Preparation and Structure of the IOF_6^- and TeF_7^- Anions

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The compounds $Me_4N^+IOF_6^-$ and $Me_4N^+IF_7^-$ have been prepared; both anions have a pentagonal bipyramidal structure, and in IOF_6^- the oxygen occupies an apical position.

Unexpectedly, octahedral IOF_5 exhibits Lewis acidic behaviour towards F^- if the latter is present as tetramethylammonium fluoride.[1] From Me_3CN solutions $Me_4N^+IOF_6^-$ can be grown as large colourless crystals (m.p. 172 °C).† The structure of this novel anion is pentagonal bipyramidal as established by NMR and vibrational spectroscopy and especially by crystallography. ^{19}F NMR spectroscopy shows a doublet at $-\delta$ 167.0 and a partially resolved binominal sextet at δ -113.6, J 195 Hz. The considerable line width of about 100 Hz may be caused by partially quadrupole-collapsed spin coupling to the iodine nucleus with J 5/2 such as in IOF_5. Oxygen must be in the second apical position. The anion does not undergo intramolecular ligand exchange within the NMR time scale. Raman spectra of IOF_6^-, if compared with TeF_7^- (see below) and IF_7 are also in accord with this peculiar structure, see Table 1. The crystallographic analysis of $Me_4N^+IOF_6^-$ suffers from a fourfold disorder or a systematic twinning. Treatment of the data with normal procedures assuming a disorder or with a mathematical procedure for twinned crystals[4] results in the structure as shown in Fig. 1.‡

Since it is the equatorial fluorine atoms that are affected by disorder or twinning, errors of bond distances and angles can be larger here than the σ-values indicate. The structure has the remarkable feature that the five equatorial fluorine atoms are

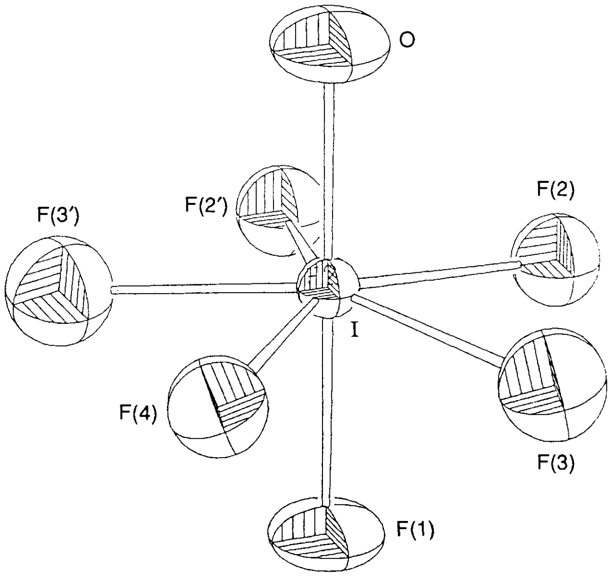

Fig. 1 Molecular structure of the IOF_6^- anion. The ellipsoids represent 50% probability. The $F(1)_1$–I–O linkage is linear due to crystallographic symmetry. Owing to disorder or twinning bond distances and angles among the equatorial fluorine atoms remain more uncertain than indicated: I–O 1.775(6), I–F(1) 1.820(5), I–F(2) 1.902(7), I–F(3) 1.871(11), I–F(4) 1.824(13) Å; O–I–F(2,3,4) 96.2–96.9 (2–4), F(2)–I–F(3) 69.5(5), F(3)–I–F(4) 76.7(18), F(2)–I–F(2′) 65.4(4)°.

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† Satisfactory elemental analysis was obtained.

‡ *Crystal data* for $Me_4N^+IOF_6^-$, P_4/nmm (No. 129) or $Pmmn$ (No. 59, twinned), $a = 8.779(2)$, $b = 8.787(3)$, $c = 6.331(1)$ Å, $U = 488.3$ Å^3, $Z = 2$, $\mu = 34.2$ cm^{-1}, $\lambda = 0.7107$ Å, $T = -163$ °C. The data were collected on an Enraf-Nonius CAD 4 diffractometer using monochromatized Mo-Kα radiation *via* the ω-2θ scan technique. 3517 reflections measured in $\pm h,+k,+l$ within $2° \le \theta \le 40°$, 210 systematically absent $(h,k,0 \ne 2n)$, 877 unique reflections tetragonal, 885 with $I \ge 3\sigma(I)$. $R_w = 0.036$, $R = 0.039$ for all atoms anisotropic, except the disordered equatorial fluorine atoms (isotropic) and H atoms (isotropic in fixed positions).

A detailed description of the twinning problem and listings of the atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 Raman spectra of IOF_6^-, TeF_7^- and IF_7^{-a}

$Me_4N^+IOF_6^-$	$Me_4N^+TeF_7^-$	$Cs^+TeF_7^-$ (ref. 2)	IF_7 (ref. 3)
871m (νIO, A_1)			
655m (νIF, A_1)	640s ($\nu_s TeF_2$, A_1')	652vs	675s
583s ($\nu_s IF_5$, A_1)	597m ($\nu_s TeF_5$, A_1')	593s	629vs
456m ($\nu_{as} IF_5$, E_2)	459m ($\nu_{as} TeF_5$, E_2')	455s	509m
343s (δ)	325m ($\delta_{as} TeF_5$, E_2')	305m	342m
333w (δ)	287s ($\delta_s TeF_5$, A_2'')		308m

[a] Lines of the Me_4N^+ cation have been omitted. The assignments are based on $C_{5h}(IOF_6^-)$ and $D_{5h}(TeF_7^-)$ symmetries.

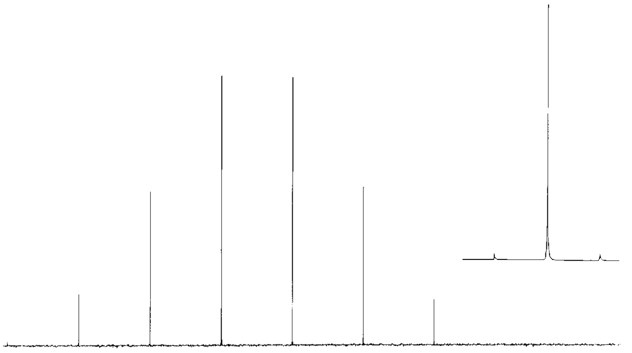

Fig. 2 ^{125}Te NMR spectrum of $Me_4N^+TeF_7^-$ in MeCN solution, 25 °C [24.83 MHz, δ −129.7, H_6TeO_6–H_2O ext, $J(^{125}Te$–$^{19}F)$ 2876 Hz]. Insert: ^{19}F NMR of TeF_7^- [84.25 MHz; δ 17.0, $CFCl_3$ ext. $J(^{125}Te$–^{19}F 2875 Hz].

approximately in one plane, below the iodine atom if viewed from the oxygen atom. No puckering of the equatorial fluorine atoms, as proposed for IF_7,[5] is observed. The single apical fluorine bond distance is shorter than the average of the equatorial ones.

Reaction of TeF_6 with $Me_4N^+F^-$ in MeCN affords $Me_4N^+TeF_7^-$ and insoluble $(Me_4)_2TeF_8$ that are analogous to the previously described $CsTeF_7$ and Cs_2TeF_8.[2] $Me_4N^+TeF_7^-$ can also be grown as large, colourless crystals that have a very similar unit cell to $Me_4N^+IOF_6^-$ but with a still unresolved twinning and/or disorder problem. The identity of this material is, however, obvious from the vibrational data by comparison with IF_7, and particularly by ^{125}Te and ^{19}F NMR, see Fig. 2. The binominal octet in the ^{125}Te NMR spectrum proves not only the composition but also the non-rigidity of the anion TeF_7^-, very much like IF_7. The unexpected rigidity of the IOF_6^- anion is probably a result of the fact that any kind of pseudorotational ligand exchange process will interchange the apical oxygen position into an unfavoured equatorial one.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Received, 22nd February 1991; Com. 1/00865J

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