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## Preparation and Crystal Structure of $S_{19}(AsF_6)_2$ and an ESR and Absorption Spectral Study of Solutions Containing the $S_{19}^{2+}$ Cation and Related Systems

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The structure of the compound previously thought to be  $S_{16}(AsF_6)_2$  has been determined from three-dimensional X-ray diffraction data and shown to be  $S_{19}(AsF_6)_2$ . The crystals are triclinic with  $a = 7.536(2) \text{ \AA}$ ,  $b = 13.406(3) \text{ \AA}$ ,  $c = 27.226(5) \text{ \AA}$ ,  $\alpha = 89.02(2)^\circ$ ,  $\beta = 91.58(2)^\circ$ ,  $\gamma = 93.24(2)^\circ$ ,  $V = 2744.9(10) \text{ \AA}^3$ , and  $d_{\text{calcd}} = 2.39 \text{ g cm}^{-3}$  for  $Z = 4$ , space group  $B\bar{1}$ . The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares to  $R_1 = 0.071$  and  $R_2 = 0.082$  for 1844 observed ( $I > 3\sigma(I)$ ) reflections. The structure contains discrete  $AsF_6^-$  anions and  $S_{19}^{2+}$  cations, the latter consisting of two seven-membered rings joined by a five-atom chain. One of the rings has a boat conformation and the other ring is disordered, existing 80% in a chair conformation and 20% in a boat conformation. The significant bond length alternations found in these two rings and related systems are discussed. The ESR and absorption spectra of solutions obtained by the oxidation of sulfur with  $AsF_5$  in  $SO_2$  have been further investigated, the presence of  $S_{19}^{2+}$ ,  $S_8^{2+}$ ,  $S_5^+$ , and two other radical species in these solutions has been confirmed, and assignments of the absorption spectral bands have been made.

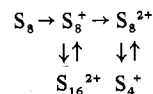
### Introduction

Sulfur may be oxidized by a variety of oxidizing agents including  $AsF_5$ ,  $SbF_5$ , and  $S_2O_6F_2$  and by strong acids such as  $H_2S_2O_7$  and  $HSO_3F$  to give several different cationic species. Evidence has been reported for the doubly charged  $S_4^{2+}$ ,  $S_8^{2+}$ , and  $S_{16}^{2+}$  cations<sup>1-3</sup> and for several singly charged radical cations, of which only  $S_5^+$  has been positively identified.<sup>4</sup> So far, these singly charged species have only been observed in solution. They do not appear to be as stable as the doubly charged species and hence are not as well characterized. In contrast, all three of the dipositive cations have been obtained in the form of relatively stable solid salts such as  $S_4(SO_3F)_2$  and  $S_8(AsF_6)_2$ .<sup>1</sup>

In the case of  $S_8(AsF_6)_2$  a single-crystal X-ray crystallographic study has shown unequivocally that this cation has an exo-endo cyclic structure with a long transannular bond.<sup>5</sup> No crystallographic studies have been reported on salts of  $S_4^{2+}$ , although both the analogous  $Se_4^{2+}$  and  $Te_4^{2+}$  species have been shown by this method to have square-planar structures.<sup>6,7</sup> However, comparison of the Raman and electronic spectra of the  $S_4^{2+}$  cation with those of  $Se_4^{2+}$  and  $Te_4^{2+}$  clearly indicates that  $S_4^{2+}$  has the same structure.<sup>1,3,8</sup> The results of a study of the magnetic circular dichroism of  $S_4^{2+}$ ,  $Se_4^{2+}$ , and  $Te_4^{2+}$  in oleum solutions also lead to the same conclusion.<sup>9</sup>

The evidence for the third of the dipositive cations,  $S_{16}^{2+}$ , was not so conclusive. The existence of this ion was first proposed as a result of the isolation of a red solid from the reaction of sulfur and  $AsF_5$  in anhydrous HF solution.<sup>2</sup> From analytical data this solid appeared to have a composition corresponding to  $S_{16}(AsF_6)_2$ . The characteristic absorption spectrum of this ion in solution showed that it was also obtained during the oxidation of sulfur by  $S_2O_6F_2$  in  $HSO_3F$ , by either  $AsF_5$  or  $SbF_5$  in  $SO_2$ , or by oleum.<sup>1</sup> In a study of the progressive oxidation of sulfur by  $S_2O_6F_2$  in  $HSO_3F$  it was also observed that some unreacted sulfur always remained until sufficient oxidant had been added to give a ratio of sulfur to

$S_2O_6F_2$  of 16:1. Similarly, cryoscopic measurements on these solutions were also consistent with the formulation of this ion as  $S_{16}^{2+}$ .<sup>1</sup> During the past few years we have made a number of attempts to obtain stable crystals of an  $S_{16}^{2+}$  salt suitable for X-ray crystallographic studies, but none of these proved successful. Even when good crystalline material was obtained, it decomposed rapidly to give elemental sulfur. Quite recently it has been possible to grow some suitable and relatively stable red crystals with both needle and platelike habits from a solution of the material believed to be  $S_{16}(AsF_6)_2$  in a 2:1 mixture of  $SO_2$  and  $SO_2ClF$  at  $-25^\circ\text{C}$ . An X-ray crystallographic study of these crystals led to the surprising and unexpected result that the compound has the composition  $S_{19}(AsF_6)_2$ , i.e., that it is a salt of the  $S_{19}^{2+}$  cation rather than the  $S_{16}^{2+}$  cation. The original analytical data would not in fact distinguish clearly between  $S_{16}(AsF_6)_2$  and  $S_{19}(AsF_6)_2$ , and the possible existence of such a bizarre species was not envisaged at that time. The composition  $S_{16}^{2+}$  also appeared to be reasonable, not only because complete solution of sulfur in  $HSO_3F$  occurred when the sulfur to  $S_2O_6F_2$  ratio was 16:1 but also because it gave a plausible explanation for the existence of the radical ions that were observed in solution. Thus it was proposed that oxidation of sulfur occurred in the following stages:



Since then good ESR evidence has been obtained which shows that the species originally thought to be  $S_4^+$  is in fact the  $S_5^+$  cation.<sup>4</sup> This, along with the evidence presented in this paper that the proposed  $S_{16}^{2+}$  is in fact  $S_{19}^{2+}$ , shows that the above scheme was a much too facile description of the oxidation of sulfur, which must be a much more complicated process. Accordingly, we have made a further study by ESR and by absorption spectroscopy of the radicals formed in the oxidation of sulfur in  $SO_2$  as solvent with particular emphasis on the early stages of this process.

### Experimental Section

**Preparation of  $S_{19}(AsF_6)_2$ .** In a typical preparation 0.994 mmol (0.169 g) of arsenic pentafluoride (Ozark Mahoning Co.) was condensed onto 5.6 mmol (0.170 g) of dry sulfur (BDH) in about 25 cm<sup>3</sup> of a frozen 2:1 mixture of  $SO_2$  and  $SO_2ClF$  at  $-196^\circ\text{C}$ . The solvent was allowed to melt, and reaction occurred as the ampule warmed to room temperature. After about 3-4 h all of the sulfur had reacted

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to give a dark red-brown solution. The solution was then filtered and placed in a "freezer" at about  $-25^{\circ}\text{C}$ . Under these conditions crystallization proceeded slowly over a period of about 2 weeks. If crystallization was not carried out at low temperatures only very small crystals were obtained, which were not suitable for X-ray examination.

**X-ray Intensity Measurements and Crystal Data.** The major crystal forms obtained from these reactions were deep red needles, although in some samples thin plates were observed. The crystals were highly reactive and generally decomposed in a few minutes even when the ampules were opened inside a drybox in an atmosphere containing less than 2–3 ppm of moisture. Most of the sample crystals were found to be too small for study, but eventually three larger, apparently single crystals were sealed in Lindemann glass capillaries. The crystals were wedged by constricting the sides of the capillaries. Only one of these crystals lasted for any length of time, and all crystallographic examination of this crystal was performed with a Syntex P2<sub>1</sub> diffractometer. In subsequent preparations more crystals of a suitable size were obtained, although in each case it was found that the process of mounting the crystals in the capillaries introduced sufficient moisture so that surface attack and consequential loss of intensity of the diffracted spots from the crystals were more pronounced than with the crystal upon which the original data set was collected. Reflection profiles and axial photographs of the crystal used showed the absence of any obvious twinning and indicated that the crystal symmetry was triclinic.

**Crystal Data.**  $\text{S}_{19}(\text{AsF}_6)_2$ : triclinic;  $a = 7.536(2)$ ,  $b = 13.406(3)$ ,  $c = 27.226(5)$  Å;  $\alpha = 89.02(2)$ ,  $\beta = 91.58(2)$ ,  $\gamma = 93.24(2)^{\circ}$ ;  $V = 2744.9(10)$  Å<sup>3</sup>;  $d_{\text{calc}} = 2.39$  g cm<sup>-3</sup> for  $Z = 4$ ;  $fw = 986.98$ ;  $F(000) = 1912$ ; Mo  $K\alpha$  radiation;  $\lambda = 0.71069$  Å;  $\mu(\text{Mo } K\alpha) = 40.34$  cm<sup>-1</sup>; space group  $B\bar{1}$  (nonstandard setting of No. 2). The unit cell parameters were obtained from a least-squares refinement of the diffracting positions of 15 high angle ( $24^{\circ} < 2\theta < 26^{\circ}$ ) reflections. The Delaunay reduced primitive triclinic cell for this compound has  $a' = 7.536$  Å,  $b' = 14.025$  Å,  $c' = 13.406$  Å,  $\alpha' = 90.05^{\circ}$ ,  $\beta' = 93.28^{\circ}$ ,  $\gamma' = 104.00^{\circ}$ , and  $V = 1373$  Å<sup>3</sup> with  $Z = 2$  and is related to the above centered cell by the transformations  $a' = a$ ,  $b' = -1/2(a + c)$ ,  $c' = b$ , although for convenience the  $B$  centered cell was used throughout.

Data were collected to  $2\theta = 46^{\circ}$  in several shells by using graphite monochromated Mo  $K\alpha$  radiation. Reflections were measured by using  $\theta$ - $2\theta$  scans over a scan range ( $K\alpha_1 - 0.7^{\circ}$ ) to ( $K\alpha_2 + 0.7^{\circ}$ ) with a variable scan rate of 6.0–29.3<sup>o</sup>/min depending on the intensity of a preliminary count. Stationary background counts were recorded at each end of the scan, each for one-quarter of the scan time. The intensities of three standard reflections were monitored after every 60 reflections and showed a rapid decline in intensities over the first few hours of data collection. At the end of the first two shells of data, with  $2\theta < 30^{\circ}$  and  $30^{\circ} < 2\theta < 35^{\circ}$ , there was a short break of 2–3 h. After this period the decomposition had slowed, and the intensities of the standard reflections were virtually constant over the last shell of data collected. The crystal was recentered several times during and at the end of the data collection, with no significant change in the orientation matrix. By this time the crystal was beginning to show an appreciable change in color from red to yellow at its edges. We attribute the unusual behavior of the standards during the data collection to initial surface decomposition of the crystal caused by small traces of moisture remaining in the capillary. Presumably, when all traces of moisture had reacted or when the surface of the crystal had been covered by a layer of sulfur (the decomposition product) there was little further crystal decomposition and hence no further decrease in the intensities of the standards.

A total of 4277 reflections (including standards) were collected in a period of 36 h. Due to the sudden change in the rate of decomposition the data were separated into two scale groups. All reflections with  $2\theta < 35^{\circ}$  were included in the first scale group, and the intensities of these reflections were rescaled by using the linear equation  $I_c = I_0(1.0 + 0.010356t)$ , where  $t$  = time in hours. The maximum rescale factor using this equation was 1.1545. The remaining data, with  $35^{\circ} < 2\theta \leq 46^{\circ}$ , were not rescaled. Lorentz and polarization factors were applied to the data in both groups, after any corrections for decomposition. Since the crystal was approximately a cylinder of radius 0.06 mm and length 0.575 mm ( $\mu R = 0.242$ ) aligned with the needle axis  $a$  almost vertical, and in view of the large rescale factors required above, no absorption corrections were applied. A total of 2004 reflections with measured intensities greater than 3 times their standard error based on counting statistics were considered observed, and after averaging equivalent reflections resulted in a data

set of 1844 reflections, which was used in the final refinement.

**Structure Solution.** An initial statistical test using normalized structure factors ( $E_{hkl}$ 's) calculated on the basis of four molecules of  $\text{S}_{16}(\text{AsF}_6)_2$  in the unit cell was interpreted as indicating that the space group was acentric. The Patterson function was therefore solved for four independent arsenic atoms in  $B1$ . A subsequent Fourier had two major peaks which were initially assumed to be additional arsenic atoms. Subsequent maps showed that these were in fact sulfur atoms at the bridgehead positions of two  $\text{S}_7$  rings and that the molecule, contrary to expectations, was not  $\text{S}_{16}^{2+}$  but a 19 sulfur atom system,  $\text{S}_{19}^{2+}$ . Location of the fluorine atoms in the structure was hampered by the diffuse nature of some of the peaks, with peak heights being as low as  $2.4$  e/Å<sup>3</sup>. Block-diagonal least-squares refinement in the acentric space group of two independent  $\text{S}_{19}(\text{AsF}_6)_2$  molecules converged to  $R_1 (= \sum ||F_o| - |F_c|| / \sum |F_o|)$  of 0.086, using anisotropic temperature factors for the arsenic atoms. There was no significant difference between the "hands" of the structure. Furthermore, the model at this point clearly contained a pseudo center of symmetry, and there was poor agreement of related bond distances and bond angles between the two equivalent molecules, especially for the  $\text{AsF}_6^-$  anions. Transformation to the centric space group  $B\bar{1}$  and further refinement resulted in a significant improvement in the crystallographic residual as well as better geometries for the  $\text{AsF}_6^-$  groups. Block-diagonal least-squares refinement using three blocks with anisotropic temperature factors for the arsenic and sulfur atoms converged to  $R_1 = 0.076$ . However, the following difference Fourier contained several peaks up to  $2.5$  e/Å<sup>3</sup>, two of which were close to sulfur atoms with high temperature factors in one of the seven-membered rings. Subsequent refinement of a model with disorder at these positions improved  $R_1$  to 0.071. The optimum population parameters for the atoms involved in the alternative conformations of ring 1 of  $\text{S}_{19}^{2+}$  resulting from this disorder were found to be 0.80 and 0.20. The highest remaining peaks in the difference Fourier are around As(2) and have peak heights up to  $1.3$  e/Å<sup>3</sup>. It is clear from the temperature factors of the fluorines in this group that they are subject to considerable libration. Refinement of the fluorine atoms with anisotropic thermal parameters reduced the size of these peaks without significantly affecting the residual and so was not pursued further. A disordered model was similarly found to be unreasonable.

In the final cycles of refinement weights were calculated by using the expression  $w = xy$  where (i)  $x = (\sin \theta) / 0.22$  if  $\sin \theta < 0.22$ , otherwise  $x = 1$ , and (ii)  $y = F / 60$  if  $F < 60$  or  $y = 140 / F$  if  $F > 140$ , otherwise  $y = 1$ . Several cycles of block-diagonal least squares (three blocks) using this weighting scheme converged to  $R_1 = 0.071$  and  $R_2 = 0.082$  ( $R_2 = [\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2]^{1/2}$ ). In the final cycle of refinement no parameter shift was greater than 12% of its standard error, and a final difference Fourier was featureless with a maximum peak and a minimum trough of  $+1.26$  e/Å<sup>3</sup> and  $-0.98$  e/Å<sup>3</sup>, respectively, around As(2). The ratio between the two scale factors at the end of the refinement was 1.1422. A final comparison of the average  $w ||F_o| - |F_c||^2$  as a function of  $F_o$  and  $\sin \theta$  revealed no systematic trends.

As an independent check on the present structure and as confirmation that no other  $\text{S}_m^{n+}$  species were to be found in the samples prepared, several other crystals were sealed in capillaries and examined on the diffractometer. In each case the crystals of both needle and platelike habit were found to be triclinic with very similar cell dimensions to those given above. A data set was collected on the best of these crystals, which was a thick plate. The standards used in this re-collection were collected every 60 reflections (ca. every 30 min) and showed a continuous linear decrease in intensities over the period of data collection. The data were rescaled for this decomposition, and a  $N(Z)$  test using this second data set and the correct unit cell contents confirmed that the centric space group  $B\bar{1}$  was correct. Input of the final coordinates from the determination above gave  $R_1 = 0.195$  with the arsenic atoms having anisotropic temperature factors and  $R_1 = 0.185$  with all the sulfur atoms anisotropic. It is clear from these residuals that this data set was of poorer quality. The temperature factors of the disordered atoms S(3) and S(4) indicated that the same proportions of conformers were present in ring 1. Although the temperature factors of some of the fluorine atoms were exceedingly high, they still gave reasonable octahedral geometries around each of the arsenic atoms. The subsequent difference Fourier was also featureless. No further work is envisaged on this data set.

The atomic scattering factors for neutral As, S, and F in the analytical form were taken from ref 10. All calculations were

Table I. Atomic Coordinates ( $\times 10^4$ ) for  $S_{19}(AsF_6)_2$ 

atom	x	y	z	atom	x	y	z
As(1)	-4450.0 (28)	-2275.3 (15)	2648.5 (8)	S(15)	6147 (11)	4608 (6)	618 (3)
As(2)	506.4 (31)	2760.6 (16)	116.7 (8)	S(16)	7484 (9)	4240 (6)	1312 (3)
S(1)	4353 (10)	11615 (5)	1514 (3)	S(17)	6461 (9)	5056 (6)	1793 (3)
S(2)	5827 (9)	11651 (6)	943 (3)	S(18)	3983 (9)	4355 (5)	1972 (2)
S(3a) <sup>a</sup>	7291 (14)	10401 (10)	1109 (6)	S(19)	2762 (8)	4047 (4)	1336 (2)
S(3b) <sup>a</sup>	7244 (58)	10441 (42)	651 (17)	F(11)	-6604 (22)	-2016 (13)	2624 (6)
S(4a) <sup>a</sup>	6372 (17)	9449 (10)	578 (4)	F(12)	-2290 (20)	-2547 (11)	2683 (6)
S(4b) <sup>a</sup>	6214 (54)	9392 (30)	1086 (15)	F(13)	-5071 (19)	-3501 (10)	2639 (5)
S(5)	3873 (11)	8876 (5)	785 (3)	F(14)	-3882 (23)	-1043 (13)	2654 (6)
S(6)	2324 (8)	10019 (5)	645 (2)	F(15)	-4406 (23)	-2230 (13)	2020 (6)
S(7)	1934 (7)	10674 (4)	1324 (2)	F(16)	-4552 (20)	-2310 (11)	3264 (6)
S(8)	2395 (8)	9583 (4)	1850 (2)	F(21)	551 (34)	3231 (19)	-465 (10)
S(9)	-119 (8)	9007 (4)	1957 (2)	F(22)	991 (39)	2295 (22)	664 (11)
S(10)	-540 (8)	7929 (4)	1440 (2)	F(23)	1067 (27)	3921 (15)	287 (8)
S(11)	263 (9)	6656 (4)	1787 (2)	F(24)	64 (28)	1602 (16)	-58 (8)
S(12)	2720 (9)	6468 (4)	1543 (3)	F(25)	-1555 (54)	2925 (30)	66 (15)
S(13)	2239 (8)	5451 (4)	999 (2)	F(26)	2659 (45)	2610 (25)	77 (12)
S(14)	5088 (14)	5834 (6)	658 (3)				

Thermal Parameters in  $S_{19}(AsF_6)_2$ <sup>b</sup>

atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
As(1)	38.1 (14)	40.5 (13)	37.7 (14)	2.9 (10)	1.8 (10)	-7.2 (10)
As(2)	57.5 (16)	39.6 (14)	32.5 (13)	6.3 (11)	-7.8 (10)	-4.1 (9)
S(1)	90 (5)	58 (4)	71 (5)	-26 (4)	-11 (4)	-10 (3)
S(2)	55 (4)	91 (5)	108 (6)	-21 (4)	17 (4)	-1 (4)
S(3a)	55 (7)	137 (11)	142 (13)	29 (7)	-13 (7)	9 (9)
S(3b)	82 (30)	136 (44)	58 (28)	32 (28)	12 (21)	-4 (25)
S(4a)	122 (10)	123 (10)	84 (8)	69 (9)	51 (7)	13 (7)
S(4b)	89 (29)	81 (27)	90 (31)	56 (24)	36 (22)	29 (21)
S(5)	123 (7)	46 (4)	73 (5)	20 (4)	14 (4)	-13 (3)
S(6)	63 (4)	68 (4)	40 (4)	3 (3)	-15 (3)	-12 (3)
S(7)	43 (3)	35 (3)	45 (3)	5 (2)	11 (3)	6 (2)
S(8)	64 (4)	47 (3)	37 (3)	5 (3)	3 (3)	3 (3)
S(9)	64 (4)	44 (3)	51 (4)	3 (3)	21 (3)	-5 (3)
S(10)	53 (4)	51 (4)	54 (4)	6 (3)	3 (3)	-4 (3)
S(11)	95 (5)	31 (3)	60 (4)	2 (3)	25 (4)	1 (3)
S(12)	64 (4)	44 (4)	84 (5)	16 (3)	-25 (4)	-25 (3)
S(13)	51 (4)	42 (3)	50 (3)	10 (3)	-10 (3)	-10 (3)
S(14)	154 (8)	75 (5)	104 (7)	21 (5)	75 (6)	41 (5)
S(15)	86 (5)	99 (6)	72 (5)	16 (4)	22 (4)	-8 (4)
S(16)	59 (5)	77 (5)	108 (6)	5 (4)	-1 (4)	-19 (4)
S(17)	62 (4)	91 (5)	78 (5)	-3 (4)	-15 (4)	-26 (4)
S(18)	83 (5)	65 (4)	44 (4)	-7 (4)	-5 (3)	8 (3)
S(19)	55 (4)	36 (3)	57 (4)	-6 (3)	2 (3)	-1 (3)

Isotropic Temperature Factors

atom	$U, \text{\AA}^2$	atom	$U, \text{\AA}^2$	atom	$U, \text{\AA}^2$
F(11)	101 (5)	F(15)	103 (5)	F(23)	129 (7)
F(12)	86 (4)	F(16)	87 (5)	F(24)	134 (7)
F(13)	77 (4)	F(21)	165 (9)	F(25)	251 (16)
F(14)	105 (5)	F(22)	190 (11)	F(26)	210 (12)

<sup>a</sup> Atoms S(3a) and S(4a) have population parameters of 0.80; atoms S(3b) and S(4b) have population parameters of 0.02. <sup>b</sup> Anisotropic thermal parameters in the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}khlb^*c^*)]$ .

performed on a CDC 6400 computer using the series of programs in the XRAY 71 system<sup>11</sup> and some local programs. The final atomic positional coordinates and temperature factors for the first refinement are given in Table I. Interatomic distances and angles and dihedral angles in the  $S_{19}^{2+}$  cation are given in Table II, and some selected inter- and intramolecular contact distances are listed in Table III. A tabulation of observed and calculated structure factors is available.<sup>12</sup>

**Electron Spin Resonance Measurements.** ESR spectra were recorded on a JEOLCO Model JES-3BS-X spectrometer. The  $g$  values were obtained by comparison with the third line ( $g = 1.981$ ), counted from the high-field side, of trace  $Mn^{2+}$  in solid MgO. They are considered accurate to  $\pm 0.001$ .

**Spectrophotometric Measurements.** Absorption spectra were obtained by using 0.5-cm rectangular silica cells and were recorded on

a Cary 14 instrument against a reference cell containing solvent.

## Results and Discussion

The structure determination shows that the compound originally formulated as  $S_{16}(AsF_6)_2$  contains instead a 19 sulfur atom cation,  $S_{19}^{2+}$ . This new cation has no symmetry and consists of two seven-membered sulfur rings linked by a five-membered sulfur atom bridge (Figure 1). There are several notable differences between the two rings in the cation. In particular, ring 1 exists in both major and minor conformations as a consequence of the disordered S(3) and S(4) positions. Furthermore, the major conformation of this ring is significantly different from that of ring 2. This is discussed in more detail below.

The sulfur-sulfur distances in  $S_{19}^{2+}$  vary greatly from 1.87 to 2.38 Å while the angles vary from 91.9 to 127.6°. The largest variations of bond lengths and angles are found in the seven-membered rings, since the distances and angles in the

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965.

(11) "X-Ray 71 System of Crystallographic Programs"; Technical Report TR-192; University of Maryland, College Park, Md.

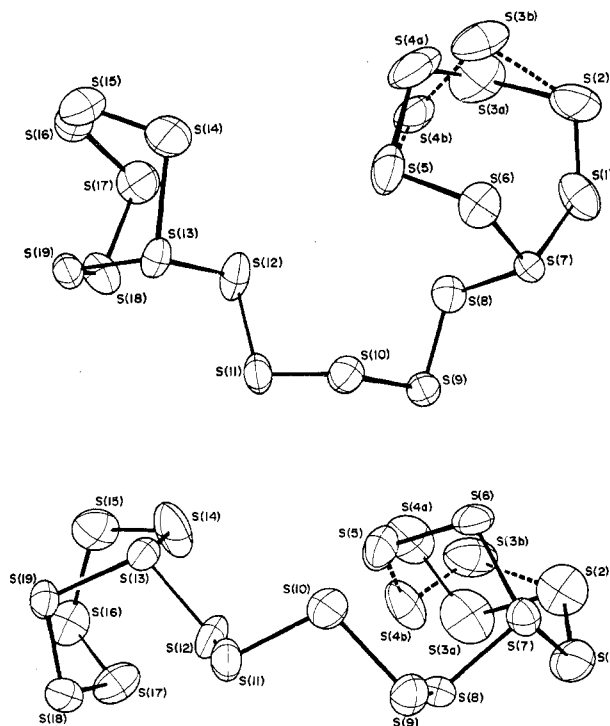
(12) Supplementary material.

Table II. Bond Distances and Bond Angles for  $S_{19}(AsF_6)_2$  with Standard Deviations in Parentheses

Bond Lengths (Å)			
S(1)-S(2)	1.934 (11)	S(9)-S(10)	2.039 (8)
S(2)-S(3a)	2.094 (15)	S(10)-S(11)	2.049 (8)
S(2)-S(3b)	2.165 (54)	S(11)-S(12)	2.015 (10)
S(3a)-S(4a)	2.027 (19)	S(12)-S(13)	2.041 (8)
S(3b)-S(4b)	1.963 (64)	S(13)-S(14)	2.389 (12)
S(4a)-S(5)	2.082 (15)	S(14)-S(15)	1.873 (12)
S(4b)-S(5)	2.016 (41)	S(15)-S(16)	2.179 (11)
S(5)-S(6)	2.003 (10)	S(16)-S(17)	1.924 (11)
S(6)-S(7)	2.096 (8)	S(17)-S(18)	2.108 (10)
S(1)-S(7)	2.212 (9)	S(18)-S(19)	1.977 (8)
S(7)-S(8)	2.066 (8)	S(19)-S(13)	2.132 (8)
S(8)-S(9)	2.031 (8)		
S(3a)···S(3b)	1.248 (50)	S(3b)···S(4a)	1.464 (55)
S(3a)···S(4b)	1.539 (41)	S(4a)···S(4b)	1.392 (43)
As(1)-F(11)	1.679 (17)	As(2)-F(21)	1.694 (26)
-F(12)	1.687 (16)	-F(22)	1.645 (30)
-F(13)	1.683 (14)	-F(23)	1.659 (21)
-F(14)	1.683 (18)	-F(24)	1.646 (22)
-F(15)	1.714 (18)	-F(25)	1.583 (41)
-F(16)	1.680 (15)	-F(26)	1.653 (34)
Bond Angles (Deg)			
S(7)-S(1)-S(2)	106.7 (4)	S(6)-S(7)-S(8)	106.0 (3)
S(1)-S(2)-S(3a)	98.8 (6)	S(7)-S(8)-S(9)	100.9 (3)
S(1)-S(2)-S(3b)	127.6 (14)	S(8)-S(9)-S(10)	105.1 (4)
S(2)-S(3a)-S(4a)	101.1 (7)	S(9)-S(10)-S(11)	104.1 (4)
S(2)-S(3a)-S(4b)	114.9 (17)	S(10)-S(11)-S(12)	105.3 (4)
S(2)-S(3b)-S(4a)	121.3 (26)	S(11)-S(12)-S(13)	102.4 (4)
S(2)-S(3b)-S(4b)	96.2 (23)	S(12)-S(13)-S(14)	91.9 (3)
S(3a)-S(4a)-S(5)	107.2 (7)	S(12)-S(13)-S(19)	104.8 (3)
S(3b)-S(4a)-S(5)	130.2 (20)	S(14)-S(13)-S(19)	98.6 (3)
S(3a)-S(4b)-S(5)	136.5 (26)	S(13)-S(14)-S(15)	105.5 (5)
S(3b)-S(4b)-S(5)	108.4 (23)	S(14)-S(15)-S(16)	110.6 (5)
S(4a)-S(5)-S(6)	103.0 (5)	S(15)-S(16)-S(17)	105.2 (5)
S(4b)-S(5)-S(6)	109.6 (12)	S(16)-S(17)-S(18)	107.1 (4)
S(5)-S(6)-S(7)	106.2 (4)	S(17)-S(18)-S(19)	105.6 (4)
S(6)-S(7)-S(1)	107.8 (3)	S(18)-S(19)-S(13)	106.1 (3)
S(1)-S(7)-S(8)	95.1 (3)		
F(11)-As(1)-F(12)	178.9 (8)	F(21)-As(2)-F(22)	165.9 (14)
-F(13)	89.0 (8)	-F(23)	85.4 (11)
-F(14)	89.5 (8)	-F(24)	94.1 (12)
-F(15)	90.0 (8)	-F(25)	83.9 (17)
-F(16)	88.4 (8)	-F(26)	87.6 (14)
F(12)-As(1)-F(13)	90.5 (7)	F(22)-As(2)-F(23)	92.7 (12)
-F(14)	90.9 (8)	-F(24)	87.0 (13)
-F(15)	91.0 (8)	-F(25)	110.2 (18)
-F(16)	90.7 (7)	-F(26)	78.4 (16)
F(13)-As(1)-F(14)	178.5 (8)	F(23)-As(2)-F(24)	176.9 (11)
-F(15)	90.9 (8)	-F(25)	94.9 (16)
-F(16)	89.3 (7)	-F(26)	86.7 (14)
F(14)-As(1)-F(15)	88.8 (8)	F(24)-As(2)-F(25)	88.1 (16)
-F(16)	91.0 (8)	-F(26)	90.2 (14)
F(15)-As(1)-F(16)	178.4 (8)	F(25)-As(2)-F(26)	171.2 (19)
Dihedral Angles (Deg) <sup>a</sup>			
ring 1		ring 2	
S(7)-S(1)-S(2)-S(3a)	-89.7	S(12)-S(13)-S(14)-S(15)	+126.3
S(7)-S(1)-S(2)-S(3b)	-69.6	S(19)-S(13)-S(14)-S(15)	+21.1
S(1)-S(2)-S(3a)-S(4a)	+112.1	S(13)-S(14)-S(15)-S(16)	-85.5
S(1)-S(2)-S(3b)-S(4b)	+7.9	S(14)-S(15)-S(16)-S(17)	+19.1
S(2)-S(3a)-S(4a)-S(5)	103.1	S(15)-S(16)-S(17)-S(18)	+79.1
S(2)-S(3b)-S(4b)-S(5)	+95.0	S(16)-S(17)-S(18)-S(19)	-48.6
S(3a)-S(4a)-S(5)-S(6)	+75.1	S(17)-S(18)-S(19)-S(13)	-66.7
S(3b)-S(4b)-S(5)-S(6)	-53.9	S(18)-S(19)-S(13)-S(14)	+82.0
S(4a)-S(5)-S(6)-S(7)	-78.5	S(18)-S(19)-S(13)-S(12)	+12.3
S(4b)-S(5)-S(6)-S(7)	119.4		
S(5)-S(6)-S(7)-S(1)	+101.4		
S(6)-S(7)-S(1)-S(2)	+8.0		
S(5)-S(6)-S(7)-S(8)	+95.0		
S(2)-S(1)-S(7)-S(8)	+116.6		
Bridging Group Angles (Deg)			
S(1)-S(7)-S(8)-S(9)	+154.8	S(9)-S(10)-S(11)-S(12)	100.2
S(6)-S(7)-S(8)-S(9)	-96.0	S(10)-S(11)-S(12)-S(13)	-97.9
S(7)-S(8)-S(9)-S(10)	+92.7	S(11)-S(12)-S(13)-S(14)	+163.9
S(8)-S(9)-S(10)-S(11)	+90.7	S(11)-S(12)-S(13)-S(19)	-97.7

<sup>a</sup> As defined by: Bucourt, R. *Top. Stereochem.* 1974, 8, 159.Table III. Significant Contact Distances ( $S\cdots S < 3.6$  Å;  $S\cdots F < 3.05$  Å)

Intramolecular			
S(1)···S(3)	3.06	S(9)···S(11)	3.22
S(1)···S(4b)	3.59	S(10)···S(12)	3.23
S(1)···S(6)	3.48	S(11)···S(13)	3.16
S(1)···S(8)	3.16	S(12)···S(14)	3.19
S(2)···S(4a)	3.18	S(12)···S(17)	3.53
S(2)···S(4b)	3.08	S(12)···S(18)	3.23
S(2)···S(6)	3.42	S(12)···S(19)	3.31
S(2)···S(7)	3.33	S(13)···S(15)	3.41
S(3a)···S(5)	3.31	S(13)···S(18)	3.29
S(3b)···S(5)	3.23	S(14)···S(16)	3.34
S(4a)···S(6)	3.20	S(14)···S(17)	3.40
S(4b)···S(6)	3.29	S(14)···S(19)	3.43
S(5)···S(7)	3.28	S(15)···S(17)	3.26
S(5)···S(8)	3.31	S(15)···S(19)	3.30
S(6)···S(8)	3.32	S(16)···S(18)	3.25
S(7)···S(9)	3.16	S(16)···S(19)	3.56
S(8)···S(10)	3.23	S(17)···S(19)	3.25
Intermolecular <sup>a</sup>			
S(1)···S(19) <sup>I</sup>	3.56	S(4b)···S(10) <sup>II</sup>	3.33
S(3a)···S(7) <sup>II</sup>	3.53	S(11)···S(17) <sup>IV</sup>	3.48
S(3a)···S(9) <sup>II</sup>	3.56	S(7)···F(22) <sup>I</sup>	2.91
S(4a)···S(6) <sup>III</sup>	3.55	S(12)···F(15) <sup>V</sup>	2.99
		S(13)···F(23)	2.93

<sup>a</sup> Roman numerals as superscripts refer to atoms related to the position  $x, y, z$  by the transformations: (I)  $x, 1+y, z$ ; (II)  $1+x, y, z$ ; (III)  $1-x, 2-y, -z$ ; (IV)  $-1+x, y, z$ ; (V)  $1+x, 1+y, z$ .Figure 1. Two views of the  $S_{19}^{2+}$  cation. Thermal ellipsoids are drawn at the 50% probability level.

five-membered sulfur bridge (average S-S = 2.04 Å, average S-S-S = 103.6°) vary only slightly and are comparable to the bond lengths and angles in  $S_8$  (2.048 Å, 107.4–109.1°)<sup>13</sup> and  $S_8^{2+}$  (2.04 Å, 91.5–104.6°).<sup>5</sup> It should be noted that the distances in  $S_{19}^{2+}$  are uncorrected for any thermal effects. It is clear from Table IV that some of the sulfur atoms in  $S_{19}^{2+}$  have significant root-mean-square vibrational amplitudes so that some of the quoted distances are likely to be shortened

(13) Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* 1977, 99, 760.

Table V. Thermal Corrections to Bond Lengths (Å) in  $S_{19}^{2+}$ <sup>a</sup>

bond <sup>b</sup>	obsd	min	max	rid	unc
S(1)–S(2)	1.934 (11)	1.935	2.094	1.946	2.014
S(2)–S(3a)	2.094 (15)	2.097	2.280	2.118	2.189
S(2)–S(3b)	2.166 (54)	2.166	2.325	2.174	2.246
S(4a)–S(3a)	2.026 (19)	2.027	2.200	2.033	2.113
S(3b)–S(4b)	1.963 (64)	1.963	2.139	1.968	2.051
S(5)–S(4a)	2.082 (15)	2.084	2.232	2.099	2.158
S(4b)–S(5)	2.016 (41)	2.016	2.130	2.018	2.073
S(6)–S(5)	2.003 (10)	2.006	2.141	2.021	2.074
S(7)–S(6)	2.095 (8)	2.097	2.193	2.107	2.145
S(7)–S(8)	2.066 (8)	2.067	2.161	2.071	2.114
S(7)–S(1)	2.212 (9)	2.217	2.320	2.234	2.268
S(8)–S(9)	2.032 (8)	2.032	2.125	2.036	2.078
S(9)–S(10)	2.040 (8)	2.040	2.148	2.040	2.094
S(10)–S(11)	2.050 (8)	2.050	2.166	2.058	2.108
S(11)–S(12)	2.015 (10)	2.015	2.126	2.016	2.071
S(13)–S(12)	2.041 (9)	2.042	2.167	2.052	2.105
S(13)–S(14)	2.388 (12)	2.397	2.513	2.422	2.455
S(15)–S(14)	1.873 (12)	1.875	2.095	1.894	1.985
S(16)–S(15)	2.179 (11)	2.179	2.319	2.184	2.249
S(17)–S(16)	1.925 (11)	1.925	2.095	1.928	2.010
S(18)–S(17)	2.108 (9)	2.109	2.240	2.116	2.174
S(19)–S(18)	1.977 (8)	1.979	2.097	1.990	2.038
S(13)–S(19)	2.132 (8)	2.132	2.226	2.134	2.179

<sup>a</sup> Following the treatment of Busing and Levy (*Acta Crystallogr.*, 1964, 17, 142). The five columns in the table are the observed bond lengths and the values after thermal corrections using the minimum, maximum, riding, and uncorrelated models. <sup>b</sup> The ordering of the atoms is such that, in the riding model, the second atom is assumed to be riding on the first.

by thermal effects, particularly in the flexible seven-membered rings. Thermal corrections to the bond lengths in  $S_{19}^{2+}$  following the treatment of Busing and Levy<sup>14</sup> have therefore been calculated by using the local program STREP and are included in Table V. Although it is not possible to decide which model will best describe the librations in the  $S_{19}^{2+}$  cation, it may be noted that the same qualitative ordering of the thermally corrected bond lengths in the two rings of  $S_{19}^{2+}$  is preserved whichever model is used, although the significance of some of the differences between individual values is somewhat reduced. This does not, however, affect the following discussion of the seven-membered rings in the  $S_{19}^{2+}$  cation.

The five atoms in the bridging group in  $S_{19}^{2+}$  have an all-cis arrangement with atoms S(8), S(9), S(11), and S(12) lying in a plane and atoms S(7), S(10), and S(13) deviating from this plane by  $-1.62$ ,  $-1.25$ , and  $-1.33$  Å, respectively. It should be noted that this arrangement of the bridging sulfur atoms in  $S_{19}^{2+}$  is a recognizable fragment of several of the higher neutral sulfur allotropes such as  $S_{12}$ ,  $S_{18}$ , and  $S_{20}$ .<sup>15,16</sup> However, the conformations of the known polysulfide anions, which form unbranched nonlinear chains with trans or cis-trans arrangements of the sulfur atoms, and the helical conformation of the sulfur chains in  $S_{\infty}$  are obviously different.<sup>17-19</sup>

In both rings of  $S_{19}^{2+}$  the bonds formed by the three-coordinate sulfur atoms are considerably longer (average 2.26 Å in ring 2 and 2.16 Å in ring 1) than the average length of the remaining bonds (2.01 Å in ring 2 and 2.07 Å in ring 1). In each case one of these bonds is the longest in the ring, 2.39 Å in ring 2 and 2.21 Å in ring 1, and adjacent to this long bond one finds the shortest bond in the ring, 1.87 Å in ring 2 and 1.93 Å in ring 1. The remaining bonds then alternate in length around the ring, the alternations being appreciably larger in

Table VI. Intramolecular Contacts (Å) Related to the Cube and Cuneane Structures

bonds	intramolecular contact			
	$S_7$	$S_7I^+$	$S_7O$	$S_{19}^{2+}$ (ring 1)
14	3.283	3.30 <sup>a</sup>	3.239	3.31
58	3.355	3.29 <sup>a</sup>	3.328	3.42
37		3.384 (S...I)	2.952 (S...O)	
34				3.31
bonds	$S_{19}^{2+}$ (ring 2)	bonds	$S_{19}^{2+}$ (ring 2)	
12	3.53	25	3.19	
34	3.25	24	3.23	
78	3.30			

<sup>a</sup> Distances kindly provided by Dr. J. Passmore, personal communication.

ring 2 than in ring 1. Similar bond length alternations have been observed in all of the other known seven-membered sulfur rings, i.e.,  $\delta S_7$ ,<sup>20</sup>  $S_7O$ ,<sup>21</sup> and  $S_7I^+$ ,<sup>22</sup> and also in  $S_8O$ .<sup>23</sup> It has been observed by Steudel<sup>20</sup> that there is a dependence of the S–S bond length between two divalent sulfur atoms in these ring systems upon the arithmetic mean of the internuclear distances of the neighboring bonds.<sup>24,25</sup> Sulfur rings containing bonds of approximately equal lengths ( $S_6$ ,  $S_8$ ,  $S_{12}$ ) have points close to a discontinuity in this graph. However, when a charge is introduced into the rings as in  $S_7I^+$  and the two rings of  $S_{19}^{2+}$  this relationship breaks down, and the resulting points are scattered below the lines relating the bond lengths in the other rings. An alternative treatment of the bond-length alternations in  $S_{19}^{2+}$  and related rings is given below.

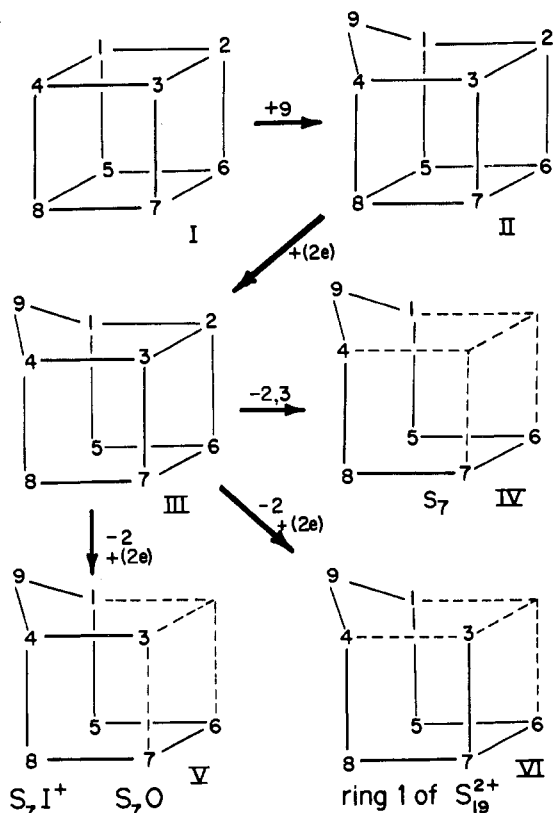
The major conformation of ring 1 is "twist-chair", being somewhat distorted from the regular chair conformation of  $\delta S_7$ .<sup>20</sup> Both ring 2 and the minor component of ring 1 have "twist-boat" conformations. This is the first time that a boat conformation has been observed for a seven-membered sulfur ring.

It has been shown elsewhere<sup>26</sup> that the structures of a large number of cage and ring compounds can be related to a small number of basic cluster structures. These are the tetrahedron, the trigonal prism, the cube, and the cuneane structure for clusters up to eight atoms. Thus the chair conformation of  $S_7$  can be related to the cube by carrying out the following transformations: (1) One edge of cube I is bridged by the additional atom (9) to give II. (2) One of the cube edges (5–8) is broken by the addition of an electron pair to give III. (3) Two atoms (2 and 3) are removed to give IV.

A similar procedure can be used to derive the structures of  $S_7I^+$ ,  $S_7O$ , and ring 1 of  $S_{19}^{2+}$  (major conformation). Starting with III atom 2 is removed and bond 3–7 is broken to give V in the case of  $S_7I^+$  and  $S_7O$ . The three-coordinate atom in the chair conformation of ring 1 of  $S_{19}^{2+}$  is at position 7 rather than 4 but occupies the same general position relative to the ring. This structure can be derived simply by breaking bond

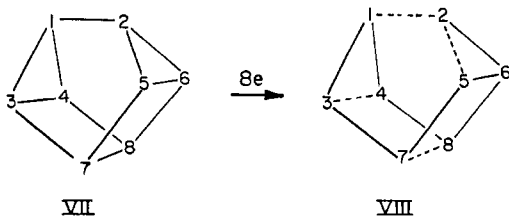
- (14) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* 1964, 17, 142.  
 (15) Kutoglu, A.; Hellner, E. *Angew. Chem., Int. Ed. Engl.* 1966, 5, 965.  
 (16) Schmidt, M.; Wilhelm, E.; Debaerdemaeker, T.; Hellner, E.; Kutoglu, A. *Z. Anorg. Allg. Chem.* 1974, 405, 153.  
 (17) Rahman, R.; Safe, S.; Taylor, A. Q. *Rev., Chem. Soc.* 1970, 24, 208.  
 (18) Meyer, B. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 287.  
 (19) Kelly, B.; Woodward, P. J. *Chem. Soc., Dalton Trans.* 1976, 1314.

- (20) Steudel, R.; Reinhardt, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 715.  
 (21) Steudel, R.; Reinhardt, R.; Sandow, T. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 716.  
 (22) Passmore, J.; Taylor, P.; Whidden, T. K.; White, P. J. *Chem. Soc., Chem. Commun.* 1976, 689. In view of the present structures of  $S_{19}^{2+}$  it is not surprising that the reaction of " $(S_{16}^{2+})(AsF_6)_2$ " and iodine gave  $S_7I^+$  and not  $S_8I^+$ .  
 (23) Luger, P.; Bradaczek, H.; Steudel, R.; Rebsch, M. *Chem. Ber.* 1976, 109, 3441.  
 (24) Similar correlations between the sulfur–sulfur bond length in dialkyl and diaryl disulfides and the dihedral angles involving the alkyl and aryl groups have been noted by, for example: Hordvik, A. *Acta Chem. Scand.* 1966, 20, 1885. Raghavan, N. V.; Seff, K. *Acta Crystallogr., Sect. B* 1977, 33, 386.  
 (25) Steudel, R. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 655.  
 (26) Gillespie, R. J. *Chem. Soc. Rev.* 1979, 8, 315.



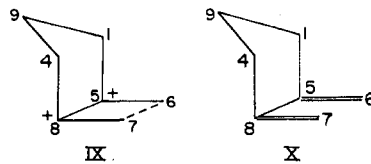
3-4 rather than 3-7 to give VI. It should be noted, however, that the structure of this ring is somewhat distorted from the "ideal" chair conformation that is observed in  $S_7$ .

Ring 2 of  $S_{19}^{2+}$  has an approximate boat conformation. The "ideal" boat conformation can be derived from the cuneane structure VII by breaking bonds 3-4, 7-8, 2-5, and 1-2 to give VIII.



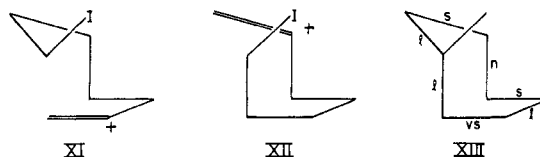
In this formalism, the structures all retain the approximate form of the cluster from which they are derived because the broken bonds still represent weak attractive interactions. This is discussed in more detail elsewhere,<sup>26</sup> but the presence of these attractions is shown by the contact distances between the corresponding atoms which are all considerably less than the van der Waals contact distances and are some of the shortest intramolecular contacts in each of the structures (Table VI). In addition to the four predicted short contacts in ring 2 of  $S_{19}^{2+}$  there is an additional contact (2-4) which reflects the distortion of the ring from an ideal boat conformation.

It is a remarkable feature of  $S_7$  that it is the only homocyclic sulfur ring that shows large variations in bond lengths (1.993-2.181 Å). Where such bond length alternations occur in other homocyclic sulfur rings, they are very small (e.g., 2.047-2.071 Å in  $S_{10}^{2+}$ ). This large bond length alternation in  $S_7$  can be rationalized in the following manner. If commencing with structure II bond 7-6 is broken instead of 5-8 and atoms 2 and 3 are removed structure IX is obtained. The



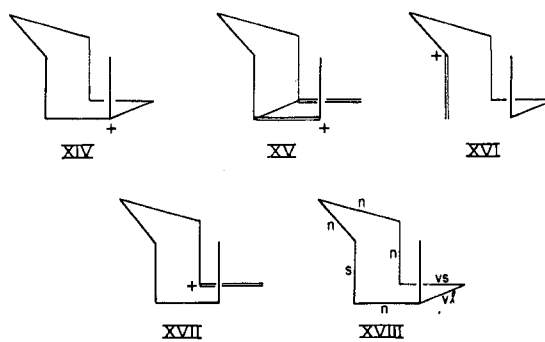
formal charges can then be eliminated by electron delocalization from atom 7 to 8 and from 6 to 5, thus transforming bonds 5-6 and 7-8 into double bonds to give X. If it is then assumed that IX and X are resonance forms for  $S_7$  with IX being the most important, we obtain an explanation of the fact that bond 6-7 is long and bonds 5-6 and 7-8 are rather short. We also note that structure X is consistent with the shortness of the 5-8 intramolecular contact. It is noteworthy that the dihedral angle 5678 is zero and thus all the electron pairs, both bonding and nonbonding, on atoms 6 and 7 are eclipsed. It is reasonable, therefore, to associate the length of the 6-7 bond with this zero dihedral angle. The perturbation caused by this long bond is apparently then propagated round the ring and produces an alternation in bond lengths which diminishes with distance from the perturbation. However, the mechanism by which this alternation of bond lengths is produced is not entirely clear.

The bond lengths in  $S_7I^+$  and  $S_7O$  and the  $S_7$  rings in  $S_{19}^{2+}$  (Figures 2 and 3), as well as in  $S_8O$ , show clearly that the introduction of a three-coordinate sulfur into a sulfur ring also causes a considerable perturbation in the bond lengths. In every case the two ring bonds formed by the three-coordinate sulfur are considerably longer than the other bonds in the ring. The adjacent bonds are much shorter and a bond length alternation then continues around the ring. The fact that the bonds adjacent to the three-coordinate sulfur are always increased in length suggests that they may be represented by valence-bond structures having no bond in these positions, e.g., structures XI and XII for  $S_7I^+$ , which also serve to delocalize the positive charge in the ring.



If the structures V, X, XI, and XII are assumed to all contribute equally to the actual structure, we conclude that the bonds will vary in length as in XIII. Thus the bonds may be classified as long (l), normal (n), short (s), and very short (vs). Comparison with the observed bond distances in  $S_7I^+$  and  $S_7O$  is made in Table VII.

For ring 1 in  $S_{19}^{2+}$  the three-coordinate atom is in a different position and structures XIV to XVII must be considered. The



bond length variations in XVIII are then predicted. It is assumed that the bond that is predicted to be long in XVI and short in XV will have an approximately "normal" length. Comparison with the observed bond distances is made in Table

(27) Reinhardt, R.; Steudel, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 57.

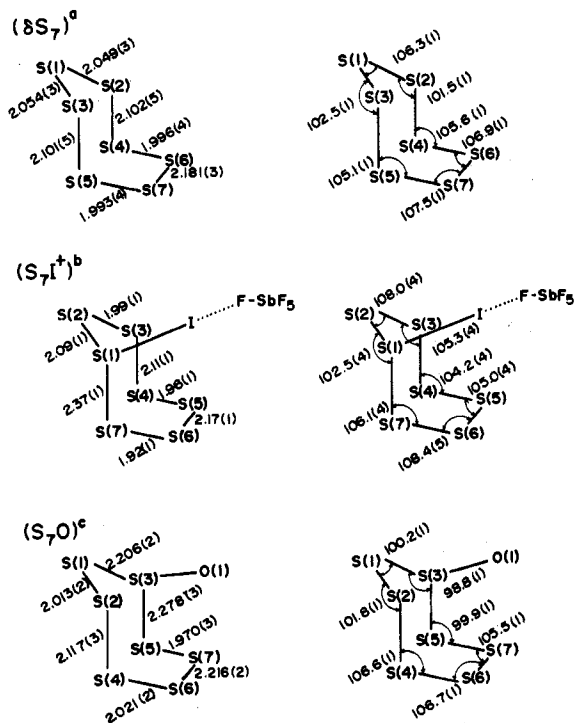


Figure 2. A comparison of the bond lengths (Å) and bond angles (deg) in the known seven-membered sulfur rings: (a) ref 20; (b) ref 22; and (c) ref 21.

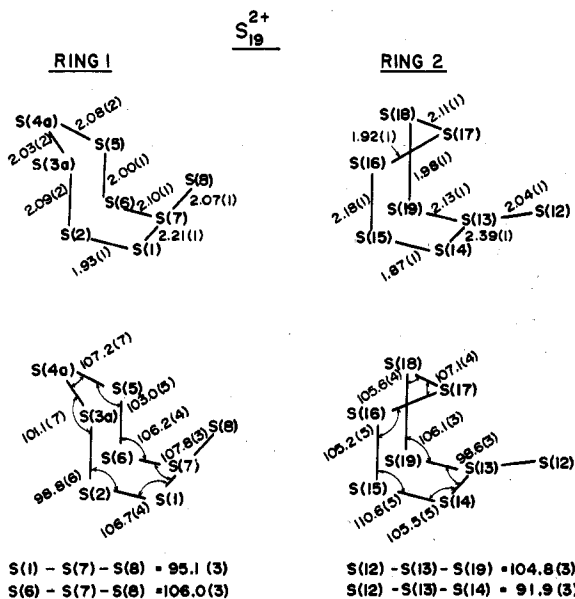


Figure 3. Bond lengths and angles in  $S_{19}^{2+}$  (only the major conformation of ring 1 has been included).

VII. Although this rather crude treatment does not account for all the bond length variations, it does nevertheless seem to account for the principal bond length variations, and in particular it correctly predicts the short and the long bonds. Although the conformation of the ring is different, the same types of resonance structures also apply to the boat conformation of ring 2 in  $S_{19}^{2+}$ . It is noticeable that the variations in bond length are greater in ring 2, which has the boat conformation, than in ring 1, which has the chair conformation. Perhaps this can be associated with the more compact nature of the boat conformation and consequently the greater interactions between the bonds.

At present it is not possible to explain the significant differences in the conformations of rings 1 and 2 in  $S_{19}^{2+}$ . As

Table VII. Predicted and Observed Bond Length Variations (Å) in  $S_7I^+$ ,  $S_7O$ , and  $S_{19}^{2+}$

predicted length	obsd length	
	$S_7I^+$	$S_7O$
l	2.37, 2.17, 2.09	2.28, 2.22, 2.21
n	2.11	2.12
s	1.99, 1.96	2.01, 2.02
vs	1.92	1.97

predicted length	obsd length	
	$S_7$ (chair)ring in $S_{19}^{2+}$	$S_7$ (boat)ring in $S_{19}^{2+}$
vl	2.21	2.39
n	2.03, 2.08, 2.09, 2.10 (av 2.07)	1.92, 2.11, 2.13, 2.18 (av 2.08)
s	2.00	1.98
vs	1.93	1.87

the energy differences between the boat and chair conformations would be expected to be small, the different environments of the two rings may be responsible for their different conformations. It is apparent from Figure 1 and the dihedral angles involving S(7) and S(13) that the two rings are rotated significantly with respect to each other and to the bridging group. Thus ring 2 is rotated about S(12)–S(13) so that the contacts S(12)–S(18) and S(12)–S(17) of 3.32 and 3.53 Å, respectively, are rather short, and this has already been discussed in the derivation of the conformation of ring 2.<sup>28</sup> Although there are differences in the bond angles at the two three-coordinate positions, between the dihedral angles S(1)–S(7)–S(8)–S(9) (+154.8°) and S(11)–S(12)–S(13)–S(14) (+163.9°), and some contact distances between atoms in the bridge and those in the two rings (excluding next-neighbor contacts), it is not possible to suggest which of these differences, if any, are responsible for the different ring conformations. Similarly, intercation contacts are for the most part greater than van der Waals distances (>~3.6 Å) with the exception of S(4b)···S(10)<sup>II</sup> (3.33 Å) and S(11)···S(17)<sup>IV</sup> (3.48 Å).

Of the two  $AsF_6^-$  groups in the asymmetric unit, that involving As(1) is a fairly well-defined octahedron with an average As–F distance of 1.69 Å and bond angles close to 90 and 180°, in good agreement with previously reported values.<sup>29</sup> The second  $AsF_6^-$  group is, however, not so well-defined with the As–F distances ranging from 1.58 (4) to 1.69 (3) Å and the cis F–As–F angles ranging from 78.4 to 110.2°, although the deviations of bond distances and bond angles from their ideal values do correlate with the thermal parameters of the fluorines. The packing of the molecules is shown in Figure 4 and the closest anion–cation contacts are 2.91, 2.93, and 2.93 Å for S(7)···F(23), S(13)···F(23), and S(12)···F(15), respectively.

#### The ESR and Absorption Spectra of Solutions Prepared by the Oxidation of Sulfur with $AsF_5$ in $SO_2$ as Solvent.

In the light of the present study of the  $S_{19}^{2+}$  cation and the recent identification of the  $S_5^+$  radical cation,<sup>4</sup> it is apparent that the oxidation of sulfur is a considerably more complicated process than originally proposed. Much of the earlier work, particularly on the radical cation, was carried out in oleum solutions.<sup>4,30–37</sup> These solutions are not as stable as the solvent

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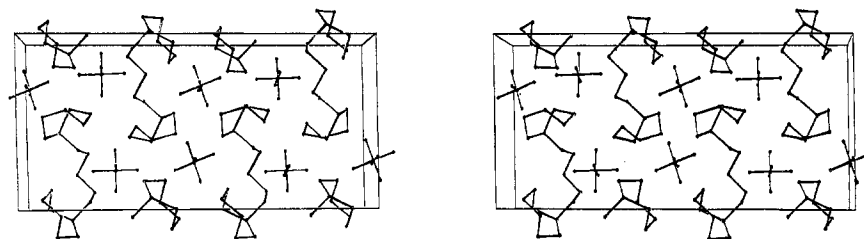


Figure 4. Stereoscopic view of the packing in  $S_{19}(AsF_6)_2$  down  $a$ . The origin is in the top left-hand corner of the diagram.

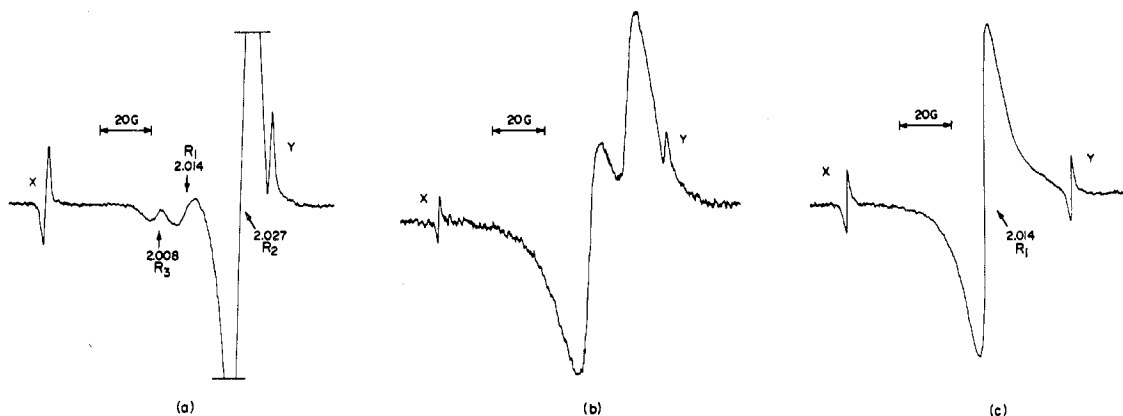
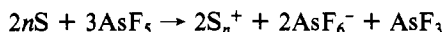


Figure 5. Typical ESR spectra in the progressive oxidation of sulfur with  $AsF_5$  in  $SO_2$ : (a) at all ratios of  $n$  between 12 and  $\sim 8$ ; (b) at  $n = \sim 4$ ; and (c) at  $n = \sim 2$ . X and Y are signals from the  $Mn^{2+}$  reference.

is also the oxidant and sulfur is slowly but continuously oxidized through the various cations to sulfur dioxide. We have, therefore, reinvestigated the oxidation of sulfur in the non-oxidizing solvent  $SO_2$  by using controlled amounts of  $AsF_5$  as the oxidizing agent and have followed the reaction by means of ESR and absorption spectroscopy. The reactions between sulfur and  $AsF_5$  can be summarized by the general equation



Here the formula  $S_n^+$  is not meant to imply that species with all possible values of  $n$  are produced. Rather it represents simply the average composition of all the sulfur cations,  $S_n^+$  and  $S_{2n}^{2+}$ , that may be present. In other words the value of  $n$  merely indicates the relative amount of sulfur that was used in the reaction. This varied from 12 to 1 as increasing amounts of  $AsF_5$  were added to a given amount of sulfur.

In  $SO_2$ , as in oleum, sulfur is initially oxidized by  $AsF_5$  to give a red-brown solution. From the initial value of  $n = 12$  to  $n = \sim 8$ , sulfur was always present in the sample, even on standing for over 1 week. At  $n = \sim 8$  all of the sulfur had reacted. This same "end point" was obtained previously in the reaction between sulfur and  $S_2O_5F_2$  in  $HSO_3F$  and was used as evidence for the original formulation of the  $S_{16}^{2+}$  cation.<sup>1</sup> It should be noted that at this end point ca. 85% of the  $AsF_5$  has been used to form  $S_{19}^{2+}$ , while the remaining oxidant has been involved in the formation of small amounts of other species. The ESR and absorption spectra of the red solutions showed no change over this range of stoichiometry. Thus in the presence of unreacted sulfur it appears that all the species present have the same relative concentrations. Typical spectra are shown in Figures 5 and 6. The ESR spectra of these solutions show three signals, with  $g$  values of 2.027, 2.014, and 2.008, the former being the most intense. The first two radicals, usually designated  $R_2$  and  $R_1$ , respectively, have been observed previously in oleum solutions,<sup>30-36</sup>

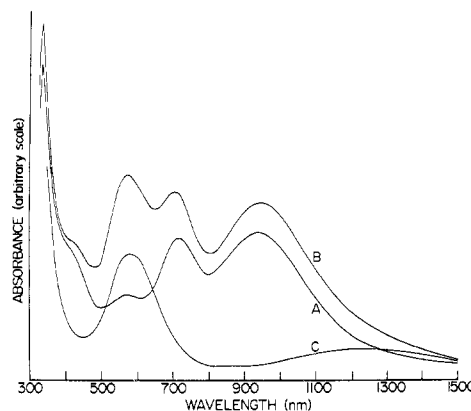


Figure 6. Typical UV-visible absorption spectra in the progressive oxidation of sulfur with  $AsF_5$  in  $SO_2$ : (A) at all ratios of  $n$  between 12 and  $\sim 8$ ; (B) at  $n = \sim 4$ ; and (C) at  $n = \sim 2$ .

Table VIII. Ionic Species Formed by the Oxidation of Sulfur in Oleum and by  $AsF_5$  in  $SO_2$

species	$g$ value	abs bands, nm
$S_{19}^{2+}$		235, 333
$S_8^{2+}$		( $\sim 220, \sim 390, \sim 600$ ) <sup>a</sup>
$S_4^{2+}$		330
$S_5^+$ ( $R_1$ )	2.014 ( $g_{\parallel} = 2.000, g_{\perp} = 2.018$ )	585
$R_2$	2.027 ( $g_1 = 2.003, g_2 = 2.031, g_3 = 2.041$ )	435, 715, 940
$R_3$	2.008	

<sup>a</sup> Absorption bands for  $S_8^{2+}$  predicted on the basis of the  $Se_8^{2+}$  spectrum.

and all three have been observed in  $HSO_3F$  and  $SO_2$  solutions.<sup>1</sup> The radical with a  $g$  value of 2.008 will be designated  $R_3$ . This radical probably occurs in oleum solution as well, but, as large concentrations of  $R_1$  always form quickly in this medium, its signal is obscured by that of  $R_1$  (see below) and it has never been observed in this solvent. The properties of these radicals are summarized in Table VIII, together with other relevant data.

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When an  $SO_2$  solution of this composition ( $n = 12$  to  $n \sim 8$ ) is cooled, the ESR signals do not disappear, and when the solution is frozen to 77 K, the primary signal ( $R_2$ ) splits into three components, with  $g_1 = 2.003$ ,  $g_2 = 2.031$ , and  $g_3 = 2.041$ . Because of their relatively lower intensities it was not possible to observe any splitting of the ESR signals of  $R_1$  and  $R_3$ . The splitting of the signal of  $R_2$  was observed by Giggenbach for frozen solutions of sulfur in 20% oleum, the latter being red.<sup>33</sup> This splitting implies that the radical has lower than axial symmetry. Similarly, a solid sample of  $S_{19}(AsF_6)_2$  at either room temperature or 77 K (where a much sharper spectrum was obtained) showed the same three signals. In view of the structure of  $S_{19}(AsF_6)_2$  this is probably due to doping or surface contamination of the sample by the radical species. In the absorption spectra of the above solutions ( $n = 12$  to  $n \sim 8$ ) bands were observed at 940, 715, 585, 435 (sh), and 333 nm. Bands at similar wavelengths have been observed in oleum solutions<sup>9,33,36-38</sup> and in  $HSO_3F$ ,<sup>1-3</sup> although with slight solvent shifts. One other band at 235 nm has been observed in the acid solutions but, because of the intense absorption from the solvent  $SO_2$  at 280 nm, this band was obscured in our work. Some interference was also noted with the intensity of the band at 333 nm relative to the bands at higher wavelengths. The absorption spectral data are also summarized in Table VIII, along with the ESR data on the radical species formed in solution.

Further addition of  $AsF_5$  to the red-brown solution with  $n \sim 8$  caused the color to change to brown-green and then to green at  $n \sim 6$ . At the same time the ESR signal of  $R_1$  increased in intensity with respect to  $R_2$ , and probably  $R_3$  as well. The signals due to species  $R_2$  and  $R_3$  appeared to remain constant in intensity relative to each other as that of  $R_1$  increased, but as the signal of  $R_3$  was quickly obscured by that of  $R_1$  and was no longer visible at  $n \sim 6$ , no quantitative comparisons could be made. Concomitant with the relative increase in the intensity of the signal of  $R_1$  the absorption band at 585 nm increased in intensity relative to the bands at 940, 715, and 435 nm. Continued addition of  $AsF_5$  caused the solution to turn from green to dark blue at  $n \sim 4$ , and the ESR signal due to  $R_1$  became even more intense than that due to  $R_2$ . It was, however, not until  $n \sim 2$  that the signal of  $R_2$  had completely vanished. A similar relationship held with the intensities of the absorption bands, so that at  $n \sim 2$  the bands at 940, 715, and 435 nm had disappeared, and the only bands present were at 585 nm and a rather broad weak band at 1240 nm. This latter band is not due to the excess  $AsF_5$  or to the reduction product  $AsF_3$ . Furthermore, this band cannot be attributed to  $S_4^{2+}$  as  $AsF_5$ , unlike  $SbF_5$  or  $S_2O_6F_2$ , is not a strong enough oxidant to oxidize  $S_8^{2+}$  to the  $S_4^{2+}$  species.<sup>2</sup> The ESR and absorption spectra of solutions at  $n \sim 4$  and  $n \sim 2$  are also shown in Figure 5.

When the blue solution obtained when  $n \sim 2$  was cooled, the ESR signal from  $R_1$  did not disappear, and like the primary signal in the red solution ( $n = 12$  to  $\sim 8$ ) it also split on freezing at 77 K. However, only two lines appeared in this case, with  $g_{||} = 2.000$  and  $g_{\perp} = 2.018$ . This same splitting was also observed by Giggenbach<sup>33</sup> for frozen solutions of sulfur in oleum, the latter being blue. In this case the splitting of the signal into two lines implies that the radical has axial symmetry. Interestingly, a solid sample of  $S_8(AsF_6)_2$  at either room temperature or 77 K also showed the same two lines, once again presumably arising from doping or surface contamination of the crystal by the radical species.

From a previous study by ESR and absorption spectroscopy of solutions of sulfur in various strengths of oleum, the bands at 235 and 333 nm were attributed to the  $S_{16}^{2+}$  cation.<sup>36</sup> This

was based on correlation of the change in the intensities of the ESR signals of the radicals with the intensity of the absorption bands as the temperature was varied. These bands must now be attributed to the  $S_{19}^{2+}$  cation. Other bands at 435, 715, and 940 nm were attributed to the radical  $R_2$ , which was assumed to be in equilibrium with the  $S_{16}^{2+}$  cation,<sup>36</sup> which has now been established as the  $S_{19}^{2+}$  species. The remaining band at 585 nm was assigned to the  $S_8^{2+}$  cation, although a prior study by Giggenbach suggested that this band could be attributed to the radical  $R_1$ .<sup>33</sup> The identity of  $R_1$  has recently been established as  $S_5^+$  from a study of the ESR spectrum of sulfur enriched to 91.8% in  $^{33}S$  in 65% oleum.<sup>4</sup> This radical has a  $g$  value of 2.0134 and a hyperfine coupling constant  $A$  of 8.92 G. Associated with the ESR signal of  $R_1$  ( $S_5^+$ ) throughout our work was the absorption band at 585 nm which, as noted above, has been attributed to the radical itself or to the  $S_8^{2+}$  cation in equilibrium with the radical. Our evidence now indicates that the 585-nm absorption band can definitely be attributed to the  $S_5^+$  radical. The ESR signal of  $R_1$  ( $g = 2.014$  and the absorption band at 585 nm were present in all solutions which were in equilibrium with undissolved sulfur. These conditions are hardly conducive to the presence of the more highly oxidized  $S_8^{2+}$ , especially as  $S_8^{2+}$  is easily reduced by elemental sulfur. Recent  $^{77}Se$  NMR data on  $Se_8^{2+}$ , which has a similar structure to  $S_8^{2+}$ , indicates that this cation retains its solid-state structure in solution.<sup>39</sup> It is reasonable to expect that  $S_8^{2+}$  would do the same. One would, therefore, expect the spectra of  $S_8^{2+}$  and  $Se_8^{2+}$  to be very similar, with only a small bathochromic shift, as is observed between the spectra of the  $S_4^{2+}$  and  $Se_4^{2+}$  cations.<sup>1,3,9</sup> Therefore, bands might reasonably be expected to occur at about 600, 390, and 220 nm for the  $S_8^{2+}$  cation. The reported absorption spectrum of  $S_8^{2+}$  is actually considerably different from the expected spectrum, being dominated by the band at 585 nm. This band appears to be much too intense from a consideration of extinction coefficients relative to the reported spectrum of  $Se_8^{2+}$ ,<sup>40</sup> and it seems clear that this band can be associated with the  $S_5^+$  radical cation. This is in accord with the suggestion by Giggenbach.<sup>33</sup> However, this author also proposed that, on the basis of reflectance spectra of frozen solutions of sulfur in oleum, a band at 23000–24000  $cm^{-1}$  (ca. 410 nm) could be attributed to the  $S_8^{2+}$  cation. In our work no band was observed in this region of the spectrum for solutions which contained this cation. Rather, the tail of a strong absorption band was observed at less than 380 nm, and this may perhaps be attributed to the  $S_8^{2+}$  cation. The position of this band is also in accord with the shift in the electronic spectrum of  $S_8^{2+}$  relative to that of  $Se_8^{2+}$  which one would expect. The band which might be expected at ca. 600 nm from  $S_8^{2+}$  is obscured by the 585-nm band of the  $S_5^+$  radical cation, while the band at ca. 220 nm was obscured by the absorption of the solvent and so could not be observed in our work.

The identities of the radicals  $R_2$  and  $R_3$  are at present unknown. The ESR spectra of solutions of sulfur enriched to 91.8% in  $^{33}S$  in 20% oleum give only a broad signal for  $R_2$ , with no resolved hyperfine structure.<sup>35</sup> Consequently, no firm conclusions can be drawn about the identity of this radical. On the basis of the  $S_{19}^{2+}$  structure it is tempting to speculate that  $R_2$  and  $R_3$  are radicals such as  $S_7^+$  and  $S_{12}^+$ . Certainly a ring containing more than five atoms with all of the sulfur atoms appearing equivalent in solution cannot be ruled out. Such a ring with the free electron in a delocalized  $\pi$ -type orbital would be expected to give a smaller hyperfine coupling constant than that of the  $S_5^+$  cation. As the observed line width of the ESR signal of  $R_2$  is about half of that of the signal

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of  $R_1$  (ca. 5 and 9.5 G, respectively; see also ref 35), the hyperfine splitting would not be resolved, assuming similar resolution. Furthermore, the signal of  $R_2$  splits into three lines on freezing at 77 K, implying less than axial symmetry, as observed for the static conformations of either of the  $S_7$  rings in the  $S_{19}^{2+}$  cation. However, other radicals such as  $S_8^+$  might also be expected to fit these criteria. It must be concluded that the progressive oxidation of sulfur to give singly charged cation radicals and doubly charged cations, several of which may be in equilibrium at any one time, is by no means well understood at present.

**Note Added in Proof:** Very recently, X-ray crystallographic studies of the compounds  $S_4(AsF_6)_2 \cdot 0.6(SO_2)$  and  $S_4(S_7I)_4 \cdot (AsF_6)_2$  have confirmed that the  $S_4^{2+}$  cation does have a

square-planar structure in the  $(S_{16}^{2+})(AsF_6)_2$  solid state.<sup>41</sup>

**Acknowledgment.** We thank the National Research Council of Canada for financial support of this work.

**Registry No.**  $S_{19}(AsF_6)_2$ , 72827-53-3; sulfur, 10544-50-0;  $S_4^{2+}$ , 12597-09-0;  $S_5^+$ , 37217-16-6;  $S_8^{2+}$ , 11062-34-3;  $AsF_5$ , 7784-36-3;  $S_{16}(AsF_6)_2$ , 12429-04-8.

**Supplementary Material Available:** Listings of structure factor amplitudes and root-mean-square amplitudes and direction cosines of thermal motion (19 pages). Ordering information is given on any current masthead page.

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## Preparation and Characterization of $Se_{10}(AsF_6)_2$ , $Se_{10}(SbF_6)_2$ , and $Se_{10}(AlCl_4)_2$ and Crystal Structure of $Se_{10}(SbF_6)_2$

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Preparative routes for the title compounds are described along with a single-crystal X-ray structural study of the  $Se_{10}(SbF_6)_2$  salt. Crystals of  $Se_{10}(SbF_6)_2$  form deep red plates which crystallize in the monoclinic space group  $P2_1/c$  with  $a = 19.869$  (5) Å,  $b = 16.200$  (4) Å,  $c = 13.282$  (3) Å,  $\beta = 109.24$  (2)°, and  $d_{\text{calcd}} = 4.15$  g cm<sup>-3</sup> for  $Z = 8$ . The structure has been determined by direct methods and refined by least squares to final agreement indices  $R_1 = 0.096$  and  $R_2 = 0.128$  for 2832 observed reflections ( $I/\sigma(I) > 3.0$ ). The  $Se_{10}^{2+}$  cation can be described as a six-membered boat-shaped ring linked across the middle by a chain of four selenium atoms, that is, a bicyclo[4.2.2]decane type structure, and is isostructural with the known  $Te_2Se_8^{2+}$  cation. The selenium-selenium bonds in the cation vary greatly in length from 2.24 to 2.44 Å. These variations in the bond lengths and the relationship of the cage structure of  $Se_{10}^{2+}$  to the cuneane and pentagonal-prism structures are discussed. The electronic absorption and diffuse reflectance spectra of the  $Se_{10}^{2+}$  cation are also reported and compared with that of the  $Se_8^{2+}$  cation.

### Introduction

Two homopolyatomic cations of selenium,  $Se_4^{2+}$  and  $Se_8^{2+}$ , are well-known, and a number of salts of both cations have been prepared.<sup>1-5</sup> X-ray crystallographic determinations of the structures of  $Se_4(HS_2O_7)_2^5$  and  $Se_8(AlCl_4)_2^4$  have established that  $Se_4^{2+}$  is square planar and that  $Se_8^{2+}$  is an eight-membered ring with an exo-endo conformation and a long cross-ring bond. The analogous cations of sulfur,  $S_4^{2+}$ <sup>7,9</sup> and  $S_8^{2+}$ ,<sup>8-10</sup> have similar shapes. In addition a third cation, which

was previously reported as  $S_{16}^{2+}$ ,<sup>8,9</sup> has recently been shown by an X-ray crystallographic study of the hexafluoroarsenate salt to be the cation  $S_{19}^{2+}$ .<sup>11</sup> This species consists of two seven-membered rings joined by a five-atom chain. No evidence has been obtained for an analogous selenium species, although the results of a recent potentiometric and spectrophotometric study of cationic species of selenium in NaCl-AlCl<sub>3</sub> melts have been interpreted as indicating the presence of the  $Se_{12}^{2+}$  and  $Se_{16}^{2+}$  cations.<sup>12</sup> Recently, the heteropolyatomic cation  $Te_2Se_8^{2+}$  has been prepared by the reaction of tellurium with  $Se_8^{2+}$ , and an X-ray crystallographic study indicated that it has a bicyclic structure with an eight-membered ring fused to a six-membered ring.<sup>13</sup> The object of the present work was to attempt the preparation of the analogous homopolyatomic cation  $Se_{10}^{2+}$  and/or other homopolyatomic cations of selenium containing the element in a lower formal oxidation state than that found in the  $Se_8^{2+}$  species. This paper reports the preparation and characterization of the compounds  $Se_{10}(AsF_6)_2$ ,  $Se_{10}(SbF_6)_2$ , and  $Se_{10}(AlCl_4)_2$ , and an X-ray

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