

The Crystal Structure of Technetium(IV) Chloride

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WE now report the crystal structure of technetium(IV) chloride as determined by a single crystal X-ray-diffraction analysis.

The crystals are orthorhombic with the centrosymmetric space group *Pbca*. There are eight TcCl_4 units in a unit cell of dimensions $a = 11.58$,

$b = 13.97$, and $c = 5.98 \text{ \AA}$. The calculated density, 3.31 g.cm.^{-3} is within the range established by flotation. All atoms were located by means of projections of the Patterson function down each of the three crystallographic axes. Trial co-ordinates were refined by several least-squares cycles using

the block diagonal approximation with partial three-dimensional data. The discrepancy factor, R , for all 390 reflections used is 0.13. The refinement will be completed when the remaining data are available.

The structure consists of octahedral groups of composition TcCl_6 linked into endless linear chains extended parallel to the c -axis by the sharing of four chlorine atoms. The mean Tc-Cl bond length is 2.36 Å, compared with the only other reported value of 2.35 Å found by Cotton and Bratton¹ in $\text{Tc}_2\text{Cl}_8^{3-}$. There are variations between individual bonds, but at this stage they are of doubtful significance. All bond angles are close to 90°. The Tc-Tc distance within the polymer chain is 3.59 Å and the mean Cl-Cl distance is 3.33 Å. There are no unusually close contacts between the chains.

The octahedral co-ordination about technetium suggests that d^2sp^3 hybrid orbitals are being used for σ -bond formation. Tc^{IV} possesses the d^3 electronic configuration and would thus be in the spin-free t_{2g}^3 state. We might therefore predict a magnetic moment close to the theoretical value for three unpaired electrons (3.88 B.M.). The figure of 3.16 B.M. reported by Knox and Coffey² is very low, even if allowance is made for some exchange phenomena between Tc atoms *via* the bridging chlorines and also some distortion of the octahedra.

The TcCl_4 structure is the first of the tetrahalides of the manganese group to be established, but its octahedral basis may be contrasted with the trinuclear structure predicted for ReCl_4 (analogous to $\text{Re}_3\text{Cl}_{12}^{3-}$) by Colton and Martin³ on the basis of magnetic evidence.

(Received, June 14th, 1965.)

¹ F. A. Cotton and W. K. Bratton, *J. Amer. Chem. Soc.*, 1965, **87**, 921.

² K. Knox and C. E. Coffey, *J. Amer. Chem. Soc.*, 1959, **81**, 7.

³ R. Colton and R. L. Martin, *Nature*, 1965, **205**, 239.