Fluoride Crystal Structures. Part XIX.[1] Dipotassium Aquopentafluoroferrate(III)

By **A. J. Edwards,** Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Crystals of dipotassium aquopentafluoroferrate(III) are monoclinic, space-group $C2/c$, $a = 9{\cdot}71$, $b = 7{\cdot}79$, $c = 7{\cdot}95$ Å, $\beta = 96{\cdot}5°$, $Z = 4$. The structure was refined by three-dimensional least-squares methods to R 0·074 for 615 reflections. The structure consists of separate K^+ and $[FeF_5(H_2O)]^{2-}$ ions. In the anion the co-ordinated oxygen atom is further from the iron atom (Fe–O 2·07 Å) than the fluorine atoms (mean Fe–F 1·92 Å) but the angles at the iron atom are all very close to 90°. The anions are linked into chains by strong hydrogen bonds (O · · · F 2·54 Å).

COMPOUNDS of formula A_2MF_5,H_2O are well characterised, and many have been assumed [2] to contain separate octahedrally co-ordinated anions. However, the only crystallographic studies reported are for K_2AlF_5,H_2O [3] and K_2MnF_5,H_2O,[4] in both of which there are endless-chain anions linked through *trans*-bridging fluorine atoms, and separate water molecules. The structure of dipotassium aquopentafluoroferrate(III) has therefore

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[1] Part XVIII, A. J. Edwards, *J. Chem. Soc.* (*A*), 1971, 3074.

[2] R. Colton and J. H. Canterford, ' Halides of the First-row Transition Metals,' Wiley–Interscience, New York, 1969.

[3] R. W. G. Wyckoff, ' Crystal Structures,' vol. III, 2nd edn., Interscience, New York, p. 574.

[4] A. J. Edwards, *J. Chem. Soc.* (*A*), 1971, 2653.

been determined to investigate the effect of the co-ordinated water molecule on the octahedral arrangement in the anion.

EXPERIMENTAL

Single crystals of dipotassium aquopentafluoroferrate(III) were prepared by an adaptation of Palmer's method.[5] Aqueous hydrofluoric acid solutions of potassium bifluoride and iron(III) alum were allowed to diffuse together in aqueous hydrofluoric acid, the reaction being carried out in a welded Polythene container. The crystals formed in aggregates, mostly twinned, and a single crystal was cut from the mass with a razor blade. The crystal was a transparent, colourless, flat plate with roughly triangular shape and the *a* axis perpendicular to the plate.

Crystal Data.—$K_2FeF_5(H_2O)$, $M = 247$, Monoclinic, $a = 9{\cdot}71 \pm 0{\cdot}01$, $b = 7{\cdot}79 \pm 0{\cdot}01$, $c = 7{\cdot}95 \pm 0{\cdot}01$ Å, $\beta = 96{\cdot}5 \pm 0{\cdot}2°$, $U = 597$ Å^3, $Z = 4$, $D_c = 2{\cdot}81$, $F(000) = 476$. Cu-K_α ($\lambda = 1{\cdot}5418$ Å) and Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation; μ(Mo-K_α) = 41·6 cm^{-1}. Single-crystal precession and Weissenberg photographs. Space-group $C2/c$ or Cc by systematic absences: $hk0$ when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$. The centrosymmetric space-group $C2/c$ (C^6_{2h}, No. 15) was indicated from the Patterson function, and the assignment shown to be correct by the subsequent successful refinement.

Structure Determination.—Integrated intensities were collected about the *b* axis (layers $h0$—$6l$) by use of Mo-K_α radiation and a Nonius integrating camera. The relative intensities of 615 reflections were measured with a photometer of similar design to that described by Jeffery[6] and were corrected for Lorentz and polarisation factors. Absorption corrections were calculated by use of the program ABSCOR.

The positions of all the atoms except hydrogen were deduced from a three-dimensional Patterson synthesis, assuming space-group $C2/c$, and structure-factors calculated by use of neutral atom scattering factors from ref. 7. The positional and isotropic temperature parameters, and layer scale-factors, were refined by full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised initially with unit weights and with $\sqrt{w} = |F_o|/13$ when $|F_o| \leqslant 13$, and $\sqrt{w} = 13/|F_o|$ when $|F_o| > 13$ during the final cycles of refinement. The final parameter shifts were $< 0{\cdot}1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$ was satisfactory. The final R was 0·074 and the weighted value R', 0·101 [$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$]. Observed and calculated structure-factors are listed in Supplementary Publication No. 20311 (9 pp., 1 microfiche),* and the final positional parameters and isotropic temperature factors, with their estimated standard deviations, in Table 1. Interatomic distances and angles are given in Table 2 (estimated standard deviations do not include cell parameter errors).

TABLE 1

Final atomic positional and thermal parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
Fe	0	0·2061(3)	$\frac{1}{4}$	0·94(3)
K	0·2984(2)	−0·0028(3)	0·4682(2)	1·69(3)
F(1)	0·0701(5)	0·2027(9)	0·4863(6)	1·92(8)
F(2)	0·1855(6)	0·1958(9)	0·1940(6)	2·05(8)
F(3)	0	0·4525(14)	$\frac{1}{4}$	1·55(13)
O	0	−0·0592(21)	$\frac{1}{4}$	2·71(23)

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Fe–F(1)	1·925(5)	F(1) · · · F(2)	2·692(7)
Fe–F(2)	1·905(5)	F(1) · · · F(3)	2·737(10)
Fe–F(3)	1·919(11)	F(2) · · · F(3)	2·761(10)
Fe–O	2·066(16)	O · · · F(1)	2·805(13)
O · · · F(2)	2·751(13)	K · · · F(1)	2·751(6)
K · · · F(2)	2·794(6)	K · · · O	3·234(3)
K · · · F(2^{I})	2·692(7)	K · · · F(3^{I})	2·781(2)
K · · · F(2^{II})	2·671(6)	K · · · F(3^{III})	2·830(2)
F(1) · · · F(2^{IV})	2·722(7)	F(1) · · · O$^{\text{II}}$	2·536(9)
K · · · F(1^{V})	3·487(6)		

(*b*) Angles

F(3)–Fe–F(1)	90·8(2)	F(1)–Fe–F(2)	89·3(2)
O–Fe–F(1)	89·2(2)	F(3)–Fe–F(2)	92·4(2)
F(1^{VI})–O–F(1^{VII})	127·6(2)	O–Fe–F(2)	87·6(2)
		F(1^{VI})–O–Fe	116·2(2)

The Roman numerals as superscripts refer to atoms in the following equivalent positions relative to the reference molecule at x, y, z:

I $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
II $x, -y, \frac{1}{2} + z$
III $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
IV $-x, y, \frac{1}{2} - z$
V $\frac{1}{2} + x, -\frac{1}{2} + y, z$
VI $-x, -y, 1 - z$
VII $x, -y, -\frac{1}{2} + z$

DISCUSSION

The atomic arrangement is shown in Figure 1. The structure consists of separate K^+ and $[FeF_5(H_2O)]^{2-}$ ions, with a slightly distorted octahedral co-ordination of the iron atom. The three independent Fe–F distances are approximately equal, mean 1·92 Å. This value is the same, within experimental error, as that of 1·910 Å in the isolated $[FeF_6]^{3-}$ anion[8] in K_2NaFeF_6, and 1·92 Å in FeF_3.[9] The Fe–O distance of 2·07 Å is very close to those of 2·08 and 2·10 Å for Fe–O reported in the $[FeCl_5(H_2O)]^{2-}$ anion, in the ammonium[10] and potassium[11] salts respectively, and to that[12] of 2·07 Å in *trans*-$[FeCl_2(H_2O)_4]^+$ in $[FeCl_2(H_2O)_4]Cl,2H_2O$.

Despite the greater distance of the oxygen atom from the iron atom the angles in the octahedron are very close to 90°, and the water molecule appears to 'fill' its octahedral co-ordination position. The two structure determinations[10,11] involving the $[FeCl_5(H_2O)]^{2-}$ anion also show angles in the octahedron close to 90°, although the Fe–Cl distances are much longer than the Fe–O distance.

Unfortunately no example of a separate $[FeF_5]^{2-}$ or $[FeCl_5]^{2-}$ ion is known which could be compared with the

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies).

[5] W. G. Palmer, 'Experimental Inorganic Chemistry,' Cambridge University Press, Cambridge, 1959, p. 523.

[6] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[7] 'International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, p. 202.

[8] K. Knox and D. W. Mitchell, *J. Inorg. Nuclear Chem.*, 1961, **21**, 253.

[9] M. A. Hepworth, K. H. Jack, R. D. Peacock, and G. J. Westland, *Acta Cryst.*, 1957, **10**, 63.

[10] I. Lindqvist, *Acta Chem. Scand.*, 1948, **2**, 530; *Arkiv Kemi Mineral. Geol.*, 1946, **24***A*, 1.

[11] A. Bellanca, *Periodico Mineral.* (*Rome*), 1948, **17**, 59.

[12] M. D. Lind, *J. Chem. Phys.*, 1967, **47**, 990.

aquo-complex, to assess the effect of the water molecule on the five-co-ordinate species. However, the pair of ions $[InCl_5(H_2O)]^{2-}$ and $[InCl_5]^{2-}$ have been structurally characterised [13,14] and this aquo-complex has a very similar structure to the iron analogue, with angles close to 90° in the octahedron.[13] In the square-pyramidal $[InCl_5]^{2-}$ species [14] the Cl(apical)–In–Cl(basal) angle is 103·9°, and hence the water molecule does have an appreciable effect on the co-ordination.

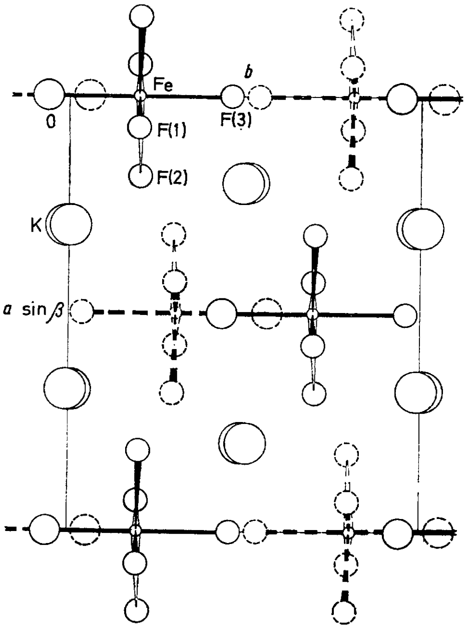

FIGURE 1 Projection of the structure down [001] showing the atom numbering. The anions at $z = \frac{1}{4}$ are shown in full and those at $z = \frac{3}{4}$ by dashed lines for clarity

The intermolecular contacts in the structure (Table 2) show one contact much shorter than the average. The distance F(1) · · · O is 2·54 Å, and presumably involves a hydrogen bond. The Fe–F(1) distance is statistically significantly longer than Fe–F(2), by 0·02 Å, and this is presumably the result of the hydrogen-bonding interaction. This O · · · F distance is shorter than previously reported hydrogen-bonded O · · · F distances of 2·68 and 2·72 Å in [15] $Fe(H_2O)_6SiF_6$, and 2·72 Å in [16] $CuF_2,2H_2O$.

hybridised. The same type of planar configuration for the water molecule and the metal atom has been found previously in $Fe(H_2O)_6SiF_6$ and $CuF_2,2H_2O$. In K_2MnF_5,H_2O the water molecule is not part of the anion.

It has recently been suggested, on the basis of CNDO MO calculations,[17] that the oxygen atoms in the co-ordinated water molecules of hexa-aquometal(II) and hexa-aquometal(III) ions have a configuration derived from a tetrahedral geometry (sp^3 hybridisation). For this co-ordination geometry to be present in the aquopentafluoroferrate(III) the hydrogen atoms would not conform to the space-group symmetry, and the two examples detailed support the planar configuration.

The hydrogen bonding in the structure links the anions into zigzag chains parallel to the c axis (Figure 2) and distorts the packing of the ions from the regular K_2PtCl_6 type of structure. The basic packing can be seen to be related to this arrangement by considering the neighbours for the ions. Thus each K^+ ion has four $[FeF_5(H_2O)]^{2-}$ ions arranged in a roughly tetrahedral

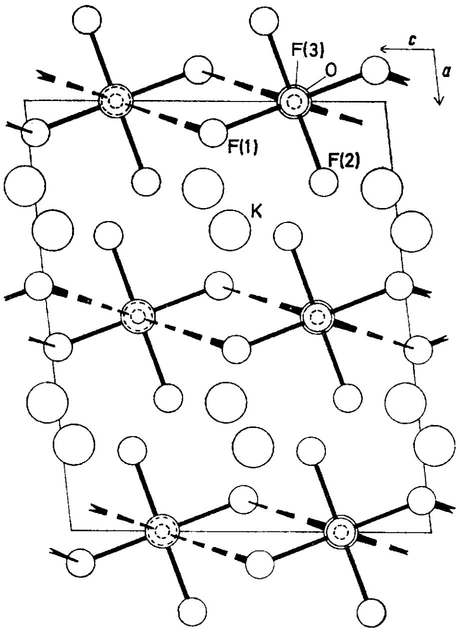

FIGURE 2 Projection of the structure down [010] showing