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High-coordination Number Fluoro- and Oxofluoro-anions; IF_6O^-, TeF_6O^{2-}, TeF_7^-, IF_8^- and TeF_8^{2-}

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The novel hypervalent, highly coordinated, high-oxidation state anions IF_6O^-, TeF_6O^{2-}, TeF_7^-, IF_8^- and TeF_8^{2-} have been synthesized in anhydrous MeCN using anhydrous $N(Me)_4^+F^-$ as the fluoride ion source; the anions have been characterized by NMR and vibrational spectroscopy and represent novel examples of seven and eight-coordinate species having symmetries C_{5v} (IF_6O^-, TeF_6O^{2-}), D_{5h} (TeF_7^-) and D_{4d} (IF_8^-, TeF_8^{2-}).

The study of fluoro-anions having coordination numbers higher than six and, in particular, those involving free valence electron pairs, have recently received considerable attention.[1–6] To a large extent, these studies have been greatly facilitated by the development of a convenient preparative scale synthesis of anhydrous $N(Me)_4^+F^-$[7] and the realization that this salt is an excellent reagent for the preparation of novel, high-oxidation state complex fluoro- or oxofluoro-anions. Furthermore, the high solubilities of these $N(Me)_4^+$ salts in solvents such as MeCN or CHF_3 permit the gathering of valuable structure information through NMR and vibrational studies and the growth of single crystals suitable for X-ray structure determinations.

Our recent success with the preparation of the XeF_5^- anion,[4] the first known example of a pentagonal planar AX_5E_2 (where E stands for a free valence electron pair) species, prompted us to study some closely related iodine and tellurium compounds. In addition, there are relatively few examples of main-group species which allow the applicability of the valence shell electron pair repulsion (VSEPR) rules to coordination numbers exceeding six to be tested.[8] In this note, we report on the syntheses and structures of the novel IF_6O^- anion and on the $N(Me)_4^+$ salts of TeF_7^-, TeF_8^{2-} and IF_8^-.

The salt, $N(Me)_4^+IF_6O^-$, was prepared according to eqn. (1) by the reaction of anhydrous $N(Me)_4^+F^-$ with a threefold excess of IF_5O in dry MeCN at −31 °C for 30 min.

$$N(Me)_4^+F^- + IF_5O \xrightarrow[-31\,^{\circ}C]{MeCN} N(Me)_4^+IF_6O^- \qquad (1)$$

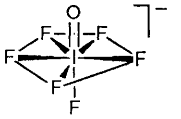
The solvent and unreacted IF_5O were pumped off at −31 °C leaving behind $N(Me)_4{}^+IF_6O^-$ as a colourless crystalline solid in quantitative yield. According to differential scanning calorimetry (DSC) and pyrolysis data, the compound starts to decompose at about 137 °C with formation of CF_4, COF_2 and IF_4O^- as the major products.

The ^{19}F NMR spectrum of $N(Me)_4^+IF_6O^-$ in MeCN solution recorded at −40 °C (Fig. 1) is consistent with the structure predicted by the VSEPR rules, consisting of a pentagonal bipyramidal structure of C_{5v} symmetry (structure **1**) in which the oxygen atom occupies an axial position. The spectrum consists of a doublet at δ 166.0, assigned to the equatorial fluorines, and a 1:5:10:10:5:1 sextet at δ 111.1, assigned to the axial fluorine trans to oxygen. Both resonances are broadened by partially quadrupole-collapsed spin coupling to ^{127}I (I = 5/2). The fluorine–fluorine scalar coupling, $^2J(^{19}F_a–F_e)$ 205 Hz, is very similar in magnitude to those for IF_5O (271–280 Hz)[9] and *cis*-$IO_2F_4^-$ (204 Hz in MeCN).[10]

The vibrational spectra of IF_6O^- are also in excellent agreement with symmetry C_{5v}. The assignments were made by comparison with the related IF_7 molecule (see Table 1) and XeF_5^- anion.[4]

The reactions between TeF_6 and alkali metal fluorides have been reported previously, although definitive characterization of the products was never achieved.[11,12] The reactions of TeF_6 with CsF and RbF suspended in C_6F_6 resulted in products approaching the limiting compositions $CsF{\cdot}TeF_6$ and $2RbF{\cdot}TeF_6$, respectively.[12] Vibrational studies on these materials were tentatively interpreted as indicating D_{5h} and D_{4d} structures for TeF_7^- and TeF_8^{2-}, respectively. However, since both compounds decomposed in solution, a fuller characterization of their nature was precluded.

The preparation of $N(Me)_4^+TeF_7^-$ was similar to that for the IF_6O^- salt except that a 5% excess of TeF_6 was allowed to



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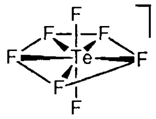

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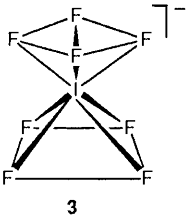

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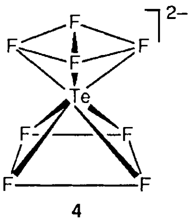

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react with $N(Me)_4{}^+F^-$ according to equation (2). The solvent and an excess of TeF_6 were pumped off at room temperature leaving a white solid in quantitative yield.

$$N(Me)_4{}^+F^- + TeF_6 \xrightarrow[-40\,°C]{MeCN} N(Me)_4{}^+TeF_7{}^- \qquad (2)$$

The room temperature ^{125}Te NMR spectrum of $N(Me)_4{}^+TeF_7{}^-$ in MeCN consists of a 1 : 7 : 21 : 35 : 35 : 21 : 7 : 1 octet centred at δ 327.4 (Fig. 2). The octet fine structure arises from the one-bond spin–spin coupling between the central ^{125}Te and the ^{19}F ligands [$^1J(^{125}Te–^{19}F)$ 2876 Hz] and is in accord with a $TeF_7{}^-$ anion structure in which all seven fluorines are rendered equivalent on the NMR time scale by a facile intramolecular exchange process. The ^{19}F NMR spectrum is also consistent with the $TeF_7{}^-$ anion undergoing a fluxional process in solution, and consists of a single environment (δ 16.1) and natural abundance satellite spectra arising from $^1J(^{123}Te–^{19}F)$ 2385 and $^1J(^{125}Te–^{19}F)$ 2876 Hz. Under high resolution at an external field strength of 11.744 T, the central line displays the isotopic shift pattern arising from the natural abundance spinless tellurium isotopes corresponding to the fluorines of the ^{130}Te, ^{128}Te, ^{126}Te, ^{124}Te and ^{122}Te isotopomers, with each isotopomer shifted successively to higher frequency of $^{130}TeF_7{}^-$, by 0.004 ppm. Earlier NMR studies have shown that the isoelectronic IF_7 molecule also undergoes rapid intramolecular exchange and gives rise to a single fluorine environment in the room temperature ^{19}F NMR spectrum with partially quadrupole-collapsed fine structure arising from $^1J(^{127}I–^{19}F)$.[13]

The vibrational spectra of $TeF_7{}^-$ have been assigned by analogy with those of the isoelectronic IF_7 molecule (Table 1) and are in agreement with a pentagonal bipyramidal structure of D_{5h} symmetry (structure **2**). In general, the $TeF_7{}^-$ frequencies are shifted to lower frequencies relative to those of IF_7, in accordance with the formal negative charge of $TeF_7{}^-$.

The syntheses of $Cs^+IF_8{}^-$,[14] $NO^+IF_8{}^-$[14,15] and $NO_2{}^+IF_8{}^-$[15] have previously been reported, and the ionic nature of these salts was established by the observation of the vibrational bands characteristic for NO^+ and $NO_2{}^+$.[14,15] Although partial Raman[14] and IR spectra[15] had been reported for $IF_8{}^-$, no conclusions could be drawn from these data about the exact structure of this interesting octacoordinated anion. To allow a

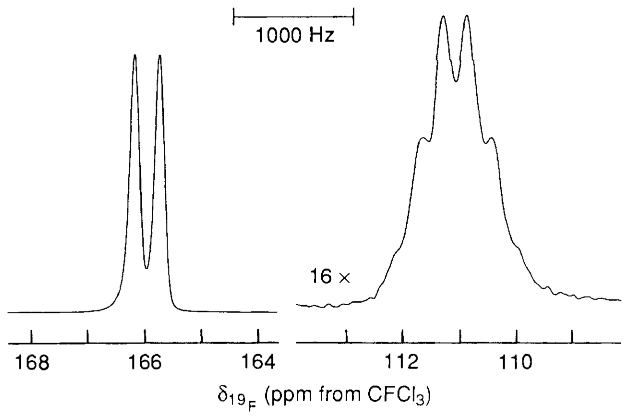

Fig. 1 The ^{19}F NMR spectrum of $N(Me)_4{}^+IF_6O^-$ recorded at 471.599 MHz in MeCN solvent at −40 °C

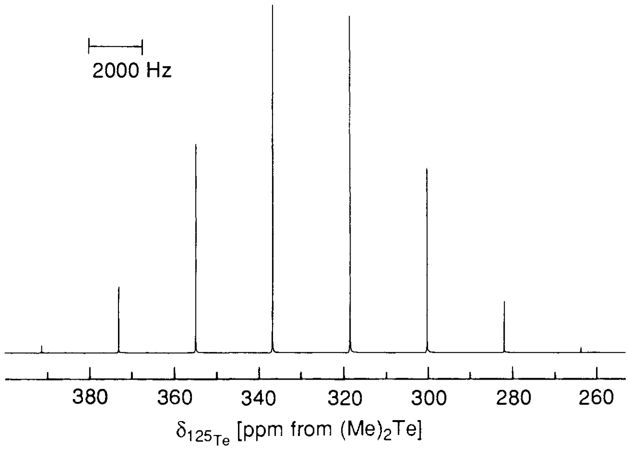

Fig. 2 The ^{125}Te NMR spectrum of $N(Me)_4{}^+TeF_7{}^-$ recorded at 157.792 MHz in MeCN solvent at 30 °C

Table 1 Vibrational frequencies (cm^{-1}) and tentative assignments for IF_6O^-, IF_7 and $TeF_7{}^-$

			IF_6O^- (C_{5v})[a]				IF_7 (D_{5h})[b]	$TeF_7{}^-$ (D_{5h})[a]
A_1	ν_1	ν I=O	873 [vs, IR; 5.3, R (p)]					
	ν_2	ν IF ax	649 [s, IR; 8.8 R (p)]	A_1'	ν_1	ν sym MF_2 ax	675 [2.0, R (p)]	597 (2.6, R)
	ν_3	ν sym IF_5	584 [10, R (p)]		ν_2	ν sym MF_5	629 [10, R (p)]	640 (10, R)
				A_2''	ν_3	ν asym MF_2 ax	746 (s, IR)	695 (vs, IR)
	ν_4	δ umbrella IF_5	359 (s, IR)		ν_4	δ umbrella MF_5	363 (s, IR)	332 (s, IR)
E_1	ν_5	ν asym IF_5	585 (vs, IR)	E_1'	ν_5	ν asym MF_5	672 (vs, IR)	625 (vs, IR)
	ν_6	δ wag I=O	457 (4.9, R)		ν_6	δ scissoring MF_2ax	425 (vs, IR)	384 (vs, IR)
	ν_7	δ wag IF ax	405 (vs, IR)		ν_7	δ asym MF_5 in plane	257 (w, IR)	[c]
	ν_8	δ asym IF_5 in plane	260 (s, IR; 0.2, R)	E_1''	ν_8	δ wag MF_2 ax	308 (0.6, R)	299 (0.6, R)
E_2	ν_9	ν asym IF_5	530 (0.4, R)	E_2'	ν_9	ν asym MF_5	509 (0.9, R)	458 (1.6, R)
	ν_{10}	δ scissoring IF_5 in plane	341 (6.2, R)		ν_{10}	δ scissoring MF_5 in plane	342 (0.6, R)	326 (0.7, R)
	ν_{11}	δ pucker IF_5	[d]	E_2''	ν_{11}	δ pucker MF_5	[d]	[d]

[a] Spectra recorded for the $N(Me)_4{}^+$ salts at 25 °C. [b] Frequencies are taken from H. H. Eysel and K. Seppelt, *J. Chem. Phys.*, 1972, **56**, 5081. A number of modes have been reassigned so that they are consistent with the corresponding assignments for $XeF_5{}^-$ (ref. 4), which have been confirmed by a force constant analysis and theoretical calculations. [c] Mode not observed. [d] Inactive in both the IR and Raman spectra.

Table 2 Vibrational frequencies (cm^{-1}) and assignments for IF_8^- in $N(Me)_4^+IF_8^-$ and TeF_8^{2-} in $[N(Me)_4^+]_2TeF_8^{2-}$ in point group D_{4d}

Raman				IR (solid 25 °C)		Assignment in D_{4d}
IF_8^-			TeF_8^{2-}	IF_8^-	TeF_8^-	
Solid		MeCN sol'n				
25 °C	−142 °C					
660 (0+)	660 (0+)					ν_{12} (E$_3$)
				590 vs, br	558 vs	ν_4 (B$_2$)
						ν_6 (E$_1$)
	595 (10)					
587 (10)		590 (10) p	582 (10)			ν_1 (A$_1$)
	588 (6.5)					
550 (0.3)	550 (0.5)	550 (0+) dp	490 (0.2), br			ν_9 (E$_2$)
463 (1.8)	463 (1.9)	462 (0.5) p	408 (1.0)			ν_2 (A$_1$)
				410 s	375 vs	ν_5 (B$_2$)
						ν_8 (E$_1$)
	419 (0.9)					
411 (0.7)		410 sh[a]	388 (1.8)			ν_{10} (E$_2$)
	410 (1.4)					
	380 (0+)[b]		325 (0.3)			ν_{13} (E$_3$)
				314 m	265 w	ν_7 (E$_1$)

[a] Shoulder on strong MeCN solvent band. [b] This band could possibly be due to the $N(Me)_4^+$ cation.

better characterization of the IF_8^- anion, we have prepared the new $N(Me)_4^+IF_8^-$ salt and its isoelectronic tellurium analogue, TeF_8^{2-}, by the reaction of $N(Me)_4^+F^-$ with excess IF_7 and a stoichiometric amount of $N(Me)_4^+TeF_7^-$, respectively. For reaction (3) the solvent and unreacted IF_7 were pumped off at −22 and 0 °C, respectively, leaving behind colourless $N(Me)_4^+IF_8^-$ in quantitative yield. In the case of reaction (4), $[N(Me)_4^+]_2TeF_8^{2-}$ was isolated in admixture with *ca.* 20–30% $N(Me)_4^+TeF_7^-$. The $[N(Me)_4^+]_2TeF_8^-$ salt

$$N(Me)_4^+F^- + IF_7 \xrightarrow[-31\,°C]{MeCN} N(Me)_4^+IF_8^- \quad (3)$$

$$N(Me)_4^+F^- + N(Me)_4^+TeF_7^- \xrightarrow[0\,°C]{MeCN} [N(Me)_4^+]_2TeF_8^{2-} \quad (4)$$

has a strong tendency to dissociate in MeCN, thus far preventing the preparation of a sample containing only the TeF_8^{2-} anion. At room temperature, dissociation of the insoluble TeF_8^{2-} anion into TeF_7^- and F^- results in rapid solvent attack by F^-[16] and formation of HF_2^- anion. Even in the presence of a fivefold excess of $N(Me)_4^+F^-$ at −5 °C, significant amounts of TeF_7^- and F^- were observed in the ^{19}F NMR spectrum, but no resonance attributable to TeF_8^{2-} could be observed. The $N(Me)_4^+IF_8^-$ salt is a crystalline solid which, according to DSC data, is stable up to *ca.* 110 °C where it undergoes exothermic decomposition.

The IF_8^- and TeF_8^{2-} anions possess eight fluorine ligands and no free central atom valence electron pair. Their structures could, therefore, be either a cube of symmetry O_h, which is unlikely owing to steric interactions,[8] a dodecahedron of symmetry D_{2d} or a square antiprism of symmetry D_{4d} (structures **3** and **4**).[17–20] Distinction among these three possibilities was made by vibrational spectroscopy. The dodecahedral structure is expected to give rise to two polarized stretching modes and four deformation modes (two polarized; two depolarized) exclusively in the Raman. The IR bands are mutually non-exclusive and comprise four stretching modes and five deformation modes which are all depolarized in the Raman. All Raman and IR bands observed for IF_8^- and TeF_8^{2-} are mutually exclusive, thereby eliminating D_{2d} symmetry. For the cubic O_h structure, two stretching modes are expected (one polarized; the other depolarized) and two depolarized deformation modes in the Raman, as well as one stretching and one deformation mode in the infrared. All these modes should be mutually exclusive.[18] For the square antiprismatic D_{4d} structure, one polarized and two depolarized stretching modes are expected as well as one polarized and three depolarized deformation modes in the Raman. In the IR spectrum, two stretching and three deformation modes are expected, which again should be mutually exclusive.[17,19,20] Although the full number of fundamentals for D_{4d} was not observed (see Table 2), probably because of either low relative intensities or coincidences, the observation of a polarized Raman deformation band at 462 cm^{-1} and of at least two IR active deformation modes at 410 and 314 cm^{-1}, respectively, establish the square antiprismatic D_{4d} structure for IF_8^-. It was not possible to obtain polarization data on TeF_8^{2-} owing to the insolubility of the salt and its tendency to dissociate in MeCN. However, the vibrational spectra of TeF_8^{2-} can be assigned by their close analogy to those of IF_8^- (Table 2) and it may be concluded that TeF_8^{2-} also possesses a square antiprismatic structure.

X-Ray crystal structure determinations on these and other closely related anions are underway both in our laboratories and in an independent effort by Dr K. Seppelt and coworkers at the Freie Universität, Berlin.

Note added in proof: The TeF_6O^{2-} anion has also been synthesized by the reaction of equimolar amounts of $N(Me)_4^+F^-$ and $N(Me)_4^+TeF_5O^-$ at −9 °C in MeCN. The vibrational assignments (ν/cm^{-1}) under C_{5v} establish that TeF_6O^{2-} is isostructural with IF_6O^-: ν_1 829 (s, IR; s, R); ν_2 613 (m, IR; vs, R); ν_3 528 (m, R), ν_4 330 (s, IR); ν_5 525 (vs, IR); ν_6 388 (m, R); ν_7 365 (vs, IR); ν_8 245 (not observed, beyond spectrometer limit; w, R); ν_9 not observed; ν_{10} 322 (s, R); ν_{11} (not observed). The ^{19}F NMR spectrum of $N(Me)_4^+IF_8^-$ has been obtained at 30 °C (δ 248.6) and is a partially quadrupole collapsed multiplet (saddle-shaped with a 'doublet' separation of 3807 Hz) arising from the ^{127}I–^{19}F scalar coupling and is consistent with the small electric field gradient at the ^{127}I nucleus that is anticipated for a square antiprismatic AX_8 geometry.

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