Novel Columnar Anion in Potassium Tetrafluorochromate(III): *X*-Ray Crystal Structure

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Summary Single crystal *X*-ray structure analysis of potassium tetrafluorochromate(III) has shown the anion to consist of approximately planar [Cr_3F_9] units linked into columns by fluorine bridges, with the columns separated by potassium ions, consistent with the extraordinary ease of cleavage of the crystals into fibres.

DETAILED structural studies have been reported on a number of alkali metal tetrafluoroferrates(III) and the structures correlated with the magnetic properties of the compounds.[1] In these compounds the anion consists of octahedrally co-ordinated iron atoms linked through fluorine bridges into corrugated sheets, with the sheets separated by potassium ions. The two terminal fluorine atoms are *trans* to one another. The corresponding tetrafluorovanadates(III) are isostructural with these ferrates, although no detailed structure analyses have been reported.[2]

We have found a completely different structural arrangement for potassium tetrafluorochromate(III), where the same sheet arrangement might have been expected. The chromium atoms are octahedrally co-ordinated but the two terminal fluorine atoms are *cis* to one another and the bridging gives a triangular column arrangement.

Potassium tetrafluorochromate(III) was prepared[3] by the medium temperature flux method by interaction of potassium hydrogen fluoride with chromium trifluoride and lead dichloride as flux. Some of the crystals appeared to consist of bundles of very fine fibres and pressure on others caused cleavage into these very fine fibres. From *X*-ray powder photography a hexagonal unit cell was reported[4] for the compound ($a = 9{\cdot}12$, $c = 7{\cdot}40$ Å). We found one good single crystal in a batch of material and have shown its crystal symmetry to be orthorhombic, related to the previously reported hexagonal cell.

Crystal data: CrF_4K, M 167, orthorhombic, space group $Pnma$ (D^{16}_{2h}, No. 62), $a = 15{\cdot}76(1)$, $b = 7{\cdot}43(1)$, $c = 18{\cdot}38(1)$ Å, $U = 2152$ Å^3, $D^4_m = 3{\cdot}13$, $D_c = 3{\cdot}09$ g cm^{-3}, $Z = 24$, $F(000) = 1896$, Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å; $\mu = 40{\cdot}8$ cm^{-1}).

Unit cell geometry and space group data were derived photographically, and intensity data were obtained by use

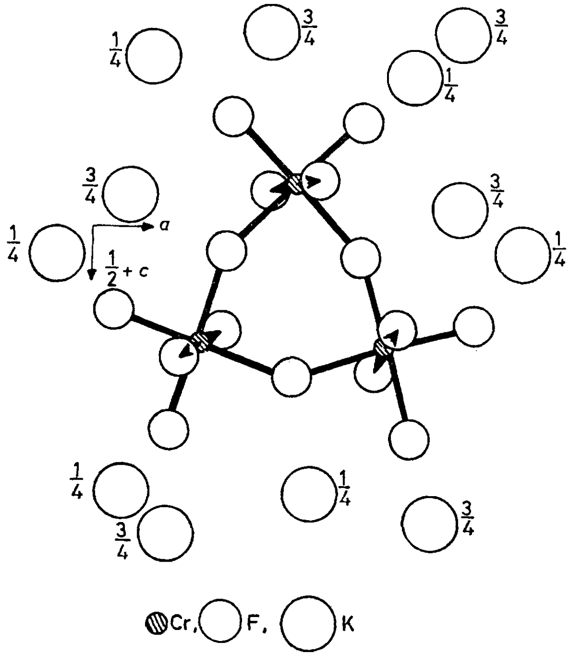

Figure. Projection of part of the structure of CrF_4K down [010] showing a section across the columnar anion and the surrounding potassium cations.

of a Stoe 2-circle diffractometer. The structure was solved by a combination of Patterson and direct methods, and 1975 independent reflections with $I_0 > 3\sigma(I)$ were refined by full-matrix least-squares methods to a present R of 0·057, with isotropic temperature parameters.

The structure consists of novel columnar anions $[CrF_4^-]_\infty$ separated by potassium cations (Figure). The symmetry of the individual columns is close to 3-fold, although no symmetry is space-group imposed. The octahedra are tilted with respect to the plane defined by the three chromium atoms, resulting in angular bridges up the column, with bridge angles of between 140 and 150° at both these fluorine atoms and those within the $[Cr_3F_9]$ unit. The mean terminal Cr–F bond distance is 1·860(15) Å, whereas the bridging Cr–F distances average 1·934(20) Å (individual e.s.d.s are ±0·005 Å).

The trimeric linking of octahedra to form $[Cr_3F_{12}]$ units is similar to that[5] in the trimeric polymorphs of technetium and molybdenum oxide tetrafluorides, but has not previously been observed for a compound containing fluorine alone.

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