

Identification of the Species $[\text{Te}_n\text{Se}_{4-n}]^{2+}$ by High Resolution ^{125}Te and ^{123}Te Fourier Transform N.M.R. Spectroscopy

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Summary High resolution ^{125}Te and ^{123}Te F.T. n.m.r. spectroscopy have been used to identify all members of the series $[\text{Te}_n\text{Se}_{4-n}]^{2+}$ ($n = 1-4$) in the Te-Se-oleum system.

THE reaction between metallic tellurium and sulphuric acid to produce a red-violet solution has been known since 1798.¹ However, it was only during the last few years that Gillespie *et al.*² and others^{3,4} characterised the reaction and concluded that the colour was due to the Te_4^{2+} species. Subsequent X-ray studies of $\text{Te}_4(\text{AlCl}_4)_2$ and $\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$ ⁴ have shown the Te_4^{2+} ion to be square-planar.

Tellurium and selenium metal were dissolved in 65% oleum at room temperature and the resulting orange-brown solutions were used in obtaining ^{125}Te and ^{123}Te high resolution F.T. n.m.r. spectra. All spectra were obtained on a home-built, crossed-coil pulse spectrometer⁵ operating at 15.06 MHz and equipped with a Nicolet 1082 data system. Non-spinning sample tubes (12 mm) were used and solutions were not degassed.

Figure 1 shows the ^{125}Te resonances of all five species of the series $[\text{Te}_n\text{Se}_{4-n}]^{2+}$ for a sample after periods of 1 day, 2 days, and 4 days. As can be seen from the series of spectra, the exchange process is very slow, requiring *ca.* 4 days for total disappearance of the Te_4^{2+} species. Chemical shifts for the various ^{125}Te resonances are given in the Table. The Te_4^{2+} species is at high field with other ^{125}Te resonances containing Se atoms moving progressively downfield with the replacement of Se atoms for Te. This is consistent with the higher electronegativity of Se than that of Te. The chemical shifts are very large in going from

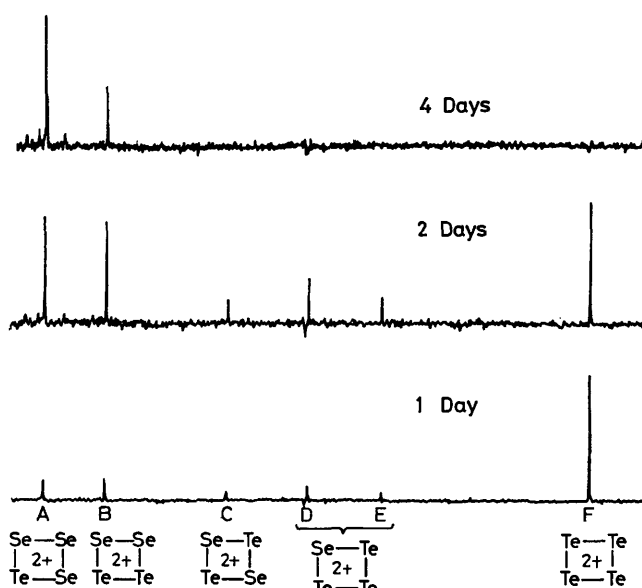


FIGURE 1. ^{125}Te n.m.r. spectrum of Te-Se-oleum mixture as slow exchange occurred over a four-day period (12.5 kHz details of 20 kHz scans); 500,000 scans (20 h) for each spectrum; resonance A is at low field and resonance F is at high field.

Te_4^{2+} to $[\text{TeSe}_3]^{2+}$ (*ca.* 700 p.p.m.) because of the very large paramagnetic contribution to the shielding term of Te. Thus the Te shift is an ideal parameter for the identification of the members of this series.

We have also been able to measure the $J(^{125}\text{Te}-^{123}\text{Te})$ couplings in Te_4^{2+} in addition to all of the $J(^{125}\text{Te}-^{77}\text{Se})$ coupling constants. Figure 2 displays the ^{123}Te spectrum of Te_4^{2+} showing the *cis*- and *trans*-coupling to magnetic

^{125}Te nuclei. This spectrum is consistent with a time-average square-planar solution structure for the parent species Te_4^{2+} . Values are reported in the Table. The

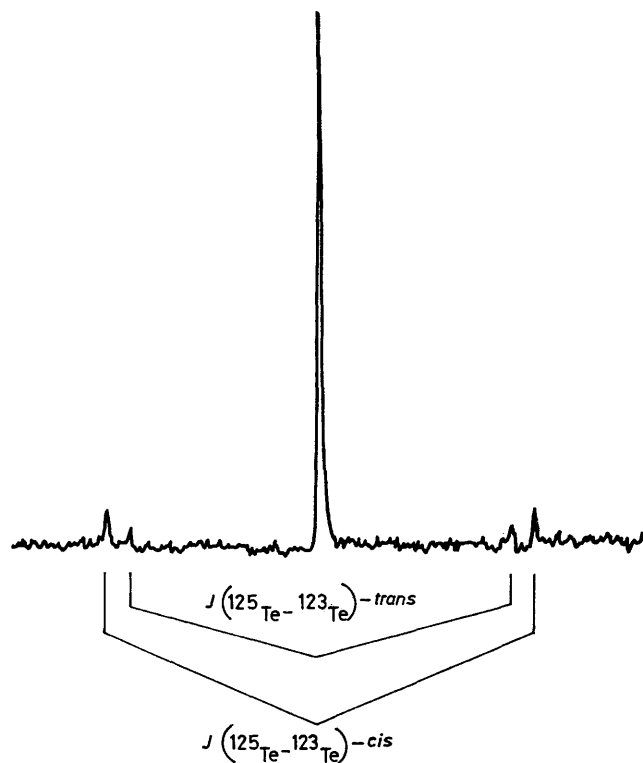


FIGURE 2. ^{123}Te n.m.r. spectrum of Te_4^{2+} showing the main resonance with two doublets (intensity 2:1) corresponding to $J(^{123}\text{Te}-^{125}\text{Te})$ -*cis*, 676 and $J(^{123}\text{Te}-^{125}\text{Te})$ -*trans*, 602 Hz. Sweep width 1000 Hz; 10^6 scans (40 h).

¹ M. H. Klaproth, *Phil. Mag.*, 1798, **1**, 78.

² J. Barr, R. J. Gillespie, G. P. Pez, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, 1976, **10**, 362; R. J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 49.

³ J. Bjerrum and G. P. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 4472; D. T. Prince, J. D. Corbett, and B. Garbisch, *Inorg. Chem.*, 1970, **9**, 2731.

⁴ T. W. Couch, D. A. Lokken, and J. D. Corbett, *Inorg. Chem.*, 1972, **11**, 357.

⁵ T. Higgs, A. Brooke, and E. J. Wells, unpublished results.

TABLE

Species	$\delta/\text{p.p.m.}^{\text{a}}$	Coupling constant/Hz
A	-3352 to -3354	$J(^{125}\text{Te}-^{77}\text{Se})$ - <i>cis</i> , 764; - <i>trans</i> , 581
B	-3254 to -3272	$J(^{125}\text{Te}-^{77}\text{Se})$ - <i>cis</i> , 457; - <i>trans</i> , 200
C	-3110 to -3147	$J(^{125}\text{Te}-^{77}\text{Se})$ - <i>cis</i> , 330 ^c
D,E	Te- <i>cis</i> , -3004 to -3008; - <i>trans</i> , -2887 to -2907	$J(^{125}\text{Te}-^{125}\text{Te})$ - <i>cis</i> , 930 ^b
F	-2665 to -2625 ^c	$J(^{125}\text{Te}-^{123}\text{Te})$ - <i>cis</i> , 676; ^d - <i>trans</i> , 602

^a Chemical shifts all downfield relative to $^{125}\text{TeMe}_2$ as external standard. Shifts are all concentration-dependent. Observed ranges are indicated. ^b Measured in liquid SO_2 solution. ^c Medium-dependent as well as concentration-dependent. ^d Medium-dependent.

intensities of the ^{77}Se satellite resonances have enabled us to positively identify these signals as belonging to the various $[\text{Te}_n\text{Se}_{4-n}]^{2+}$ species. In the $[\text{Te}_3\text{Se}]^{2+}$ case we were unable to obtain the spin-spin coupling constants in oleum because of the weakness of the signal. However, we were able to measure the expected 2:1 ratio for the two different ^{125}Te resonances belonging to this particular species. The species $[\text{Te}_3\text{Se}]^{2+}$ has been clearly observed in liquid SO_2 solution.

We feel that ^{125}Te and ^{123}Te high resolution F.T. n.m.r. spectroscopy will be invaluable in the assignment and identification of other Te-polycations in the oleum solutions. We have observed other Te resonances to much higher fields in these solutions.

Added in proof: A ^{125}Te and ^{77}Se n.m.r. study of the Te_6^{4+} , $\text{Te}_{4-n}\text{Se}_n^{2+}$, $\text{Te}_2\text{Se}_4^{2+}$, and $\text{Te}_3\text{Se}_3^{2+}$ cations is reported in the following communication.

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