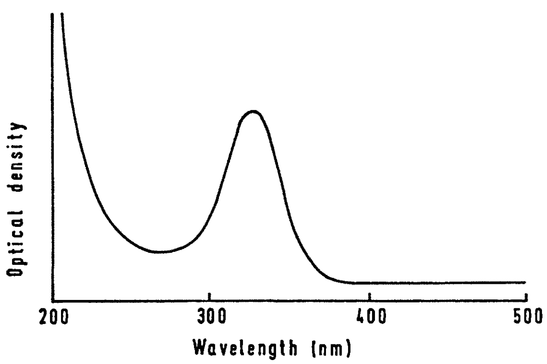
The Cation S_4^{2+}

By J. BARR, R. J. GILLESPIE,* and P. K. UMMAT
(*Department of Chemistry, McMaster University, Hamilton, Ontario, Canada*)

Summary Sulphur has been oxidized with $S_2O_6F_2$ and with SbF_5 to the compounds $S_4(SO_3F)_2$ and $S_4(SbF_6)_2$ which contain the S_4^{2+} cation.

WE reported recently[1] that sulphur is oxidized by AsF_5 to the cations S_{16}^{2+} and S_8^{2+}. We have now studied the oxidation of sulphur with $S_2O_6F_2$ and SbF_5 and have obtained new compounds containing the S_4^{2+} cation. Oxidation of sulphur with $S_2O_6F_2$ in solution in fluorosulphuric acid gave initially the spectrum of S_{16}^{2+} (strong peak at 235 and weak peaks at 350 and 430 nm), then the blue solution of S_8^{2+} (λ_{max} 595 nm), and finally with an excess of $S_2O_6F_2$ an almost colourless solution with λ_{max} 330 nm which must be due to a species containing sulphur in a higher oxidation state than in S_8^{2+}. By condensing an excess of $S_2O_6F_2$ on to powdered sulphur in liquid SO_2 at $-196°$ and then allowing the mixture to warm up to $-23°$ slowly over several days, a pale yellow amorphous powder was obtained after removing the SO_2 by pump. Careful temperature control was necessary as any rapid increase in the temperature resulted in an explosion. Elemental analysis of the product was consistent with the composition S_2SO_3F. The solid was found to be diamagnetic, hence by analogy with the previously reported Se_4^{2+} and Te_4^{2+} cations[2] it is reasonable to formulate this compound as $S_4(SO_3F)_2$. It did not give a stable solution in fluorosulphuric acid as the characteristic peak of the S_8^{2+} cation at 595 nm appeared and increased in intensity with time. However, a stable colourless solution was obtained in HSO_3F–SbF_5 which had the absorption spectrum shown in the Figure with a strong peak at 330 nm and a weak poorly resolved peak at *ca.* 280 nm. The Raman spectrum of the solid showed all the bands of the SO_3F^- ion.



FIGURE

Ruff *et al.*[3] reported that a white solid SbF_5S could be obtained from the reaction of SbF_5 with S. Peacock *et al.*[4] obtained a blue solution of sulphur in SbF_5 from which on removal of the excess of SbF_5 they obtained a white solid which they claimed to have the composition $(SbF_5)_2S$. In the present investigation we found that when sulphur is treated with SbF_5 in liquid SO_2 in the stoicheiometric ratio S_8–$SbF_5 = 1{\cdot}5$ a dark red product was formed which contains S_{16}^{2+} formed according to the equation

$$2S_8 + 3SbF_5 = S_{16}^{2+}(SbF_6)_2 + SbF_3.$$

With a larger quantity of SbF_5 a blue product was obtained which contains S_8^{2+}, and with a large excess of SbF_5 the first product was a dark blue solution which on heating under reflux at 140° for several days became colourless. After removal of the excess of SbF_5 and SbF_3 by heating under vacuum at 100° a white solid was obtained. The Raman spectrum of the solid showed that it contained SbF_6^- and the absorption spectrum of a solution of the compound in HSO_3F gave a spectrum identical to that in the Figure. The compound therefore appears to be $S_4(SbF_6)_2$.

The absorption spectra of Te_4^{2+}, Se_4^{2+}, and S_4^{2+} are very similar in shape each having a strong peak at longer wavelengths and a weak peak at shorter wavelengths, the λ_{max} decreasing steadily in the series Te_4^{2+}, Se_4^{2+}, and S_4^{2+} as shown in the Table. This similarity in the spectra lends further support to our identification of the species S_4^{2+} and also strongly suggests that it has the same square planar structure that has been established[2] for Se_4^{2+}.

Recently Stephens[5] has drawn attention to the similarity in the m.c.d. of the absorption bands of Se_4^{2+} and Te_4^{2+} and the 330 nm band observed in solutions of sulphur in oleum. Accordingly he has attributed this 330 nm band to the S_4^{2+} cation. Our work thus confirms Stephens' assignment of the 330 nm band of S in oleum to S_4^{2+}. We have also shown from absorption spectra and e.s.r. spectra that S_{16}^{2+} and S_8^{2+} and radicals derived from these diamagnetic cations are also present in solutions of sulphur in oleum of various concentrations.

	λ_{max} (nm)	
	Strong	Weak
Te_4^{2+}	510	420
Se_4^{2+}	410	320
S_4^{2+}	330	∼280

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

(*Received, December 22nd*, 1969; *Com.* 1927.)

[1] R. J. Gillespie and J. Passmore, *Chem. Comm.*, 1969, 1333.
[2] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Canad. J. Chem.*, 1968, **46**, 169; I. D. Brown, D. B. Crump, R. J. Gillespie and D. P. Santry, *Chem. Comm.*, 1968, 853; J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, 1968, **90**, 6855.
[3] O. Ruff, H. Graf, W. Heller, and Knoch, *Ber.*, 1906, **39**, 4310.
[4] E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. and Ind.*, 1951, 1117.
[5] P. J. Stephens, *Chem. Comm.*, 1969, 1496.