

Preparation of a Dico-ordinate Sulphur Dication

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Summary The first dico-ordinate sulphur dication, $(\text{Me}_2\text{N})_2\text{S}^{2+}$, has been prepared by treatment of $(\text{Me}_2\text{N})_2\text{SF}_2$ with fluoride ion acceptors.

THE isoelectronic principle suggests the existence of several six-electron main-group cations such as R_3Si^+ , R_3P^{2+} , R_2P^+ , and R_2S^{2+} . Thus far only phosphonium (R_3P^+) ions have been found to exist in the condensed phases,^{1,2} although, of course, silicium ions are well known species in the vapour phase.³ Two-co-ordinate sulphur dications, R_2S^{2+} , have been postulated as one of the possible transition states involved in the racemisation of sulphonium cations,⁴ however, such compounds have never been isolated previously.

Treatment of $(\text{Me}_2\text{N})_2\text{SF}_2$ (**1**) with 1 equiv. of a fluoride ion acceptor such as PF_5 , AsF_5 , or BF_3 in SO_2 solution results in the generation of the cation $(\text{Me}_2\text{N})_2\text{SF}^+$ (**2**) as described previously.⁵ However, when an excess of AsF_5 is employed, the ^1H resonance of (**2**), which appears as a doublet because of coupling to F (δ 2.95, $J_{\text{F-SNCH}}$ 7.0 Hz), is replaced by a singlet at lower field (δ 3.75) which we assign to the dico-ordinate sulphur dication, $(\text{Me}_2\text{N})_2\text{S}^{2+}$ (**3**). The ^{13}C resonance of (**3**) (δ 41.6 p.p.m., s) was also downfield from that of (**2**) (δ 37.9 p.p.m., s). Moreover, no ^{19}F resonance attributable to (**3**) could be detected. Particularly compelling is the fact that two anion resonances were detected by n.m.r. spectroscopy when the fluoride ion

abstraction from (**1**) was conducted with two F^- acceptors. For example, treatment of (**1**) with 1 equiv. of PF_5 followed by 1 equiv. of AsF_5 resulted in the detection of PF_6^- (^{31}P n.m.r.: δ 144 p.p.m., septet, J_{PF} 711 Hz, ^{19}F n.m.r.: δ 72.5 p.p.m., d, J_{PF} 711 Hz), AsF_6^- (^{19}F n.m.r.: δ 59.4 p.p.m., q \dagger), and (**3**).

Vibrational spectroscopy has also been useful for the characterisation of (**3**). Since $(\text{Me}_2\text{N})_2\text{P}^+$ and (**3**) are isoelectronic the vibrational spectra of these cations are expected to be somewhat similar. This is indeed the case. For example, $(\text{Me}_2\text{N})_2\text{P}^+$ exhibits strong Raman peaks at 997 and 1300 cm^{-1} while for (**3**) peaks of very similar appearance and relative intensity are observed at 961 and 1247 cm^{-1} . Parry and his co-workers¹ have detected peaks at 996 and 1309 cm^{-1} in the i.r. spectrum of $(\text{Me}_2\text{N})_2\text{P}^+$ and assigned them to CN...P stretching. When (**3**) is generated by treating (**1**) with 2 equiv. of PF_5 , a strong Raman peak at 742 cm^{-1} is detected which has been assigned⁶ to $\nu_1(A_{1g})$ of PF_6^- . Similarly, when AsF_5 is used as the fluoride ion acceptor, an analogous band at 685 cm^{-1} is detected which is characteristic⁶ of AsF_6^- . When (**1**) is treated with equimolar quantities of PF_5 and AsF_5 the $\nu_1(A_{1g})$ modes of both PF_6^- and AsF_6^- are detected.

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\dagger The quartet is due to quadrupolar broadened coupling with the ^{75}As nucleus, $I = 3/2$.

¹ See, e.g., M. G. Thomas, C. W. Schultz, and R. W. Parry, *Inorg. Chem.*, 1977, **16**, 994, and references therein.

² For characterization by X-ray crystallography, see A. H. Cowley, M. C. Cushner, and J. S. Szobota, *J. Amer. Chem. Soc.*, 1978, **100**, 7784.

³ See, e.g., M. K. Murphy and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 1976, **98**, 5781; M. K. Murphy and J. L. Beauchamp, *ibid.*, 1977, **99**, 2085; Y. Apeloig and P. v. R. Schleyer, *Tetrahedron Letters*, 1977, 4687.

⁴ S. Oae, *Quart. Reports Sulfur Chem.*, 1970, **5**, 53.

⁵ A. H. Cowley, D. J. Pagel, and M. L. Walker, *J. Amer. Chem. Soc.*, 1978, **100**, 7065.

⁶ G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.