gen atoms. In fact, the hole size (the approximate radius is 3.5 Å taking phenyl hydrogens into account) seems large enough to accommodate larger anions. Thus, the structure of the trifluoroacetonitrile adduct of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$,[28] which is currently under investigation, might be expected to have a similar overall geometry.

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Polyatomic Cations of Sulfur. II. The Crystal Structure of Octasulfur Bis(hexafluoroarsenate), $S_8(AsF_6)_2$

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The structure of $S_8(AsF_6)_2$ has been determined from three-dimensional X-ray diffraction data by a direct sign determination procedure. The crystals are monoclinic, mol wt 634.3, $a = 15.005 \pm 0.005$ Å, $b = 13.401 \pm 0.005$ Å, $c = 16.489 \pm 0.005$ Å, $\beta = 107.96 \pm 0.01°$, $V = 3154$ Å^3, $Z = 8$, $d_m = 2.6 \pm 0.1$ g cm^{-3}, $d_c = 2.66$ g cm^{-3}, space group $P2_1/c$. The least-squares refinement of this structure gave a conventional R index of 0.067 for 1975 reflections. The configuration of the S_8^{2+} cation is that of a folded ring with approximate C_s symmetry having an endo–exo conformation. The average S–S bond distance around the ring is 2.04 Å, and the S–S–S bond angles average 102° excluding the two end angles which average 93°. The cross-ring S–S distances between atoms related by the pseudo mirror plane range between 2.83 and 3.05 Å. The average As–F bond length in the approximately octahedral AsF_6^- ion is 1.67 Å.

Introduction

Sulfur, selenium, and tellurium can be oxidized by various oxidizing agents such as SO_3, $S_2O_6F_2$, AsF_5, and SbF_5 to colored cations containing the element in low oxidation states of 1+ or less. For example sulfur can be oxidized with arsenic pentafluoride to the two compounds $S_{16}^{2+}(AsF_6^-)_2$ and $S_8^{2+}(AsF_6^-)_2$[1,2] and with antimony pentafluoride to $S_{16}^{2+}(SbF_6^-)_2$ and $S_8^{2+}(Sb_2F_{11}^-)_2$.[2] Stable solutions of these cations as well as S_4^{2+} have been obtained by oxidizing sulfur with SO_3 in solution in oleum or with $S_2O_6F_2$ in solution in fluorosulfuric acid.[2,3] The white crystalline material $S_4^{2+}(SO_3F^-)_2$ has been obtained by oxidizing sulfur with $S_2O_6F_2$ in solution in SO_2.[2,3] The oxidation state and molecular weight of the cations have been established by chemical analysis of their compounds, by cryoscopic and conductometric measurements on their solutions, and by magnetic and spectroscopic measurements on the solids and the solutions. Similar studies have shown that selenium can be oxidized to Se_4^{2+} and Se_8^{2+} and tellurium to Te_4^{2+} and Te_n^{n+}.[4] These ions thus constitute a new class of homopolyatomic cations which contain the elements sulfur, selenium, and tellurium in hitherto unknown oxidation states. Their structures are of obvious interest. The first structure to be determined was that of Se_4^{2+}. A single-crystal X-ray crystallographic study of the orange crystalline compound $Se_4^{2+}(HS_2O_7^-)_2$ has shown that Se_4^{2+} has a square-planar structure.[5,6] Comparison of the absorption spectra, the infrared and Raman spectra, and the magnetic circular dichroism of S_4^{2+} and Te_4^{2+} with those of Se_4^{2+} lead to the conclusion that these ions also have a square-planar structure.[4] Very recently this conclusion has been confirmed for Te_4^{2+} by an X-ray crystallographic study of $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$.[7]

The present paper reports a single-crystal X-ray crystallographic investigation of the structure of $S_8^{2+}(AsF_6^-)_2$. While our investigation was in progress, a preliminary communication on the structure $Se_8(AlCl_4)_2$ was published[8] which showed that Se_8^{2+} has the structure of a folded ring with an endo–exo conformation and a long cross-ring bond giving a bicyclic structure reminiscent of bicyclo[3.3.0]octane. The results of this work on Se_8^{2+} are compared with our own in the discussion.

Experimental Section

The preparation of the compound $S_8(AsF_6)_2$ from arsenic pentafluoride and sulfur has been described previously.[1,2] Slow recrystallization from hydrofluoric acid yielded dark blue crystals. These were pumped dry on a vacuum line and subsequently handled in a drybox. The crystals were mounted in 0.3-mm thin-walled quartz capillary tubes for the subsequent X-ray examination.

Precession photographs of the 0*kl*, 1*kl*, 2*kl*, and *hk*0, *hk*1, *hk*2 planes using Cu Kα radiation showed the systematic absences characteristic of the space group $P2_1/c$ (no. 14, C_{2h}^5). The crystals are monoclinic, mol wt 634.3, $a = 15.005 \pm 0.005$ Å, $b = 13.401 \pm 0.005$ Å, $c = 16.489 \pm 0.005$ Å, $\beta = 107.96 \pm 0.01°$, $V = 3153.9$ Å^3, $Z = 8$, $d_m = 2.6\ (1)$ g cm^{-3}, $d_c = 2.66$ g cm^{-3}. The density was determined by the standard displacement method using Fluorolube oil as the inert liquid. All weighings were performed in a drybox. The unit cell parameters were found by least-squares refinement of the Bragg angle and crystal

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TABLE I[a]

(a) Atomic Coordinates ($\times 10^4$) in $S_8(AsF_6)_2$

Atom type	*x*	*y*	*z*
As(1)	6878 (2)	371 (2)	4,152 (2)
As(2)	73 (2)	361 (2)	7,518 (2)
As(3)	7311 (2)	570 (2)	9,267 (2)
As(4)	3710 (2)	2303 (2)	3,664 (2)
S(11)	1670 (5)	1757 (5)	6,345 (4)
S(12)	1156 (5)	3036 (5)	6,704 (4)
S(13)	178 (5)	3456 (5)	5,622 (5)
S(14)	−574 (5)	2189 (5)	5,199 (5)
S(15)	−581 (5)	2278 (6)	3,958 (5)
S(16)	771 (5)	1755 (6)	4,180 (5)
S(17)	1461 (5)	3029 (5)	4,671 (4)
S(18)	2415 (4)	2582 (5)	5,755 (4)
S(21)	5460 (5)	1286 (5)	706 (4)
S(22)	6596 (5)	0628 (5)	1,577 (5)
S(23)	7272 (4)	1858 (5)	2,178 (4)
S(24)	7370 (5)	2756 (5)	1,221 (4)
S(25)	7051 (5)	4082 (5)	1,683 (5)
S(26)	5640 (5)	3768 (5)	1,249 (5)
S(27)	5600 (5)	2817 (6)	2,205 (4)
S(28)	4814 (4)	1647 (5)	1,595 (4)
F(11)	6095 (10)	425 (11)	4,685 (9)
F(12)	7440 (12)	1352 (13)	3,435 (10)
F(13)	6233 (11)	1150 (13)	3,435 (10)
F(14)	7575 (12)	−402 (13	4,890 (10
F(15)	6358 (12	−639 (13)	3,622 (12)
F(16)	7667 (11)	326 (12)	3,585 (10)
F(21)	54 (12)	424 (13)	8,545 (1)
F(22)	355 (15)	1543 (17)	7,308 (14)
F(23)	488 (12)	−830 (14)	7,707 (11)
F(24)	1138 (14)	811 (15)	7,781 (12)
F(25)	−1012 (13)	−94 (14)	7,229 (12)
F(26)	110 (12)	282 (13)	6,494 (11)
F(31)	8344 (14)	58 (15)	9,349 (12)
F(32)	7595 (10)	1568 (12)	8,750 (10)
F(33)	7838 (13)	1126 (15)	10,204 (12)
F(34)	6841 (17)	19 (19)	8,384 (16)
F(35)	7034 (10)	−448 (12)	9,772 (10)
F(36)	6362 (16)	1160 (17)	9,326 (14)
F(41)	2599 (14)	2072 (16)	3,444 (13)
F(42)	3949 (16)	1081 (19)	3,735 (15)
F(43)	3643 (13)	2289 (15)	2,630 (12)
F(44)	3798 (12)	2300 (14)	4,701 (11)
F(45)	3535 (23)	3494 (25)	3,637 (20)
F(46)	4826 (13)	2466 (15)	3,907 (12)

(b) Thermal Parameters in $S_8(AsF_6)_2$[b]

Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As(1)	3.7 (1)	2.5 (1)	2.9 (1)	0.6 (1)	1.1 (1)	0.1 (1)
As(2)	5.1 (2)	3.3 (1)	3.2 (1)	−1.3 (1)	1.6 (1)	0.1 (1)
As(3)	3.4 (1)	2.5 (1)	3.3 (1)	0.3 (1)	1.2 (1)	−0.1 (2)
As(4)	3.3 (1)	3.2 (1)	2.7 (1)	0.1 (1)	1.3 (1)	−0.1 (1)
S(11)	5.2 (3)	4.8 (3)	3.0 (4)	−1.2 (3)	0.5 (3)	−1.1 (3)
S(12)	6.2 (4)	2.7 (3)	4.8 (3)	−0.0 (3)	2.3 (3)	−0.2 (3)
S(13)	4.9 (4)	3.9 (4)	4.5 (4)	1.3 (3)	1.5 (3)	−0.5 (3)
S(14)	3.7 (4)	4.8 (4)	5.7 (4)	−0.5 (3)	1.5 (3)	0.6 (3)
S(15)	3.8 (4)	6.3 (5)	4.6 (4)	−0.6 (3)	0.2 (3)	−0.5 (4)
S(16)	4.2 (4)	5.5 (4)	4.2 (4)	−0.5 (4)	0.3 (4)	−2.7 (3)
S(17)	4.0 (3)	4.0 (4)	3.7 (4)	−0.5 (3)	1.4 (3)	−0.0 (3)
S(18)	3.2 (3)	3.6 (4)	4.5 (4)	−0.2 (3)	1.2 (3)	0.1 (3)
S(21)	5.2 (4)	4.8 (4)	3.0 (3)	−1.2 (3)	0.5 (3)	−1.1 (3)
S(22)	5.8 (4)	4.5 (4)	3.2 (4)	0.4 (3)	2.0 (3)	−0.8 (3)
S(23)	3.7 (3)	3.8 (4)	2.7 (3)	0.5 (3)	0.3 (2)	0.2 (3)
S(24)	4.3 (4)	3.8 (4)	4.6 (4)	−0.2 (3)	2.4 (3)	−0.0 (3)
S(25)	5.2 (4)	3.3 (3)	3.7 (4)	−0.5 (3)	2.0 (3)	−0.3 (3)
S(26)	4.2 (4)	3.5 (4)	5.3 (4)	0.6 (3)	1.4 (3)	1.1 (3)
S(27)	4.0 (3)	4.0 (4)	3.4 (3)	−0.3 (3)	1.8 (3)	−0.0 (3)
S(28)	3.3 (3)	4.9 (4)	3.9 (4)	−1.1 (3)	0.7 (3)	0.0 (3)

Isotropic Temperature Factors

Atom type	*B*	Atom type	*B*	Atom type	*B*	Atom type	*B*
F(11)	5.4 (3)	F(21)	7.4 (4)	F(31)	8.9 (5)	F (41)	9.6 (6)
F(12)	7.2 (4)	F(22)	10.8 (6)	F(32)	8.8 (4)	F (42)	119.1 (7)
F(13)	6.8 (4)	F(23)	8.0 (5)	F(33)	8.7 (5)	F (43)	8.7 (5)
F(14)	7.1 (4)	F(24)	9.1 (5)	F(34)	12.0 (7)	F (44)	7.8 (5)
F(15)	7.1 (4)	F(25)	7.8 (5)	F(35)	6.0 (3)	F (45)	17.1 (10)
F(16)	5.9 (4)	F(26)	7.2 (4)	F(36)	10.8 (6)	F (46)	8.8 (5)

[a] The number in parentheses is the estimated standard error in the last significant figure. [b] The B_{ij}'s in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

orientation for 24 reflections in the region $5° \leqslant 2\theta \leqslant 20°$, measured on a GE XRD6 automatic diffractometer using Mo Kα (λ 0.71069 Å) radiation. An approximately spherical crystal (radius 0.08 mm) was mounted with its [$\bar{1}$21] axis coincident with the ϕ axis of the diffractometer for intensity measurements. The θ–2θ moving-crystal, moving-counter technique was used with a scan range for each reflection equal to $1.8° + \tan 2\theta$. The reflections in the range $2.5° < 2\theta < 33.8°$ were recorded at a scan rate of 1°/min as were also those in the range $33.8° < 2\theta < 45°$ which satisfied the condition that a 10-sec stationary count at the Bragg peak was twice the corresponding background count. Stationary 40-sec gackground counts were taken at the beginning and end of the 2θ scan for each reflection.

Two equivalent sets of reflections were measured and averaged to give a total of 2482 inequivalent reflections. Of these, 1975 had intensities greater than 3 times the standard error derived from counting statistics. The recorded intensities were corrected for background, Lorentz, and polarization effects. A standard deviation was applied to each reflection according to the formula $\sigma(I) = 0.31623\sqrt{I + kB}$, where I is the integrated scan in decacounts $- B$, $B = k(B_1 + B_2)$, and $K = (60\Delta 2\theta)/80$. B_1 and B_2 are the background counts in decacounts at the extremes of the 2θ scan about a Bragg peak. Reflections having an intensity $I < 3\theta(I)$ were not included in the refinement of the structure.

The set of intensities up to 45° was completed by assigning to each reflection not scanned a value half that of the minimum scanned intensity in the region 33.8–45°. Eight standard reflections randomly distributed in the sphere of reflection were recorded every 100 measurements to monitor the stability of the crystal and its alignment. No distinct time-dependent trend was observed, the maximum intensity variation of these standards being of the order of 3%.

The linear absorption coefficient (μ) has the value of 5.604 mm^{-1} for Mo Kα radiation. Assuming the crystal to be a sphere (radius 0.08 mm), the transmission factor at $\theta = 0°$ is 0.481, and at $\theta = 25°$, 0.488. The variation between the two values is of the order of 1% which is smaller than other uncertainties in the measured intensities and could therefore be neglected in the refinement of the structure.

Solution and Refinement of the Structure.—The structure factors were put on an absolute scale by calculating the statistical distribution of the E values for all the inequivalent reflections with $0° < 2\theta < 45°$. The final averaged statistics ($|E|_{av} = 0.814$, $|E^2 - 1|_{av} = 1.00$; theoretical for centric distribution, $|E|_{av} = 0.798$, $|E^2 - 1|_{av} = 0.968$) confirm the centrosymmetric space group and support the assignment of intensities to the nonscanned reflections. A total of 546 reflections had E values above 1.5. The most consistent set of signs for 488 reflections was determined using the program PHASE of the X-ray 67 system. Using these phases, an E map was calculated which showed clearly the positions of four arsenic atoms in the asymmetric unit.

The arsenic positions and estimated isotropic temperature factors were refined by two cycles of full-matrix least squares to give an agreement index $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ of 0.44. The 1975 observed structure factors were used together with their

TABLE II[a]

BOND LENGTHS AND INTRAMOLECULAR CONTACTS

Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Distance, Å
			(a) $(AsF_6)^-$				
As(1)–F(11)	1.672 (17)	As(2)–F(21)	1.705 (19)	As(3)–F(31)	1.663 (21)	As(4)–F(41)	1.623 (21)
As(1)–F(12)	1.691 (17)	As(2)–F(22)	1.703 (23)	As(3)–F(32)	1.710 (17)	As(4)–F(42)	1.673 (25)
As(1)–F(13)	1.650 (16)	As(2)–F(23)	1.707 (18)	As(3)–F(33)	1.677 (18)	As(4)–F(43)	1.678 (20)
As(1)–F(14)	1.691 (16)	As(2)–F(24)	1.710 (19)	As(3)–F(34)	1.591 (24)	As(4)–F(44)	1.673 (18)
As(1)–F(15)	1.670 (17)	As(2)–F(25)	1.666 (18)	As(3)–F(35)	1.714 (17)	As(4)–F(45)	1.615 (34)
As(1)–F(16)	1.720 (18)	As(2)–F(26)	1.635 (20)	As(3)–F(36)	1.657 (25)	As(4)–F(46)	1.612 (19)
						Av As–F 1.67	
	(b) Sulfur Atoms in Ring 1				(c) Sulfur Atoms in Ring 2		
S(21)–S(22)	2.059 (9)	S(21)–S(23)	3.132 (8)	S(11)–S(12)	2.041 (10)	S(11)–S(13)	3.157 (9)
S(22)–S(23)	2.027 (9)	S(21)–S(27)	3.169 (10)	S(12)–S(13)	2.010 (9)	S(11)–S(17)	3.175 (10)
S(23)–S(24)	2.027 (10)	S(21)–S(24)	3.364 (10)	S(13)–S(14)	2.039 (10)	S(11)–S(14)	3.364 (9)
S(24)–S(25)	2.049 (10)	S(21)–S(26)	3.433 (10)	S(14)–S(15)	2.046 (11)	S(11)–S(16)	3.404 (10)
S(25)–S(26)	2.058 (10)	S(22)–S(28)	3.010 (11)	S(15)–S(16)	2.068 (11)	S(12)–S(18)	2.866 (11)
S(26)–S(27)	2.043 (10)	S(22)–S(24)	3.228 (10)	S(16)–S(17)	2.031 (10)	S(12)–S(14)	3.196 (9)
S(27)–S(28)	2.033 (9)	S(23)–S(27)	2.832 (10)	S(17)–S(18)	2.006 (8)	S(13)–S(17)	2.889 (12)
S(28)–S(21)	2.048 (11)	S(23)–S(25)	3.082 (9)	S(18)–S(11)	2.022 (11)	S(13)–S(15)	3.065 (10)
		S(24)–S(26)	2.942 (10)			S(14)–S(16)	3.053 (12)
		S(25)–S(27)	3.084 (11)			S(15)–S(17)	3.092 (10)
		S(26)–S(28)	3.221 (10)			S(16)–S(18)	3.179 (9)

[a] The number in parentheses is the estimated standard error in the last significant figure.

TABLE III[a]

BOND ANGLES (DEG)

(a) In the Sulfur Rings

Ring 1		Ring 2	
S(22)–S(21)–S(28)	94.3 (4)	S(12)–S(11)–S(18)	89.7 (4)
S(21)–S(22)–S(23)	100.1 (4)	S(11)–S(12)–S(13)	102.4 (4)
S(22)–S(23)–S(24)	104.3 (4)	S(12)–S(13)–S(14)	104.2 (4)
S(23)–S(24)–S(25)	98.3 (4)	S(13)–S(14)–S(15)	97.2 (5)
S(24)–S(25)–S(26)	91.5 (4)	S(14)–S(15)–S(16)	95.8 (4)
S(25)–S(26)–S(27)	97.5 (4)	S(15)–S(16)–S(17)	97.9 (4)
S(26)–S(27)–S(28)	104.5 (4)	S(16)–S(17)–S(18)	103.9 (4)
S(27)–S(28)–S(21)	101.9 (4)	S(11)–S(18)–S(17)	104.6 (4)

(b) Around the Arsenic Atoms

As(1)		As(2)		As(3)		As(4)	
F(11)–F(12)	88.6 (9)	F(21)–F(22)	92.0 (10)	F(31)–F(32)	89.6 (9)	F(41)–F(42)	90.7 (11)
F(11)–F(13)	89.8 (8)	F(21)–F(23)	88.9 (9)	F(31)–F(33)	86.9 (10)	F(41)–F(43)	92.0 (10)
F(11)–F(14)	91.6 (8)	F(21)–F(24)	178.9 (8)	F(31)–F(34)	91.2 (12)	F(41)–F(44)	88.8 (10)
F(11)–F(15)	91.1 (9)	F(21)–F(25)	89.3 (9)	F(31)–F(35)	89.6 (9)	F(41)–F(45)	92.0 (14)
F(11)–F(16)	178.7 (7)	F(21)–F(26)	91.9 (10)	F(31)–F(36)	171.4 (10)	F(41)–F(46)	176.6 (10)
F(12)–F(13)	89.7 (8)	F(22)–F(23)	178.7 (8)	F(32)–F(33)	89.6 (9)	F(42)–F(43)	90.2 (11)
F(12)–F(14)	88.8 (8)	F(22)–F(24)	89.0 (10)	F(32)–F(34)	90.8 (11)	F(42)–F(44)	88.8 (11)
F(12)–F(15)	176.8 (8)	F(22)–F(25)	90.5 (10)	F(32)–F(35)	178.1 (8)	F(42)–F(45)	176.8 (13)
F(12)–F(16)	91.8 (9)	F(22)–F(26)	89.4 (10)	F(32)–F(36)	90.4 (10)	F(42)–F(46)	86.1 (11)
F(13)–F(14)	177.9 (9)	F(23)–F(24)	90.1 (9)	F(33)–F(34)	178.1 (8)	F(43)–F(44)	176.8 (9)
F(13)–F(15)	93.5 (8)	F(23)–F(25)	88.7 (9)	F(33)–F(35)	91.3 (8)	F(43)–F(45)	91.4 (14)
F(13)–F(16)	88.9 (8)	F(23)–F(26)	91.4 (9)	F(33)–F(36)	84.5 (10)	F(43)–F(46)	89.2 (10)
F(14)–F(15)	88.1 (8)	F(24)–F(25)	91.1 (9)	F(34)–F(45)	88.2 (11)	F(44)–F(45)	89.5 (14)
F(14)–F(16)	89.7 (8)	F(24)–F(26)	87.7 (10)	F(34)–F(36)	97.4 (12)	F(44)–F(46)	89.9 (10)
F(15) F(16)	88.6 (9)	F(25)–F(26)	178.8 (10)	F(35)–F(36)	90.6 (10)	F(45)–F(46)	91.2 (14)

[a] The number in parentheses is the estimated standard error in the last significant figure.

signs as determined from the calculated structure factors using the arsenic atom positions to calculate a three-dimensional Fourier map which revealed the sulfur atoms.

These positions, when included in another two cycles of least-squares refinement, reduced R_1 to 0.25. A new three-dimensional Fourier map was calculated and the clearly resolved peaks in the vicinity of the arsenic atoms were assumed to be fluorine atoms. Two cycles of least-squares analysis, varying the positional and isotropic temperature coordinates of all the atoms, reduced R_1 to 0.087. At this point the sulfur and arsenic atoms were allowed to refine with anisotropic temperature factors and R fell to 0.067. Final refinement was performed with the Cruickshank weighting scheme, $w = a + b|F_o| + c|F_o|^2 + \cdots$, in which $a = 5.012$, $b = 0.002$, and $c = 0.00$. These values, obtained from analysis of the structure factors, correspond to almost equal weighting of every reflection and as expected there was no further change in the agreement index R_1. The value for $R_2 = \sqrt{\Sigma w(F_o - F_c)^2/\Sigma w F_o^2}$ was found to be 0.077. A difference fourier map was computed and, except for a maximum peak height value of 1.4 e/Å^3 in the vicinity of the arsenic atoms, was essentially featureless.

The atomic scattering curves for arsenic and fluorine were taken from the "International Tables for X-Ray Crystallography" and for sulfur from Dawson.[9] All calculations were performed on a CDC 6400 computer using the series of programs in the X-ray 67 system.[10,11] The final positional coordinates

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[9] B. Dawson, *Acta Crystallogr.*, **13**, 403 (1960).

[10] J. M. Stewart, *et al.*, "X-ray 67 System," University of Maryland.

and temperature factors for all atoms are given in Table I which also gives the standard errors as derived from the least-squares analysis.

Description of the Structure.—Figure 1 shows the configuration of the S_8^{2+} ion. Tables II and III list the bond lengths and angles for $S_8(AsF_6)_2$.

The structure consists of discrete S_8^{2+} and AsF_6^- ions, two of the former and four of the latter forming the asymmetric unit of the cell. The configuration of the S_8^{2+} ion is within experimental error the same in both crystallographically distinct ions (Figure 1). The close similarity of the two S_8 ring suggests that their conformation is the most stable one for the ion and is not forced by the exigencies of crystal packing.

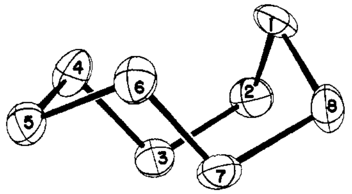
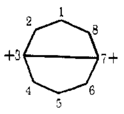
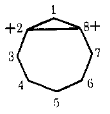


Figure 1.—The configuration of the S_8^{2+} ring in $S_8(AsF_6)_2$.

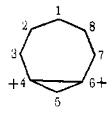
The sulfur–sulfur bonds around the ring have an average length of 2.04 Å which is the same as the sulfur–sulfur bond length of 2.048 Å in the S_8 molecule.[12] The structure of S_8^{2+} however differs from that of the crown-shaped S_8 molecule in several ways. The cross-ring S(3)–S(7) distance is only 2.86 Å compared with 4.68 Å in the S_8 ring. This is significantly shorter than the van der Waals distance of approximately 3.7 Å and we take this to indicate definite although weak bonding between these two atoms which thus produces a bicyclic system. The distortion of the ring produced by this cross-ring bonding causes all the bond angles which range from 91.5 to 104.3° to be smaller than the angle of 107.9° found in the S_8 ring. The conformation of S_8^{2+} also differs from that of S_8 in that the S(1) atom is in an endo rather than an exo position. The reason for this conformation change is not clear but presumably results from changes in nonbonded repulsions brought about by the cross-ring bonding. Two other cross-ring distances, *i.e.*, S(4)–S(6) = 3.00 Å and S(2)–S(8) = 2.94 Å, are not much longer than S(3)–S(7) and are significantly shorter than the van der Waals contact; they may also indicate weak cross-ring bonding. It seems reasonable therefore to describe the molecule by means of mixture of primarily structure **1** with some contribution from structures **2** and **3**.



1



2



3

In this connection it is probably of significance that the four sulfur atoms S(2), S(8), S(3), and S(7) lie in a plane as do also the four atoms S(3), S(7), S(4), and S(6) (see Table IV). Presumably there is some delocalization of charge in these approximately square-planar groups of four sulfur atoms somewhat analogous to the delocalization of charge found in the square-planar Se_4^{2+} molecule. Such delocalization would also be consistent with the small but probably significant shortening of the S(2)–S(3), S(3)–S(4), S(6)–S(7), and S(7)–S(8) bonds (2.03 Å) compared to the remaining four ring bonds (2.05 Å).

This may be conveniently described by structure **4** in which the circles indicate the delocalized electrons.

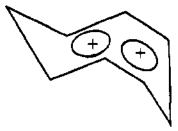
The structure of S_8^{2+} is very similar to that of Se_8^{2+} which also has the same exo–endo conformation.[8] In particular the two smallest bond angles in the S_8^{2+} ring are S(2)–S(1)–S(8) = 94.3° and S(4)–S(5)–S(6) = 91.5° while the two similar angles in the Se_8^{2+} ring are also the smallest and have values of 93.3 and 89.8°, respectively. The cross-ring Se–Se distance in Se_8^{2+} is significantly shorter than the van der Waals contact distance of approximately 3.8 Å and is proportionately shorter than the corresponding S–S cross-ring distance indicating a rather stronger cross-ring bond than in S_8^{2+}.

Table IV

Mean Planes in Sulfur Rings and Atomic Displacements Therefrom

Atoms	Distance, Å	Equations Defined by $Ax + By + Cz = D^a$ A	B	C	D
S(12)	0.011	4.85	12.5	0.687	4.81
S(13)	−0.011				
S(17)	0.011				
S(18)	−0.011				
S(13)	−0.008	5.51	−6.84	10.33	3.55
S(14)	0.008				
S(16)	−0.008				
S(17)	0.008				
S(22)	0.003	−3.05	−5.66	14.89	0.0241
S(23)	−0.004				
S(27)	0.004				
S(28)	0.003				
S(23)	0.004	5.21	8.74	8.81	7.32
S(24)	−0.004				
S(26)	0.004				
S(27)	−0.004				

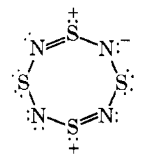
[a] In direct crystal coordinate system.



4

Comparison with the structure of S_4N_4 is of obvious interest. Indeed S_8^{2+} has a structure which is intermediate between that of the crown-shaped S_8 which has an exo–exo conformation[13] and S_4N_4 which has an endo–endo conformation. Although S_4N_4 has often been represented by ring structures such as **5**, the two cross-ring sulfur–sulfur distances are only 2.58 Å which indicates bonding between these sulfur atoms. Hence structure **6** is a better representation of the structure of S_4N_4. This is also the conclusion of a recent molecular orbital treatment of S_4N_4.[14] It is of interest that S_4N_4 is isoelectronic with S_8^{4+}, which is not known as this oxidation state of sulfur has been found only as the square-planar molecule S_4^{2+}. Thus on removing two electrons from S_8 a cross-ring bond is formed and one end of the molecule flips into the endo position; then on removing another two electrons to give S_4N_4 (or hypothetical S_8^{4+}) the other end of the molecule flips into the endo position and a second cross-ring bond is formed.

The four AsF_6^- groups in the unit cell have an octahedral structure in which the observed As–F distances vary over a considerable range from 1.59 to 1.72 Å, the average being 1.67 Å which agrees well with a previously reported literature value[15] of 1.67 Å for a regular AsF_6^- octahedron.



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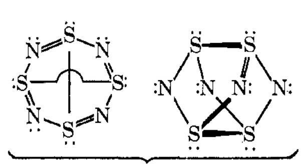

6

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(11) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(12) A. S. Cooper, W. L. Bond, and S. C. Abrahams, *Acta Crystallogr.*, **14**, 1008 (1961).

(13) B. D. Sharma and J. Donohue, *ibid.*, **16**, 891 (1963).

(14) A. W. Turner and F. S. Mortimer, *Inorg. Chem.*, **5**, 906 (1966).

(15) F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. De Boer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).