The Compounds $S_8(AsF_6)_2$ and $S_{16}(AsF_6)_2$

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Summary From the reaction between sulphur and arsenic pentafluoride the new compounds $S_8(AsF_6)_2$ and $S_{16}(AsF_6)_2$ have been isolated and identified.

CRYSTALLINE compounds of composition S_4AsF_6 (blue) and S_8AsF_6 (red) have been prepared. We have obtained evidence that the blue compound contains the S_8^{2+} cation, and it appears to be the species that is responsible for the blue colour of solutions of sulphur in oleum,[1] the supposed compound "S_2O_3,"[2] and the blue product formed in the reaction of SbF_5 with sulphur.[3] The red compound contains the S_{8n}^{n+} cation and is very probably S_{16}^{2+}.

In a typical experiment, arsenic pentafluoride (0·0533 moles) was condensed on to powdered sulphur (0·0177 moles of S_8) in HF at $-78°$ and the mixture was allowed to warm up to 0° over several days. Large quantities of arsenic trifluoride were identified (in the condensable products) by i.r. spectroscopy. The solid product consisted of a mass of glistening blue crystals the weight and elemental analysis of which corresponded to quantitative conversion of the sulphur into $S_8(AsF_6)_2$ (0·0172 moles).

The reaction can be formulated as:

$$S_8 + 3AsF_5 \rightarrow S_8(AsF_6)_2 + AsF_3.$$

In a similar reaction S_8 (0·0218 moles) was treated with AsF_5 (0·0327 moles) to yield a red solid in the amount (0·0217 moles) expected for quantitative reaction according to the equation:

$$2S_8 + 3AsF_5 \rightarrow 2S_8AsF_6 + AsF_3.$$

Elemental analysis was in agreement with the composition S_8AsF_6.

I.r. spectra of the solids at $-196°$ showed the presence of the AsF_6^- ion: blue compound, 700, (shoulder at 674), 397 cm.$^{-1}$; red compound, 698, 397 cm.$^{-1}$; $CsAsF_6$,[4] 699, 392 cm.$^{-1}$. The ^{19}F n.m.r. spectra at room temp. of solutions of both compounds in fluorosulphuric acid had only one signal in addition to that from the solvent at δ (CCl_3F) 58 p.p.m. for the blue compound and at δ (CCl_3F) 60 p.p.m. for the red compound. A solution of $Bu_4N^+AsF_6^-$ in fluorosulphuric acid gave a signal at δ (CCl_3F) 63 p.p.m. in addition to the solvent peak. The spectra remained essentially unchanged on cooling the solutions to $-80°$. Sulphur dioxide solutions of both compounds gave a single very broad resonance. On adding pyridine to the SO_2 solutions, sulphur was precipitated and the 1 : 1 : 1 : 1 quartet of AsF_6^- [δ (CCl_3F) 60 p.p.m., J_{As-F} 930 Hz.] was observed in both cases. Magnetic susceptibility measurements on the blue solid and its solutions in fluorosulphuric acid showed that the compound is essentially diamagnetic in the temperature range $-80°$ to $-10°$. The red compound, and solutions of the red compound in fluorosulphuric acid, were slightly paramagnetic in the same temperature range. On heating (up to 100°), the paramagnetism increased reversibly as the temperature was increased. Solutions of the blue compound showed a similar increase in paramagnetism on heating up to 100°. Tentatively, the paramagnetism in these solutions may be assigned to equilibria of the type

$$S_{2n}^{2+} \rightleftharpoons 2S_n^+$$

The paramagnetism of the solid red compound may be due to the presence of a small amount of the same radical that is formed at higher temperatures in solution.

The u.v. spectra of solutions of the compounds in fluorosulphuric acid are given in the Figure. The compounds completely dissolved in fluorosulphuric acid, ruling out the possibility of elemental sulphur impurity. The red compound gives only one absorption at 210 nm., suggesting that it is pure material. The main absorption of the blue compound is at 599 nm. The weak shoulders at *ca.* 400 and *ca.* 320 nm. increase slowly with time and almost certainly arise from a slow reaction of S_8^{2+} with the solvent.

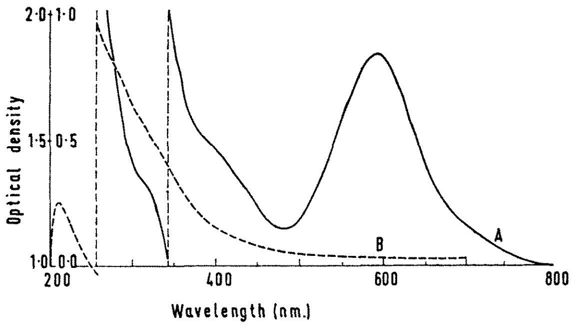

FIGURE. *Absorption spectra*: A 0·026M *solution of* $S_8(AsF_6)_2$ *in fluorosulphuric acid* (*path length,* 0·0124 cm.); B 0·0088M *solution of* $S_{16}(AsF_6)_2$ *in fluorosulphuric acid* (*path length,* 0·0032 cm.).

Single crystal data for the blue compound shows that there are sixteen S_4AsF_6 units per unit cell: space group $P2_1/c$, $a = 15{\cdot}0$, $b = 13{\cdot}4$, $c = 16{\cdot}5$ Å, $\beta = 107°\ 53''$, $D_m = 2{\cdot}61$ for sixteen units of S_4AsF_6, $D_c = 2{\cdot}69$. The asymmetric unit for $P2_1/c$ is one quarter of the unit cell, therefore, given that the cation is not polymeric, the upper limit for the molecular formula is $(S_4AsF_6)_4$. The compound is diamagnetic, therefore the cation can be either S_8^{2+} or S_{16}^{4+}. As the analogous selenium cation has been shown[5] to be Se_8^{2+}, the formula S_8^{2+} is preferred for the blue cation of sulphur. A complete crystal structure analysis is in progress.

The stoicheiometry of the preparative reaction, the chemical analysis, and the spectroscopic results show clearly that the red compound is $S_{8n}^{n+}(AsF_6^-)_n$. The magnetic data rules out odd-electron species of low molecular weight such as S_8^+ and S_{24}^{3+}. We therefore suggest that it is most likely that the cation has the formula S_{16}^{2+}. Single crystals have been obtained and the crystal structure determination is continuing.

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