. Barr, R. J. Gillespie, and P. K. Ummat, *ibid.*, 264 (1970).
(23) R. J. Gillespie and P. K. Ummat, unpublished work.

TABLE I
FREEZING POINTS AND CONDUCTIVITIES OF
RED SOLUTIONS OF SULFUR IN HSO_3F

Molality of S_8	$10^3\kappa$, ohm^{-1} cm^{-1}	Molality of S_8	Fp depression, °C
0.0064	1.675	0.0224	0.14
0.0280	5.367	0.0346	0.19
0.0534	9.456	0.0628	0.36
0.0830	13.92	0.0630	0.39
0.1034	16.77	0.0906	0.54
0.1110	17.81	0.110	0.62
		0.116	0.74
		0.119	0.76

value of 1.5 (Figure 2). This value is consistent with the formation of the $S_{16}{}^{2+}$ cation according to the equation

$$2S_8 + S_2O_6F_2 \longrightarrow S_{16}{}^{2+} + 2SO_3F^- \qquad (1)$$
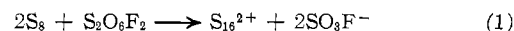
The conductivities of the solutions were close to those for $Ba(SO_3F)_2$ and $Sr(SO_3F)_2$ if the molalities were calculated on the assumption that the compound is $S_{16}(SO_3F)_2$ (Figure 2). Thus the conductivity results are
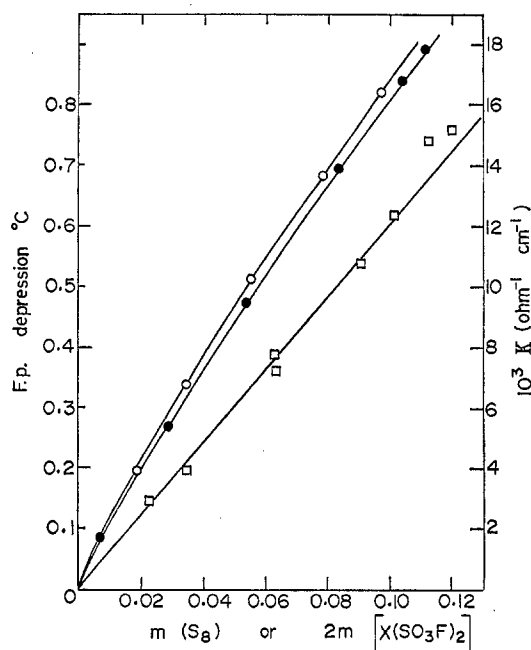

Figure 2.—Freezing points and conductivities of red solutions of sulfur in HSO_3F: □, freezing points; ●, conductivities; ○, $Sr(SO_3F)_2$.

also consistent with the reaction of S_8 to form the $S_{16}{}^{2+}$ cation according to eq 1.

At the ratio $S/S_2O_6F_2 = 8$, the solution had a deep blue color and the absorption spectrum shown in Figure 1 (curve B) with an intense maximum at 590 nm and no trace of the spectrum that we have assigned to $S_{16}{}^{2+}$. Presumably the blue species is a sulfur cation containing sulfur in the +0.25 oxidation state, formed according to the equation

$$S_8 + S_2O_6F_2 \longrightarrow S_8{}^{2+} + 2SO_3F^- \qquad (2)$$
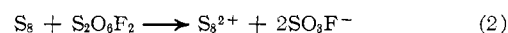
but it was not possible to confirm this by cryoscopic and conductometric measurements as these solutions were not stable slowly depositing sulfur on standing. Further evidence on the nature of the blue species and confirmatory evidence for the red $S_{16}{}^{2+}$ species was obtained from studies of the reactions between sulfur and AsF_5 and sulfur and SbF_5.

When an excess of $S_2O_6F_2$ was used in solution in sulfur dioxide and the temperature of the reaction mixture was allowed to rise slowly from $-63°$ to room temperature over a period of a few days, a red compound formed first which was then replaced by a blue compound, and finally a white crystalline material was obtained after excess $S_2O_6F_2$ and SO_2 had been removed. The white product was extremely hygroscopic, reacted with moist air to give the red species, and instantaneously decomposed to elemental sulfur when added to water. The elemental analysis results were in good agreement with the calculated values expected for the formulation $S_2(SO_3F)$ containing sulfur in the $+0.5$ oxidation state. The solid was found to be diamagnetic. By analogy with the previously reported Se_4^{2+} and Te_4^{2+} cations it seems reasonable to formulate this compound as $S_4(SO_3F)_2$. The compound did not give a stable solution in HSO_3F as the characteristic peak of the blue S_8^{2+} cation appeared and increased in intensity with time. However a stable colorless solution was obtained in HSO_3F–SbF_5 which had the absorption spectrum shown in Figure 1 (curve C), with a strong peak at 330 nm and a weak, poorly resolved peak at 280 nm. The absorption spectra of Te_4^{2+}, Se_4^{2+}, and S_4^{2+} are very similar in shape, each having a strong peak at longer wavelengths and a weak peak at shorter wavelengths, the λ_{max} decreases steadily in the series Te_4^{2+}, Se_4^{2+}, and S_4^{2+} as shown in Table II. This similarity in the

TABLE II
COMPARISON OF THE ABSORPTION SPECTRA OF
Te_4^{2+}, Se_4^{2+}, AND S_4^{2+} CATIONS

Cation	λ_{max}, nm	
	Strong	Weak
Te_4^{2+}	510	420
Se_4^{2+}	410	320
S_4^{2+}	330	$\sim$280

spectra lends further support to the identification of the cation as S_4^{2+}.

The Raman frequencies of $S_4(SO_3F)_2$ are given in Table III together with the assignments made on the

TABLE III
RAMAN FREQUENCIES OF $S_4^{2+}(SO_3F^-)_2$

Rel intens[a]	Shift, cm^{-1}	Assignment	
		S_4^{2+}	SO_3F^-
2	300 }	Lattice vib?	
2	313 }		
16	330	$\nu_3(B_{2g})$	
15	382		$\nu_6(E)$
5	460	$\nu_4(E_u)$	
10	530	$\nu_2(B_{1g})$	
50	564		$\nu_3(A_1)$
100	584	$\nu_1(A_{1g})$	
75	591 }		
5	635 }		$\nu_5(E)$
13	709 }		
13	866		$\nu_2(A_1)$
39	1070		$\nu_1(A_1)$
35	1230 }		
40	1240 }		$\nu_4(E)$
10	1303 }		
6	1434	?	

[a] Peak height.

basis of a predominantly ionic model, *i.e.*, $S_4^{2+}(SO_3F^-)_2$ containing a square planar cation similar to the cations Se_4^{2+} [24] and Te_4^{2+}.[25] The anion vibrations are

(24) R. J. Gillespie and G. Pez, *Inorg. Chem.*, **8**, 1229 (1969).
(25) J. D. Corbett, private communication.

assigned using previously published assignments for SO_3F^-.[26-28] The frequency 584 cm^{-1} assigned to the A_{1g} mode of the square-planar S_4^{2+} cation is slightly higher than the frequency of the S–S stretch in S_2Cl_2[29,30] (540 cm^{-1}) which presumably contains a single bond between the sulfur atoms, just as the frequency (327 cm^{-1}) assigned to the A_{1g} mode of Se_4^{2+} is a little higher than the Se–Se stretching frequency (290 cm^{-1}). The frequencies assigned to the B_{1g}, B_{2g}, and A_{1g} modes are in approximately the same ratio as the frequencies of the same vibrational modes of the Se_4^{2+} cation (Table IV). The weak band observed at 460 cm^{-1} does not

TABLE IV
VIBRATIONAL FREQUENCIES OF THE
S_4^{2+}, Se_4^{2+}, AND Te_4^{2+} IONS

Vibrational mode	S_4^{2+}	Se_4^{2+}	Te_4^{2+}
$\nu_1(A_{1g})$	584	327	219
$\nu_2(B_{1g})$	530	319	...
$\nu_3(Eu)$	460	306	...
$\nu_4(B_{2g})$	330	192	139

appear to be an anion frequency. It may be the E_u mode of the cation, which though Raman inactive in an isolated M_4^{2+} cation with D_{4h} symmetry, could become weakly allowed in the Raman if the site symmetry of the cation is lower in the solid. The E_u mode of Se_4^{2+}–$(SO_3F^-)_2$ is observed weakly in the Raman spectrum.[24]

The Reaction of Sulfur with Arsenic Pentafluoride.— Arsenic pentafluoride in anhydrous hydrogen fluoride solution reacts with powdered sulfur at $0°$ over a period of several days to give a red solid, S_8AsF_6, or a blue solid, S_4AsF_6, depending on the ratio of the reactants. The reactions may be formulated in the manner

$$S_8 + 3AsF_5 \longrightarrow S_8(AsF_6)_2 + AsF_3$$

$$2S_8 + 3AsF_5 \longrightarrow S_{16}(AsF_6)_2 + AsF_3$$
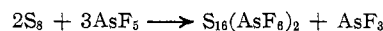
Stoichiometric amounts of reactants gave the weight of product corresponding to complete conversion to one of the compounds after removal of the solvent HF and AsF_3 under vacuum. Intermediate ratios of arsenic pentafluoride to sulfur gave a mixture of red and blue solids which generally crystallized in separate parts of the reaction vessel. Excess arsenic pentafluoride did not appear to lead to further oxidation under these experimental conditions nor under more extreme conditions. For example when the reaction was carried out with excess AsF_5 in solution in SO_2 at $80°$ in a sealed tube, only the blue compound was obtained.

The blue compound crystallized from solution as shiny deep blue plates. The elemental analysis results were in excellent agreement with the calculated values expected for the formulation S_4AsF_6. The compound was soluble in fluorosulfuric acid and the solution had an absorption spectrum identical with that in Figure 1 (curve B) and an extinction coefficient of 2.5×10^3 mol of S kg^{-1} cm^{-1}.

The infrared spectrum of the solid and the ^{19}F nmr spectrum of a solution in HSO_3F showed the presence of the AsF_6^- ion. The mass spectrum showed peaks attributable to S_n^+ ($n = 1$–8) and AsF_n^+ ($n = 1$–4). This result is consistent with the supposition that the

(26) H. Siebert, *Z. Anorg. Allg. Chem.*, **289**, 15 (1957).
(27) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 644 (1962).
(28) J. Goubean and J. B. Milne, *ibid.*, **45**, 2321 (1967).
(29) J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950); **19**, 139 (1951).
(30) H. Stamreich and R. Forneris, *Spectrochim. Acta*, **8**, 46 (1956).

compound contains a polycation of sulfur and the AsF_6^- anion and is additional evidence for absence of sulfur–fluorine and arsenic–sulfur bonds. The analytical results and the spectroscopic evidence imply that the compound has the ionic structure $S_{4n}{}^{n+}(AsF_6{}^-)_n$. The weight of sulfur precipitated on hydrolysis was consistent with sulfur in the $+0.25$ oxidation state disproportionating to elemental sulfur and sulfur dioxide according to the equation $2S_8{}^{2+} + 2H_2O \rightarrow 15S + SO_2 + 4H^+$.

Solutions of the compound in fluorosulfuric acid were found to be diamagnetic over the temperature range -70 to $-10°$. The solid was very slightly paramagnetic but the paramagnetism was much less than would be expected for a radical species such as $S_4{}^+$ or $S_{12}{}^{3+}$; hence the cation must be $S_8{}^{2+}$, $S_{16}{}^{4+}$, or in general $S_{8n}{}^{2n+}$.

Crystal X-ray diffraction data allowed the space group to be uniquely determined as $P2_1/C$. The number of S_4AsF_6 units in the unit cell was found to be 16 from density and unit cell dimensions. The asymmetric unit for the $P2_1/C$ space group is one-quarter of the unit cell; therefore assuming that the cation is not an infinite polymer, the upper limit for the molecular formula is $(S_4AsF_6)_4$. The compound is diamagnetic; therefore the molecular formula is either $S_8(AsF_6)_2$ or $S_{16}(AsF_6)_4$. As the selenium analog has been established[1] as $Se_8{}^{2+}$, it seems reasonable to prefer the $S_8(AsF_6)_2$ formulation for the sulfur compound.

The red compound is generally prepared as a microcrystalline powder, although sometimes the product contains platelike crystals. The reaction product was completely soluble in fluorosulfuric acid, showing it to be free from elemental sulfur. The analysis results give excellent agreement with the calculated values expected for the empirical formula S_8AsF_6. The infrared, ^{19}F nmr, and mass spectrum results were similar to those obtained for the blue compound; hence the compound can be formulated as $S_{8n}{}^{n+}(AsF_6{}^-)_n$. The weight of elemental sulfur precipitated on hydrolysis was consistent with sulfur of oxidation state $^1/_8$, disproportionating to elemental sulfur and sulfur dioxide

$$2S_{16}{}^{2+} + 2H_2O \longrightarrow 31S + SO_2 + 4H^+$$

The absorption spectra of solutions in fluorosulfuric acid were identical with curve A in Figure 1.

The solid red compound and solutions of the compound in fluorosulfuric acid were found to be very slightly paramagnetic. However, the paramagnetism was very much less than would be expected for a radical species such as $S_8{}^+$ and hence we conclude that the most probable formulation is $S_{16}{}^{2+}(AsF_6{}^-)_2$. This agrees with our conclusion that $S_2O_6F_2$ oxidizes sulfur to $S_{16}{}^{2+}$ in solution in HSO_3F.

Reaction of Sulfur with Antimony Pentafluoride.— On stirring elemental sulfur with antimony pentafluoride in approximately the molar ratio $^2/_3$ in anhydrous HF or liquid SO_2 at room temperature for approximately 3 days, a red solid was obtained when the HF or SO_2 was removed under vacuum. This solid was extracted several times with sulfur dioxide leaving a white residue which was shown to be antimony(III) fluoride. On evaporation of the red sulfur dioxide solution a microcrystalline red solid was obtained which had an elemental analysis consistent with the composition

S_8SbF_6. A solution in fluorosulfuric acid had an absorption spectrum identical with curve A in Figure 1, which we have attributed to $S_{16}{}^{2+}$. We conclude that the red solid may be formulated as $S_{16}{}^{2+}(SbF_6{}^-)_2$ and that it is formed according to the equation $2S_8 + 3SbF_5 \rightarrow S_{16}{}^{2+}(SbF_6{}^-)_2 + SbF_3$. The presence of the $SbF_6{}^-$ ion in the solid was confirmed by infrared and ^{19}F nmr spectroscopy.

When sulfur was oxidized with excess antimony pentafluoride in sulfur dioxide solution in a sealed system at room temperature for a few days, a dark blue solid product and a blue solution were obtained. On extracting the product with sulfur dioxide all the blue material dissolved leaving a white solid which was shown to be antimony trifluoride. On evaporation the sulfur dioxide solution gave a dark blue solid. The weight obtained and the elemental analyses were consistent with the formulation $S_8(Sb_2F_{11})_2$ formed according to the equation $S_8 + 5SbF_5 \rightarrow S_8(Sb_2F_{11})_2 + SbF_3$. This material gave blue solutions in oleum and fluorosulfuric acid. The absorption spectrum of the solution in fluorosulfuric acid was identical with that in Figure 1 (curve B) with an absorption maximum at 590 nm and an extinction coefficient of 2.32×10^3 mol of S kg^{-1} cm^{-1}. The $Sb_2F_{11}{}^-$ ion was identified in the solid by means of its characteristic infrared spectrum and by the nmr spectra of SO_2 and HSO_3F solutions.

When elemental sulfur was heated with a large excess of SbF_5 at $140°$ for several days, the dark blue product first formed was gradually replaced by a white solid. This was isolated by removal of the excess SbF_5 by heating to $100°$ under vacuum. This solid turned blue when exposed to moist air and decomposed to elemental sulfur when treated with water. It was insoluble in liquid SO_2 and decomposed to the blue species on prolonged heating at $100°$ under vacuum. The reduced product which was presumably the compound $SbF_5 \cdot SbF_3$ could not be separated from the white sulfur compound by either SO_2 extraction or sublimation. The white product had a slight solubility in HSO_3F and the solution showed the characteristic absorption of $S_4{}^{2+}$ at 330 nm as shown in Figure 1. Mainly because of the difficulties involved in separating $SbF_5 \cdot SbF_3$ from the reaction product, it was not further investigated. Presumably the white materials which Ruff, et al.,[17] and Peacock, et al.,[18] obtained from the reaction of sulfur and excess SbF_5 were also mixtures.

Esr of Solutions.—The yellow-orange solutions in HSO_3F obtained from the mole ratio $S/S_2O_6F_2 = 16$ had a strong esr signal at $g = 2.027$ and weak signals at $g = 2.014$ and 2.006. On increasing the amount of $S_2O_6F_2$, the signal at $g = 2.027$ decreased in intensity and that at $g = 2.014$ increased in intensity.

The red solution of $S_{16}(SbF_6)_2$ in liquid SO_2 gave a strong absorption at $g = 2.027$, a very weak absorption at $g = 2.014$, and a barely detectable absorption at $g = 2.006$. The blue solution of $S_8(Sb_2F_{11})_2$ in SO_2 had a strong absorption at $g = 2.014$.

It seems clear that the $g = 2.027$ absorption can be attributed to a radical species arising from $S_{16}{}^{2+}$ and the $g = 2.014$ absorption to a species arising from $S_8{}^{2+}$. It seems reasonable to suppose that these species are the radicals $S_8{}^+$ and $S_4{}^+$, small amounts of which are presumably in equilibrium with $S_{16}{}^{2+}$ and $S_8{}^{2+}$, respectively: $S_{16}{}^{2+} \rightleftharpoons 2S_8{}^+$ and $S_8{}^{2+} \rightleftharpoons 2S_4{}^+$.

We suppose that the first stage of oxidation of S_8 involves the loss of one electron to give the S_8^+ radical ion which then dimerizes extensively leaving only a small equilibrium concentration of S_8^+. On further oxidation S_8^+ presumably loses another electron to become S_8^{2+} which appears to have a slight tendency to dissociate into S_4^+ radical ions. On further oxidation S_4^+ presumably loses another electron to become S_4^{2+} which appears to have no tendency to dissociate into radical ions.

Conclusions

The cations S_4^{2+}, S_8^{2+}, and S_{16}^{2+} are strong Lewis acids and they are stable only under very weakly basic conditions. We have shown that they can be obtained in solvents such as HSO_3F, oleum, and HSO_3F–SbF_5 in which the most basic species is the solvent anion. The solid compounds that have been isolated contain anions such as SbF_6^-, $Sb_2F_{11}^-$, or AsF_6^- which are very weakly basic; *i.e.*, they are the anions of extremely strong acids. The S_{16}^{2+} and S_8^{2+} cations are stable in sulfur dioxide solution; however, the S_4^{2+} cation slowly disproportionates to give S_8^{2+} and SO_2 in this solvent. In fluorosulfuric acid S_{16}^{2+} is relatively stable, but S_8^{2+} appears to undergo a disproportionation reaction which eventually gives elemental sulfur and SO_2, while the S_4^{2+} cation is very rapidly disproportionated to give the blue S_8^{2+} cation and SO_2. The S_4^{2+} ion is however stabilized by the higher acidity (lower basicity) of an HSO_3F–SbF_5 solvent.

The structures of these cations are clearly of considerable interest. Presumably the structure of S_8^{2+} resembles that of Se_8^{2+} which was recently determined by Corbett, *et al.*[5] Confirmation of this suggestion awaits the completion of the determination of the structure of $S_8^{2+}(AsF_6^-)_2$ which is in progress.[31] It seems reasonable to speculate that the S_{16}^{2+} cation consists of two S_8^+ rings held together by a single sulfur–sulfur bond. In view of the difference in conformation between the Se_8 ring in elemental selenium and in Se_8^{2+} the conformations of the rings in both S_8^{2+} and S_{16}^{2+} are obviously of considerable interest. The esr and magnetic results indicate that both S_8^{2+} and S_{16}^{2+} are in equilibrium with small concentrations of radicals and we propose that these are the radical cations S_4^+ and S_8^+.

Experimental Section

Reactions of Sulfur with $S_2O_6F_2$.—These reactions were carried out either in HSO_3F as solvent at 0° or in SO_2 as solvent.

Reactions were carried out in HSO_3F solvent by adding a solution of $S_2O_6F_2$ in HSO_3F dropwise to sulfur in HSO_3F at 0° with constant stirring. It was not found possible to isolate pure compounds from these solutions. Reactions were also carried out in liquid sulfur dioxide as solvent with the primary objective of isolating a compound of sulfur in the +0.5 oxidation state. In a typical experiment an excess of $S_2O_6F_2$ (0.05 mol) was condensed onto powdered sulfur (0.0078 mol) in liquid SO_2 at −196° and the mixture was then allowed to warm up to −23° through intermediate temperatures over a period of several days. At −63° sulfur reacted very slowly to give the red species, but at −23° a greenish blue solution was obtained. The reaction vessel was set at −23° for a further few days until a deep greenish blue solution was obtained. At this point the reaction vessel was left at room temperature and the solution further stirred until a white crystalline product was obtained. Excess $S_2O_6F_2$ and SO_2 were pumped off under vacuum leaving a white product. Careful temperature control was necessary as any rapid increase in the temperature resulted in an *explosion*.

Elemental analysis gave the following results. *Anal.* Calcd for $S_2(SO_3F)$: S, 58.80; F, 11.62; O, 29.50. Found: S, 57.93; F, 11.15; O (by difference), 30.92. The solid was found to be diamagnetic with a gram-atom susceptibility of −24 × 10^{-6} cgsu.

This reaction and others using HF as solvent were carried on in an apparatus constructed from Monel tubing, Kel-F and copper traps, stainless steel 1KS4-316 valves, and Swagelok compression fittings. Gas pressures were measured with a Monel Bourdon gauge. Infrared spectra of gases were obtained using a Monel gas cell fitted with silver chloride windows. All solids were handled in a good drybox.

In a typical experiment, arsenic pentafluoride (0.0533 mol) was condensed onto powdered sulfur (0.0177 mol, S_8) in anhydrous hydrogen fluoride contained in a Kel-F trap. A mixture of red and blue solids was formed on standing overnight at −78°. On keeping at 0° for several days complete conversion to the blue material was observed. All volatile material was removed from the trap and condensed onto sodium fluoride. The solvent was absorbed by the sodium fluoride leaving a large quantity of arsenic trifluoride which was identified by its infrared spectrum. The blue solid reaction product was evacuated at 5 × 10^{-4} Torr for 2 days giving 0.0172 mol of $S_8(AsF_6)_2$ as glistening blue crystals in the form of · plates. *Anal.* Calcd for $S_8(AsF_6)_2$: S, 40.43; As, 23.62; F, 35.94. · Found: S, 40.53; As, 23.63; F, 36.12. Sulfur precipitated on hydrolysis: calcd for $2S_8^{2+} \rightarrow 15S + SO_2$, 37.95%; found, 37.88%; mp 128°. The infrared spectrum had bands at 700 and 395 cm^{-1}. $CsAsF_6$ has bands at 699 and 392 cm^{-1}.[21] The ^{19}F nmr spectrum of a solution in fluorosulfuric acid had a single broad peak in the fluorine on arsenic(V) region in addition to the solvent peak δ_{CCl_3F} 58 ppm; *cf.* (n-$C_4H_9)_4NAsF_6$ in HSO_3F, δ_{CCl_3F} 63 ppm.

In a similar reaction 0.0218 mol of S_8 was treated with 0.0327 mol of AsF_5 to yield 0.0217 mol of a red microcrystalline solid. *Anal.* Calcd for $S_8(AsF_6)$: S, 57.50; As, 16.82; F, 25.59. Found: S, 57.64; As, 16.62; F, 25.81. Sulfur precipitated on hydrolysis: calcd for $2S_{16}^{2+} \rightarrow 31S + SO_2$, 55.7%; found, 55.5%; mp 112–115° dec. The infrared spectrum had bands at 698 and 397 cm^{-1}. The ^{19}F nmr spectrum had a single broad peak at δ_{CCl_3F} 64 ppm in addition to the solvent peak.

When a large excess of AsF_5 (0.12 mol) was condensed onto finely powdered sulfur (0.012 mol) in a thick-walled Pyrex glass tube in liquid SO_2 at −196° and the reaction mixture was allowed to warm up to room temperature, a deep blue solution containing a blue solid was obtained. On further heating this solution at 80° for 2 weeks, there was no apparent change in the blue color.

Reactions of Sulfur with Antimony Pentafluoride.—(1) In a typical experiment sulfur (0.0078 mol) was stirred with antimony pentafluoride (0.0117 mol) in anhydrous HF at room temperature for 3 days. On removing the solvent under vacuum a red solid was obtained. This was extracted several times with sulfur dioxide leaving a white residue which was shown to be antimony trifluoride. The Raman spectrum was identical with that of an authentic sample and the +3 oxidation state of antimony was confirmed by the Rhodamine B test. On evaporating the sulfur dioxide extract under vacuum a red solid was obtained the weight of which corresponded to the quantitative formation of $S_{16}(SbF_6)_2$ (0.0077 mol). *Anal.* Calcd for $S_{16}(SbF_6)_2$: S, 52.06; Sb, 24.76; F, 23.18. Found: S, 51.75; Sb, 24.05; F, 23.95. The infrared spectrum of the solid had the characteristic strong broad band of SbF_6^- at 699 cm^{-1}. The ^{19}F nmr spectrum of a solution in fluorosulfuric acid had in addition to the solvent resonance a strong resonance at 166 ppm from HSO_3F which may be assigned to SbF_6^- and a weak spectrum characteristic of $SbF_5(SO_3F)^-$[32] resulting from some solvolysis of SbF_6^-. The ^{19}F spectrum of a solution in liquid SO_2 had only one broad signal at δ_{CCl_3F} 105.5 ppm (*cf.* $C_6H_5N(CH_3)_3^+SbF_6^-$ in SO_2, δ_{CCl_3F} 104.8 ppm).

(2) In a typical experiment antimony pentafluoride (0.048 mol) was added to powdered sulfur (0.00816 mol) in sulfur dioxide at −63° and the mixture was allowed to warm to room temperature and then stirred for a few days. A very dark blue solution containing some dark solid was obtained. The blue solid was extracted four times with 50 ml of sulfur dioxide until the remaining solid residue was white. This white solid was identified as antimony trifluoride as before. The sulfur dioxide extract was evaporated under vacuum and a dark blue crystalline solid was obtained the weight of which corresponded to quantitative formation of $S_8(Sb_2F_{11})_2$ (0.0081 mol). *Anal.* Calcd for

(31) C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, unpublished work.

(32) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

$S_8(Sb_2F_{11})_2$: S, 22.03; Sb, 41.60; F, 36.00. Found: S, 21.21; Sb, 40.71; F, 37.74. The infrared spectrum was essentially the same as that of $CsSb_2F_{11}$ over the range 450–1800 cm^{-1} and in particular contained a broad band at 650–770 cm^{-1} assigned to Sb–F stretching modes and a weaker band at 478 cm^{-1} which appears to be a stretching mode associated with the Sb–F–Sb bridge in $Sb_2F_{11}^-$ and which has been previously observed at 523 cm^{-1} in $VO_2^+Sb_2F_{11}^-$,[33] at 485 cm^{-1} in $Se_4^{2+}(Sb_2F_{11}^-)_2$,[24] and a 479 cm^{-1} in $CsSb_2F_{11}$.[34] The ^{19}F nmr spectrum in SO_2 at $-90°$ consisted of a multiplet at 92 ppm, a doublet of doublets at 111 ppm, and a quintet at 133 ppm from external $CFCl_3$ with coupling constants of 59 and 102 Hz. The chemical shifts and coupling constants agree well with those observed previously for $Sb_2F_{11}^-$.[35] The ^{19}F spectrum of a solution in HSO_3F had a broad peak at 166 ppm from HSO_3F which may be assigned to SbF_6^-, a doublet at 155 ppm, and a quintet at 183 ppm with a coupling constant of 100 Hz which may be assigned to the $SbF_5SO_3F^-$ anion.[22] The areas of the peaks were consistent with the formation of equal amounts of SbF_6^- and $SbF_5SO_3F^-$ according to the equation $Sb_2F_{11}^- + SO_3F^- \rightarrow SbF_6^- + SbF_5(SO_3F)^-$.

(3) In a typical experiment a large excess of SbF_5 (0.55 mol) was treated with elemental sulfur (0.012 mol) at 140° for several days during which time the dark blue product which was first formed was gradually replaced by a white solid. This was isolated by removal of the excess SbF_5 by heating at 100° under vacuum. As it was not found possible to separate the sulfur compound from the reduction product which was presumably $SbF_3 \cdot SbF_5$, no attempt was made to analyze this material.

Spectrophotometric Measurements.—Absorption spectra were obtained on a Cary Model 14 spectrometer using 1-cm path length quartz cells and quartz inserts to give path lengths down to 0.005 cm. The cells were rigorously dried and filled with the fluorosulfuric acid solutions in a drybox. Concentrated solutions and short path lengths were used in order to minimize any effects of reaction with the solvent or with impurities present in the solvent, e.g., SO_3 or H_2O.

Magnetic Susceptibility Measurements.—Measurements were made by the Gouy method using an Alpha Scientific Laboratories Model AL7500 electromagnet, a Sartorius Vacuum Electrono microbalance, and a variable-temperature experimental arrangement built after a design from Earnshaw.[27] The usual tube corrections and, in the case of solution work, correction for the contribution of the solvent were applied. The sample tubes were calibrated with solid $Hg[Co(CNS)_4]$ and distilled water. The molar susceptibility for the solid $S_8(AsF_6)_2$ was found to be -160×10^{-6} and to be independent of temperature from $+20$ to $-170°$. The diamagnetic contribution is estimated to be -316×10^{-6} cgsu using diamagnetic susceptibility values taken from ref 36. Hence the solid appears to have a very slight para-

magnetism. The magnetic susceptibility of a solution in HSO_3F was found to be constant over the ranges -70 to $-10°$ and to correspond to a molar susceptibility of -280×10^{-6} cgsu which within experimental error is equal to the value of the diamagnetic correction and implies that the compound is diamagnetic.

The molar susceptibility of the solid $S_{16}(AsF_6)_2$ and its solution in HSO_3F was found to be -224×10^{-6} cgsu over the temperature range -70 to $+70°$. The diamagnetic contribution for the ligands is estimated to be -436×10^{-6} cgsu. This implies that the compound is diamagnetic over this temperature range; the small paramagnetism is presumably being due to radical impurity. The molar susceptibility of the solid S_4-$(SO_3F)_2$ was found to be -24×10^{-6} cgsu after making ligand corrections and to be independent of temperature from $+20$ to $-170°$.

X-Ray Diffraction.—Diffraction photographs of single crystals of the blue compound $S_8(AsF_6)_2$ were obtained using both Weissenburg and precession cameras. The crystals were mounted in thin-walled quartz tubes. They gave the following information for S_4AsF_6: mol wt 317.17; monoclinic cell with $a = 15.00$, $b = 13.40$, $c = 16.49$ Å, $\beta = 107.96°$, $V = 3154.0$ Å^3, $d_m = 2.61$, $Z = 16$, $d_c = 2.69$; space group $P2_1/c$. The density was determined by displacement of Fluorolube oil.

Mass Spectra.—Mass spectra were obtained on a CEC mass spectrometer, 21-110, by the direct-inlet method, at an ionizing voltage of 70 eV, an accelerating potential of 8 kV, and a source temperature of 80°. The spectra of both the red and the blue compounds consisted of peaks attributable to the S_8^+, S_7^+, S_6^+, S_4^+, S_3^+, S_2^+, S^+, AsF_4^+, AsF_3^+, AsF_2^+, AsF^+, and As^+ ions.

Esr.—The esr spectra of the solids at room temperature were obtained on a Joelco Model JES 3BS-X spectrometer. The g values were obtained by comparison with the manganous ion.

Infrared Spectroscopy.—Samples for infrared spectroscopy were prepared by coating CsI windows with the powder at approximately 196° in the low-temperature cell described by Gillespie and Pez.[5] Infrared spectra of gases were obtained using a Monel gas cell fitted with silver chloride windows. Infrared spectra were obtained on a Beckman IR-12 spectrometer over the range 200–2000 cm^{-1}.

Raman Spectroscopy.—Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing amplifier and recorder. The exciting radiation was the green 5165-Å line of a Spectra-Physics Model 140 argon ion laser or the 6328-Å line of a Spectra-Physics Model 125 helium–neon laser. Standard samples, both solids and liquids, were sealed in 2-mm o.d. glass capillary tubes and mounted horizontally in a brass holder.

^{19}F Nmr Spectroscopy.—The ^{19}F nmr spectra were obtained using a Varian DP-60 nmr spectrometer.

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(34) P. A. W. Dean and R. J. Gillespie, unpublished observation.

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(36) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960.