Trisulphates of Unusual Tellurium Cations

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Tellurium forms red and yellow solutions when dissolved in disulphuric acid. From u.v., cryoscopic, conductance, and magnetic susceptibility measurements, it has been found that the red and yellow solutions are due to Te_4^{2+} and Te_2^{2+} cations respectively. Solid compounds of composition $Te_4S_3O_{10}$ and $Te_2S_3O_{10}$ have been obtained on treating tellurium with sulphur trioxide. From u.v. and i.r. spectra, cryoscopic and conductance studies in highly acidic media it has been found that these compounds are ionic in nature and tellurium is present as cation in an unusual oxidation state.

RECENTLY some interest has been shown in coloured solutions of iodine,[1-3] sulphur,[4,5] selenium,[6,7] tellurium,[8,9] arsenic,[10] and antimony[11] in highly acidic media. These solutions have been obtained by the oxidation of these elements with peroxydisulphuryl difluoride or sulphur trioxide. For sulphur and selenium solid compounds having these elements in unusual oxidation states have been isolated. From *X*-ray[12] studies of $Se_4(HS_2O_7)_2$, it has been shown that the cation Se_4^{2+} has a square-planar structure. In an earlier communication[8] the existence of the cations Te_4^{2+} and Te_2^{2+} in disulphuric acid has been shown. We report here the isolation of solid compounds containing unusual tellurium cations.

EXPERIMENTAL

Preparation of the solvent and design of the conductivity cells, and cryoscopic apparatus have been described.[13] The conductometric and cryoscopic factors γ and ν were obtained by comparison of the curves obtained from conductance and depression in freezing point of solutions at various concentrations with similar curves obtained from compounds of known behaviour.[14] Fluorosulphuric acid was prepared as already described.[15]

Tellurium powder was heated in an oven at 100—110° for 4 h and kept overnight over P_2O_5 in a desiccator.

Preparation of $Te_4S_3O_{10}$ *and* $Te_2S_3O_{10}$.—An excess of sulphur trioxide was distilled into a flask, cooled in hydrochloric acid–ice, containing dry tellurium powder (10 g). The contents were set aside for 24 h. The excess of sulphur trioxide, and sulphur dioxide formed during the reaction, were removed *in vacuo* when a reddish brown hygroscopic solid of composition $Te_4S_3O_{10}$ was obtained (Found: Te, 64·9; S, 12·43. $Te_4S_3O_{10}$ requires Te, 66·59; S, 12·53%). When the excess of sulphur trioxide is allowed to remain in contact with tellurium for 2 weeks at room temperature, a yellow compound of composition $Te_2S_3O_{10}$ is formed (Found: Te, 47·7; S, 18·6. $Te_2S_3O_{10}$ requires Te, 49·9; S, 18·8%).

U.v. spectra of the solutions were observed on a Beckmann DB recording instrument with a cell of path length 1 mm. I.r. spectra of the solid compounds were observed on a Perkin-Elmer 337 spectrophotometer using Nujol mulls between Teflon sheets. Magnetic measurements of the solutions were carried out on a Guoy-type magnetic balance at room temperature; the sample tube was calibrated with nickel chloride solution. The susceptibility per g.-atom of Te was found to be -12×10^{-6} c.g.s.u. for the red species and -10×10^{-6} c.g.s.u. for the yellow species at 25 °C. All transferences of materials wherever possible were carried out in a dry box.

RESULTS AND DISCUSSION

Tellurium forms a red solution in disulphuric acid which changes to yellow after a week. A similar red solution of tellurium is obtained in sulphuric acid at 60 °C. The dissolution of tellurium in these cases is accompanied by the evolution of sulphur dioxide, suggesting that there is a redox reaction. When these solutions are poured onto crushed ice, tellurium separates out quantitatively which implies that it is present in the positive oxidation state and that the yellow solution has a higher oxidation state than the red.

The absorption spectra of the solutions of tellurium in disulphuric acid having different colours show clearly the existence of two distinct species which are stable and obey the Beer–Lambert Law. In Figure 1, curve A represents the spectrum of the red solution whereas curve B represents the spectrum of the yellow solution. The red solution has an intense absorption band at 520 nm and a weak shoulder at 420 nm; the yellow solution has three absorption bands at 280, 380, and 480 nm. It is observed that with time the intensity of the 520 nm peak decreases. Similar absorption spectra for red and yellow coloured solutions of tellurium have been attributed to Te_4^{2+} and Te_{2n}^{n+} by Gillespie and his co-workers. Spectrum (A) can be attributed to Te_4^{2+} but spectrum (B) cannot be attributed with certainty

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[1] R. J. Gillespie and J. B. Milne, *Chem. Comm.*, 1966, 158.

[2] R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, 1966, **5**, 1577.

[3] R. J. Gillespie and K. C. Malhotra, *Inorg. Chem.*, 1969, **8**, 1751.

[4] R. J. Gillespie and J. Passmore, *Chem. Comm.*, 1969, 1333.

[5] J. Barr, R. J. Gillespie, and P. K. Ummat, *Chem. Comm.*, 1970, 264.

[6] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Canad. J. Chem.*, 1968, **46**, 149.

[7] J. Barr, D. B. Crump, R. J. Gillespie, R. Kapoor, and P. K. Ummat, *Canad. J. Chem.*, 1968, **46**, 3607.

[8] J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, 1968, **90**, 6855.

[9] R. C. Paul, J. K. Puri, and K. C. Malhotra, *Chem. Comm.*, 1970, 776.

[10] R. C. Paul, J. K. Puri, R. D. Sharma, K. K. Paul, and K. C. Malhotra, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 725.

[11] R. C. Paul, K. K. Paul, and K. C. Malhotra, *Chem. Comm.*, 1970, 453.

[12] I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Comm.*, 1968, 853.

[13] R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.* (*A*), 1967, 1994.

[14] R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.* (*A*), 1968, 1933.

[15] R. C. Paul, S. K. Vashist, K. C. Malhotra, and S. S. Pahil, *Analyt. Chem.*, 1962, **34**, 820.

to any particular species. Molar extinction coefficients for various species are given in Table 1.

TABLE 1

Molar extinction coefficients for red and yellow species in disulphuric acid

	nm	$\varepsilon_{max.}$
A (Red solution)	520	1870
	420	320
B (Yellow solution)	480	1120
	380	760
	280	940

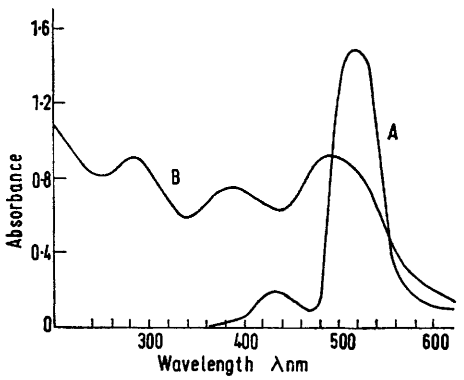

FIGURE 1 U.v. spectra of $Te_4S_3O_{10}$ and $Te_2S_3O_{10}$ in disulphuric acid; A, red solution, $Te_4S_3O_{10}$; B, yellow solution, $Te_2S_3O_{10}$

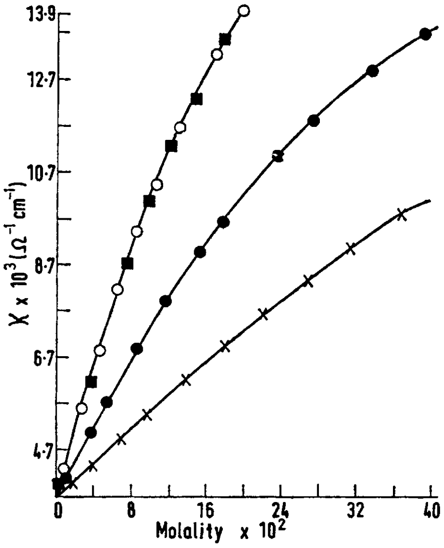

FIGURE 2 Conductivities of various solutes in disulphuric acid at 25 °C; ○, $Te_2S_3O_{10}$; ■, $Te_4S_3O_{10}$; ●, red solution; × yellow solution

Further light has been thrown on the nature of these ions by carrying out cryoscopic, conductance, and magnetic susceptibility measurements. The mode of the ionisation of the solutes in disulphuric acid is best established by the determination of γ and ν values as already indicated in the Experimental section. The γ and ν values obtained from Figures 2 and 3 and given in Tables 2 and 3 clearly establish the overall reaction which produces the red solution as:

$$4Te + 6H_2S_2O_7 \longrightarrow Te_4^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

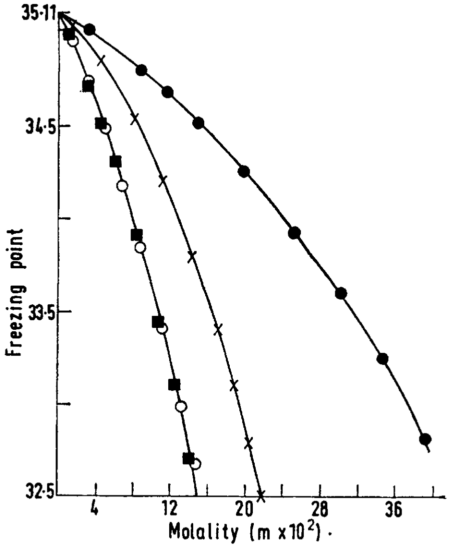

FIGURE 3 Freezing points of solutions of some solutes in disulphuric acid; symbols as for Figure 2

TABLE 2

Conductivities of various solutes in disulphuric acid at 25 °C

Tellurium (red solution)		Tellurium (yellow solution)	
Molality × 10^2	$10^3\kappa/\Omega^{-1}$ cm^{-1}	Molality × 10^2	$10^3\kappa/\Omega^{-1}$ cm^{-1}
1·84	3·9468	1·06	4·1390
4·06	4·3187	3·99	5·0684
7·59	4·827	5·86	5·6686
10·38	5·3264	9·14	6·7817
14·40	6·0998	11·68	7·8946
18·54	6·8813	15·39	8·0396
22·32	7·5739	17·66	9·6274
26·90	8·4106	33·54	11·0638
31·34	9·1058	27·28	11·8006
36·74	9·8480	33·48	12·9215
42·34	10·3896	39·07	13·7468
48·87	11·6432		
$Te_4S_3O_{10}$		$Te_2S_3O_{10}$	
0·82	4·2998	0·38	4·0642
3·04	5·5840	4·06	6·1533
4·96	6·8517	7·72	8·7605
6·88	8·1835	9·98	10·1054
8·63	9·4452	12·04	11·3196
10·72	10·4684	14·88	12·2877
13·18	11·6738	17·74	13·4260
16·99	13·2792		
19·76	13·9856		

Sulphur dioxide is soluble in disulphuric acid and behaves as a non-electrolyte. The value of the molar extinction coefficient supports the above mode of the reaction. This finds further support from cryoscopic titrations against sulphur trioxide which shows that 1·30 moles of sulphuric acid are produced per g.-atom of tellurium dissolved. The somewhat high experimental value may be explained by the slow oxidation of Te_4^{2+} to a higher oxidation state by the solvent,

TABLE 3

Freezing points of solutions of electrolytes in $H_2S_2O_7$

Tellurium (red)		Tellurium (yellow)	
Molality × 10^2	Freezing point	Molality × 10^2	Freezing point
3·24	35·02	1·54	35·04
8·82	34·79	4·48	34·85
10·61	34·82	8·20	34·53
14·78	34·51	11·22	34·30
19·64	34·25	14·16	33·79
25·18	33·91	17·20	33·41
30·18	33·59	18·79	33·10
34·68	33·24	20·42	32·79
39·12	32·82	21·98	32·51
42·06	32·54		
$Te_4S_3O_{10}$		$Te_2S_3O_{10}$	
1·48	34·95	1·18	34·98
3·21	34·73	3·16	34·72
4·78	34·49	4·70	34·50
6·80	34·17	6·02	34·31
8·76	33·84	8·38	33·90
11·20	33·40	10·72	33·43
13·16	32·97	12·41	33·10
14·80	32·68	14·08	32·69
18·18	31·86	16·92	32·28
21·26	31·18	18·75	31·85

which involves the formation of more sulphuric acid per g.-atom of tellurium.

In the yellow solution the comparison of the freezing point and conductivity curves with the calibrated curves (Figures 2 and 3) establishes the overall reaction as:

$$2Te + 6H_2S_2O_7 \longrightarrow Te_2^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

This mode of the reaction finds support from cryoscopic titrations against sulphur trioxide which show that 2·5 moles of sulphuric acid are produced per g.-atom of tellurium.

Magnetic measurements of both the solutions (red and yellow) show that they are diamagnetic and this rules out the possibility of the presence of odd electron cations such as Te_6^{3+}.

Although these cations have been characterised in solution in a highly acidic medium, it is of interest to isolate the solid compounds where such cations of tellurium are present. Two compounds of composition $Te_4S_3O_{10}$ and $Te_2S_3O_{10}$ are obtained when tellurium is treated with sulphur trioxide. These compounds are highly susceptible to hydrolytic attack and develop a pink and finally a black colour when exposed to moisture. They are insoluble in the conventional organic and aprotic solvents. However, they are readily soluble in disulphuric and fluorosulphuric acids to give red and yellow solutions respectively. The u.v. spectra for the red and yellow solutions are exactly the same as has been reported for Te_4^{2+} and Te_2^{2+} indicating that in these solid compounds tellurium is present in the unusual oxidation states already indicated in the solutions. These compounds are not simple molecular adducts of sulphur trioxide and tellurium (Te,SO_3) as was previously thought.[16]

These compounds form highly conducting solutions in di- and fluoro-sulphuric acids and there is no change in their conductance with time. From cryoscopic and conductance studies, the nature of these solutions may be represented as:

$$Te_4S_3O_{10} + 2H_2S_2O_7 \longrightarrow Te_4^{2+} + 2HS_3O_{10}^- + H_2SO_4$$

Cryoscopic titrations against sulphur trioxide show the production of one mole of sulphuric acid per mole of the compound dissolved, which supports the above solvolytic reaction and the fact that in this compound tellurium is present in $+\frac{1}{2}$ oxidation state. A compound of Te_4^{2+} has already been reported,[8] where tellurium is present in this oxidation state. Comparison of the conductance of its solution in fluorosulphuric acid with potassium fluorosulphate (Figure 4) indicates that the value of γ is somewhat less than 2. The solvolytic reaction may be represented by either of the following two equations:

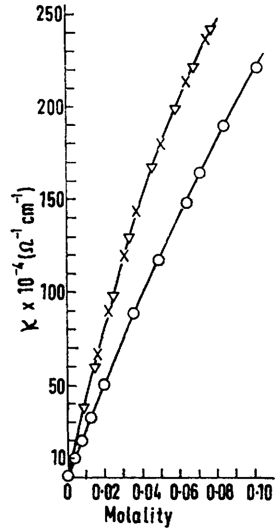

FIGURE 4 Conductances of various compounds in fluorosulphuric acid at 25 °C; ○, KSO_3F; ▽, $Te_2S_3O_{10}$; ×, $Te_4S_3O_{10}$

$$Te_4S_3O_{10} + 2HSO_3F \longrightarrow Te_4^{2+} + 2SO_3F^- + H_2S_3O_{10}$$

$$Te_4S_3O_{10} + 3HSO_3F \longrightarrow Te_4^{2+} + 2SO_3F^- + HS_2O_6F + H_2S_2O_7$$

From the conductance data only, it is very difficult to differentiate between the two modes of reaction. It is not unreasonable to believe that in an excess of fluorosulphuric acid, instead of the existence of trisulphuric acid, there is a greater possibility of the existence of pyrofluorosulphuric and disulphuric acids. A lower value of conductance than required for $2SO_3F^-$ may partly be due to the acidic character of disulphuric or trisulphuric acids, in fluorosulphuric acid and partly due to the low mobility of the Te_4^{2+} cation as compared to that of K^+ in the case of KSO_3F.

Similarly the compound $Te_2(S_3O_{10})$ when dissolved in disulphuric and fluorosulphuric acids forms highly

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[16] J. J. Doolan and J. R. Partington, *J. Chem. Soc.*, 1924, 1402.

conducting yellow solutions. From the cryoscopic and conductance studies, the mode of the solvolytic reaction in disulphuric acid may be represented as:

$$Te_2S_3O_{10} + 2H_2S_2O_7 \longrightarrow Te_2^{2+} + 2HS_3O_{10}^- + H_2SO_4$$

whereas the solvolytic reaction in fluorosulphuric acid may be represented as:

$$Te_2S_3O_{10} + 3HSO_3F \longrightarrow Te_2^{2+} + H_2S_2O_7 + HS_2O_6F + 2SO_3F^-$$

The ionic nature of these compounds in supported by i.r. spectral studies. Because of the limited transparency of the material of the window used, it has not been possible to observe any bands corresponding to the cations which occur in the far-i.r. region. However, the bands corresponding to the anions have been observed and are reported in Table 4; the bands due to $K_2S_2O_7$ have been included from the literature.[17]

TABLE 4

Infrared spectra (cm^{-1})

$K_2S_2O_7$ [a]	$Te_2S_3O_{10}$	$Te_4S_3O_{10}$
855	835	845
875	875	880
1015	1005	1010
1080	1085	1190
1170	1180	1175
1280	1290	1280
2480	2565	2395
3100	3060	2975

[a] Ref. 17.

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[0/1489 *Received, 28th August,* 1970]

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[17] J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2582.