

SHORT STRUCTURAL PAPERS

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The Molecular Adduct Cyclotetra(azathiene) – Arsenic Pentafluoride

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Abstract. $S_4N_4 \cdot AsF_5$, monoclinic, $P2_1/m$, $a = 5.593$ (1), $b = 11.062$ (2), $c = 7.682$ (1) Å, $\beta = 109.10$ (1)°, $U = 449.2$ (2) Å³, $D_c = 2.62$ Mg m⁻³ for $Z = 2$; $R_1 = 0.036$ for 848 non-zero data. The structure of this compound is comparable to those of all the other 1:1 adducts of S_4N_4 , with the exception of the adduct $S_4N_4 \cdot CuCl$. The coordination of the AsF_5 group to one of the N atoms results in the opening of the S_4N_4 cage structure to a puckered boat-shaped ring with the four S atoms in a plane.

Introduction. During attempts to prepare cationic derivatives of S_4N_4 , the reactions of S_4N_4 with the compounds $S_8(AsF_6)_2$ and $Se_8(AsF_6)_2$ in SO_2 have been observed to give the species $S_6N_4(AsF_6)_2$ and its selenium analogue $Se_4S_2N_4(AsF_6)_2$ (Gillespie, Kent & Sawyer, 1980). However, when the corresponding reactions of S_4N_4 with both $Te_4(AsF_6)_2$ in SO_2 and $Se_8(AsF_6)_2$ in methylene chloride were attempted, they gave a deep-red crystalline product which has been characterized by X-ray crystallography as a 1:1 adduct of S_4N_4 with the Lewis acid AsF_5 .

Crystals of $S_4N_4 \cdot AsF_5$ exist in a variety of forms depending on the reaction conditions. An approximately spherical crystal of this material was selected from the product of the reaction of $Se_8(AsF_6)_2$ with S_4N_4 and sealed in a Lindemann capillary. Accurate unit-cell dimensions were obtained by least-squares refinement with 15 high-angle reflections measured on a Syntex $P2_1$ diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Data were originally collected to a maximum 2θ of 50° using a B -centred cell $a' = 5.593$, $b' = 11.062$, $c' = 14.561$ Å with $\beta' = 92.33^\circ$ and later transferred to the primitive cell above. Reflections were measured using θ - 2θ scans over a 2θ scan range ($K\alpha_1 - 0.9^\circ$) to ($K\alpha_2 + 0.9^\circ$) and variable scan rates of 4–29.3° min⁻¹ depending on the intensity of preliminary count. A total of 2260 data in the

quadrants ($h, \pm k, \pm l$) were collected. Lorentz and polarization corrections were applied to all the data. No absorption corrections were considered necessary as the crystal was approximately a sphere of radius 0.088 mm ($\mu = 4.93$ mm⁻¹; and hence $\mu R = 0.43$). Averaging 677 equivalent data (R merge = 0.03) and excluding 485 data which either were systematically absent or had observed structure amplitudes equal to zero gave a final data set of 848 non-zero reflections.

The structure was solved using conventional Patterson and Fourier methods. Least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$ with all atoms having anisotropic temperature factors converged to final agreement indices $R_1 = 0.036$ ($R_2 = 0.032$) for all 848 non-zero data and $R_1 = 0.023$ ($R_2 = 0.028$) for 651 observed data [$I/\sigma(I) > 3.0$] [$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$]. In the final cycle of refinement weights were calculated using the expressions $w = xy$ where: (1) $x = F/8$ if $F < 8$, or $x = 30/F$ if $F > 30$, otherwise $x = 1.0$, and (2) $y = \sin \theta / 0.28$ if $\sin \theta < 0.28$, or $y = 0.40 / \sin \theta$ if $\sin \theta >$

Table 1. Final atomic positional parameters ($\times 10^4$) with standard deviations in parentheses for the molecular adduct $S_4N_4 \cdot AsF_5$

	x	y	z	U_{eq}^* (Å ² × 10 ³)
As	1526 (1)	2500	1490 (1)	33.9 (3)
F(1)	-620 (5)	3598 (2)	398 (3)	50.1 (14)
F(2)	3676 (5)	3613 (2)	2519 (3)	51.3 (14)
F(3)	421 (10)	2500	3311 (5)	76.3 (29)
S(1)	3463 (2)	1245 (1)	-1466 (1)	38.4 (5)
S(2)	-1769 (2)	1175 (1)	-3966 (1)	38.0 (5)
N(1)	2830 (8)	2500	-518 (6)	30.6 (22)
N(2)	979 (6)	771 (3)	-2988 (4)	39.9 (17)
N(3)	-2579 (9)	2500	-3703 (6)	34.9 (23)

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Table 2. Bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses

Primed atoms are related to the corresponding unprimed atoms by reflection through the mirror plane at $y = \frac{1}{2}$. Values in square brackets are interatomic distances corrected for thermal motion assuming a riding model.

As—F(1)	1.721 (2) [1.734]	S(1)—N(1)	1.659 (3)
—F(2)	1.722 (3) [1.740]	—N(2)	1.584 (3)
—F(3)	1.704 (5) [1.737]	S(2)—N(2)	1.540 (3)
—N(1)	1.910 (5)	—N(3)	1.567 (2)
F(1)—As—F(2)	89.4 (1)	As—N(1)—S(1)	123.2 (2)
—F(3)	91.0 (1)	S(1)—N(1)—S(1')	113.6 (3)
—N(1)	89.8 (1)	N(1)—S(1)—N(2)	109.9 (2)
—F(1')	89.8 (1)	S(1)—N(2)—S(2)	139.3 (2)
—F(2')	178.3 (1)	N(2)—S(2)—N(3)	119.5 (2)
F(2)—As—F(3)	90.5 (1)	S(2)—N(3)—S(2')	138.7 (4)
—N(1)	88.7 (1)		
—F(2')	91.3 (1)		
F(3)—As—N(1)	178.9 (2)		
—F(1')	91.0 (1)		
—F(2')	90.5 (1)		
F(1')—As—N(1)	89.8 (1)		
F(2')—As—N(1)	88.7 (1)		

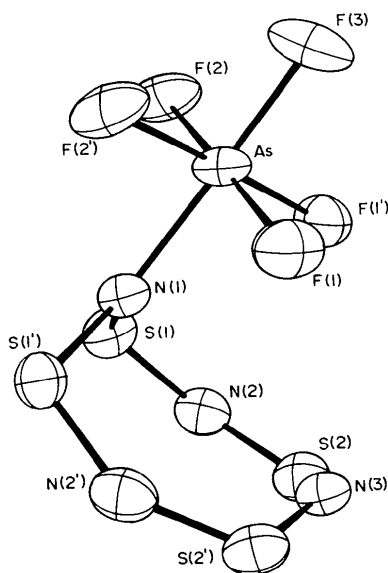


Fig. 1. ORTEP view (Johnson, 1965) of the molecular adduct $S_4N_4 \cdot AsF_5$.

0.40, otherwise $y = 1.0$, and no parameter shift was greater than 9% of its standard error. A final difference Fourier map was featureless, with a maximum peak of $0.5 \text{ e } \text{Å}^{-3}$ close to the arsenic. 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. Computing was carried out using the XRAY system (1972) and the program SHELX on a CDC 6400 computer. The final atomic coordinates from the refinement using all data are

included in Table 1,* and bond distances and angles in the $S_4N_4 \cdot AsF_5$ adduct are included in Table 2. A view of the adduct is shown in Fig. 1.

Discussion. It is well documented that tetrasulphur tetranitride [cyclotetra(azathiene)] will form adducts with a variety of Lewis acids and several structures for these adducts are known from crystallographic determinations or have been postulated from infrared spectra and chemical evidence (Alange & Banister, 1978). The molecule of the $S_4N_4 \cdot AsF_5$ adduct has crystallographic mirror symmetry and is very similar to the molecules of the 1:1 adducts of S_4N_4 with BF_3 (Drew, Templeton & Zalkin, 1967), $SbCl_5$ (Neubauer & Weiss, 1960), SO_3 (Gieren, Dederer, Roesky, Amin & Petersen, 1978) and FSO_2NCO (Gieren, Hahn, Dederer, Roesky & Amin, 1978), although it differs significantly from that of the adduct with $CuCl$ (Thewalt, 1976). In all of the former compounds the S_4N_4 ring has a modified saddle conformation with the four S atoms in a plane, and the Lewis acid coordinated to a N atom. The structure of the $S_4N_4 \cdot CuCl$ adduct differs in that the S_4N_4 bridges Cu atoms *via* two N atoms without any change in the conformation of the S_4N_4 from that in the free state in which there is a plane of N atoms and tetrahedron of S atoms (DeLucia & Coppens, 1978).

In the S_4N_4 ring of the AsF_5 adduct, there are four different S—N distances and markedly different angles around the ring. The three bonds at the substituted N are coplanar (the sum of the angles around N is 360°) and the N—S bonds to this N are the longest in the ring [1.659 (3) Å]. The S—N—S angle at this N is also markedly smaller (114°) than those at the other N atoms (139° av.). The two independent N—S—N angles in the ring also differ significantly (110 and 120°) and as a result the remaining S—N bonds have slightly different lengths (1.540–1.584 Å). The bond lengths and angles involving S and N in $S_4N_4 \cdot AsF_5$ are very similar to those in all the other adducts in which the S_4N_4 is monodentate. In all of these adducts with the exception of $S_4N_4 \cdot FSO_2NCO$ (Gieren, Hahn, Dederer, Roesky & Amin, 1978), the three bonds at the coordinated N do not deviate significantly from planarity.

The As—N bond has a length of 1.910 (5) Å in $S_4N_4 \cdot AsF_5$ and is shorter than the corresponding distance of 1.985 (16) Å found in the *N*-methyl-*S*,*S*-difluorosulphoximine–arsenic pentafluoride adduct (Bellard, Rivera & Sheldrick, 1978). The small difference in the As—F bond lengths in $S_4N_4 \cdot AsF_5$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34874 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[1.722 (3) and 1.704 (5) Å] can be attributed to the thermal motion of F(3) although it is noteworthy that the average bond length (1.716 Å av.) is very similar to that of 1.719 (3) Å found in KAsF_6 (Gafner & Kruger, 1974), indicative of the strength of the coordination. The average As–F distance after application of a riding correction is 1.737 (3) Å. In the *N*-methyl-*S,S*-difluorosulphoximine adduct the As–F distances are shorter than those in KAsF_6 and this along with the long As–N distance is considered to be evidence for a fractional bond order for the As–N bond. An even longer, weaker As–N bond of 2.29 (2) Å is found in the adduct $\text{Cl}_3\text{As}\cdot\text{NMe}_3$, although in this case As^{III} is involved (Webster & Keats, 1971).

There are no intermolecular contacts of note. The chemistry of the reactions producing this adduct will be discussed elsewhere (Gillespie, Kent & Sawyer, 1980).

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Caesium Lithium Tungstate: A Stuffed *H*-Cristobalite Structure

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Abstract. CsLiWO_4 , cubic, $F\bar{4}3m$, $a = 8.350(1)$ Å, $Z = 4$, $D_x = 4.42$ Mg m⁻³. The crystals were prepared by heating a mixture of Cs_2CO_3 , Li_2CO_3 and WO_3 at 1173 K for 3 h in a platinum crucible. Colourless and transparent prismatic crystals were obtained. The substance is a stuffed derivative of the *H*-cristobalite structure, with W–O and Li–O distances of 1.78 (3) and 1.87 (3), and Cs–O distances of 3.22 (3) and 3.60 (3) Å.

Introduction. A preliminary X-ray study with Weissenberg photographs revealed that the crystals were cubic with Laue symmetry $m\bar{3}m$. As the hkl reflexions were systematically missing for $h + k$, $k + l$ and $l + h$ odd, the possible space groups were restricted to $F\bar{4}3m$, $F432$ and $Fm\bar{3}m$. $F\bar{4}3m$ gave a satisfactory result for the structure refinement. A prismatic crystal with approximate dimensions 0.15 × 0.05 × 0.05 mm was used for intensity collection. With the ω – 2θ scan tech-

nique, intensities were measured on a Philips PW1100 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The scan speed was 4° min⁻¹ in ω and scanning was repeated twice when the total counts were less than 10 000. The scan width was determined according to $(1.2 + 0.3 \tan \theta)^\circ$. Intensities were corrected for the Lorentz–polarization and absorption effects ($\mu = 27.18$ mm⁻¹). Corrections for isotropic secondary extinction were carried out in the final stage of the structure refinement (the crystal was assumed to be a sphere 0.1 mm in diameter). Intensities of 187 independent reflexions, with $|F| > 3\sigma(|F|)$, were obtained and used for the structure determination.

The positions of the Cs and W atoms were obtained from the Patterson map and those of the Li and O atoms were then found on Fourier and difference Fourier maps synthesized with phases derived from the Cs and W atoms. The structure was refined with the