Synthesis and Structure Approach of $K_3Ba_7Al_6F_{33}Cl_2$

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An approach of the structure of $K_3Ba_7Al_6F_{33}Cl_2$ is performed despite many defects: systematic twinning, partial order of the K and Ba atoms at the same sites, and correlated orientational disorder of some $[AlF_6]$ octahedra. The structure is refined to $R_F = 0.031$ in the $P\bar{3}m1$ space group from 1500 unique reflections merged in the $6/mmm$ Laue symmetry (two equal volume domains with overlapping hkl and $hk\bar{l}$ reflections); $Z = 3$; $a = 18.863(4)$ Å, $c = 7.636(2)$ Å. It is built up from isolated dimeric $[Al_2F_{11}]$ groups of corner-sharing $[AlF_6]$ octahedra. The Cl atoms are octahedrally coordinated by the Ba and K cations, forming infinite chains of face-sharing $[Cl(Ba,K)_6]$ octahedra, parallel to $[001]$. © 1993 Academic Press, Inc.

Introduction

An unusual $[ClM_6^{II}]$ (M^{II} = Sr, Pb, Ba) octahedral coordination was recently established in $Sr_{10}Al_2F_{25}Cl$ (*1*), $Pb_{10}Al_2F_{25}Cl$, and the series $Ba_{10}M_2F_{25}Cl$ (M^{3+} = Al, Ti, V, Cr, Fe). Of course, such an octahedral coordination is characteristic of the common NaCl structure type. However, one must consider that, more generally, the chlorine ion in complex chlorofluoride compounds containing $3d$ cations (or cations having similar behavior, i.e., forming $[MF_6]$ or $[MCl_6]$ octahedra) is found as part of these cations' environment. For instance, the chlorine ions belong exclusively to the $[ZnCl_6]$ octahedra in $Ba_6Mn_2ZnF_{12}Cl_6$ (*2*); they are in the axial position in $[Cr^{II}F_4Cl_2]$ octahedra for $K_2Cr_3Cl_2F_6$ (*3*). Both compounds were synthesized by using a chloride flux method (*4–6*), such as $Sr_{10}Al_2F_{25}Cl$. Indeed, it is rare for the Cl atom to integrate compounds synthesized in this way, which are more commonly fluorides. It was verified in some cases that the same chlorofluorides could be synthesized by the more classical heated-sealed-tube method. In fact, generalizations in chlorofluoride crystal chemistry are not yet

possible since syntheses of chlorofluorides have not been extensively investigated: from the Inorganic Crystal Structure Database (ICSD) (*7*), one can estimate that probably no more than 20 different structure types have been established; they are dominated by Sb-, Nb-, Ta-, Te-, and As-based compounds. Thus, general knowledge of this class of materials needs to be increased.

During investigation of the KF-BaF_2-AlF_3 system by means of the chloride flux method, single crystals of $K_3Ba_7Al_6F_{33}Cl_2$ were obtained. This paper deals with the preparation and the crystal structure determination of this new chlorofluoride, presenting another example of chlorine in octahedral cationic coordination. Due to the presence of various systematic defects, the structure determination from single-crystal X-ray diffraction data was far from being a routine study.

Experimental

Single crystals were grown using a chloride flux method in a platinum crucible under an argon atmosphere, from the composition KF + BaF_2 + AlF_3 + 0.44 KCl + 1.67

$ZnCl_2$. The mixture was heated at 650°C for 12 hr and then slowly cooled (5°C/hr) to room temperature. Following this procedure, well-shaped hexagonal single crystals of $K_3Ba_7Al_6F_{33}Cl_2$ were obtained.

The same compound has been synthesized from a stoichiometric mixture of halogenides: KF, KCl, BaF_2, and AlF_3. The solid-state reaction was carried out in a gold tube sealed under a dry argon atmosphere by heating at 800°C for 1 day and then air quenching.

Laue and Buerger precession film techniques were used in a preliminary study of various crystals; all of them appeared to be of sufficiently high quality, presenting sharp spots.

Structure Determination

The translucent crystal selected for X-ray data collection on a Siemens AED2 four-circle diffractometer had an approximate volume of 0.0015 mm^3 and was limited by many faces (001, $22\bar{1}$, 110, $\bar{1}10$, $\bar{1}20$, $1\bar{2}0$, $2\bar{1}0$, 210). The lattice parameters were refined from 36 reflections by the double scan technique. The conditions of the diffraction experiment are summarized in Table I. No extinction condition was observed; the Laue class was determined as 6/mmm from the satisfying $R_{avg} = 0.028$ obtained after absorption correction from a preliminary data collection (full space up to $2\theta_{max} = 25°$ with 2246 measured reflections merged to 141 unique).

The Patterson and Direct methods were both tried (SHELXS program (8)) in all the possible space groups (P6/mmm, $P\bar{6}2m$, . . .) without obtaining any convenient part of the solution. Then, careful examination of the data revealed that all the hhl reflections were weak when $l = 2n + 1$, leading to a structure which could be described, in a first approximation, in one of the $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$ space groups. Moreover, it was established that a hexagonal subcell having $a' = 10.88$ and $c' = 7.64$ Å ($\mathbf{a'} = -1/3\mathbf{a} - 2/3\mathbf{b}$; $\mathbf{b'} = 2/3\mathbf{a} + 1/3\mathbf{b}$;

$\mathbf{c'} = \mathbf{c}$) as cell parameters could be deduced from the weakness of the superstructure reflection intensities (the most intense ($\bar{8}01$) represented no more than 5% of the largest subcell reflection (004)). A good approach of the heavy atom positions was obtained in this subcell with the $P6_3/mcm$ space group deduced from pseudo-extinction conditions. Refinements of their coordinates followed by Fourier difference synthesis suggested possible positions for the Cl, Al, and some F atoms. As the formula was not established before the structure determination, the presence of Cl atoms was deduced from crystal chemistry considerations (identification of probable $[ClBa_6]$ octahedra). In this subcell, the final R factor was 0.061 (anisotropic thermal motion) for 560 reflections and 32 refined parameters (calculations were made with the SHELX76 program (9); ionic scattering factors and dispersion correction terms were taken from International Tables for X-Ray Crystallography (10)). Because all the fluorine atoms were not located, $[AlF_6]$ octahedra were not completed; some abnormally large thermal motions indicated that a probable special ordering of these octahedra was responsible for the superstructure.

This result was then extended as the starting part of the solution in the supercell considering in a first step the pseudo-extinction (hhl, $l = 2n$). After time-consuming systematic tests, an almost satisfactory solution was obtained by using the $P6_3mc$ space group with $R = 0.116$ and $R = 0.076$, respectively, with isotropic and anisotropic thermal motions (139 refined parameters and 1500 reflections). At this stage, the apparent formulation was "$KBa_4Al_3F_{17}Cl$." Three different sites of Al atoms led to $[AlF_6]$ octahedra, 2/3 of which were connected by a corner, forming isolated $[Al_2F_{11}]$ dimers, and the remaining 1/3 were isolated octahedra. To obtain electrical neutrality, and also to improve the quality of the refinement, it was clear that the potassium atom should share one site with a barium atom with a 50%/50% occupancy; however, refining the

TABLE I

Crystal Data and Conditions of Data Collection and Refinement for $K_3Ba_7Al_6F_{33}Cl_2$

Symmetry	Trigonal
Space group	$P\bar{3}m1$ (No. 164)
Cell parameters	$a = 18.863(4)$ Å
	$c = 7.636(2)$ Å
	$V = 2353.0$ Å^3
	$Z = 3$
Calculated density	4.10
Radiation	Mo$K\alpha$ (graphite monochromatized)
Scanning mode	ω-2θ
Learnt profile, isotropic linewidth	$\omega = 0.897 + 0.044\mathrm{tg}\theta$
Number of profile points	36
Min. and max. measuring time	1–4 sec
Time interval between standards	60 min.
Data collection range	$2.5 \leq 2\theta \leq 70°$
Maximum h,k,l	26, 30, 12
Absorption correction	Gauss method
Absorption coefficient	$\mu = 95.9$ cm^{-1}
Min. and max. transmission factors	0.405, 0.566
Reflections measured	4382
Independent	1980 (merged in $6/mmm$)
R_{avg}	0.027
Used in refinement	1500 ($F_o > 6\sigma(F_o)$)
Number of refined parameters	165
Agreement factors	$R_F = (\Sigma\|F_o\| - k\|F_c\|)/\Sigma\|F_o\| = 0.031$
	$R_I = (\Sigma\|I_o - kI_c\|)/\Sigma I_o = 0.030$

occupancy factor showed a clear departure from this value, leading to 57%/43% of potassium and barium atoms, respectively. Other anomalies were noted: generally high thermal motion and particularly high values for the fluorine atoms belonging to the isolated [AlF$_6$] octahedra; unsatisfying Al–F distances ranging from 1.66 to 1.99 Å. Moreover, the Fourier difference synthesis shown one clear peak: a ghost at 0.7 Å along the c axis from the Al atom site corresponding to isolated [AlF$_6$] octahedra. As no improvement of this result could be obtained by testing possible disorder on these octahedra, it was considered that all the anomalies (high thermal motion, apparent disorder, pseudo-extinction, existence of a subcell) could indicate twinning. Such a problem is more frequently encountered than solved, particularly in trigonal symmetry, leading to apparent hexagonal symmetry when micro-

domains, with equipartition in volume, superpose their hkl and $hk\bar{l}$ reflections (as a mean). Numerous tests were made following this hypothesis, restricting this first approach to the trigonal maximal nonisomorphic subgroups of the $P6_3mc$ space group ($P31c$ and $P3m1$). Calculations were performed by using the TMACLE program (11), which minimizes the function $\chi^2 = \Sigma \omega(I_o - I_c)^2$, with $I_c = \Sigma_i k_i|F_i(hkl)|^2$, where k_i is the scale factor for the twin domain i and $\omega = 1/I_o$. Examples of applications of this program may be found in Refs. (12–16). A quite satisfying result was obtained with the $P3m1$ space group; it was then observed that this solution should be described by using the centrosymmetrical $P\bar{3}m1$ space group. The R_F factor dropped to 0.085 and 0.052, respectively, with isotropic and anisotropic thermal motion. Then, keeping the 50%/50% K/Ba exchange on two sites in

$P\bar{3}m1$ equivalent to the site previously described in $P6_3mc$, the formula was "KBa$_4$Al$_3$F$_{16.5}$Cl," and so was not equilibrated. The main change from the previous $P6_3mc$ proposition was that all [AlF$_6$] octahedra were involved in [Al$_2$F$_{11}$] dimers. This proposition appeared convincing not only because of the clear decrease in the R value, but because of crystal chemistry arguments: interatomic distances and angles were slightly improved, the Al–F distances ranging now from 1.67 to 1.91 Å. Moreover, most of the abnormally high thermal motions reduced to more tolerable values, with exceptions concerning some fluoride atoms all belonging to the coordination of one of the three Al atoms' independent sites. So the problem did not appear completely solved. We first look at the possibility that the formula may become equilibrated by refining the K/Ba exchange rate: this was not obtained until all the Ba sites previously considered as pure Ba sites were considered to represent some Ba/K exchange. In this way the R_F factor dropped to 0.047 for a formulation refined to K$_{1.45}$Ba$_{3.55}$, not very far from the K$_{1.5}$Ba$_{3.5}$Al$_3$F$_{16.5}$Cl expected. At this stage three peaks clearly appeared on the Fourier difference synthesis map. It must be emphasized that Fourier difference performed from such data with a twinning hypothesis, leading to strict overlapping of reflections, has the same limitations as those inherent in the Rietveld method applied to powder diffraction data (17); i.e., the overlapping "observed" data are regenerated (in the TMACLE program (11)) by apportionment according to the calculated data and are thus biased. One must note, however, that many reflections unaffected by the twinning problem are present ($hk0$, hhl). The interpretation of these three peaks was not obvious since their distances to the same Al atom suggested fluorine atoms, whereas the corresponding [Al(1)F$_6$] octahedron was already completed, and so distances between these peaks and previous F atoms were as short as 1.4 Å. These observations suggested that as in the K/Ba substitution, the

[Al(1)F$_6$] octahedron could take two orientations. Indeed, it was possible to construct a quasi-regular [AlF$_6$] octahedron from these three peaks, generating the four fluorines atoms coplanar with the Al(1) atom (i.e., the basal plane of the octahedron) and completing the octahedra with two of the preexisting fluorine atoms, one (F(8)) shared with an independent neighboring octahedra to form a dimer [Al$_2$F$_{11}$] and the other (F(9)) being at the opposite octahedron corner. Therefore, an hypothesis of orientational disorder for one octahedron with two variants, each deriving from the other by rotation of nearly 90° along the F(8)–Al(1)–F(9) axis, was tested by refining the fluorine occupancy factors with appropriate constraints. The R_F factor dropped to 0.031 (the TMACLE program did not allow extinction correction; the two most intense reflections at low angle ($\bar{3}60$, 004) showing some possible effect were excluded). Then, residual peaks on the subsequent Fourier difference synthesis did not exceed one electron. No improvement could be obtained from the whole data set (without merging in the $6/mmm$ Laue symmetry) and refining the domain's volumes. Interestingly for the problematic [AlF$_6$] octahedra, the proportion of orientational variants was refined to 63%/37%, a value very close to some of the K/Ba exchange rates. The thermal motion of the F(3) and F(4) atoms, previously the most abnormally high, were now more reasonable because their occupancy decreased from 100 to 63%. Such a near 2/3 : 1/3 ratio could suggest a superstructure cell which may have escaped detection. However, no superstructure or satellite reflections could be detected by a careful check of long-time exposures from rotation and Buerger-precession photographic diffraction techniques.

This "structure determination" was not a routine one. Several hypotheses have been formulated, and we have admitted as support both the decreasing R factor and the satisfaction of elementary crystal chemistry rules of fluoroaluminate compounds. The twinning hypothesis ($P\bar{3}m1$ together with

TABLE IIA

Atomic Coordinates, Occupancy Numbers, and Isotropic Temperature Factors

Atom	Site	Occupancy	x	y	z	B (Å^2)
Al1	$6i$	1	0.1339(1)	$-x$	0.7263(6)	1.7(1)
Al2	$6i$	1	0.2009(1)	$-x$	0.3241(5)	1.6(1)
Al3	$6i$	1	0.5345(1)	$-x$	0.1903(5)	1.2(1)
Ba	$6i$	1	0.75003(2)	$-x$	0.2339(1)	1.96(3)
Ba/K1	$6i$	0.891/0.109(6)	0.08657(3)	$-x$	0.2574(1)	2.39(6)
Ba/K2	$6i$	0.852/0.148(6)	0.42039(2)	$-x$	0.2680(1)	1.68(4)
K/Ba1	$6h$	0.650/0.350(5)	0.33355(7)	0	0	2.00(8)
K/Ba2	$6g$	0.547/0.453(5)	0.32891(7)	0	1/2	1.75(6)
Cl1	$1a$	1	0	0	0	3.1(4)
Cl2	$1b$	1	0	0	1/2	4.7(6)
Cl3	$2d$	1	1/3	2/3	0.4900(9)	1.8(2)
Cl4	$2d$	1	1/3	2/3	0.9932(9)	2.1(2)
F1	$12j$	1	0.2367(4)	0.3396(5)	0.2275(8)	3.5(5)
F2	$12j$	1	0.4349(3)	0.0036(5)	0.2787(7)	2.8(3)
F3	$12j$	0.63(1)	0.2370(5)	0.3426(6)	0.7806(13)	2.5(5)
F4	$12j$	0.63(1)	0.0378(5)	0.8304(6)	0.6165(16)	3.8(7)
F5	$12j$	1	0.1256(3)	0.4962(4)	0.9331(7)	2.4(3)
F6	$12j$	1	0.1601(3)	0.4542(3)	0.4508(7)	2.2(3)
F7	$3e$	1	1/2	0	0	2.1(5)
F8	$6i$	1	0.1604(3)	$-x$	0.5056(12)	3.3(5)
F9	$6i$	1	0.1055(4)	$-x$	0.9244(17)	8.5(9)
F10	$6i$	1	0.2399(3)	$-x$	0.1637(13)	4.3(6)
F11	$6i$	1	0.5725(3)	$-x$	0.3560(12)	3.7(5)
F12	$6i$	0.37(1)	0.1781(6)	$-x$	0.8464(27)	6.8(9)
F13	$12j$	0.37(1)	0.0392(9)	0.7775(9)	0.7371(25)	4.5(7)
F14	$6i$	0.37(1)	0.0844(7)	$-x$	0.6271(26)	2.6(5)

Note. esd's are given in parentheses.

apparent $6/mmm$ Laue symmetry) is a school-case already encountered (see, for instance, the recent case of $Ba_6IrNb_2O_{12}Cl_2$ (*18*)). Thus, our final proposition may be considered imperfect; however, it is the best current view available for the structure of this compound. Its formulation will be considered stoichiometric $(K_3Ba_7Al_6F_{33}Cl_2)$; this will be supported by arguments developed in the following description of the structure and discussion. A semiquantitative chemical analysis was performed by using a JEOL 2010 electron microscope equipped with a KEWEX analyzer. The mean atom percentages from nine independent measurements were 67.6, 10.2, 4.2, 4.9, and 13.0%, respectively, for F, Al, Cl, K, and Ba atoms. These rough values compare well with the calculated ones (64.7, 11.8, 3.9, 5.9, and 13.7%).

Tables IIA and IIB list the atomic coordinates and the thermal motion parameters, and Table III gives the main interatomic distances and angles. A table specifying the observed and calculated intensities (separated as two contributions from two domains) can be obtained from the authors upon request.

Description of the Structure and Discussion

Projections of the structure of $K_3Ba_7Al_6F_{33}Cl_2$ along [001] are shown Figs. 1 and 2, respectively, for the two $[Al(1)F_6]$ octahedra orientational variants. An inter-

TABLE IIB

ANISOTROPIC THERMAL PARAMETERS $U_{ij}x10^4$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al1	193(10)	193(10)	299(17)	17(7)	−17(7)	113(11)
Al2	166(10)	166(10)	198(15)	4(7)	−4(7)	26(12)
Al3	136(9)	136(9)	180(15)	27(6)	−27(6)	66(11)
Ba	192(2)	192(2)	284(3)	49(2)	−49(2)	37(3)
Ba/K1	334(4)	334(4)	297(7)	2(2)	−2(2)	209(4)
Ba/K2	201(3)	201(3)	209(4)	−19(2)	19(2)	81(3)
K/Ba1	277(7)	261(8)	218(6)	62(6)	31(3)	130(4)
K/Ba2	234(6)	184(6)	229(5)	−52(4)	−26(2)	92(3)
Cl1	378(34)	378(34)	421(54)	0	0	189(17)
Cl2	326(33)	326(33)	1125(114)	0	0	163(17)
Cl3	202(17)	202(17)	260(23)	0	0	101(9)
Cl4	280(20)	280(20)	252(22)	0	0	140(10)
F1	438(35)	718(44)	323(25)	−135(37)	15(30)	402(36)
F2	268(26)	457(29)	278(21)	132(32)	117(25)	145(25)
F3	266(41)	302(40)	416(45)	−82(42)	−210(41)	169(34)
F4	194(40)	418(57)	852(85)	123(56)	−8(47)	163(40)
F5	228(24)	340(27)	386(29)	58(24)	11(22)	180(22)
F6	264(22)	318(26)	315(25)	−28(21)	−18(21)	199(21)
F7	273(35)	284(49)	248(45)	−106(45)	−53(22)	142(24)
F8	527(39)	527(39)	258(33)	−22(21)	22(21)	302(45)
F9	1765(136)	1765(136)	559(73)	−101(32)	101(32)	1520(145)
F10	542(41)	542(41)	392(44)	−122(27)	122(27)	162(49)
F11	438(34)	438(34)	459(50)	210(24)	−210(24)	173(41)
F12	1779(360)	1779(360)	167(89)	10(37)	−10(37)	1740(370)
F13	489(96)	278(73)	599(106)	76(80)	88(95)	−74(63)
F14	319(74)	319(74)	300(94)	98(46)	−98(46)	116(86)

Note. The vibrational coefficients relate to the expression $T=\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

esting feature of this complex chlorofluoride structure is the presence of isolated vertex-sharing bioctahedral dimers $[Al_2F_{11}]$ between which K and Ba ions are inserted with a partial order. To our knowledge, it is the second time that such dimeric clusters have been evidenced, after the case of $CsBa_2Cr_2F_{11}$ (*19*). The Cl atoms are octahedrally coordinated by Ba and Ba/K atoms. The $[Cl(Ba/K)_6]$ octahedra are not isolated as were the $[ClSr_6]$ octahedra in $Sr_{10}Al_2F_{25}Cl$ (*1*): instead, they form infinite chains of face-sharing octahedra directed along the *c* axis. There are two sites dominantly occupied by Ba atoms (Ba/K), one site fully occupied by Ba atoms, and two sites dominantly occupied by K atoms (K/Ba). None of the (K/Ba) sites has any chlorine atom in its coordination. Due to similar ionic radii, the occurrence of Ba/K exchange is not unusual, particularly in silicate compounds. Few fluorides simultaneously presenting both Ba and K cations have been structurally studied, none chlorofluorides. Among fluorides, one can note the series KBa $M_2^{III}F_9$ (M^{III} = V, Cr, Fe, Ga) (*20*) and Ba_2 $KM_2^{II}F_9$ (M^{II} = Fe, Co, Ni, Zn) (*21*), where K may be replaced by a Cs or Rb atom. No structure determination was performed for any of the compounds of the first series; they are isotypical with Ba_2CoFeF_9 (*22*). Among the compounds of the second series (isostructural with $Ba_3Re_2O_9$ (*23*)), the structure investigation of $Ba_2KNi_2F_9$ revealed Ba/K exchange at two sites (with 85.8/14.2 and 57.1/42.9 proportion), preserving the stoi-

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $K_3Ba_7Al_6F_{33}Cl_2$

Al1 octahedron ⟨Al1–F⟩ = 1.806 (63% in this configuration)

Al1	F9	F3	F3	F4	F4	F8
F9	**1.775(12)**	2.714(13)	2.714(13)	2.660(15)	2.660(15)	3.667(11)
F3	99(1)	**1.789(11)**	2.479(10)	2.539(9)	3.551(13)	2.464(13)
F3	99(1)	87.7(9)	**1.789(11)**	3.551(13)	2.539(9)	2.464(13)
F4	96(1)	90.2(9)	164(1)	**1.795(10)**	2.486(10)	2.386(15)
F4	96(1)	164(1)	90.2(9)	87.7(9)	**1.795(10)**	2.386(15)
F8	175.7(7)	84(1)	84(1)	80.5(9)	80.5(9)	**1.895(9)**

Al1 octahedron ⟨Al1–F⟩ = 1.772 (37% in this configuration)

Al1	F12	F13	F13	F9	F14	F8
F12	**1.711(16)**	2.463(20)	2.463(20)	2.446(8)	3.489(5)	2.666(21)
F13	91(1)	**1.734(12)**	3.458(31)	2.392(20)	2.449(22)	2.654(17)
F13	91(1)	171(2)	**1.734(12)**	2.392(20)	2.449(22)	2.654(17)
F9	89(1)	86(1)	86(1)	**1.775(12)**	2.373(23)	3.667(11)
F14	172.7(4)	88(1)	88(1)	84(1)	**1.786(17)**	2.651(8)
F8	95(1)	94(1)	94(1)	175.7(7)	92.1(8)	**1.895(9)**

Al2 octahedron ⟨Al2–F⟩ = 1.810

Al2	F10	F1	F1	F6	F6	F8
F10	**1.767(11)**	2.660(12)	2.660(12)	2.565(10)	2.565(10)	3.683(6)
F1	**91.1(7)**	**1.780(7)**	2.524(8)	3.577(9)	2.532(6)	2.489(11)
F1	97.1(8)	90.3(7)	**1.780(7)**	2.532(6)	3.577(5)	2.489(11)
F6	91.7(7)	171.1(6)	89.8(6)	**1.807(6)**	2.528(5)	2.554(9)
F6	91.7(7)	89.8(6)	171.1(4)	88.7(5)	**1.807(4)**	2.554(9)
F8	177.5(4)	84.6(7)	84.6(8)	86.6(6)	86.6(6)	**1.916(9)**

Al3 octahedron ⟨Al3–F⟩ = 1.805

Al3	F11	F2	F2	F5	F5	F7
F11	**1.773(9)**	2.697(10)	2.697(10)	2.560(9)	2.560(9)	3.606(4)
F2	98.6(7)	**1.786(9)**	2.524(7)	2.567(5)	3.596(6)	2.475(5)
F2	98.6(7)	89.9(7)	**1.786(9)**	3.596(9)	2.567(5)	2.475(5)
F5	90.8(7)	90.7(6)	170.4(6)	**1.822(5)**	2.513(6)	2.459(8)
F5	90.8(7)	170.4(4)	90.7(5)	87.2(6)	**1.822(5)**	2.459(8)
F7	173.3(3)	86.1(5)	86.1(4)	84.4(5)	84.4(5)	**1.839(3)**

Ba/K–F/Cl distances

Ba [11], [10]		Ba/K1 [10], [11]		Ba/K2 [12]	
F12	*2.427(14)*	2× F4	2.506(8)	2× F6	2.754(4)
2× F5	2.640(5)	F9	2.617(13)	F11	2.881(9)
2× F6	2.820(5)	*F14*	2.824(20)	2× F5	2.902(6)
2× F3	2.856(12)	2× *F14*	*2.930(13)*	2× F2	2.945(10)
F10	3.054(10)	2× *F13*	*2.951(13)*	2× F10	3.060(7)
2× F11	3.062(5)	2× F1	3.007(10)	F7	3.309(1)
Cl4	3.229(4)	2× F4	3.062(12)	Cl3	3.311(4)
Cl3	3.444(4)	F8	3.068(8)	Cl4	3.535(4)
		Cl2	3.381(1)		
		Cl1	3.444(1)		

TABLE III—*Continued*

K/Ba–F distances		
K/Ba1 [9], [*11*]		K/Ba2 [12], [*10*]
2 × F3 2.542(9)		2 × *F13* 2.524(20)
2 × F1 2.565(9)		2 × F2 2.593(7)
2 × *F13* 2.723(20)		2 × F6 2.777(6)
2 × F5 2.832(8)		2 × F1 2.783(8)
2 × F2 2.839(7)		2 × F3 2.848(11)
F7 3.140(1)		2 × F4 2.861(12)
2 × *F12 3.378(13)*		2 × F8 3.105(7)

Cl environment			
Cl1	Cl2	Cl3	Cl4
6 × Ba/K1 3.444(7)	6 × *F14 2.923(13)*	3 × F11 3.294(8)	3 × Ba 3.229(4)
6 × F9 3.495(9)	6 × Ba/K1 3.381(7)	3 × Ba/K2 3.311(4)	3 × F10 3.319(9)
		3 × Ba 3.444(4)	3 × Ba/K2 3.535(4)

Note. Either F3 and F4 or *F12, F13*, and *F14* are present; correspondingly, the Ba, Ba/K1, and K/Ba atoms coordinations are given within brackets as either [] or *[]*.

chiometry, whereas the Cs- and Rb-based compounds presented a full Ba/Cs or Ba/Rb order. For K$_3$Ba$_7$Al$_6$F$_{33}$Cl$_2$, the K/Ba exchange seems also to preserve the stoichiometry and this could mean that the [AlF$_6$] octahedra resist being isolated in this structure (the contrary was suggested by the first structure approach leading to the estimated KBa$_4$Al$_3$F$_{17}$Cl formulation with 1/3 of [AlF$_6$] octahedra being isolated). However, if K atoms could be replaced by Rb or Cs atoms in K$_3$Ba$_7$Al$_6$F$_{33}$Cl$_2$, a full Rb/Ba or Cs/Ba order could not be described in the same $P\bar{3}m1$ space group because there would be
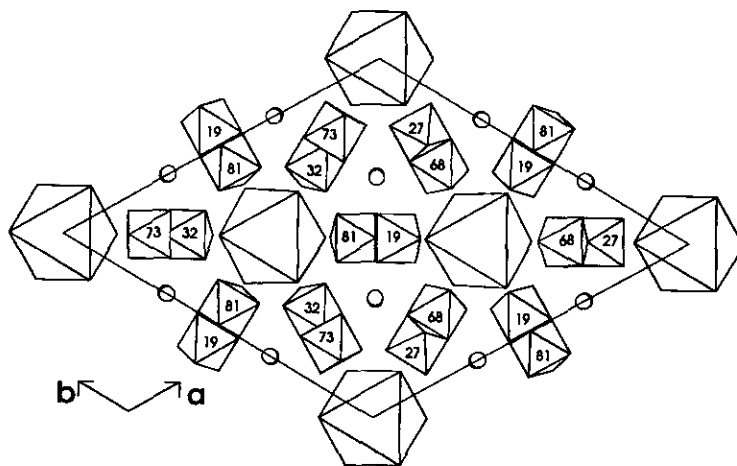
FIG. 1. [001] projection of the K$_3$Ba$_7$Al$_6$F$_{33}$Cl$_2$ structure. Small octahedra are [AlF$_6$] ones, all linked by a corner, forming isolated [Al$_2$F$_{11}$] dimers at various z levels (the Al z coordinate is indicated (×100)). Large octahedra are the [Cl(Ba,K)$_6$] ones involving the Ba, Ba/K(1), and Ba/K(2) sites at $z \approx 1/4$ or 3/4, the Cl atoms being at $z \approx 0$ and 1/2. Empty circles are the K/Ba(1) and K/Ba(2) atoms, respectively, at $z = 0$ and $z = 1/2$. The [Al(1)F$_6$] octahedra are shown in the main orientation possibility (63%).
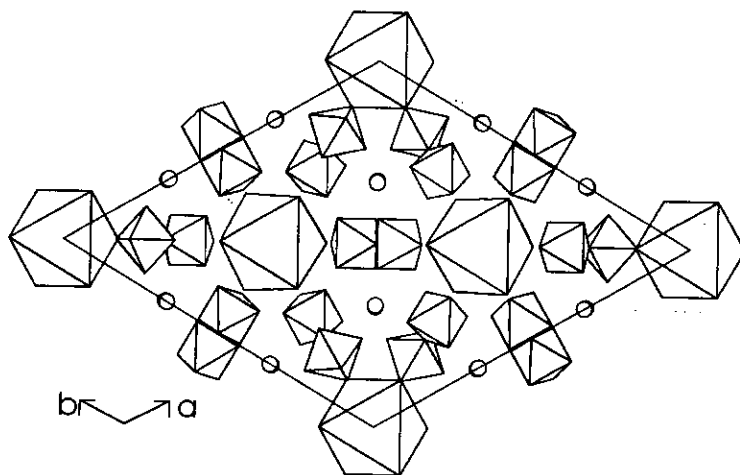
FIG. 2. As in Fig. 1, but for the [Al(1)F$_6$] octahedra shown in the less occupied position (37%).

nine Rb or Cs atoms in the cell and all the Ba or K atom sites have multiplicity 6.

In K$_3$Ba$_7$Al$_6$F$_{33}$Cl$_2$, the K/Ba exchange seems to have the additional effect of correlatively influencing the [Al(1)F$_6$] octahedron orientation since the K/Ba(1) and K/Ba(2) proportions (0.65/0.35 and 0.55/0.45) are quite similar to the independently estimated occupancy of the F(3), F(4), F(12), F(13), and F(14) atom sites. Because of these two possible orientations for the [Al(1)F$_6$] octahedra, each barium or potassium atom having these latter fluorine atoms in its environment will present two possible polyhedra. The Ba/K(2) site is the only site not affected,

presenting a large coordination number of 12 (10 F and 2 Cl atoms). Its distorted polyhedron, with a tetragonal face of 4 F atoms capped by one additional F atom, opposed to a nearly hexagonal face (5 F and one Cl atoms) capped by a Cl atom, is difficult to define (Fig. 3). In its dominant form, the polyhedron characterizing the fully occupied Ba site is very similar to the previous one; however, the cap of the tetragonal face is absent. The alternative is obtained by changing the tetragonal face by a triangle (Fig. 4). The dominant form of the Ba/K(1) polyhedra has a pentagonal equatorial plane of fluorine atoms with a fluorine triangle on one side and two chlorine atoms on the other side; the alternative has a distorted hexagonal equatorial plane instead of the pentagonal one (Fig. 5). Thus, all Ba-dominant sites
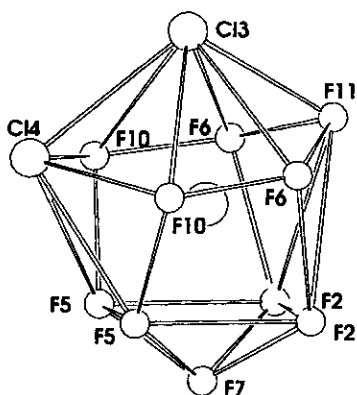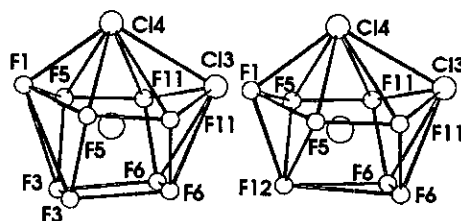

FIG. 3. Ba/K(2) polyhedron.

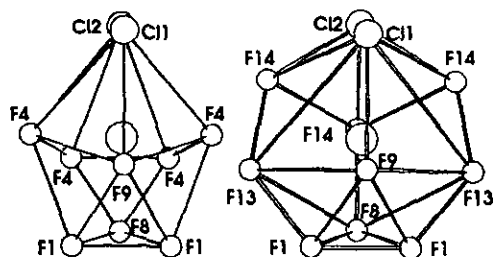FIG. 4. The two possible polyhedra of Ba (left, 63%; right, 37%).

FIG. 5. The two possible polyhedra of Ba/K(1) (left, 63%; right, 37%).

FIG. 7. The two possible polyhedra of K/Ba(2) (left, 63%; right, 37%).

have 2 Cl atom neighbors; the polyhedron symmetry is *m*, a mirror passing through these three atoms. Concerning the K-dominant sites, with F(3) in its environment, the K/Ba(1) polyhedron is a monocapped square antiprism, with the noncapped square face changing to a distorted hexagonal one when F(3) is replaced by F(12) and F(13) (Fig. 6). The latter polyhedron has similitude with the Ba/K(2) and Ba polyhedra. This fact seems to confirm the hypothesis of a correlation between the 37% [Al(1)F₆] octahedron orientation and the occupation of these latter K/Ba(1) polyhedra exclusively by Ba atoms (occupancy refined to 35%); the question of why the correlation would exist for this particular K/Ba(1) site and not for the Ba/K and Ba sites or even to a less extent for the K/Ba(2) site is not fully understood. The dominant form of the K/Ba(2) polyhedra is a bicapped pentagonal antiprism changing to a polyhedron defined
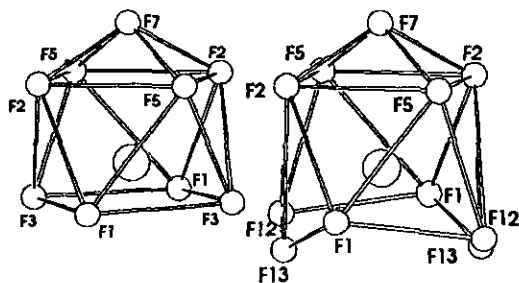
by an equatorial square plane with a triangle on each side (Fig. 7).

Concerning distances, it is a disordered structure, so there are some anomalies. One must not consider the [F(3),F(4)]–[F(12),F(13),F(14)] distances among the anomalies since they cannot occur. All intra-octahedron interfluorine shortest distances are tolerable (>2.386 Å), as well as the interoctahedron ones, with the exception of the very short F(4)–F(4) = 2.17(2) Å distance, which probably reflects some inaccuracy in the location of F(4). Indeed, the U_{33} thermal motion of the F(4) atom is the most important of all the U_{33} values relative to fluorine atoms and may indicate additional static disorder not accounted for in the final refinement. Such additional disorder may also apply to the Cl(2), F(9), and F(12) atoms, which present very elongated thermal motion ellipsoids.

The mean Al–F distance for [AlF₆] octahedra in fluoride crystal chemistry is 1.80 Å, with discrepancies rarely exceeding ±0.01 Å. Satisfactory mean Al–F distances are thus obtained for K₃Ba₇Al₆F₃₃Cl₂, with the exception of the [Al(1)F₆] octahedron in its less occupied orientation; thus, its position is known with much less accuracy. Another source of inaccuracy may be the consideration of only one position for Al(1), whereas there are two octahedron orientations. We have not tried to split the Al(1) site because its thermal motion was not so high. It is however the highest of the three different Al atoms, the medium value being taken by Al(2), and is certainly affected by

FIG. 6. The two possible polyhedra of K/Ba(1) (left, 63%; right, 37%).

the disorder since the $[Al(2)F_6]$ and $[Al(1)F_6]$ octahedra share a corner. On the other hand, the longest Al–F distances correspond to fluorine atoms bridging two octahedra (F(8) and F(7), a fact generally observed for fluoride compounds.

The Ba–F, Ba/K–F, and K/Ba–F distances are quite acceptable. The shortest K–F distance in $K_2Cr_3Cl_2F_6$ (3) is 2.554(2) Å, not far from 2.54 or 2.52 Å obtained for the K/Ba(1) or K/Ba(2) atom sites. Concerning the Ba-dominant sites, two distances are really too short; again they concern fluorine atoms not so well located (F(12) and F(4); see Table III).

Some Cl–F distances are similar or even shorter than the Cl–Ba or Cl–Ba/K shortest distances; this was not unexpected due to the similar sizes of Ba, K, and F. All the fluorine atoms belong to $[AlF_6]$ octahedra in this structure. In the crystal chemistry of complex $3d$ transition metal fluorides (or based on assimilated cations forming $[MF_6]$ octahedra), there are few known examples where some of the fluorine atoms may not belong to these octahedra. They are called, maybe improperly, "independent" fluorines (24). For instance, they may be found as [FCa₃Na], [FBa₄], [FSr₃Na], or [FPb₄] tetrahedra in, respectively, $Na_2Ca_3Al_2F_{14}$ (25), Ba_3AlF_9 (26, 27), $NaSr_2CrF_8$ (28), and $Pb_8MnFe_2F_{24}$ (29). Clearly, the Cl ion plays the same role here, its larger size than the F ion leading to an increase in the coordination. Further investigations on chlorofluoride compounds may reveal that the $[Cl(Ba,K)_6]$ octahedra are not so unusual after all. Such compounds may have interesting optical properties; work is in progress.

Acknowledgment

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