The Crystal Structure of a Trimeric Form of Technetium Oxide Tetrafluoride

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TRANSITION-METAL pentafluorides and oxide tetrafluorides have been shown to polymerise in the solid state to give tetrameric or endless chain arrangements.[1] We have shown previously that technetium oxide tetrafluoride, formed as blue needles during the fluorination of technetium metal,[2] is isostructural with its rhenium analogue, and has a chain structure.[1]

Small amounts of a green, volatile solid, which also resulted from the fluorination of technetium,[2] have now been found, by crystal structure analysis, to be a trimeric polymorph of technetium oxide tetrafluoride.

Crystal data were determined photographically by Weissenberg techniques with Cu-K_α and Mo-K_α radiation: $TcOF_4$, $M = 191$, hexagonal, $a = 9{\cdot}00 \pm 0{\cdot}01$, $c = 7{\cdot}92 \pm 0{\cdot}01$ Å, $U = 556$ Å.[3] Space group $P\ 6_3/m$ (C_{6h}^2, No. 176). The volume is consistent with $Z = 6$, since with 30 light atoms in the unit cell, the volume per light atom is 18·4 Å,[3]

close to the usual value for approximate close-packing.[3] Intensity data were determined photometrically from integrated Weissenberg films, giving 368 independent reflections. The technetium atom positions were determined from the three-dimensional Patterson function, and those of the light atoms from a subsequent electron density map. Full-matrix least-squares refinement of positional and isotropic temperature parameters gave an R value of 0·108.

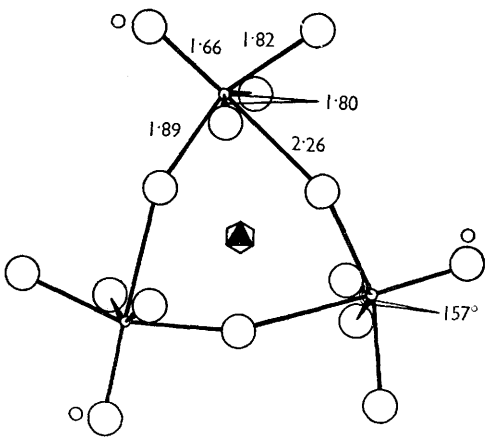

FIGURE. *Projection of the structure down* [001] *with slight displacements of out-of-plane fluorine atoms, for clarity. Estimated standard deviations in bond lengths are* ± 0·03 Å

The structure consists of trimeric units, with a distorted octahedral co-ordination of the technetium atoms, and *cis*-bridging fluorine atoms (see Figure). The terminal positions of the oxygen atoms (which could not be distinguished from fluorine in the presence of the technetium atoms by X-ray methods) were inferred from the geometry. The bond lengths and angles around technetium are almost identical with those around molybdenum in the chain structure of molybdenum oxide tetrafluoride, being within ± 0·03 Å and ± 6° respectively.[1]

The [MOF_4] units can be linked either as endless chains or trimeric units, without disturbing the geometry around the metal atom. The bridge angles are 151° ($MoOF_4$) and 161° ($TcOF_4$).

This is the first example of polymorphism in the oxide tetrafluorides, and we have also found a hexagonal form of molybdenum oxide tetrafluoride, with cell dimensions a = 8·95, and c = 7·91 Å, almost isodimensional with the technetium polymorph described here.

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[1] A. J. Edwards, G. R. Jones, and B. R. Steventon, *Chem. Comm.*, 1967, 462.
[2] A. J. Edwards, D. Hugill, and R. D. Peacock, *Nature*, 1963, **200**, 672.
[3] W. H. Zachariasen, *Acta Cryst.*, 1949, **2**, 390.