

## A New Structure Type in Mixed Valence Fluorinated Compounds: $K_5Cr_4^{2+}Cr_6^{3+}F_{31}$

Y. LALIGANT, A. LE BAIL, M. LEBLANC, AND G. FERÉY

*Laboratoire des Fluorures, URA C.N.R.S 449, Faculté des Sciences,  
 route de Laval, 72017 Le Mans Cedex, France*

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$K_5Cr_4^{2+}Cr_6^{3+}F_{31}$  is monoclinic (space group  $C2/m$ ,  $Z = 8$ ) with  $a = 21.576(1)$  Å,  $b = 7.6081(6)$  Å,  $c = 32.865(4)$  Å, and  $\beta = 109.24(4)^\circ$ ,  $V = 5093.6(2)$  Å<sup>3</sup>. The structure was refined from single crystal data using 4756 independent X-ray reflections to  $R = 0.040$  ( $R_w = 0.040$ ). The complex three-dimensional structure can be described as the intergrowth between  $NH_4MnFeF_6$  and  $Ba_2CuV_2F_{12}$  structure types, and exhibits three types of tunnels fully occupied by  $K^+$ . © 1990 Academic Press, Inc.

### Introduction

In contrast to tungsten bronze-like iron fluorides (1-7), extensively studied over the years, only little work has been devoted to mixed valence chromium fluorides. This is mainly due to the difficult chemistry of Cr(II). The binary systems  $MF-CrF_2$  and  $MF-CrF_3$  ( $M = \text{alkali}$ ) were carefully determined (8-15) and  $Cr_2F_5$  (16, 17) is the only compound which exists in the  $CrF_2-CrF_3$  system. Dumora (18, 19) first studied the ternary systems  $AF-CrF_2-CrF_3$  ( $A = K, Rb, Cs$ ). The observed bronze domains  $K_xCrF_3$  ( $\alpha$ , hexagonal;  $\beta$ , pyrochlore (Rb, Cs); and  $\gamma$ , perovskite) are similar to those encountered in the iron system, except when  $A = K$  and  $x \approx 0.5$ . Dumora proposed that  $\beta'-K_xCrF_3$  ( $0.44 < x < 0.60$ ) has a relationship with  $BaTa_2O_6$  (20). Using electron diffraction and high resolution electron microscopy, Sharma *et al.* determined in  $\alpha-Rb_xCrF_3$  four different superstructure types related to the hexagonal tungsten bronze

structure (21). Recently, Courbion *et al.* discovered a new mixed valence chromium fluoride  $Cs_4Cr_5F_{18.25}$  (22), which corresponds to the 2D homolog of the modified pyrochlore structure-type  $RbNiFeF_6$ . In this trigonal compound (SG  $P-3m1$ ),  $Cr^{2+}$  and  $Cr^{3+}$  are randomly distributed over the 3c site of the structure. Recently, Wanklyn *et al.* (23) reported the existence of  $KCr_2F_{6.5}$  ( $KCr_{10.5}^{2+}Cr_{1.5}^{3+}F_{6.5}$ ). Its powder pattern differs from that of our compound. The strong peaks of the latter coincide with those of  $\beta'-K_xCrF_3$ . This work was undertaken in order to clarify the crystal chemistry of these phases. It leads to a new mixed valence compound  $K_5Cr_4^{2+}Cr_6^{3+}F_{31}$ , whose composition is deduced from its crystal structure as described below.

### Experimental

The synthesis of  $K_5Cr_4^{2+}Cr_6^{3+}F_{31}$  was carried out by long heating (850°C, 3 weeks) in a sealed platinum tube of a mixture of ele-

TABLE I  
CONDITIONS OF INTENSITY DATA COLLECTION  
AND REFINEMENT

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Temperature during data collection 20°C  
 Symmetry Monoclinic  
 Space group  $C2/m$  (No. 12)  
 Parameters  $a = 21.576(1) \text{ \AA}$ ,  $b = 7.6081(6) \text{ \AA}$ ,  $c = 32.865(4) \text{ \AA}$ ,  $\beta = 109.24(4)^\circ$   
 $V = 5093.6(2) \text{ \AA}^3$ ,  $Z = 8$   
 Crystal size  $0.114 \times 0.065 \times 0.068 \text{ mm}^3$   
 Radiation Graphite monochromated:  $\text{MoK}\alpha(\lambda = 0.71069 \text{ \AA})$   
 Scan mode  $\omega - 2\theta$   
 Profile fitting data collection  $0.7103 + 0.4541 \tan(\theta)$   
 Detector aperture (mm) 2.5  
 Scan range:  $\theta_{\min}/\theta_{\max} 1-35^\circ$   
 Range of measurement  $-30 < h < 30$   
 $0 < k < 8$   
 $0 < l < 47$   
 Standard reflections (3) 0 2 0; 4 0 -2; -10 0 9  
 Maximum intensity variation 0.4%  
 Reflections measured (without standards) 9015  
 Reflections rejected ( $F/\sigma(F) < 6$ ) 2708  
 Independent reflections 4756  
 Absorption coefficient  $\mu = 50.38 \text{ cm}^{-1}$   
 Transmission factors  $A_{\max}$ , 0.7658;  $A_{\min}$ , 0.6009  
 Shift/ESD mean, 0.001; max, 0.007  
 $R$  (from averaging) 0.042  
 Weighting scheme, Unit weights  
 $R = 0.040$   
 $R_w = 0.040$

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mentary fluorides  $\text{KF-CrF}_2\text{-CrF}_3$  in the ratio 1/1/1. The composition of our compound ( $\text{KCr}_2\text{F}_{6.2}$ ) corresponds to a small amount of disproportionation of  $\text{Cr}^{2+}$ .

A single crystal was isolated by optical examination; its shape is limited by (0 2 0), (2 0 -2), and (0 0 1) faces. Intensity data collection (Table I) was made with an AED2 SIEMENS STOE four circle diffractometer. Ionic scattering factors were taken from International Tables for X-ray Crystallography (24). Some difficulties were encountered during the resolution of this structure, and we think that giving a summary of the different steps of the resolution could be useful.

Automatic indexing of 28 reflections initially suggested a pseudo-orthorhombic cell

with parameters  $a = 7.615(4) \text{ \AA}$ ,  $b = 21.57(1) \text{ \AA}$ ,  $c = 62.04(3) \text{ \AA}$ ,  $\alpha = 90.09(3)^\circ$ ,  $\beta = 90.00(3)^\circ$ ,  $\gamma = 89.97(3)^\circ$ , and F Bravais lattice. In fact, examination of the equivalent reflections showed that the true symmetry is monoclinic, in agreement with the fact that  $\alpha$  slightly deviates from  $90^\circ$ : after a careful absorption correction (Gaussian method), intensity discrepancies between ( $h k l$ ) and ( $h -k l$ ) reflections were never larger than 20%. The cell was transformed into the final monoclinic  $C$  cell whose parameters refined from 44 reflections are listed in Table I.

Direct or Patterson methods of the SHELX program (25) were unable to give any clear proposition. At this stage, the intensities were carefully examined and eventually a superstructure of a smaller cell was found, keeping in mind analogous problems recently encountered during the structure determination of  $\text{Rb}_2\text{Cr}_5\text{F}_{17}$  (26). The monoclinic distortion is itself a superstructure and was neglected as a first approximation. In the orthorhombic description found during automatic indexing, the most intense reflections were systematically observed for  $h = 2n$ ,  $k = 2n$ , and  $l = 10n$ . So the minimal subcell was 1/40 of the initial volume. Data were merged in this subcell using the space group  $Pbam$ , and direct methods gave a clear indication for all the cationic positions. It will be shown later that the cationic arrangement in the final supercell derives closely from the model obtained at this stage. Furthermore, successive Fourier synthesis revealed the position of some fluorine atoms, leading to a final value  $R = 0.23$ .

The extension of this model immediately to the supercell was unsuccessful. After various tests in other subcells, the complete structure was obtained in an orthorhombic cell with parameters  $a = 10.7834 \text{ \AA}$ ,  $b = 31.020 \text{ \AA}$ ,  $c = 3.8077 \text{ \AA}$  (1/8 of the final volume) with the space group  $Pbam$ . Among the excluded reflections from the final cell,

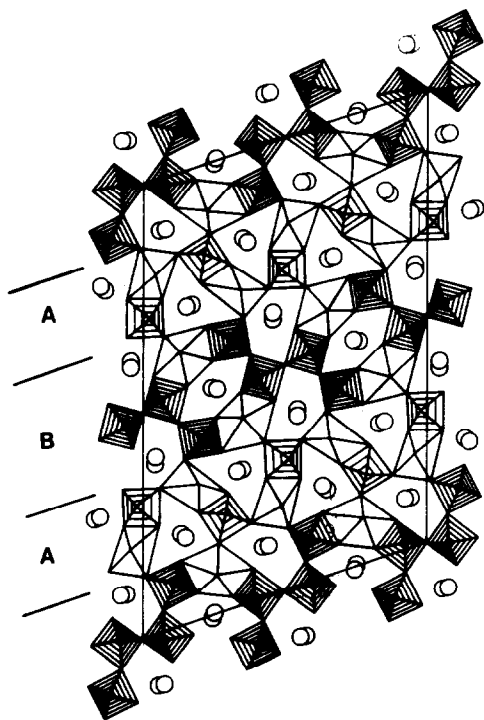


FIG. 1. [0 1 0] projection of  $\text{KCr}_2\text{F}_{6.2}$ .  $\text{Cr}^{3+}$  are hatched (slightly for Cr(5) and Cr(6), heavily for Cr(7)–Cr(10)).  $\text{KCr}_2\text{F}_{6.2}$  is described as an intergrowth of A and B motifs (see text). (A)  $[\text{Cr}^{\text{II}}\text{F}_{6/2}]_2 [\text{Cr}^{\text{III}}\text{F}_{6/2}]_2$  or  $\text{Cr}_2^{\text{II}}\text{Cr}_2^{\text{III}}\text{F}_{12}$ . (B)  $[\text{Cr}^{\text{II}}\text{F}_{6/2}]_2 [\text{Cr}^{\text{III}}\text{F}_{6/2}]_2 [\text{Cr}^{\text{III}}\text{F}_{5/2}\text{F}_{1/1}]$  or  $\text{Cr}_2^{\text{II}}\text{Cr}_4^{\text{III}}\text{F}_{19}$ .

only 8 have intensities greater than 1% of the most intense; the  $R_{\text{average}}$  being 0.094; this attests the weak departure from orthorhombic symmetry. For 1968 reflections and 141 parameters, an  $R = 0.070$  was obtained with anisotropic thermal motion: some large values of the latter indicate the atoms responsible for the superstructure.

When going to the final monoclinic cell, averaging of equivalent reflections yields a  $R_{\text{av}}$  value of 0.042. With a correct choice of the origin, the reliability factor drops to  $R = 0.081$  for all atoms with isotropic thermal parameters (215 parameters). The final refinement with anisotropic thermal motion (Table II) falls to  $R = 0.040$  ( $R_w = 0.040$ ) for 461 refined parameters. Table III lists

the interatomic distances. The list of the structure factors may be obtained on request to the authors.

### Description of the Structure

$\text{K}_5\text{Cr}_4^{2+}\text{Cr}_6^{3+}\text{F}_{31}$  exhibits a new complicated 3D structure type (Fig. 1). The description is greatly simplified when the different subcells, used successively in the structure determination, are presented together with the final one. By using the cationic sublattice only (Fig. 2), it is clear that  $\text{K}_5\text{Cr}_4^{2+}\text{Cr}_6^{3+}\text{F}_{31}$  exhibits an enormous super-

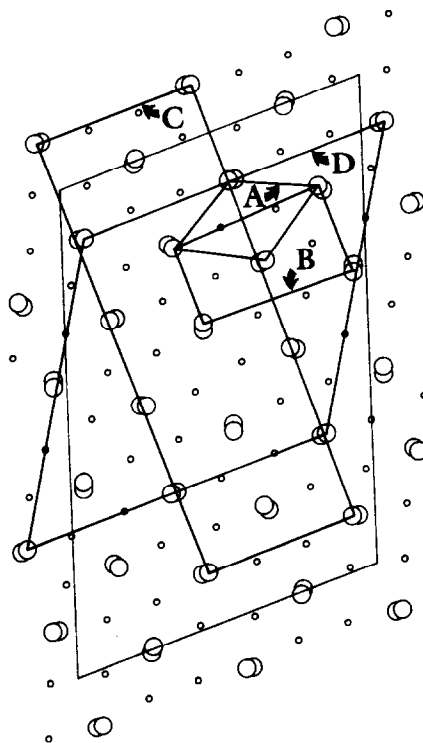


FIG. 2. Different subcells used in the structure determination. For the sake of clarity, only the cationic network is given (small and large circles correspond, respectively, to chromium and potassium). (A) Pseudo hexagonal cell of the  $\text{AlB}_2$  structure type (SG  $P-3m1$ ). (B) Minimal subcell retained (SG  $Pbam$ ). (C)  $B \times 5$  (SG  $Pbam$ ). (D) Pseudo hexagonal cell close to the  $\text{BaTa}_2\text{O}_6$  structure suggested for  $\text{KCr}_2\text{F}_6$  by Dumora (Refs. (18, 19)).

TABLE II  
FINAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS IN  $K_5Cr_4^{2+}Cr_6^{3+}F_{31}^{6-}$   
( $U_{ij} \times 10^4$ —ESD IN PARENTHESES)

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$B(\text{\AA}^2)$
Cr(1)	262(1)	2492(2)	1989(0)	185(4)	65(5)	86(3)	-1(5)	39(3)	-5(5)	0.89(4)
Cr(2)	3255(0)	2517(2)	3019(0)	162(4)	62(5)	86(3)	6(5)	14(3)	7(5)	0.87(4)
Cr(3)	1379(1)	2497(2)	4045(0)	184(4)	57(5)	93(4)	-11(5)	-19(3)	-9(5)	1.01(4)
Cr(4)	2315(1)	2486(2)	946(0)	234(4)	54(5)	86(4)	-4(5)	69(3)	0(5)	0.95(4)
Cr(5)	27(0)	2495(2)	2933(0)	91(3)	53(5)	74(3)	4(4)	26(3)	5(5)	0.58(4)
Cr(6)	2099(0)	2502(2)	2056(0)	92(3)	60(4)	74(3)	-3(4)	28(3)	-5(5)	0.59(4)
Cr(7)	8958(0)	2504(2)	978(0)	83(3)	57(4)	64(3)	1(4)	22(3)	5(4)	0.54(4)
Cr(8)	2986(0)	2486(2)	4023(0)	91(3)	53(4)	65(3)	-1(4)	22(3)	6(5)	0.56(4)
Cr(9)	784(0)	2501(2)	4875(0)	75(3)	57(4)	72(3)	3(4)	27(3)	-6(4)	0.53(3)
Cr(10)	907(0)	2504(2)	121(0)	81(3)	47(4)	68(3)	3(4)	26(3)	1(4)	0.51(3)
K(1)	2594(1)	0	5033(1)	207(13)	116(11)	205(10)	0	31(9)	0	1.5(1)
K(2)	2531(1)	0	-51(1)	239(9)	131(11)	131(11)	0	108(8)	0	1.2(1)
K(3)	8499(1)	0	1927(1)	230(11)	136(12)	198(11)	0	48(9)	0	1.5(1)
K(4)	8658(1)	5000	2040(1)	332(13)	116(12)	219(12)	0	113(10)	0	1.7(1)
K(5)	1505(1)	0	3008(1)	144(10)	130(12)	240(10)	0	67(8)	0	1.4(1)
K(6)	1695(1)	5000	3005(1)	207(11)	134(13)	281(12)	0	25(9)	0	1.7(1)
K(7)	9562(1)	0	3925(1)	341(14)	139(14)	360(15)	0	-111(11)	0	2.6(2)
K(8)	9563(2)	5000	3781(1)	387(15)	146(14)	300(14)	0	-122(11)	0	2.7(1)
K(9)	768(2)	0	1141(1)	520(17)	147(14)	401(15)	0	331(14)	0	2.5(2)
K(10)	566(2)	5000	1121(1)	467(16)	161(14)	417(16)	0	328(13)	0	2.4(2)
F(1)	432(4)	0	2069(2)	560(48)	99(37)	285(36)	0	136(33)	0	2.5(4)
F(2)	97(4)	5000	1906(2)	610(50)	44(35)	158(30)	0	-69(30)	0	2.5(4)
F(3)	3425(3)	0	3039(2)	349(36)	103(35)	225(32)	0	-12(27)	0	2.0(4)
F(4)	3040(3)	5000	3018(2)	392(38)	136(37)	177(30)	0	39(27)	0	2.0(4)
F(5)	1288(4)	0	3935(3)	597(53)	122(41)	304(40)	0	-119(35)	0	3.2(5)
F(6)	1490(3)	5000	4146(2)	292(32)	58(32)	204(30)	0	1(24)	0	1.6(3)
F(7)	2221(4)	0	1035(2)	725(57)	111(39)	288(38)	0	234(38)	0	2.8(5)
F(8)	2377(3)	5000	860(2)	343(34)	59(32)	247(31)	0	174(27)	0	1.6(3)
F(9)	227(3)	0	2983(2)	200(28)	48(31)	228(29)	0	84(23)	0	1.2(3)
F(10)	9841(3)	5000	2891(2)	257(32)	116(35)	222(31)	0	74(25)	0	1.6(3)
F(11)	2136(3)	0	1964(2)	398(38)	63(33)	239(32)	0	149(28)	0	1.8(3)
F(12)	2086(3)	5000	2140(2)	335(34)	80(33)	133(27)	0	39(24)	0	1.5(3)
F(13)	8839(3)	0	971(2)	220(29)	17(31)	341(35)	0	121(26)	0	1.5(3)
F(14)	9121(3)	5000	972(2)	248(31)	72(33)	248(31)	0	124(25)	0	1.4(3)
F(15)	3121(3)	0	4059(2)	330(37)	70(34)	182(30)	0	-6(26)	0	1.7(3)
F(16)	2905(3)	5000	3994(2)	282(35)	67(34)	229(33)	0	1(26)	0	1.7(3)
F(17)	587(3)	0	4832(2)	189(27)	73(31)	181(28)	0	44(22)	0	1.2(3)
F(18)	981(3)	5000	4925(2)	212(28)	45(31)	213(28)	0	91(23)	0	1.2(3)
F(19)	769(3)	0	167(2)	205(28)	136(33)	174(27)	0	106(22)	0	1.3(3)
F(20)	1054(3)	5000	73(2)	151(25)	89(31)	193(27)	0	80(21)	0	1.1(3)
F(21)	659(2)	2806(5)	2639(1)	126(14)	103(25)	127(15)	2(13)	66(12)	-28(14)	0.9(2)
F(22)	3030(2)	2496(7)	2369(1)	123(14)	293(23)	108(14)	-36(21)	5(11)	42(21)	1.4(2)
F(23)	8675(2)	2657(7)	1451(1)	348(20)	218(26)	172(16)	-2(20)	176(15)	31(22)	1.8(2)
F(24)	2240(2)	2342(7)	3542(1)	256(19)	180(25)	187(17)	15(19)	-96(14)	-38(21)	2.0(2)
F(25)	9857(2)	2200(6)	1342(1)	119(15)	174(27)	108(15)	-36(14)	-15(12)	-7(15)	1.2(2)
F(26)	3540(2)	2596(7)	3671(1)	208(16)	262(24)	104(15)	13(20)	82(12)	-4(21)	1.5(2)
F(27)	8087(2)	2811(6)	622(1)	89(14)	170(27)	157(16)	32(14)	8(12)	9(14)	1.2(2)
F(28)	2454(2)	2339(7)	4372(1)	146(15)	240(25)	160(15)	47(18)	91(12)	35(19)	1.4(2)
F(29)	1998(2)	2214(7)	2592(1)	333(21)	325(33)	192(18)	52(19)	196(17)	2(21)	2.0(2)

TABLE II—Continued

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>	<i>B</i> (Å <sup>2</sup> )
F(30)	9420(2)	2215(7)	2383(1)	187(17)	280(32)	135(16)	-14(17)	-49(13)	-30(18)	1.8(2)
F(31)	9415(2)	2198(6)	3221(1)	258(19)	157(28)	289(20)	69(17)	205(16)	74(17)	1.6(2)
F(32)	1196(2)	2577(8)	1751(1)	94(14)	341(27)	234(18)	0(24)	-6(13)	39(22)	1.9(2)
F(33)	1554(2)	2122(6)	4742(1)	153(16)	186(27)	123(15)	2(14)	63(13)	4(15)	1.2(2)
F(34)	1811(2)	2160(6)	258(1)	95(14)	187(27)	152(16)	-9(14)	55(12)	14(14)	1.1(2)
F(35)	1059(2)	2712(6)	712(1)	296(19)	186(26)	72(14)	-24(16)	79(13)	11(19)	1.4(2)
F(36)	344(2)	2697(6)	4284(1)	203(16)	169(25)	75(14)	8(16)	-23(12)	2(18)	1.3(2)
F(37)	9267(2)	2283(7)	491(1)	200(16)	252(27)	66(13)	-12(16)	63(12)	39(18)	1.3(2)
F(38)	3775(2)	2770(6)	4516(1)	153(15)	204(27)	66(14)	-6(14)	-2(11)	-32(16)	1.2(2)
F(39)	0	2967(8)	5000	132(22)	204(37)	242(27)	0	107(20)	0	1.4(3)
F(40)	0	2971(8)	0	85(21)	203(38)	341(31)	0	106(21)	0	1.6(3)
F(41)	722(2)	2930(6)	3459(1)	388(24)	172(28)	97(17)	15(15)	-91(16)	-26(19)	2.1(2)
F(42)	2324(2)	2925(6)	1550(1)	384(23)	233(30)	114(17)	-2(15)	136(16)	-30(19)	1.8(2)

<sup>a</sup> The vibrational coefficients *U<sub>ij</sub>* relate to the expression  $T = \exp[-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12})]$  and for *B*,  $T = \exp[-B \sin \theta/\lambda]^2$ .

structure based on the cationic arrangement found in the AIB<sub>2</sub> structure type (27, 28). Each potassium atom is 12-coordinated by chromium in a prism with hexagonal basis; each chromium atom is coordinated by six potassium in a triangular prism tri-capped by three other chromium. Such a cationic ordering is known in the PbSb<sub>2</sub>O<sub>6</sub> structure (29), in layers of PbNb<sub>2</sub>O<sub>6</sub> (30–33) and also partly in the BaTa<sub>2</sub>O<sub>6</sub> structure (20) (Note that the two last structures were not refined to a better value than *R* = 0.15, value which must be obtained without locating oxygen atoms when such heavy atoms are present). Difference occurs in the anionic packing, the fluorine atoms being principally responsible for the superstructures.

The superstructures exist at different levels:

— The *a* and *b* parameters could be reduced by a factor of two without a subtle tilting mode of the chromium polyhedra which is propagated along these directions. Also, the potassium atoms show little displacements.

— The main superstructure arises from the arrangement of fluorine atoms at nearly

the same *x* coordinates as chromium (i.e., equatorial fluorines). They lead to the identification of three different types of tunnels surrounding K<sup>+</sup>. Their section is pseudo-hexagonal, -pentagonal, or -trigonal.

Two main features arise from the examination of the three-dimensional structure: (i) the unusual coordination around one-half of the Cr<sup>2+</sup> sites, (ii) the strict ordering between Cr<sup>2+</sup> and Cr<sup>3+</sup>. Cr<sup>3+</sup> (Cr(5)–Cr(10)) are octahedrally surrounded by six F<sup>-</sup>. Cr<sup>2+</sup> atoms show more complicated polyhedra. As indicated in Table III, Cr(1) and Cr(2) octahedra present four short and two long distances: this elongation is due to the Jahn–Teller effect associated with the *d*<sup>4</sup> ion. The mean Cr(1)–F and Cr(2)–F distances (respectively, 2.149 and 2.158 Å) are larger than the sum of the ionic radii which correspond to 2.10 Å (34). This poor agreement for Cr<sup>2+</sup>–F distance was previously observed in Cr<sub>2</sub>F<sub>5</sub> ((Cr–F) = 2.179 Å (16, 17)), which also exhibits two long distances (2.572 Å). For Cr(3) and Cr(4), examination of Cr<sup>2+</sup>–F distances leads us to consider that these two chromium are sevenfold-coordinated, and they then build up pentagonal bipyramids such as Mn<sup>2+</sup> in MnCrF<sub>5</sub>

TABLE III  
 INTERATOMIC DISTANCES (Å) IN  $K_3Cr_4^{2+}Cr_6^{3+}F_{31}$  (ESD ARE GIVEN IN PARENTHESES)

Cr(1) polyhedron		Cr(6) polyhedron		K(1) polyhedron		K(6) polyhedron	
Cr-F(1)	1.934(2)	Cr-F(29)	1.857(7)	K-F(33)	2.673(5) (2×)	K-F(24)	2.688(5) (2×)
Cr-F(2)	1.946(2)	Cr-F(32)	1.874(5)	K-F(28)	2.750(6) (2×)	K-F(29)	2.712(5) (2×)
Cr-F(25)	2.030(3)	Cr-F(42)	1.908(7)	K-F(6)	2.770(6)	K-F(21)	2.732(5) (2×)
Cr-F(21)	2.034(3)	Cr-F(12)	1.924(6)	K-F(33)	2.799(6) (2×)	K-F(4)	2.887(7)
Cr-F(32)	2.390(5)	Cr-F(22)	1.931(5)	K-F(28)	2.842(6) (2×)	K-F(12)	3.220(8)
Cr-F(30)	2.561(5)	Cr-F(11)	1.936(6)	K-F(18)	3.030(7)	$\langle K-F \rangle = 2.796 \text{ Å}$	
$\langle Cr-F \rangle = 2.149 \text{ Å}$		$\langle Cr-F \rangle = 1.905 \text{ Å}$		$\langle K-F \rangle = 2.793 \text{ Å}$			
Cr(2) polyhedron		Cr(7) polyhedron		K(2) polyhedron		K(7) polyhedron	
Cr-F(4)	1.947(4)	Cr-F(23)	1.852(4)	K-F(34)	2.680(6) (2×)	K-F(36)	2.673(5) (2×)
Cr-F(3)	1.948(4)	Cr-F(27)	1.873(4)	K-F(27)	2.713(4) (2×)	K-F(26)	2.774(5) (2×)
Cr-F(22)	2.028(4)	Cr-F(13)	1.924(2)	K-F(8)	2.730(8)	K-F(31)	2.790(5) (2×)
Cr-F(26)	2.028(5)	Cr-F(25)	1.926(4)	K-F(34)	2.791(5) (2×)	K-F(17)	3.070(6)
Cr-F(31)	2.378(4)	Cr-F(37)	1.933(4)	K-F(27)	2.869(4) (2×)	$\langle K-F \rangle = 2.792 \text{ Å}$	
Cr-F(29)	2.620(4)	Cr-F(14)	1.934(2)	K-F(20)	3.076(7)		
$\langle Cr-F \rangle = 2.158 \text{ Å}$		$\langle Cr-F \rangle = 1.907 \text{ Å}$		$\langle K-F \rangle = 2.791 \text{ Å}$			
Cr(3) polyhedron		Cr(8) polyhedron		K(3) polyhedron		K(8) polyhedron	
Cr-F(5)	1.933(6)	Cr-F(24)	1.851(3)	K-F(23)	2.660(5) (2×)	K-F(36)	2.609(5) (2×)
Cr-F(6)	1.937(4)	Cr-F(28)	1.873(4)	K-F(30)	2.661(4) (2×)	K-F(31)	2.769(5) (2×)
Cr-F(41)	2.007(3)	Cr-F(15)	1.913(2)	K-F(22)	2.782(5) (2×)	K-F(3)	2.835(6)
Cr-F(28)	2.214(4)	Cr-F(26)	1.919(4)	K-F(42)	2.895(4) (2×)	K-F(26)	2.896(6) (2×)
Cr-F(33)	2.216(4)	Cr-F(16)	1.922(2)	$\langle K-F \rangle = 2.749 \text{ Å}$		K-F(10)	3.174(8)
Cr-F(36)	2.605(5)	Cr-F(38)	1.935(3)			$\langle K-F \rangle = 2.820 \text{ Å}$	
Cr-F(24)	2.866(5)	$\langle Cr-F \rangle = 1.902 \text{ Å}$					
$\langle Cr-F \rangle = 2.254 \text{ Å}$							
Cr(4) polyhedron		Cr(9) polyhedron		K(4) polyhedron		K(9) polyhedron	
Cr-F(7)	1.936(8)	Cr-F(36)	1.865(3)	K-F(23)	2.643(5) (2×)	K-F(35)	2.688(5) (2×)
Cr-F(8)	1.947(8)	Cr-F(33)	1.872(5)	K-F(30)	2.693(5) (2×)	K-F(32)	2.741(5) (2×)
Cr-F(42)	2.006(5)	Cr-F(39)	1.901(2)	K-F(22)	2.753(5) (2×)	K-F(25)	2.823(6) (2×)
Cr-F(34)	2.179(5)	Cr-F(38)	1.924(3)	K-F(10)	3.104(6)	K-F(19)	3.201(8)
Cr-F(27)	2.264(5)	Cr-F(18)	1.945(2)	K-F(11)	3.207(7)	K-F(7)	3.266(9)
Cr-F(35)	2.566(5)	Cr-F(17)	1.946(2)	K-F(2)	3.275(9)	K-F(11)	3.281(6)
Cr-F(23)	2.856(5)	$\langle Cr-F \rangle = 1.909 \text{ Å}$		$\langle K-F \rangle = 2.863 \text{ Å}$		$\langle K-F \rangle = 2.917 \text{ Å}$	
$\langle Cr-F \rangle = 2.250 \text{ Å}$							
Cr(5) polyhedron		Cr(10) polyhedron		K(5) polyhedron		K(10) polyhedron	
Cr-F(30)	1.861(5)	Cr-F(35)	1.867(6)	K-F(29)	2.607(6) (2×)	K-F(35)	2.630(5) (2×)
Cr-F(31)	1.874(6)	Cr-F(34)	1.868(5)	K-F(24)	2.634(6) (2×)	K-F(32)	2.772(5) (2×)
Cr-F(41)	1.907(4)	Cr-F(40)	1.898(3)	K-F(9)	2.731(7)	K-F(25)	2.853(5) (2×)
Cr-F(21)	1.926(5)	Cr-F(37)	1.928(6)	K-F(21)	2.814(5) (2×)	K-F(14)	2.991(8)
Cr-F(9)	1.943(7)	Cr-F(20)	1.942(8)	K-F(1)	3.190(7)	K-F(2)	3.066(9)
Cr-F(10)	1.945(7)	Cr-F(19)	1.943(8)	K-F(5)	3.233(9)	$\langle K-F \rangle = 2.821 \text{ Å}$	
$\langle Cr-F \rangle = 1.909 \text{ Å}$		$\langle Cr-F \rangle = 1.908 \text{ Å}$		$\langle K-F \rangle = 2.807 \text{ Å}$			

(35). To our knowledge, it is the first example of such a polyhedron for  $\text{Cr}^{2+}$  in fluorine chemistry.

Despite the great originality of this structure, one can try, after some simplifications, to describe it as an intergrowth of two other known structures. Indeed let us consider first the  $\text{Cr}^{3+}$  octahedral subnetwork (Fig. 1). It forms either single chains or four-membered slabs of corner sharing octahedra which run along the  $b$  axis. The single chains correspond to Cr(5) and Cr(6), the slabs to Cr(7–10). In the (0 1 0) plane, the four octahedra of the slab are *cis*-linked by corners.

Sixfold-coordinated  $\text{Cr}^{2+}$  share one edge and one corner with Cr(5) $\text{F}_6$  and Cr(6) $\text{F}_6$  octahedra in the (0 1 0) plane, and draw along the  $a$  axis a motif (labeled A in Fig. 1) which was already encountered in  $\text{NH}_4\text{MnFeF}_6$  (36) and  $\text{BaNb}_2\text{O}_6$  (37). They share also one vertex with four member slabs described above.

The sevenfold-coordinated  $\text{Cr}^{2+}$  ensure the connection between two slabs at the same  $z$  coordinate and form hexagonal crowns (motif B in Fig. 1) built up with four  $\text{Cr}^{3+}$  and two  $\text{Cr}^{2+}$ , the latter sharing edges with the former in the plane, the last equatorial fluorine of the  $\text{Cr}^{2+}$  polyhedron being shared with one  $\text{Cr}^{3+}$  of the A motif. Note that if one considers only the octahedral coordination of  $\text{Cr}^{2+}$  in this arrangement, one obtains a topology for the B motif which is close to that encountered in the  $\text{Ba}_2\text{CuV}_2\text{F}_{12}$  compound (38). Therefore, this new structure can be considered as an intergrowth between the two structure types corresponding to the motifs A ( $\text{Cr}_2^{2+}\text{Cr}_2^{3+}\text{F}_{12}$ ) and B ( $\text{Cr}_2^{2+}\text{Cr}_4^{3+}\text{F}_{19}$ ) (Fig. 1).

The formula of our compound is very close to that claimed by Dumora for  $\beta'$ - $\text{K}_x\text{CrF}_3$ , but does not belong to the pseudobinary system  $\text{KCrF}_3$ – $\text{CrF}_3$ . Finally, it seems that this structure cannot represent a new fluorinated bronze structure. Indeed, from the crystal chemistry point of view,

$\text{K}_5\text{Cr}_4^{2+}\text{Cr}_6^{3+}\text{F}_{31}$  would represent the upper limit of a bronze domain since all the tunnels are filled by  $\text{K}^+$  atoms. A nonstoichiometric domain would imply a  $\text{K}^+$  content lower than 5, and therefore an increase of the  $\text{Cr}^{3+}$  amount by substituting  $\text{Cr}^{2+}$  by  $\text{Cr}^{3+}$ . This would lead to a significant amount of edge sharing  $\text{Cr}^{3+}$  octahedra, whereas it is well-known in fluorine chemistry that octahedra of trivalent cations share quasi-exclusive corners (if one accepts  $\text{BaTiF}_5$  (39) where isolated dimers of edge sharing octahedra of  $\text{Ti}^{3+}$  were evidenced). This casts some doubts on the real existence of the bronze  $\beta'$ - $\text{K}_x\text{CrF}_3$ . Additional experiments are in progress to verify this possibility.

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