Tetrafluorotellurates(VI): *cis*- and *trans*-$(HO)_2TeF_4$, $HOTeF_4OMe$, and $(MeO)_2TeF_4$

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Summary Preparative methods based on the fluorination of orthotelluric acid with HF and on the hydrolysis of pentafluorotellurates(VI) lead to the isolation of stereoisomers of tetrafluorotellurates(VI).

WHEREAS an extensive chemistry of pentafluorotellurates(VI), compounds containing the F_5TeO group, exists,[1] little is known of the tetrafluorotellurates(VI), compounds containing the F_4TeO_2 group. Some evidence has been given for $(HO)_2TeF_4$ and the corresponding anion formed in solution as intermediates in the hydrolysis of TeF_6 or in the interaction of orthotelluric acid with HF.[2] Although a range of alkoxy-fluorotellurates is known,[3] no alkoxy-fluorotelluric acids have been reported so far. We have now succeeded in isolating the title compounds and in separating them into *cis*- and *trans*-isomers. Moreover all the tetrafluorotellurates(VI) appearing in the Scheme have also been isolated and characterized by spectroscopic means and elemental analysis. Some spectroscopic properties are given in the Table.

The preparative route for the *trans*-series of compounds started from orthotelluric acid dissolved in 48% HF. After addition of pyridine (Pyr) [mol. ratio $(HO)_6Te : HF : Pyr = 1 : 10 : 3$] the solution was evaporated to dryness. The *ca.* 90% yield of *trans*-$HOTeF_4O^-PyrH^+$ was separated from the corresponding *cis*-salt and less fluorinated tellurates using acetonitrile. Pure *trans*-$(HO)_2TeF_4$ can be sublimed out of a solution of the *trans*-salt in 96% H_2SO_4 at 130—150 °C *in vacuo*. Straightforward alkylation reactions led to the other members of the *trans*-series.

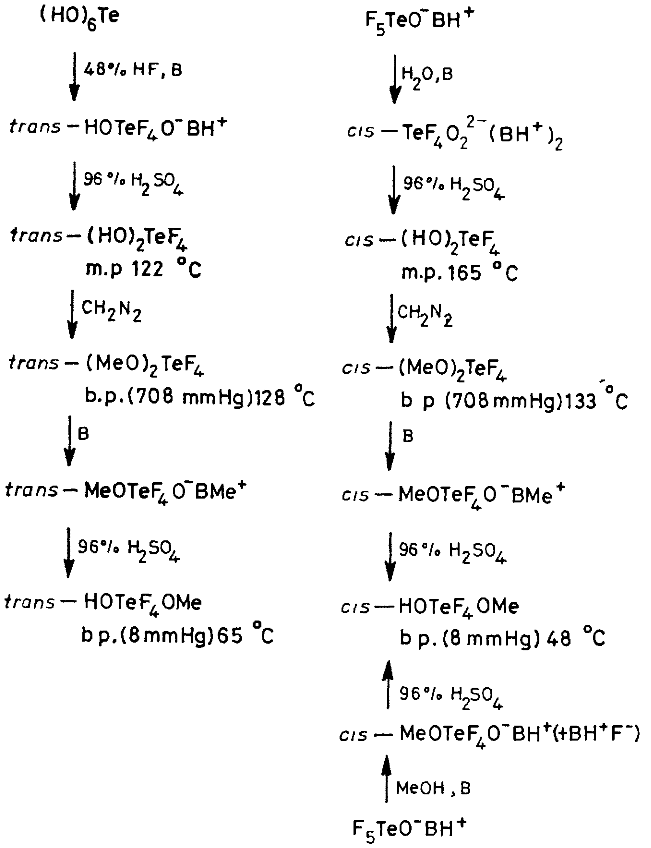
Preparation of the *cis*-series started either by precipitating the imidazolium salt of *cis*-$(HO)_2TeF_4$ from a solution of imidazolium pentafluorotellurate(VI) in dioxan in the presence of a stoicheiometric amount of water, or by

TABLE. Some spectroscopic properties of tetrafluorotellurates(VI).

		cis-$(HO)_2TeF_4$[a]	*trans*-$(HO)_2TeF_4$[a]	*cis*-$HOTeF_4OMe$	*trans*-$HOTeF_4OMe$	*cis*-$(MeO)_2TeF_4$	*trans*-$(MeO)_2TeF_4$
^{19}F-n.m.r.	spin system	A_2B_2	A_4	AB_2CM_3	A_4M_3	$A_2B_2M_6$	A_4M_6
	δ_F[b]	33·0,42·0	41·0	34·4, 49·5, 50·3	51·5	52·0, 62·0	68·8
	J/Hz	155	—	AB 167, AC 145 BC79	1·6	AB 150, BM 1·4	1·7
^{125}Te-n.m.r.	spin system	A_2B_2X	A_4X	AB_2CM_3X	A_4M_3X	$A_2B_2M_6X$	A_4M_6X
	δ_{Te}[c]	653	649	645	640	642	648
	J[d]/Hz	3247, 3307	3443	AX 3250 (B,C)X 3464 MX 125	AX 3569 MX 148	AX 3348 BX 3519 MX 125	AX3672 MX 148
^{1}H-n.m.r.	δ_H[e]	7·0	7·0	OH 6·8, CH_3 4·8	OH 6·2, CH_3 4·2	4·6	4·1
	J_{HF}/Hz	—	—	1·2[f]	1·6	1·4	1·7
m/e[g] (%)		240(5) M^+ 223(77) $M^+ - OH$ 221(12) $M^+ - F$ 203(43) $OTeF_3^+$ 187(100) TeF_3^+	240(8) M^+ 223(100)$M^+ - OH$ 221(23) $M^+ - F$ 203(68) $OTeF_3^+$ 187(62) TeF_3^+	253(27) $M^+ - H$ 237(5) $M^+ - OH$ 236(3) $M^+ - OH,H$ 235(20) $M^+ - F$ 235(13) $M^+ - OMe$ 187(100) TeF_3^+	253(83) $M^+ - H$ 237 (18) $M^+ - OH$ 236(10)$M^+ - OH,H$ 235(28) $M^+ - F$ 223(24)$M^+ - OMe$ 165(100)$TeFO^+$	267(1) $M^+ - H$ 249 (17) $M^+ - F$ 237(40) $M^+ - OMe$ 187(100) TeF_3^+	267(57) $M^+ - H$ 249 (18) $M^+ - F$ 237(64)$M^+ - OMe$ 187(100) TeF_3^+

[a] In MeCN solution. As a consequence of the state of ionization chemical shifts and coupling constants are considerably concentration- and solvent-dependent. [b] In p.p.m. rel. to $CFCl_3$. [c] In p.p.m. rel. to Me_2Te. [d] Te–H Coupling constants are higher than those for other hydrogen-containing tellurium compounds by a factor of *ca.* 10. [e] In p.p.m. rel. to Me_4Si. [f] Approximate quartet. [g] At 70 eV. Masses are related to ^{130}Te; only characteristic high-mass fragments are given.

precipitating the imidazolium salt of *cis*-$HOTeF_4OMe$ out of a solution of imidazolium pentafluorotellurate(VI) in methanol in the presence of an excess of imidazole. Subsequent synthetic steps were akin to those for the *trans*-series.



(B = organic base,
e.g. pyridine, imidazole,
trimethylamine)

Surprisingly, the tetrafluorotelluric acids were stable under these rather harsh preparative conditions. No hydrolysis or isomerization occurred in 96% H_2SO_4 up to 150 °C. In addition the preparative routes were stereospecific. Only *cis*-$(HO)_2TeF_4$ was formed in the hydrolysis of $HOTeF_5$ and fluorination of orthotelluric acid with HF led predominantly to *trans*-$(HO)_2TeF_4$.

All acids are strong, liberating HCl from alkali metal chlorides with formation of the corresponding anions. *trans*-$(HO)_2TeF_4$ appears to be thermodynamically more stable than *cis*-$(HO)_2TeF_4$; only above 150 °C is *cis*-$(HO)_2TeF_4$ partially isomerized into the *trans*-isomer.

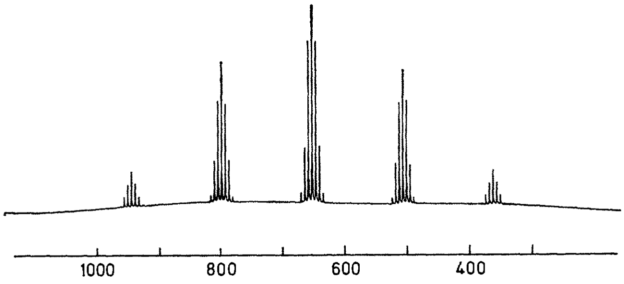


FIGURE. ^{125}Te-n.m.r. spectrum of *trans*-$(MeO)_2TeF_4$.

Identification of the compounds was greatly facilitated by ^{125}Te-n.m.r. spectroscopy. As an example the ^{125}Te-n.m.r. spectrum of *trans*-$(MeO)_2TeF_4$ is shown in the Figure. ^{19}F-n.m.r. spectroscopy was less useful since it could not differentiate between the five $(HO)_nTeF_{6-n}$ species, which exhibit a single resonance line only.

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