

## 125-Tellurium and 77-Selenium Multinuclear Magnetic Resonance Studies of $\text{Te}_6^{4+}$ , $\text{Te}_{4..n}\text{Se}_n^{2+}$ , $\text{Te}_2\text{Se}_4^{2+}$ , and $\text{Te}_3\text{Se}_3^{2+}$ Polyatomic Cations

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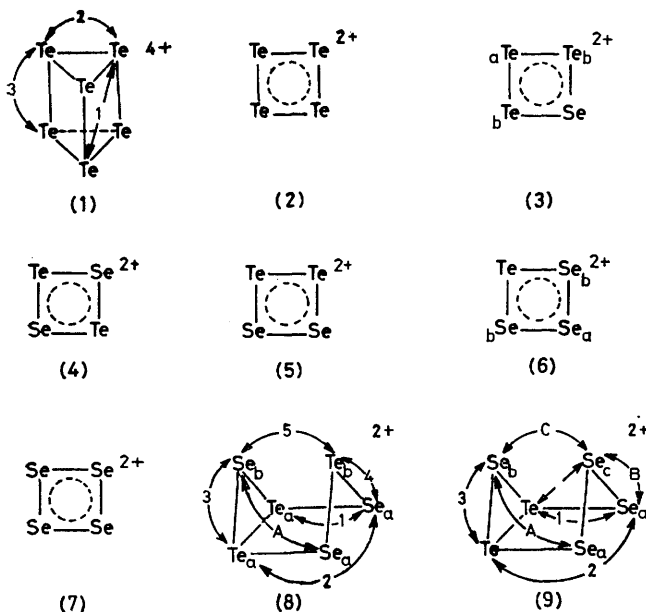
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**Summary** High-resolution  $^{125}\text{Te}$  and  $^{77}\text{Se}$  Fourier transform n.m.r. spectroscopy has been used to characterize the previously known  $\text{Te}_6^{4+}$ ,  $\text{Te}_4^{2+}$ ,  $\text{Se}_4^{2+}$ , and  $\text{Te}_2\text{Se}_4^{2+}$  cations for the first time and several new mixed species in the  $+1/2$  ( $\text{Te}_3\text{Se}^{2+}$ , *cis*- and *trans*- $\text{Te}_2\text{Se}_2^{2+}$ , and  $\text{TeSe}_3^{2+}$ ) and

$+1/3$  ( $\text{Te}_3\text{Se}_3^{2+}$ ) oxidation states; the  $^{125}\text{Te}$ - $^{123}\text{Te}$ ,  $^{125}\text{Te}$ - $^{77}\text{Se}$ , and  $^{77}\text{Se}$ - $^{77}\text{Se}$  spin-spin couplings have been observed in both natural abundance and 94.4%  $^{77}\text{Se}$  enriched preparations and used to assign the structures.

It has been known for some time that selenium and tellurium will dissolve in oleums to give yellow-green and red-violet solutions, respectively.<sup>1,2</sup> It is difficult to isolate solids from oleum solutions, but selective oxidation of the elements with  $\text{AsF}_5$ ,  $\text{SbF}_5$ ,  $\text{S}_2\text{O}_6\text{F}_2$ , or with the halide of the element in molten  $\text{NaAlCl}_4$  has allowed the isolation of salts of the polyatomic cations  $\text{Se}_4^{2+}$ ,  $\text{Se}_3^{2+}$ ,  $\text{Te}_4^{2+}$ ,  $\text{Te}_6^{4+}$ ,  $\text{Te}_2\text{Se}_4^{2+}$ , and  $\text{Te}_2\text{Se}_3^{2+}$  and determination of their structures by X-ray crystallography.<sup>3-6</sup>



Both selenium and tellurium possess naturally abundant spin 1/2 isotopes,  $^{77}\text{Se}$  (7.50%),  $^{125}\text{Te}$  (7.03%), and  $^{123}\text{Te}$  (0.89%). In the present study, we have undertaken the characterization of the previously known cations  $\text{Te}_6^{4+}$ ,  $\text{Te}_4^{2+}$ ,  $\text{Se}_4^{2+}$ , and  $\text{Te}_2\text{Se}_4^{2+}$  by means of  $^{77}\text{Se}$  and  $^{125}\text{Te}$  Fourier transform n.m.r. spectroscopy and investigation of the existence of hitherto unreported mixed tellurium-selenium species in the +1/2 and +1/3 oxidation states.<sup>7</sup>

The  $\text{Te}_6^{4+}$  cation has recently been shown to consist of a distorted trigonal prism in the solid state<sup>4</sup> while  $\text{Se}_4^{2+}$  and  $\text{Te}_4^{2+}$  have been shown to be square-planar.<sup>3</sup> Solutions of  $\text{Te}_6^{4+}$  and  $\text{Te}_4^{2+}$  have been prepared by quantitatively oxidizing tellurium powder in 30% oleum and 100%  $\text{H}_2\text{SO}_4$ , respectively. It has been possible to observe both long-range and directly bonded natural abundance  $^{125}\text{Te}$ - $^{123}\text{Te}$  spin-spin couplings in both cations. The square-planar  $\text{Te}_4^{2+}$  cation exhibits both *cis*- and *trans*- $^{125}\text{Te}$ - $^{123}\text{Te}$  couplings whose component lines have relative intensities of 2:1, respectively (Table). The  $^{125}\text{Te}$ - $^{123}\text{Te}$  coupling pattern observed for  $\text{Te}_6^{4+}$  (Figure) is consistent with a rigid, *regular* trigonal prismatic species in solution and, as such, the  $\text{Te}_6^{4+}$  cation exhibits three couplings: two unique directly bonded *cis*-couplings along the triangular edges and unique rectangular edges and a long-range *trans*-coupling across the rectangular face of the prism (Table). The respective intensities of the component lines are 2:1:2.

Oxidation of equimolar quantities of  $^{77}\text{Se}$  (94.4% enriched) and natural abundance tellurium in  $\text{SO}_2$  solvent with  $\text{AsF}_5$

followed by dissolution of the dry product in 98%  $\text{D}_2\text{SO}_4$  gives rise to a mixture of predominantly +1/3 oxidation state species. Both  $^{77}\text{Se}$  and  $^{125}\text{Te}$  n.m.r. spectra have been recorded and the principal species present have been identified with the aid of the observed  $^{125}\text{Te}$ - $^{77}\text{Se}$  and  $^{77}\text{Se}$ - $^{77}\text{Se}$  spin-spin coupling patterns. In addition to  $\text{Te}_2\text{Se}_4^{2+}$ , whose crystal structure has been reported,<sup>5</sup> we have been able to identify a new +1/3 oxidation state species,  $\text{Te}_3\text{Se}_3^{2+}$ , in these solutions (Table).

Equimolar mixtures of tellurium and selenium powders in 30% oleum and solutions of  $\text{Te}_2\text{Se}_4^{2+}(\text{AsF}_6^-)_2$  and a substance tentatively formulated as  $[\text{Te}_4\text{Se}_3^{2+}(\text{AsF}_6^-)_2]$  in 68% oleum are readily oxidized, giving rise to new resonances which occur at considerably higher  $^{77}\text{Se}$  and  $^{125}\text{Te}$  frequencies relative to the +1/3 oxidation state species. These new environments can be assigned, with the aid of natural abundance  $^{125}\text{Te}$ - $^{77}\text{Se}$  and  $^{77}\text{Se}$ - $^{77}\text{Se}$  couplings, to the series of hitherto unreported square-planar species  $\text{TeSe}_3^{2+}$ , *cis*- and *trans*- $\text{Te}_2\text{Se}_2^{2+}$ , and  $\text{Te}_3\text{Se}^{2+}$  (Table).

Interestingly, mixtures of  $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$  and  $\text{Se}_4^{2+}(\text{AsF}_6^-)_2$  in 68% oleum show no evidence for selenium-tellurium scrambling even after several days at room temperature. However, mixtures of selenium and tellurium powders dissolved in 30% oleum initially show the presence of a substantial concentration of  $\text{Te}_2\text{Se}_4^{2+}$  which is slowly oxidized over a period of *ca.* two days to give  $\text{Te}_{4-n}\text{Se}_n^{2+}$  species. Likewise, samples of  $\text{Te}_2\text{Se}_4^{2+}(\text{AsF}_6^-)_2$  dissolved in 68% oleum are remarkably stable and are only slowly oxidized to  $\text{Te}_{4-n}\text{Se}_n^{2+}$  species at room temperature, requiring *ca.* one day to go to completion. This reaction yields mainly selenium-rich species. In contrast, the solid formulated as  $[\text{Te}_4\text{Se}_3^{2+}(\text{AsF}_6^-)_2]$  is oxidized almost instantaneously in 68% oleum to give predominantly the tellurium-rich  $\text{Te}_{4-n}\text{Se}_n^{2+}$  species, showing no evidence for +1/3 oxidation state species. We conclude that formation of mixed +1/3 oxidation state cations is a necessary precursor to the formation of mixed +1/2 square-planar cations in strong oleums and that selenium-tellurium scrambling among +1/2 square-planar cations is not mechanistically significant in these media.

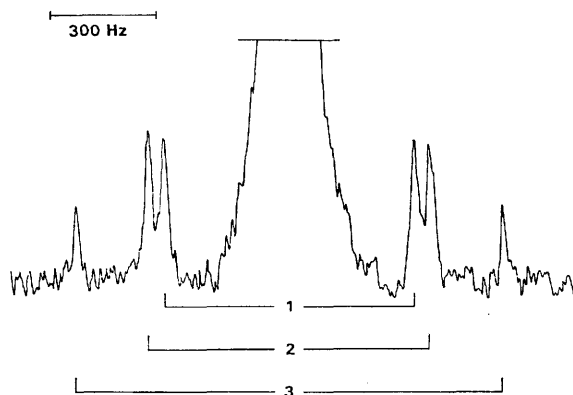


FIGURE. The natural abundance  $^{125}\text{Te}$  n.m.r. spectrum of the  $\text{Te}_6^{4+}$  cation [ $0.155 \text{ mol kg}^{-1} \text{ Te}_6^{4+}(\text{HS}_2\text{O}_7^-)_4$  in 30% oleum;  $\delta(^{125}\text{Te}) = -559 \text{ p.p.m.}$  with respect to  $(\text{HO})_6\text{Te}$ ] showing the three  $^{125}\text{Te}$ - $^{123}\text{Te}$  couplings of the trigonal prism: (1) *trans*-coupling across the rectangular faces, (2) *cis*-coupling along the triangular edges, and (3) *cis*-coupling along the unique rectangular edges.

TABLE  $^{125}\text{Te}$  and  $^{77}\text{Se}$  n.m.r. parameters for the  $\text{Te}_6^{4+}$ ,  $\text{Te}_{4-n}\text{Se}_n^{2+}$ ,  $\text{Te}_3\text{Se}_3^{2+}$ , and  $\text{Te}_2\text{Se}_4^{2+}$  polyatomic cations.<sup>a</sup>

Cation	$^{125}\text{Te}$	$\delta/\text{p.p.m.}^b$	$^{77}\text{Se}$	Coupling constants/Hz <sup>c</sup> ( $^{77}\text{Se}$ - $^{77}\text{Se}$ , $^{125}\text{Te}$ - $^{77}\text{Se}$ , $^{125}\text{Te}$ - $^{125}\text{Te}$ )
(1)	-559 <sup>d</sup>			Te-Te: <sup>d</sup> 701(1), 791(2), 1196(3)
(2)	1949 <sup>e</sup>			Te-Te: <sup>e</sup> 604 ( <i>trans</i> ), 608 ( <i>cis</i> )
	1912 <sup>f</sup>			
	2093 <sup>g</sup>			
	2100 <sup>h</sup>			
(3)	2173(a), 2294(b) <sup>f</sup>		129.6 <sup>f</sup>	Te-Se: <sup>f</sup> 207 ( <i>cis</i> )
	2219(a), 2290(b) <sup>f</sup>			
(4)	2417 <sup>f</sup>		362.2 <sup>f</sup>	Te-Se: <sup>f</sup> 531 ( <i>cis</i> )
	2376 <sup>g</sup>		391.1 <sup>g</sup>	Te-Se: <sup>g</sup> 554 ( <i>cis</i> )
	2391 <sup>h</sup>		360.9 <sup>h</sup>	Te-Se: <sup>h</sup> 550 ( <i>cis</i> )
	2409 <sup>i</sup>			
(5)	2539 <sup>f</sup>		340.4 <sup>f</sup>	Te-Se: <sup>f</sup> 195 ( <i>trans</i> ), 470 ( <i>cis</i> )
	2538 <sup>f</sup>		336.0 <sup>f</sup>	
(6)	2641 <sup>f</sup>		455.2(a), 566.3(b) <sup>f</sup>	Te-Se: <sup>f</sup> 757 ( <i>cis</i> )
	2632 <sup>h</sup>		444.8(a), 592.2(b) <sup>h</sup>	Se-Se: <sup>h</sup> 188
(7)			457.0(a), 561.2(b) <sup>i</sup>	Te-Se: <sup>h</sup> 597 ( <i>trans</i> ), 750 ( <i>cis</i> )
	2643 <sup>i</sup>			
(8)			637.3 <sup>f</sup>	
			645.7 <sup>h</sup>	
			636.1 <sup>i</sup>	
(9)	586.8(a), 217.7(b) <sup>j</sup>	-700.5(a), -1149.6(b) <sup>j</sup>		Se-Se: <sup>j</sup> 17.4(A)
				Te-Se: <sup>j</sup> 157(1), 96(2), 140(3), 231(4), 48(5)
(9)	595.4 <sup>k</sup>		-483.9(a), -1186.9(b), -622.6(c) <sup>k</sup>	Se-Se: <sup>k</sup> 13(A), 92(B), 39(C)
				Te-Se: <sup>k</sup> 168(1), 95(2), 122(3), 95(4)

<sup>a</sup>  $^{77}\text{Se}$  and  $^{125}\text{Te}$  spectra were recorded in the Fourier transform mode at 17.19 and 28.43 MHz, respectively, on a Bruker WH-90 multinuclear magnetic resonance spectrometer using quadrature phased detection.  $\text{D}_2\text{O}$  was used as the external  $^2\text{H}$ -lock substance. Between 100,000 and 300,000 scans were accumulated in 16K of memory using a spectral width of 35,000 Hz, yielding a resolution of 4.38 Hz per data point and a pulse repetition time of 0.229 s. The respective pulse widths used for all  $^{77}\text{Se}$  and  $^{125}\text{Te}$  spectra were 17 and 20  $\mu\text{s}$ . Line broadenings of 3–5 Hz were applied in the exponential smoothing of the free induction decays. <sup>b</sup> The 'high-frequency positive sign' convention for chemical shifts as outlined in the I.U.P.A.C. convention (*Pure Appl. Chem.*, 1972, 29, 627) has been employed. <sup>c</sup>  $^{125}\text{Te}$  and  $^{77}\text{Se}$  chemical shifts have been referenced with respect to external samples of saturated aqueous  $(\text{HO})_6\text{Te}$  and  $\text{H}_2\text{SeO}_3$ , respectively, at 26 °C. Conversions to chemical shifts (p.p.m.) with respect to neat  $\text{Me}_2\text{Se}$  and  $\text{Me}_2\text{Te}$  at 26 °C are given by  $\delta(\text{Me}_2\text{Se}) = \delta(\text{H}_2\text{SeO}_3) + 1302.6$ , and  $\delta(\text{Me}_2\text{Te}) = \delta[(\text{HO})_6\text{Te}] + 710.9$ . <sup>e</sup> Numbers and letters in parentheses refer to the chemical shifts and couplings indicated in the structural formulae. <sup>d</sup> 0.155 mol  $\text{kg}^{-1}$   $\text{Te}_6^{4+}$  in 30% oleum; prepared *in situ* by oxidizing tellurium powder with  $\text{SO}_3$ . <sup>e</sup> 0.250 mol  $\text{kg}^{-1}$   $\text{Te}_4^{2+}$  in ca. 100%  $\text{H}_2\text{SO}_4$ ; prepared *in situ* by oxidizing tellurium powder with 100%  $\text{H}_2\text{SO}_4$ . <sup>f</sup> 0.126 mol  $\text{kg}^{-1}$  ( $^{125}\text{Te}$  sample) and 0.115 mol  $\text{kg}^{-1}$  ( $^{77}\text{Se}$  sample) ' $\text{Te}_4\text{Se}_2^{2+}(\text{AsF}_6^-)_2$ ' in 68% oleum. The solute was prepared by oxidizing stoichiometric amounts of tellurium and selenium powders at room temperature with 1.50 mol. equiv. of  $\text{AsF}_5$  in liquid  $\text{SO}_2$  solvent followed by removal of  $\text{SO}_2$  and  $\text{AsF}_5$  *in vacuo* after several days. <sup>g</sup> 0.204 mol  $\text{kg}^{-1}$   $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$  and 0.168 mol  $\text{kg}^{-1}$   $\text{Se}_4^{2+}(\text{HS}_2\text{O}_7^-)_2$  in 100%  $\text{H}_2\text{SO}_4$ . <sup>h</sup> The sample was prepared by dissolving a mixture of equimolar amounts of tellurium and selenium powders in 30% oleum; 0.10 mol  $\text{kg}^{-1}$  'Te' and 0.10 mol  $\text{kg}^{-1}$  'Se'. <sup>i</sup> 0.335 mol  $\text{kg}^{-1}$  ( $^{125}\text{Te}$  sample) and 0.211 mol  $\text{kg}^{-1}$  ( $^{77}\text{Se}$  sample)  $\text{Te}_2\text{Se}_4^{2+}(\text{AsF}_6^-)_2$  in 68% oleum. The method of solute preparation was identical to that used in (f) above. <sup>j</sup> An equimolar mixture of natural abundance tellurium and 94.4%  $^{77}\text{Se}$ -enriched selenium powders was allowed to react at room temperature with 0.75 mol. equiv. of  $\text{AsF}_5$  in liquid  $\text{SO}_2$  for 2 days. Isolation of the solid material, consisting largely of  $\text{Te}_3\text{Se}_3^{2+}(\text{AsF}_6^-)_2$  and  $\text{Te}_2\text{Se}_4^{2+}(\text{AsF}_6^-)_2$  was followed by dissolution in 98%  $\text{D}_2\text{SO}_4$  (also used as the  $^2\text{H}$ -lock substance). 0.155 mol  $\text{kg}^{-1}$  'Te' and 0.155 mol  $\text{kg}^{-1}$  'Se'. <sup>k</sup> Sample preparation was identical to (j) above except that the relative molar amount of  $\text{AsF}_5$  was increased to 1.50 and oxidation allowed to proceed for 10 days. 0.187 mol  $\text{kg}^{-1}$  'Te' and 0.187 mol  $\text{kg}^{-1}$  'Se'. The n.m.r. spectra showed that the sample was essentially free of  $\text{Te}_3\text{Se}_3^{2+}(\text{AsF}_6^-)_2$ .

Chemical shifts among tellurium- and selenium-containing polyatomic cations are very large, ranging from +2650 to -560 p.p.m. for  $^{125}\text{Te}$  and from +650 to -1200 p.p.m. for  $^{77}\text{Se}$  in the present study. It may, therefore, be concluded that paramagnetic contributions dominate the chemical shift trends. A monotonic decrease in  $^{77}\text{Se}$  chemical shift and a parallel increase in  $^{125}\text{Te}$  chemical shift with increasing selenium number in the series  $\text{Te}_{4-n}\text{Se}_n^{2+}$  is consistent with the higher effective electronegativity of selenium (Table). Although the  $^{125}\text{Te}$  and  $^{77}\text{Se}$  chemical shifts of the +1/3 oxidation state species,  $\text{Te}_3\text{Se}_3^{2+}$  and  $\text{Te}_2\text{Se}_4^{2+}$ , occur at lower frequencies than the series of +1/2 oxidation state species,  $\text{Te}_{4-n}\text{Se}_n^{2+}$ , the frequency of

$\text{Te}_6^{4+}$ , the only known example of a +2/3 oxidation state species, shows that the  $^{125}\text{Te}$  environment is considerably more shielded than those of the aforementioned lower oxidation states. Several new resonances not reported here have also been observed and can be reasonably associated with a new series of mixed  $\text{Te}_{6-n}\text{Se}_n^{4+}$  species.

It is clear that high-resolution multinuclear magnetic resonance techniques will continue to prove invaluable for the identification of new diamagnetic polyatomic cations in oleums and other non-aqueous solvents and for pin-pointing the conditions and reaction mechanisms operative in their formation.

*Added in proof.* A  $^{125}\text{Te}$  n.m.r. study of the  $\text{Te}_{4-n}\text{Se}_n^{2+}$

cations is reported in the preceding communication.

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<sup>7</sup> The structure of the *trans*-Te<sub>2</sub>Se<sub>2</sub><sup>2+</sup> cation has been determined by X-ray crystallography in the compound (Te<sub>2</sub>Se<sub>2</sub><sup>2+</sup>)(Sb<sub>3</sub>F<sub>14</sub><sup>-</sup>) (SbF<sub>6</sub><sup>-</sup>); P. Boldrini, I. D. Brown, R. J. Gillespie, E. M. Maharajh, and D. R. Slim, unpublished observations.