Structural Studies† of Potassium Tetrafluorochromate(III), K[CrF_4], and the Novel Mixed Chloride Fluoride, Dipotassium Dichlorohexafluorotrichromate(II), $K_2[Cr_3Cl_2F_6]$

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The crystal structures of potassium tetrafluorochromate(III), K[CrF_4] (**1**), and dipotassium dichlorohexafluorotrichromate(II), $K_2[Cr_3Cl_2F_6]$ (**2**), are reported. The structure of (**1**) consists of infinite triangular anionic columns comprising approximately planar Cr_3F_9 units linked above and below by fluoride bridges, the columns being separated by K^+ ions. Each Cr^{III} atom is octahedrally co-ordinated by six F atoms. The structure of (**2**) contains two crystallographically independent Cr^{II} atoms which have distorted octahedral co-ordination by four equatorial F atoms and two axial Cl atoms. The Cr atoms are linked together by single Cr–F–Cr bridges and also by a novel chloride fluoride double bridge. The structure can also be thought of as comprising two-dimensional CrF_2 sheets, held together by Cl atom bridges. Charge balance is maintained by K^+ ions. Crystal data for (**1**) are: a = 15.76(1), b = 7.43(1), c = 18.38(1) Å, Z = 24, orthorhombic, space group *Pnma*, final R = 0.041 for 1 975 diffractometer data with $I_o > 3\sigma(I_o)$. Crystal data for (**2**) are: a = 6.726(1), b = 11.157(5), c = 7.391(3) Å, β = 125.31(4)°, Z = 2, monoclinic, space group $P2_1/c$, final R = 0.041 for 1 044 diffractometer data with $I_o > 2\sigma(I_o)$.

Medium-temperature flux growth has proved to be a useful method for the preparation of single-crystal samples of complex transition metal fluorides that are difficult to prepare by growth from the melt.[1–4] Flux growth of crystals, using CrF_3, KHF_2, and $PbCl_2$ as starting materials,[4] produced a mixture of products consisting of dark green platelets of $K_2[CrF_5]$ and fibrous green rods of K[CrF_4] (1), both of which contain chromium in the +3 oxidation state. The crystals of $K_2[CrF_5]$ had unit-cell dimensions in agreement with those given in a previous report.[5] Also, the powder pattern agreed closely with that reported for the isomorphous $K_2[FeF_5]$ on which a full structure determination has appeared.[6] We therefore presumed that $K_2[CrF_5]$ was isostructural with $K_2[FeF_5]$ and further work on these crystals was not performed.

Crystals of (1), however, had previously been reported[7] to possess a hexagonal unit cell and this did not agree with our experiments which indicated that the crystals belonged to the orthorhombic crystal system. We therefore undertook a full structure determination on these crystals and a report on the structure of (1) has previously been published in a preliminary communication.[8] In this paper we report further details of that structure.

Apart from the two major green crystalline products, a very small amount of a blue crystalline material was also present in the reaction products mentioned above. We initially believed that this material was Na[CrF_3], based largely on a consideration of unit-cell dimensions,[9a,10,11] but we show here that the crystals are in fact the novel mixed chloride fluoride having the composition $K_2[Cr_3Cl_2F_6]$ (2), containing chromium in the unexpected +2 oxidation state, the chloride being incorporated presumably from the $PbCl_2$ that was used as the flux material.

Experimental

K[CrF_4] (1).—Green rod-shaped crystals of the compound were prepared by the medium-temperature flux method[1–4] by heating KHF_2 (5.6 g), CrF_3 (7.9 g), and $PbCl_2$ (15.6 g) to 930 °C and cooling at a rate of 6 °C h^{-1} to a final temperature of 350 °C.[4] This procedure leads to a mixture of (1) and $K_2[CrF_5]$ along with a very small amount of (2). Crystals could be separated by hand. The crystals of (1) consisted of bundles of very fine fibres and pressure on the crystals caused cleavage into these fibres. One crystal, which had not separated into fibres, was suitable for *X*-ray work and preliminary oscillation, Weissenberg, and precession photographs showed it to have *mmm* Laue symmetry. The systematic absences indicated the space group to be either *Pnma* (D_{2h}^{16}, no. 62) or its non-centrosymmetric equivalent $Pn2_1a$ (C_{2v}^{9}, no. 33) in a non-standard setting.[12a] The structure has been successfully solved and refined in the centrosymmetric space group. An earlier report,[7] using *X*-ray powder photography, suggested that the compound had a hexagonal unit cell with dimensions a = 9.12 and c = 7.40 Å. This hexagonal cell appears to be a pseudo-cell, since it can be recast using the transformations: $a_{\text{orthorhombic}} = a_{\text{hexagonal}}(\tan 60°) = 15.80$; $b_{\text{orthorhombic}} = c_{\text{hexagonal}} = 7.40$; $c_{\text{orthorhombic}} = 2a_{\text{hexagonal}} = 18.24$ Å. This is in excellent agreement with the present results. Intensity data were collected on a Stoe STADI-2 two-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å); 2 538 unique reflections were obtained in the range $4 < 2\theta < 55°$. Further details of the data collection and refinement methods appear in ref. 13.

The structure was solved by a combination of Patterson and direct methods and refinement of the 188 variables was by full-matrix least-squares methods using the 1 975 reflections with $I_o > 3\sigma(I_o)$. Final residual indices[14] were R = 0.041 and R' = 0.056. Neutral-atom scattering factors and corrections for anomalous dispersion were obtained from ref. 15. All atoms were refined anisotropically and no evidence for disorder was observed in any part of the structure. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 0.8409/[\sigma^2(F_o)]$. In the final cycle of refinement the largest parameter shift was 0.12 while all remaining parameter shifts were less than 0.04 of their estimated standard deviation. The final difference Fourier map showed no significant features and the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Table 1. Positional parameters with estimated standard deviations in parentheses for (1)

Atom	x	y	z	Atom	x	y	z
Cr(1)	0.368 48(5)	−0.000 60(10)	0.630 95(4)	F(4)	0.251 8(2)	0.046 2(4)	0.659 3(2)
Cr(2)	0.135 69(5)	−0.001 87(10)	0.626 42(4)	F(5)	0.101 6(2)	−0.037 9(5)	0.721 3(2)
Cr(3)	0.252 95(5)	−0.000 91(10)	0.453 00(4)	F(6)	0.385 1(3)	0.25	0.607 7(3)
K(1)	−0.044 6(1)	0.25	0.532 1(1)	F(7)	0.107 7(3)	0.25	0.639 8(3)
K(2)	0.460 3(1)	0.75	0.476 8(1)	F(8)	0.353 3(3)	−0.25	0.652 1(3)
K(3)	0.431 2(1)	0.75	0.819 3(1)	F(9)	0.165 1(3)	−0.25	0.611 4(2)
K(4)	0.100 4(1)	0.75	0.834 2(1)	F(10)	0.026 5(2)	−0.041 7(4)	0.591 0(2)
K(5)	0.219 7(1)	0.75	0.289 3(1)	F(11)	0.221 3(3)	−0.25	0.461 0(2)
K(6)	0.041 8(1)	0.25	0.787 4(1)	F(12)	0.336 8(2)	−0.056 1(4)	0.385 0(2)
F(1)	0.403 0(2)	0.037 7(4)	0.726 4(2)	F(13)	0.169 3(2)	0.048 3(4)	0.527 0(2)
F(2)	0.335 3(2)	−0.037 5(4)	0.530 4(2)	F(14)	0.171 9(2)	0.017 8(4)	0.380 8(2)
F(3)	0.480 9(2)	−0.036 6(4)	0.600 4(2)	F(15)	0.285 8(3)	0.25	0.448 0(2)

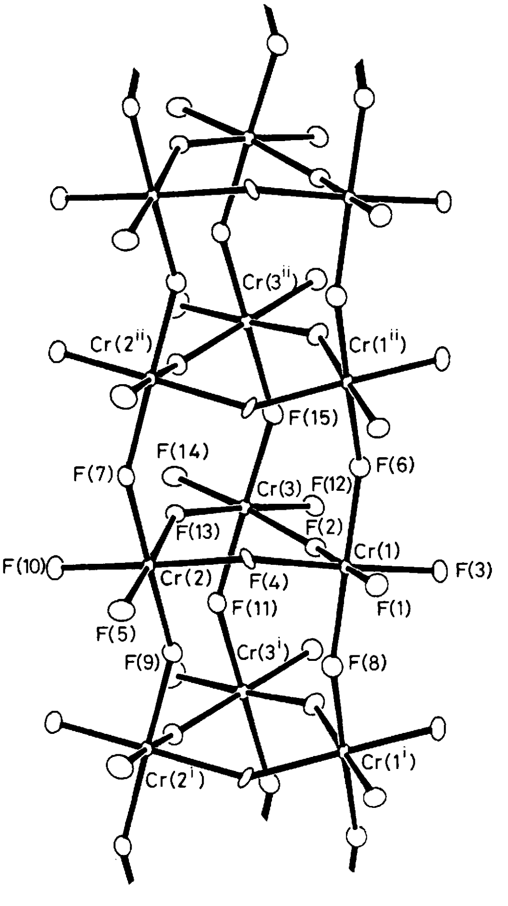

Figure 1. One of the infinite triangular anionic columns in the structure of (1); the K^+ ions are not shown

Table 2. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for (1)*

Cr(1)–F(1)	1.859(4)	Cr(2)–F(5)	1.844(4)
Cr(1)–F(2)	1.940(4)	Cr(2)–F(13)	1.939(4)
Cr(1)–F(3)	1.878(3)	Cr(2)–F(10)	1.864(3)
Cr(1)–F(4)	1.943(3)	Cr(2)–F(4)	1.960(3)
Cr(1)–F(6)	1.928(2)	Cr(2)–F(7)	1.938(2)
Cr(1)–F(8)	1.908(2)	Cr(2)–F(9)	1.921(2)
Cr(3)–F(12)	1.865(4)	Cr(3)–F(14)	1.847(4)
Cr(3)–F(13)	1.929(4)	Cr(3)–F(2)	1.945(4)
Cr(3)–F(11)	1.922(2)	Cr(3)–F(15)	1.937(2)
F(1)–Cr(1)–F(2)	178.4(1)	F(5)–Cr(2)–F(13)	177.1(2)
F(3)–Cr(1)–F(4)	177.3(1)	F(2)–Cr(3)–F(14)	176.0(1)
F(6)–Cr(1)–F(8)	178.8(2)	F(11)–Cr(3)–F(15)	178.3(2)
F(4)–Cr(2)–F(10)	177.2(2)	F(12)–Cr(3)–F(13)	177.0(1)
F(7)–Cr(2)–F(9)	178.7(2)	Cr(2)–F(7)–Cr(2^{ii})	149.8(3)
Cr(1)–F(2)–Cr(3)	149.0(2)	Cr(2)–F(9)–Cr(2^{i})	147.4(3)
Cr(1)–F(4)–Cr(2)	140.2(2)	Cr(2)–F(13)–Cr(3)	144.6(2)
Cr(1)–F(8)–Cr(1^{i})	152.3(3)	Cr(3)–F(11)–Cr(3^{i})	148.6(3)
Cr(1)–F(6)–Cr(1^{ii})	149.9(3)	Cr(3)–F(15)–Cr(3^{ii})	148.5(3)
min. *cis* F–Cr–F	86.7	max. *cis* F–Cr–F	94.5
mean *cis* F–Cr–F	90.0		

* Superscripts refer to atoms at positions generated by the following symmetry operations: i, $x, -\frac{1}{2} - y, z$; ii, $x, \frac{1}{2} - y, z$.

average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, $(\sin\theta)/\lambda$, $|h|$, $|k|$, or $|l|$, showed good consistency and the weighting scheme was considered to be satisfactory. All calculations were performed with SHELX 76[16] on the ICL 1906A computer at the University of Birmingham.

Final atomic positional parameters are given in Table 1 and interatomic distances and angles in Table 2. Figure 1 shows a view of one of the triangular columns of (1).

Crystal Data for (1).—CrF_4K, $M = 167.09$, orthorhombic, space group *Pnma*, $a = 15.76(1)$, $b = 7.43(1)$, $c = 18.38(1)$ Å, $U = 2\,152.2$ Å^3, $D_m = 3.13$ g cm^{-3} (ref. 7), $Z = 24$, $D_c = 3.094$ g cm^{-3}, $F(000) = 1\,680$, μ(Mo-K_α) = 40.8 cm^{-1}.

$K_2[Cr_3Cl_2F_6]$ (2).—Blue crystals of this compound were obtained as a very minor component from the preparation of (1) as described above.[4] Only a few crystals of (2) were available and that which was suitable for data collection had dimensions 0.40 × 0.07 × 0.07 mm. Preliminary oscillation, Weissenberg, and precession photographs showed the crystal to have $2/m$ Laue symmetry and the systematic absences indicated the space group to be $P2_1/c$ (C_{2h}^5, no. 14).[12b] Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromated Mo-K_α radiation; 1 330 unique reflections were obtained in the range $2 < 2\theta < 50°$. Further details of the data collection and refinement methods appear in ref. 17.

The structure of (2) was solved by multisolution Σ_2 sign expansion using renormalized E-values to upweight those reflections with l odd.[16] Four E-maps, based on 2^{20} starting sets and using the 320 reflections with $E > 1.1$, were obtained. One of these E-maps yielded all atomic positions, although atomic designations were finally decided upon at a later stage.

Before the structure of (2) was solved it was presumed that the compound was $Na[CrF_3]$ and there were some compelling reasons for this assumption. The space group of (2) can be

Table 3. Positional parameters with estimated standard deviations in parentheses for (**2**)

Atom	*x*	*y*	*z*
Cr(1)	0.00	0.00	0.00
Cr(2)	0.162 07(13)	0.253 03(6)	−0.116 10(11)
K(1)	0.699 41(18)	0.047 48(9)	0.335 88(17)
Cl(1)	−0.335 52(21)	0.171 24(10)	−0.308 27(19)
F(1)	0.259 5(4)	0.090 8(2)	0.012 7(4)
F(2)	0.058 4(5)	0.084 8(2)	0.262 1(4)
F(3)	0.142 4(5)	0.188 7(2)	−0.373 9(4)

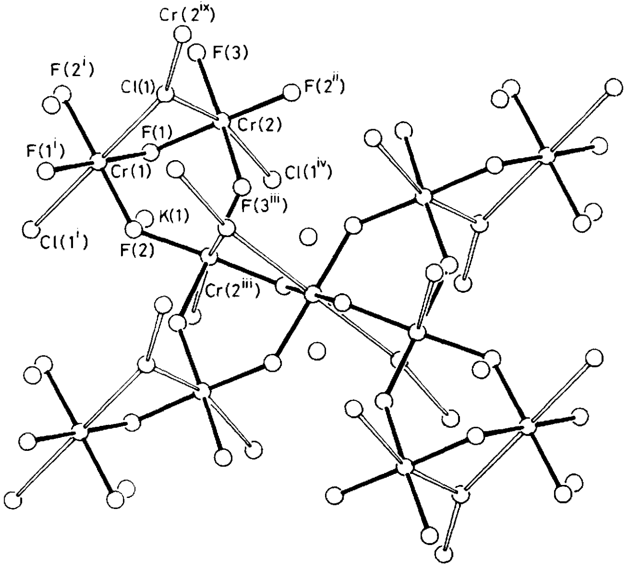

Figure 2. Structure of (**2**) projected approximately down the *a* axis. Atom Cr(1) lies at (0,0,0) which is a point of $\bar{1}$ symmetry. All the Cr–Cl bonds are open while all Cr–F bonds are filled. Note that not all bonds to atoms at the boundaries of the diagram are shown but they can be deduced from the body of the structure

transformed from $P2_1/c$ to $B2_1/c$ to give a unit cell with dimensions a = 10.983(7), b = 11.157(5), c = 7.391(3) Å, and β = 88.00(5)°. These cell dimensions are strikingly similar to those reported for Na[CuF$_3$] (a = 11.01, b = 11.37, c = 7.52 Å, and β = 86.9°).[9–11] (Note that the value of the *a* unit-cell dimension for Na[CuF$_3$] listed in Table 9.25 of ref. 9 is misprinted.) A full structure determination on Na[CuF$_3$] has not been reported. The space group for Na[CuF$_3$] has been assigned as $C2$, Cm, or $C2/m$ and this was not consistent with our assignment of $B2_1/c$ although, given the fact that crystal system and space group assignments in this field are not always completely accurate, as in the case of (**1**) for example, this discrepancy was easily discounted. The blue colour of the crystals of (**2**) also suggested Cr$^{\text{II}}$ rather than Cr$^{\text{III}}$ and this would be consistent with the Cr$^{\text{II}}$ compound being isomorphous with the Cu$^{\text{II}}$ compound. That we had K[CrF$_3$] was ruled out, although this would be more consistent with the fact that K$^+$ rather than Na$^+$ salts were used in the synthesis, since the structure of K[CrF$_3$] is known[9b,18,19] and its unit-cell dimensions and crystal system are different from those reported for Na[CuF$_3$]. Our conclusions, however, although seemingly quite sound have turned out to be incorrect and this held up the progress of the structure solution quite considerably. Also, the very limited amount of material available precluded chemical analysis of (**2**).

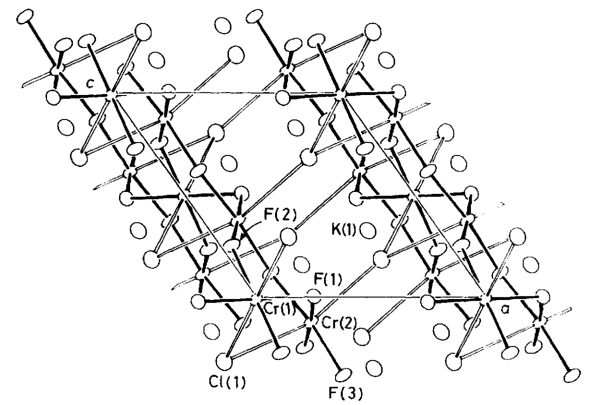

Figure 3. Diagram of (**2**) projected down the *b* axis showing the sheet-like nature of the structure. The sheets, of composition CrF$_2$, are bridged by Cl atoms. All Cr–Cl bonds are open and Cr–F bonds filled. Note that not all bonds to atoms at the boundaries of the diagram are shown but they can be deduced from the body of the structure

The true nature of (**2**) was eventually deduced from the direct methods solution as follows. The seven largest peaks on the correct *E*-map were assigned as two Cr atoms, one on a two-fold special position and the other on a four-fold general position,[12b] and three F and two Na atoms all on general positions; the distances between the various peaks seemed reasonable for the expected bond distances. Several cycles of least-squares refinement gave R = 0.102. At this stage the thermal parameters for the two Na atoms were very low which suggested that they were incorrectly assigned. Changing them to K atoms lowered the R value to 0.058 and produced more realistic thermal parameters for all the atoms. Changing Na to K was also more realistic since no Na salts were added to the reaction mixture[4] and any that were present would presumably only be there as minor impurities. On closer inspection the problem was now that the octahedral co-ordination spheres of both Cr atoms were completed by a K atom at *ca.* 2.85 Å in each case and that the stoicheiometry of '$K_4[Cr_3F_6]$' was obviously wrong. If this K atom, associated with the Cr atoms, was assigned as Cl the charge balance for (**2**) was now satisfactory with both Cr atoms in the +2 oxidation state, consistent with the blue colour of the crystals and giving a formula of $K_2[Cr_3Cl_2F_6]$. This would also be consistent with the fact that a large amount of PbCl$_2$ was present in the reaction mixture[4] and that the thermal parameters would be little affected by the change since the scattering powers of K and Cl are similar. With these changes the structure refined readily to a final R value of 0.041 with a featureless final difference Fourier map and meaningful thermal parameters for all atoms.

Final refinement of the 59 variables was by full-matrix least-squares methods using the 1 044 reflections with $I_o > 2\sigma(I_o)$. Final residual indices[14] were R = 0.041 and R' = 0.044. Neutral-atom scattering factors and corrections for anomalous dispersion were obtained from ref. 15. All atoms were refined anisotropically and no evidence for disorder was observed in any part of the structure. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1.6071/[\sigma^2(F_o) + 0.000\,400\,F_o^2]$, and in the final cycle of refinement no parameter shifted by more than 0.002 of its estimated standard deviation. The average $w\Delta^2$ for groups of data sectioned as for (**1**) showed good consistency and the weighting scheme was considered satisfactory. All calculations were performed with SHELX 76[16] on the IBM 370/165 computer at the University of Cambridge.

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for **(2)***

Cr(1)–F(1)	1.973(3)	Cr(2)–F(1)	1.973(2)
Cr(1)–F(2)	1.981(3)	Cr(2)–F(3)	1.968(3)
Cr(1)–Cl(1)	2.827(1)	Cr(2)–Cl(1)	2.925(1)
Cr(1)–F(1^{i})	1.973(3)	Cr(2)–F(2^{ii})	1.961(2)
Cr(1)–F(2^{i})	1.981(3)	Cr(2)–F(3^{iii})	1.980(4)
Cr(1)–Cl(1^{i})	2.827(1)	Cr(2)–Cl(1^{iv})	2.902(1)
Cr(1) ··· Cr(2)	3.313(1)	Cr(2) ··· Cr(2^{iii})	3.696(1)
Cr(1) ··· Cr(2^{i})	3.313(1)	Cr(1) ··· Cr(2^{iii})	3.641(1)
Cr(1) ··· Cr(2^{x})	3.641(1)	Cr(2) ··· Cr(2^{ix})	5.492(1)
Cr(1) ··· Cr(2^{ix})	5.516(1)	K(1)–Cl(1^{viii})	3.097(1)
K(1)–F(1)	2.554(2)	K(1)–F(1^{v})	3.149(3)
K(1)–F(3^{v})	2.794(3)	K(1)–Cl(1^{iv})	3.279(1)
K(1)–F(2^{vi})	2.797(4)	K(1)–Cl(1^{i})	3.378(1)
K(1)–F(2^{vii})	2.840(3)	K(1)–K(1^{xi})	3.467(1)
K(1)–F(3^{viii})	2.928(3)		
F(1)–Cr(1)–F(2)	92.2(1)	F(1)–Cr(2)–F(3)	87.1(1)
F(1)–Cr(1)–F(2^{i})	87.8(1)	F(1)–Cr(2)–F(3^{iii})	92.4(1)
F(1)–Cr(1)–Cl(1)	87.9(1)	F(1)–Cr(2)–Cl(1)	85.2(1)
F(1)–Cr(1)–Cl(1^{i})	92.1(1)	F(1)–Cr(2)–Cl(1^{iv})	88.7(1)
F(1)–Cr(1)–F(1^{i})	180.0	F(1)–Cr(2)–F(2^{ii})	177.6(2)
F(2)–Cr(1)–F(1^{i})	87.8(1)	F(3)–Cr(2)–F(2^{ii})	94.9(1)
F(2)–Cr(1)–Cl(1)	94.6(1)	F(3)–Cr(2)–Cl(1)	89.9(1)
F(2)–Cr(1)–Cl(1^{i})	85.4(1)	F(3)–Cr(2)–Cl(1^{iv})	105.2(1)
F(2)–Cr(1)–F(2^{i})	180.0	F(3)–Cr(2)–F(3^{iii})	173.3(2)
Cl(1)–Cr(1)–F(1^{i})	92.1(1)	F(2^{ii})–Cr(2)–F(3^{iii})	85.4(1)
Cl(1)–Cr(1)–F(2^{i})	85.4(1)	F(2^{ii})–Cr(2)–Cl(1)	93.5(1)
Cl(1)–Cr(1)–Cl(1^{i})	180.0	F(2^{ii})–Cr(2)–Cl(1^{iv})	92.0(1)
F(1^{i})–Cr(1)–F(2^{i})	92.2(1)	F(3^{iii})–Cr(2)–Cl(1)	83.4(1)
F(1^{i})–Cr(1)–Cl(1^{i})	87.9(1)	F(3^{iii})–Cr(2)–Cl(1^{iv})	81.5(1)
F(2^{i})–Cr(1)–Cl(1^{i})	94.6(1)	Cl(1)–Cr(2)–Cl(1^{iv})	163.4(1)
Cr(1)–F(1)–Cr(2)	114.2(1)	Cr(1)–Cl(1)–Cr(2)	70.3(1)
Cr(1)–F(2)–Cr(2^{iii})	135.0(2)	Cr(1)–Cl(1)–Cr(2^{ix})	148.7(1)
Cr(2)–F(3^{iii})–Cr(2^{iii})	138.9(1)	Cr(2)–Cl(1)–Cr(2^{ix})	141.0(1)

* Superscripts refer to atoms at positions generated by the following symmetry operations: i, $-x, -y, -z$; ii, $x, \frac{1}{2} - y, -\frac{1}{2} + z$; iii, $x, \frac{1}{2} - y, \frac{1}{2} + z$; iv, $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; v, $1 - x, -y, -z$; vi, $1 + x, y, z$; vii, $1 - x, -y, 1 - z$; viii, $1 + x, y, 1 + z$; ix, $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; x, $-x, -\frac{1}{2} + y, -\frac{1}{2} - z$; xi, $2 - x, -y, 1 - z$.

Final atomic positional parameters are given in Table 3 and interatomic distances and angles in Table 4. Figures 2 and 3 depict two different views of the structure of **(2)**.

Crystal Data for **(2)**.—$Cl_2Cr_3F_6K_2$, $M = 419.08$, monoclinic, space group = $P2_1/c$, $a = 6.726(1)$, $b = 11.157(5)$, $c = 7.391(3)$ Å, $\beta = 125.31(4)°$, $U = 452.6$ Å^3, $D_c = 3.075$ g cm^{-3}, $Z = 2$, $F(000) = 396$, μ(Mo-K_α) = 52.1 cm^{-1}.

Results and Discussion

K[CrF$_4$] **(1)**.—We have reported a brief account of this structure in a preliminary communication.[8] Some further refinement has been carried out but the structure is little changed from that reported earlier. It consists of anions comprising approximately planar Cr_3F_9 units linked into infinite columns by fluoride bridges (Figure 1), the columns being separated by K^+ ions. A view down one such column and also showing the positions of the K^+ ions is given in ref. 8. The novel columnar feature of the structure is consistent with the ease of cleavage of the crystals into fibres.

The asymmetric unit of the structure consists of three Cr atoms located on eight-fold general positions of the unit cell, six K^+ ions all of which lie on four-fold special positions on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$, and 15 F atoms with nine lying on general positions and six lying on the mirror planes of the cell, in a manner similar to the K^+ ions. The three Cr atoms are arranged in a triangle and are bridged by F atoms in general positions. Each Cr atom is also bound to two terminal F atoms all of which lie on general positions and are approximately in the plane of the three Cr and three bridging F atoms. This approximately planar Cr_3F_9 unit is linked to similar units above and below by F atom bridges where these F atoms lie on the four-fold special positions of the unit cell and thus lie on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. The symmetry of the individual columns is close to three-fold, although this symmetry is not space group imposed. Each Cr atom is six-co-ordinate and the octahedra thus formed are tilted with respect to the plane defined by the three Cr atoms, resulting in angular bridges up the column, with Cr–F–Cr bridge angles of between 140.2 and 152.3° at these F atoms and also those within the Cr_3F_9 unit.

Table 5. Average Cr–F distances (Å) and Cr–F–Cr angles (°) in tetrafluorochromates(III)

	Na[CrF$_4$]	K[CrF$_4$]	Cs[CrF$_4$]
Cr–F(terminal)	1.860	1.860	1.851
Cr–F(bridge) in triangle		1.943	1.940
Cr–F(bridge) in chain or sheet	1.931	1.926	1.929
Cr–F–Cr in triangle		144.6	149.5
Cr–F–Cr in chain		149.4	177.9
Cr–F–Cr in sheet	148.9		

When the preliminary communication[8] of this work was published we were unaware of the earlier report by Babel *et al.*[20] of the similar structure for Cs[CrF$_4$], full details of which were published later.[21] These workers have also reported details of the structure of the corresponding sodium salt[22] and a comparison of the three structures is of interest.

The caesium salt has a hexagonal unit cell and the trimeric chain anion has strictly planar Cr_3F_9 units, linked by almost linear bridges. The sodium salt contains a two-dimensional, buckled sheet anion, and is similar to the corresponding iron compound,[23] having the Na[NbO$_2$F$_2$] structure.[24] In all three compounds the CrF_6 octahedra are little distorted and the Cr–F distances very similar (Table 5). The Cr–F(bridge) distance in the chains or sheets is greater than the terminal distance by an average of 0.72 Å, whereas the corresponding average for the bridge distance in the triangle is 0.86 Å. This increase presumably corresponds to the steric requirements of the three adjacent bridging fluorine atoms in the triangle which have an average F–F distance of 2.74 Å compared with the larger average distance of 3.71 Å between the three bridging fluorines along the chain.

The Cr–F–Cr angles for the potassium and sodium salts, and for the triangular unit in the caesium salt are essentially the same and the differences in the overall geometry of the anions must result from the change in size of the cation. Thus the caesium ion is large enough to hold the chains with virtually linear bridges, the potassium ion allows the chains to buckle to give the (apparently) preferred bridge angle of about 149°, and the sodium ion is too small to stabilise the chain structure.

The trimeric linking of octahedra to form Cr_3F_{12} units in **(1)** is similar to that in the trimeric polymorphs of technetium and molybdenum oxide tetrafluorides.[25]

K$_2$[Cr$_3$Cl$_2$F$_6$] **(2)**.—The structure consists of K^+ ions, in rather asymmetric environments (Table 4), and an extended three-dimensional anionic array whose simplest unit is [Cr$_{1.5}$ClF$_3$]$^-$. The stoicheiometry of the asymmetric unit is thus K[Cr$_{1.5}$ClF$_3$] with four of these units making up the complete unit cell. There are, therefore, two independent Cr^{II} ions in the asymmetric unit, one of which, Cr(1), occupies the two-fold special positions at (0,0,0) and $(0,\frac{1}{2},\frac{1}{2})$ in the unit cell with the other Cr^{II} ion, Cr(2), occupying four-fold general positions (Figures 2 and 3). All other atoms occupy general positions. The Wyckoff *a* special positions in space group $P2_1/c$ have point symmetry $\bar{1}$ and thus the co-ordination geometry of Cr(1) has this symmetry crystallographically imposed upon it. This means that the octahedral co-ordination sphere of Cr(1) has all *trans* angles constrained to be 180°. The co-ordination geometry of Cr(2) is also octahedral but the *trans* angles are not constrained and they range from 163.4(1) to 177.6 (2)° (Table 4).

We have presumed that Cr(1) and Cr(2) are both in the +2 oxidation state and the initial evidence for this was the blue colour of the crystals of (**2**) whereas a green colour would be expected for the +3 oxidation state. The crystal structure has provided further evidence for this assignment of oxidation state, first from the stoicheiometry of the compound, and second from a consideration of the chromium–ligand distances. Both of the Cr^{II} ions are octahedrally co-ordinated by four F atoms in equatorial positions and two Cl atoms in axial positions and the Cr–F and Cr–Cl distances around Cr(1) and Cr(2) are comparable. Both octahedra adopt the usual Jahn-Teller distorted (4 short + 2 long) ligand arrangement expected for the Cr^{II} ion having a d^4 electronic configuration; as expected, the Cl atoms are in the axial positions. The equatorial Cr–F distances for Cr(1) are 1.973(3) and 1.981(3) Å and these distances are similar for Cr(2), ranging from 1.961(2) to 1.980(4) Å. These distances compare well with the equatorial Cr–F distances[26] of 1.98 and 2.01 Å in Cr^{II}F$_2$ and are significantly longer than those observed in (**1**) where comparable Cr^{III}–F distances average 1.860 Å (terminal F) and 1.943 Å (bridging F). This again indicates that Cr^{II} is present in (**2**) and not Cr^{III}. The Cr(1)–Cl axial distance is 2.827(1) Å and the two similar distances for Cr(2) are 2.902(1) and 2.925(1) Å. These distances agree well with the corresponding axial Cr–Cl distances[27,28] of 2.915 Å in Cr^{II}Cl$_2$ and are quite different from the equatorial Cr–Cl distances of 2.395 Å in that compound confirming that the Cl atom in (**2**) occupies the long, or axial, position of the Jahn-Teller distorted octahedron.

In the structure of (**2**) each of the three independent F atoms bridges between two Cr atoms (Figure 2). The F atoms designated as F(1) and F(2) bridge between Cr(1) and Cr(2) atoms and that designated as F(3) bridges between two symmetry-related Cr(2) atoms. Each of the F atoms is therefore two-co-ordinate. The Cl atom, on the other hand, is three-co-ordinate and bridges between Cr(1) and two symmetry-related Cr(2) atoms. The structure can also be viewed as being made up of two-dimensional sheets, of composition CrF$_2$ (Figure 3), with the Cl atoms bridging between these sheets *via* a bond to one of the Cr(2) atoms [specifically Cr(2^{ix}) in Figure 2] in one sheet, and two bonds, to Cr(1) and Cr(2), in the neighbouring CrF$_2$ sheet. There are two Cr ··· Cr distances of 3.641(1) and 3.696(1) Å [Cr(1) ··· Cr(2^{iii}) and Cr(2) ··· Cr(2^{iii}), Figure 2], with the metal atoms linked by single Cr–F–Cr bridges with angles of 135.0(2) and 138.9(1)°, respectively, and one distance of 3.313(1) Å [Cr(1) ··· Cr(2), Figure 2] where the linkage is a *novel chloride fluoride double bridge*, with a Cr–F–Cr angle of 114.2(1)° and a Cr–Cl–Cr angle of 70.3(1)°. The remaining links through Cr–Cl–Cr bridges, with angles 141.0(1) and 148.7(1)°, have much longer Cr ··· Cr distances of 5.492(1) and 5.516(1) Å [Cr(2) ··· Cr(2^{ix}) and Cr(1) ··· Cr(2^{ix}), Figure 2] and represent distances between the Cr atoms in neighbouring CrF$_2$ sheets. Thus, in Figure 2 it can be seen that the Cl atom participates in the chloride fluoride double bridge between Cr(1) and Cr(2), in one CrF$_2$ sheet, and also bridges to another CrF$_2$ sheet *via* the bond to Cr(2^{ix}).

The structure of (**2**) can also be thought of as consisting of linked, distorted octahedra, with K$^+$ ions filling holes with rather asymmetric environments. In terms of the linking of octahedra, that defined by Cr(1) is linked to two others by edges and two by vertices, whereas that defined by Cr(2) is linked to one other by an edge and four by vertices.

Compound (**2**) is different from the simple formulation of Na[CrF$_3$] that we originally envisaged for it. The structure of Na[CuF$_3$], whose unit-cell dimensions originally led us to our incorrect assumption, has not been reported and we obviously cannot explain any similarities between it and the structure of (**2**) which might have led to such similar unit cells. Indeed, it may simply be a coincidence since the reported space groups of the two compounds are different. A structure determination on Na[CuF$_3$] might be informative. The composition of (**2**) is interesting since it seems to have incorporated Cl$^-$ from the PbCl$_2$ flux material. Given that the amount of PbCl$_2$ in the reaction mixture is quite large it is perhaps surprising that larger quantities of other chloride species, such as K[CrCl$_4$], are not produced.

Acknowledgements

We thank the S.E.R.C. for financial support, the University of Birmingham Computer Centre for assistance, and Dr. B. M. Wanklyn and Mr. B. J. Garrard (Clarendon Laboratory, University of Oxford) for providing crystals of (**1**) and (**2**).

References

1 G. Garton and B. M. Wanklyn, *J. Cryst. Growth*, 1967, **1**, 49.
2 B. M. Wanklyn, *J. Cryst. Growth*, 1969, **5**, 279.
3 B. J. Garrard, B. M. Wanklyn, and S. H. Smith, *J. Cryst. Growth*, 1974, **22**, 169.
4 B. M. Wanklyn, *J. Mater. Sci.*, 1975, **10**, 1487.
5 A. de Kozak, *C. R. Acad. Sci. (Paris), Ser. C*, 1969, **268**, 416.
6 M. Vlasse, G. Matejka, A. Tressaud, and B. M. Wanklyn, *Acta Crystallogr., Sect. B*, 1977, **33**, 3377.
7 A. de Kozak, *Rev. Chim. Minerale*, 1971, **8**, 301.
8 J. C. Dewan and A. J. Edwards, *J. Chem. Soc., Chem. Commun.*, 1977, 533.
9 R. Colton and J. H. Canterford, 'Halides of The First Row Transition Metals,' Wiley-Interscience, London, 1969, (*a*) p. 529; (*b*) p. 199.
10 W. Rudorff, G. Lincke, and D. Babel, *Z. Anorg. Allg. Chem.*, 1963, **320**, 150.
11 W. Rudorff and D. Babel, *Naturwissenschaften*, 1962, **49**, 230.
12 'International Tables for *X*-Ray Crystallography,' 3rd edn., Kynoch Press, Birmingham, 1969, vol. 1, (*a*) pp. 119, 151; (*b*) p. 97.
13 J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J. Chem. Soc., Dalton Trans.*, 1975, 2171.
14 L. D. Silverman, J. C. Dewan, C. M. Giandomenico, and S. J. Lippard, *Inorg. Chem.*, 1980, **19**, 3379.
15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
16 G. M. Sheldrick, in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Delft University Press, Delft, 1978, p. 34.
17 J. J. Guy, P. G. Jones, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1976, **32**, 1937.
18 A. J. Edwards and R. D. Peacock, *J. Chem. Soc.*, 1959, 4126.
19 K. Knox, *Acta Crystallogr.*, 1961, **14**, 583.
20 D. Babel, W. Verscharen, and G. Knoke, presented at the 6th European Fluorine Symposium, Dortmund, 1977.
21 D. Babel and G. Knoke, *Z. Anorg. Allg. Chem.*, 1978, **442**, 151.
22 D. Babel, W. Verscharen, and G. Knoke, *J. Chem. Res.*, 1979, (*S*) 213, (*M*) 2579.
23 J. M. Dance, A. Tressaud, W. Massa, and D. Babel, *J. Chem. Res.*, 1981, (*S*) 202, (*M*) 2282.
24 S. Andersson and J. Galy, *Acta Crystallogr., Sect. B*, 1969, **25**, 847.
25 A. J. Edwards, G. R. Jones, and R. J. C. Sills, *J. Chem. Soc. A*, 1970, 2521.
26 K. H. Jack and R. Maitland, *Proc. Chem. Soc.*, 1957, 232.
27 J. W. Tracey, N. W. Gregory, E. C. Lingafelter, J. D. Dunitz, H. C. Mez, R. E. Scheringer, H. Y. Yakel, and M. K. Wilkinson, *Acta Crystallogr.*, 1961, **14**, 927.
28 H. R. Oswalt, *Helv. Chim. Acta*, 1961, **44**, 1049.

Received 27th January 1986; *Paper* 6/185