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The Crystal Structure of $Ba_5Cu_2Al_3F_{23}$: A Complex Barium, Copper, Aluminum Fluoride, with Copper (II) in Trigonal Prismatic Environment

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$Ba_5Cu_2Al_3F_{23}$ is monoclinic: $a = 28.44(2)$ Å, $b = 7.322(4)$ Å, $c = 27.95(2)$ Å, $\beta = 108.95(3)^\circ$, $Z = 12$. The crystal structure was solved in the space group $P2_1/c$ (no. 14), from X-ray single crystal data using 14,235 unique reflections (5307 with $F_o/\sigma(F_o) > 4$). It is built up from a complex tridimensional arrangement of $[MF_6]$ octahedra ($M = Al^{3+}$ and/or Cu^{2+}) and $[CuF_6]$ trigonal prisms, which form infinite tilted *cis* chains running perpendicular to the *bc* plane of the cell. Each chain is connected, roughly in the *c* direction, to four others, two up and two down, by octahedra vertices. The barium ions, 12- and 13-coordinated to fluorine atoms, ensure the electroneutrality of the structure. They are inserted between the chains. © 1999 Academic Press

I. INTRODUCTION

Crystal chemistry of inorganic complex copper (II) fluorides has considerably increased for the past few years and numerous structures with new features have been described. The study of the ternary system BaF_2–CuF_2–AlF_3 by X-ray techniques is presently in progress and many compounds, with new formulations, were disclosed in a small domain of the system, roughly centered around 50% BaF_2, 25% CuF_2, 25% AlF_3. This implies a great diversity in formulae and crystal structures. Recent papers describe the structures of some of these new fluorides, for example, $Ba_4Cu_2Al_3F_{21}$ (1), $Ba_2Cu_2AlF_{11}$ (2), and Ba_2CuAlF_9 (3). New modes of linkage involving edges and vertices between $[MF_6]$ octahedra ($M = Al^{3+}$ and/or Cu^{2+}) were found in these compounds and are also observed in the crystal structure of a new fluoride: $Ba_5Cu_2Al_3F_{23}$.

II. SYNTHESIS OF $Ba_5Cu_2Al_3F_{23}$

The starting fluorides BaF_2, CuF_2, and AlF_3 used in the investigation of the ternary system BaF_2–CuF_2–AlF_3 were prepared in the laboratory and their modes of preparation already described in a previous paper (1).

The investigation by X-ray techniques of the domain of the system mentioned above reveals the existence of numerous compounds with new and hitherto unknown powder patterns. In order to give an indexation to these diffractograms and to determine the formulae and the crystal structures of the disclosed fluorides, trials to obtain single crystals were undertaken. A mixture of the three elementary fluorides with a composition close to 50% BaF_2, 20% CuF_2, and 30% AlF_3, was melted and then annealed in a sealed copper tube at 770°C for 12 days. Irregular shaped single crystals of different fluorides were obtained and among them some, colorless, of $Ba_5Cu_2Al_3F_{23}$ and probably also of $Ba_{45}Cu_{28}Al_{17}F_{197}$, the crystal structure of which is presently under examination.

Weissenberg and Buerger X-ray photographs of one of these single crystals showed a monoclinic symmetry and the reflections conditions: $h0l$, $l = 2n$ and $0k0$, $k = 2n$, are in agreement with the space group $P2_1/c$. The measured cell parameters of $Ba_5Cu_2Al_3F_{23}$ are $a = 28.44(2)$ Å, $b = 7.322(4)$ Å, $c = 27.95(2)$ Å, $\beta = 108.95(3)^\circ$. A colorless powder of $Ba_5Cu_2Al_3F_{23}$ could be prepared in a sealed copper tube placed under inert argon atmosphere, by direct solid state reaction at 720°C during 30 h of the stoichiometric mixture of the three fluorides. The observed X-ray powder pattern of $Ba_5Cu_2Al_3F_{23}$, reported in Table 1, was collected on a 17 cm vertical Philips PW 1050/25 diffractometer (copper anticathode: $\lambda = 1.5418$ Å). It is similar to the calculated one, using the atomic coordinates of the crystal structure determination (program Fullprof (4)).

III. STRUCTURE DETERMINATION

A single crystal was mounted on a Siemens SMART system using a three-circle diffractometer equipped with a CCD bidimensional detector. A sum of 35,014 intensities was measured and the conditions of the data collection are

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TABLE 1
X-Ray Powder Pattern of $Ba_5Cu_2Al_3F_{23}$

$d_{meas.}$	$d_{calc.}$	h	k	l	I/I_0 peak height	$d_{meas.}$	$d_{calc.}$	h	k	l	I/I_0 peak height
6.402	6.405	0	1	2	4	2.688	2.689	10	0	0	25
4.653	4.658	2	0	−6	7	2.361	2.361	1	3	−3	16
4.334	4.335	5	1	0	22	2.326	2.326	12	0	−6	18
3.931	3.930	2	1	−6	60	2.223	2.222	8	1	6	42
3.663	3.661	0	2	0	13	2.164	2.163	4	3	3	47
3.525	3.527	3	0	6	76	2.112	2.112	9	2	3	60
3.406	3.407	1	2	−3	100	1.962	1.962	7	1	9	14
3.173	3.170	7	1	−6	58	1.956	1.956	13	1	−9	13
3.042	3.041	7	0	−8	9	1.919	1.919	3	3	−9	14
2.880	2.880	4	2	3	54	1.830	1.831	0	4	0	16
2.858	2.859	3	1	−9	18						

summarized in Table 2. The data were corrected for Lorentz and polarization effects and the SADABS program (5) was used for absorption correction. The scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-ray Crystallography" (6). The structure of the crystal was solved in the space group $P2_1/c$ (no. 14). All the refinement calculations were performed with the SHELX-97 programs (7). Barium, copper, and aluminum atoms were first located using the direct method analysis (TREF instruction). Thirty independent sites were found

TABLE 2
Crystal Data, Data Collection, and Refinement Characteristics

Formula: $Ba_5Cu_2Al_3F_{23}$
Symmetry: Monoclinic
Space group: $P2_1/c$ (no. 14)
Cell parameters: $a = 28.44(2)$ Å, $b = 7.322(4)$ Å, $c = 27.95(2)$ Å, $\beta = 108.95(33)^\circ$ $Z = 12$
Volume: 5505(12) Å^3
Formula weight: 1331.7 g. mol^{-1}
Density (calculated): 4.82 g. cm^{-3}
Radiation: Mo$K\alpha$ ($\lambda = 0.71073$ Å)
$F(000) = 7008$
Linear absorption coefficient: 13.2 mm^{-1}
Crystal size: $0.1 \times 0.1 \times 0.1$ mm^{-3} (irregular shaped) Colorless
Theta range for data collection: 0.7 to 30°
Index range: $-39 \le h \le 38$; $-8 \le k \le 10$; $-28 \le l \le 38$.
35,014 *reflections collected*, 14,235 *unique*, 5307 *with* $F_o/\sigma(F_o) > 4$
$R_{int} = 0.0379$
Refinement method: full-matrix least-squares on F^2
896 refined parameters
Extinction coefficient: $x = 0.0$ (9.10^{-6})
Electron density in Fourier difference map: Max. height: 10.44 e$^-$. Å^{-3}
Min. height: −9.75 e$^-$. Å^{-3}
Reliability factors: Goodness-of-fit on $F^2 = 1.078$
Final R indices ($F_o/\sigma(F_o) > 4$) $R_1 = 0.0809$ $wR_2 = 0.2569$
R indices (all data) $R_1 = 0.1585$ $wR_2 = 0.3191$

TABLE 3
Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Parameters (Å$^2 \times 10^3$), with e.s.d. in Parentheses, in the Crystal Structure of $Ba_5Cu_2Al_3F_{23}$

Atom	x	y	z	U_{eq}
Ba(1)	0515(1)	8699(2)	2926(1)	11(1)
Ba(2)	4485(1)	6278(2)	2594(1)	13(1)
Ba(3)	3458(1)	1285(2)	1738(1)	12(1)
Ba(4)	2570(1)	8701(2)	3592(1)	13(1)
Ba(5)	1530(1)	3725(2)	2738(1)	11(1)
Ba(6)	2470(1)	6272(2)	1939(1)	11(1)
Ba(7)	1410(1)	1360(2)	1083(1)	15(1)
Ba(8)	3524(1)	3708(2)	3391(1)	12(1)
Ba(9)	4589(1)	8514(2)	4226(1)	19(1)
Ba(10)	0473(1)	6304(2)	1265(1)	10(1)
Ba(11)	4470(1)	8622(2)	0909(1)	14(1)
Ba(12)	1523(1)	1452(2)	4445(1)	13(1)
Ba(13)	0561(1)	6540(2)	4534(1)	16(1)
Ba(14)	3473(1)	3447(2)	0138(1)	17(1)
Ba(15)	2489(1)	8480(2)	0205(1)	15(1)
Cu(1)	1540(1)	8674(4)	2452(1)	20(1)
Cu(2)	2444(1)	1301(4)	2204(1)	16(1)
Cu(3)	9501(1)	6587(5)	3222(1)	44(1)
Cu(4)	3523(1)	8568(5)	3014(2)	92(2)
Cu(5)/Al(5)	4474(1)	1364(4)	2893(1)	6(1)
Cu(6)/Al(6)	1529(1)	6741(5)	3889(1)	14(1)
Cu(7)/Al(7)	5508(1)	8297(4)	3538(1)	5(1)
Cu(8)/Al(8)	2463(1)	3227(6)	0759(1)	25(1)
Al(9)	9506(2)	8570(7)	1760(2)	1(1)
Al(10)	3491(2)	6457(7)	1396(2)	5(1)
Al(11)	3536(2)	6729(7)	4613(2)	1(1)
Al(12)	2520(2)	3519(8)	3952(2)	9(1)
Al(13)	1492(2)	6523(8)	0688(2)	6(1)
Al(14)	5521(2)	6584(8)	5354(2)	8(1)
Al(15)	0473(2)	3353(8)	0020(2)	4(1)
F(1)	3998(3)	3210(16)	2713(4)	15(2)
F(2)	9978(4)	6795(18)	1941(4)	18(2)
F(3)	3963(4)	8184(17)	1572(4)	17(2)
F(4)	2951(4)	1722(17)	0697(4)	18(2)
F(5)	4014(4)	6838(18)	3271(4)	19(3)
F(6)	1974(3)	3172(16)	2046(4)	13(2)
F(7)	1047(3)	8289(17)	3952(3)	15(2)
F(8)	2012(4)	6790(16)	2633(3)	13(2)
F(9)	1041(4)	6888(18)	2274(4)	19(3)
F(10)	0018(3)	8137(17)	3605(3)	15(2)
F(11)	9029(4)	6881(17)	1562(4)	22(3)
F(12)	9031(3)	8196(16)	3286(4)	13(2)
F(13)	3008(4)	8134(17)	1214(4)	17(2)
F(14)	2956(4)	3142(16)	2385(4)	15(2)
F(15)	4968(4)	3104(17)	3091(4)	19(2)
F(16)	5033(4)	6727(16)	3628(4)	17(2)
F(17)	3039(4)	6826(18)	2967(4)	21(3)
F(18)	2985(4)	1823(19)	4123(4)	24(3)
F(19)	2040(4)	1840(2)	3774(4)	24(3)
F(20)	2033(5)	0508(17)	2792(4)	30(3)
F(21)	3988(3)	9595(16)	2608(4)	16(2)
F(22)	3069(4)	8273(19)	4653(3)	20(3)
F(23)	1042(4)	0482(17)	2399(4)	22(3)
F(24)	2489(4)	3627(18)	4590(3)	24(3)
F(25)	9991(4)	0326(16)	2026(4)	24(3)
F(26)	1026(4)	8189(19)	0554(4)	25(3)

TABLE 3—*Continued*

Atom	*x*	*y*	*z*	U_{eq}
F(27)	0936(4)	1704(18)	0030(4)	24(3)
F(28)	2021(4)	8210(2)	4289(4)	28(3)
F(29)	4967(4)	9517(16)	2966(4)	20(2)
F(30)	6020(4)	6862(17)	3951(3)	15(2)
F(31)	2448(4)	2003(18)	1316(4)	23(3)
F(32)	5051(5)	8250(2)	5277(5)	36(3)
F(33)	2546(3)	3676(18)	3338(4)	23(3)
F(34)	1956(5)	8160(2)	0898(6)	38(4)
F(35)	1941(3)	9521(17)	1880(4)	22(3)
F(36)	9006(4)	0353(18)	1644(5)	27(3)
F(37)	3468(4)	6441(18)	2044(4)	26(3)
F(38)	3527(4)	6240(19)	0770(4)	26(3)
F(39)	3988(4)	4667(18)	1633(4)	20(3)
F(40)	2999(4)	4585(17)	1260(4)	24(3)
F(41)	2534(4)	4687(17)	0262(4)	23(3)
F(42)	1543(3)	8080(18)	3325(4)	22(3)
F(43)	1530(4)	6610(2)	0061(4)	35(3)
F(44)	2916(4)	9497(15)	2210(3)	14(2)
F(45)	1968(4)	1840(2)	0352(4)	30(3)
F(46)	3508(4)	5399(19)	5121(5)	30(3)
F(47)	1491(4)	5192(17)	4374(4)	22(3)
F(48)	1449(4)	6220(2)	1318(4)	39(4)
F(49)	4005(4)	8120(2)	4981(4)	41(4)
F(50)	3006(5)	5330(19)	4128(5)	38(3)
F(51)	2026(5)	5290(19)	3743(5)	34(3)
F(52)	3582(4)	7740(2)	4045(4)	29(3)
F(53)	9583(8)	8830(3)	1146(5)	88(8)
F(54)	5979(5)	8110(3)	5601(5)	62(6)
F(55)	0001(5)	1900(3)	9662(6)	58(5)
F(56)	9491(4)	8450(2)	2449(6)	44(4)
F(57)	0566(4)	4520(2)	9497(4)	30(3)
F(58)	5510(4)	6760(2)	2900(7)	64(6)
F(59)	1992(5)	4720(2)	0892(5)	38(4)
F(60)	3168(6)	0460(2)	3196(5)	50(4)
F(61)	5562(6)	6960(3)	4724(5)	72(7)
F(62)	0412(4)	2490(2)	0594(4)	47(5)
F(63)	5405(8)	9940(3)	3973(6)	96(9)
F(64)	1012(6)	4700(2)	0500(6)	61(5)
F(65)	5460(5)	5830(3)	5913(5)	60(6)
F(66)	9289(8)	4750(2)	3590(5)	80(7)
F(67)	4003(7)	5100(3)	4519(8)	88(7)
F(68)	4236(13)	0740(3)	3501(6)	172(17)
F(69)	1/2	1/2	1/2	127(16)
F(70)	0	1/2	0	170(2)

for the metallic cations. The positions of the 70 independent fluorine atoms were found by successive difference Fourier syntheses. In general the fully occupied aluminum and copper sites were attributed on the basis of clearly different Al–F and Cu–F distances. When for some sites this was not possible, it was first supposed that they were mixed Al/Cu occupied and the site occupation factors were released in order to distinguish their nature: copper, aluminum or mixed. In the text and figures, the four mixed occupied sites (50% Al^{3+}/50% Cu^{2+}) are labeled as *M*.

The refinement of all anisotropic thermal parameters for all atoms leads to $R_1(F_o) = 0.081$ and $wR_2(F_o^2) = 0.257$ for 5307 unique reflections with $F_o > 4\sigma(F_o)$ and 896 refined parameters. The poor *R* factors are probably a consequence of the great number (100!) of independent atoms in the structure and also of the mixed occupation Al/Cu of four sites, as already observed for the crystal structure determination of Ba_2CuAlF_9 (3). To save room, only the atomic coordinates and the isotropic thermal motion parameters are listed in Table 3. All the anisotropic displacement parameters, the principal bond lengths and angles, and a list of the structure factors may be obtained from the authors on request.

IV. DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure of $Ba_5Cu_2Al_3F_{23}$ is built up from a complex tridimensional arrangement of copper, aluminum, and mixed occupied Al/Cu fluorine octahedra and copper fluorine trigonal prisms. The (010) projection of the structure is represented in Fig. 1. It consists in infinite

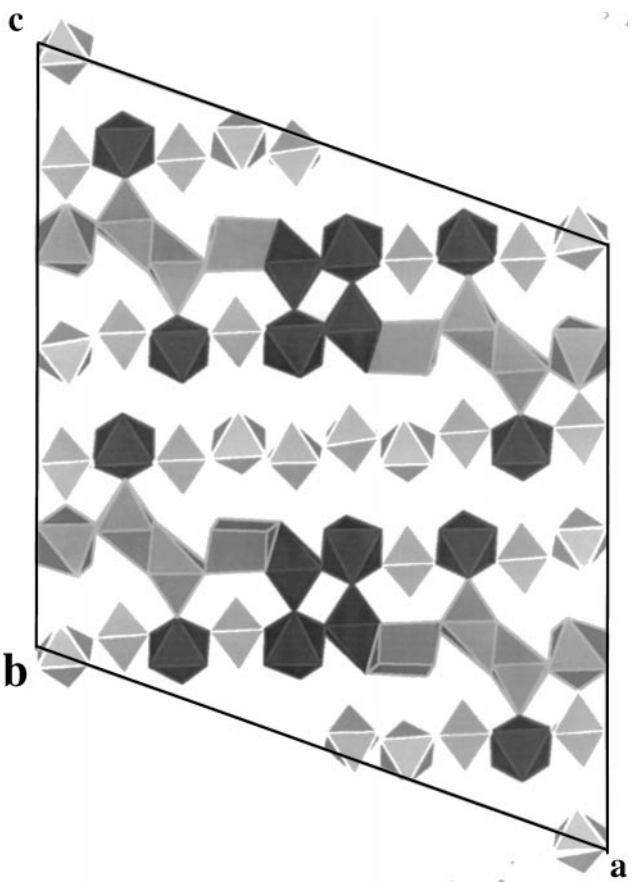

FIG. 1. (010) projection of the structure of $Ba_5Cu_2Al_3F_{23}$. Pale polyhedra are aluminum, medium are copper, and dark are mixed occupied aluminum–copper. Barium atoms are omitted.

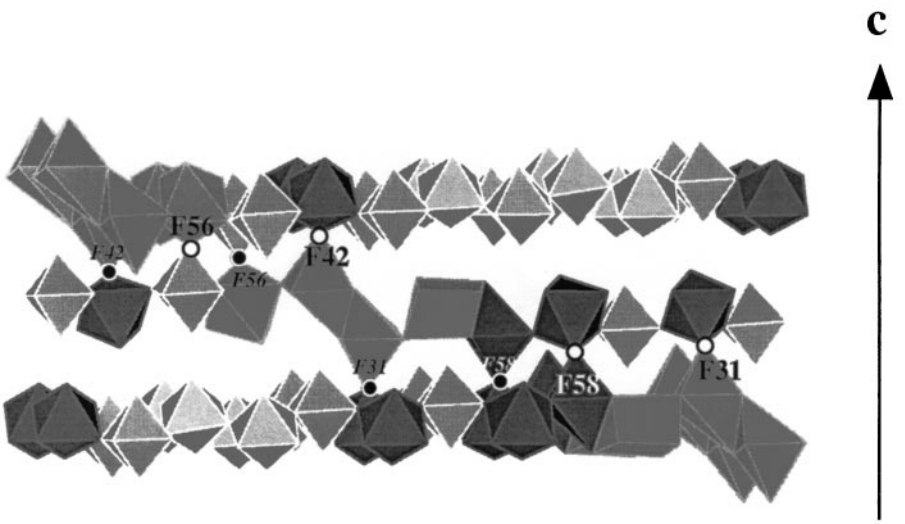

FIG. 2. One infinite tilted *cis* chain is linked, roughly in the *c* direction, to four others, two up and two down, by eight vertices (two per chain). White circles are fluorine atoms connecting the front chain and black circles are fluorine atoms connecting the posterior chain. Front and posterior chains are not directly connected together.

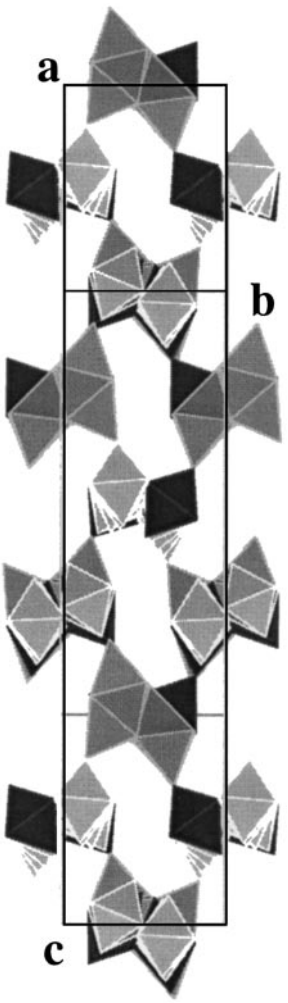

FIG. 3. (100) projection of the structure of $Ba_5Cu_2Al_3F_{23}$, showing that one chain is linked to four others.

complex tilted *cis* chains of polyhedra which develop perpendicular to the *bc* plane of the cell. Each chain is constituted by the infinite association of fifteen polyhedra: twelve octahedra, one bioctahedral unit (two copper octahedra sharing one edge), and one copper trigonal prism connected by one corner and one edge to its neighbors. The periodicity in that direction (which is not a cell direction) is of thirty polyhedra, because of the presence of an inversion center. Each chain is linked, approximately in the *c* direction, to four others, two up and two down. by eight octahedra vertices (two per chain) every 15 polyhedra (Figs. 2 and 3). The bond lengths and angles observed in the trigonal prism (Fig. 4) are given in Tables 4 and 5.

The disposal of the polyhedra, represented in Fig. 5 between the two hatched lines, allows the build up of the crystal structure of $Ba_5Cu_2Al_3F_{23}$ using the symmetry operations of the $P2_1/c$ space group. It shows the different kinds of linkage existing between these polyhedra in the structure. A collection of the bond lengths observed in the

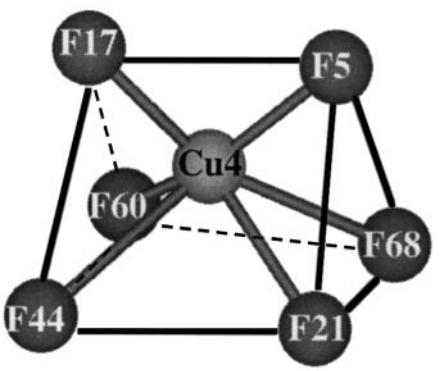

FIG. 4. The $[Cu(4)F_6]$ trigonal prism.

TABLE 4
Interatomic Distances (Å) and Bond Angles (°) in the [Cu(4)F_6] Trigonal Prism

Cu(4)	F(5)	F(17)	F(60)	F(21)	F(44)	F(68)
F(5)	**1.849(13)**	2.623	3.541	2.725	4.040	2.951
F(17)	90.3	**1.850(13)**	2.733	3.763	2.818	4.328
F(60)	143.5	94.3	**1.879(12)**	3.321	2.706	2.883
F(21)	85.9	141.1	111.3	**2.139(11)**	2.887	2.507
F(44)	140.1	80.8	76.3	77.8	**2.444(10)**	4.375
F(68)	81.5	154.0	78.6	63.2	120.7	**2.589(25)**

Note. Mean $\langle Cu-F \rangle = 2.125$ Å.

polyhedra, coupled to a bond valence analysis according to the Brese and O'Keeffe model (8), is given in Table 6. It shows the good agreement between the attribution of the sites and the electrostatic compensation of the electric charge in each polyhedron.

The aluminum fluorine octahedra are fairly regular, with mean Al–F distances ranging between 1.778 and 1.848 Å, close to the sum of the ionic radii (1.820 Å) calculated with Shannon's table (9). As generally observed in crystal chemistry, copper (II) presents a strong Jahn–Teller effect due to the combination of its electronic configuration $3d^9$ and the particularities of the crystal structure. The mean Cu–F distances range between 2.045 and 2.086 Å for an octahedral coordination and is 2.125 Å for a trigonal prismatic environment. They are slightly greater than the sum of the ionic radii: 2.015 Å (9), particularly in the trigonal prism (Table 4). The barium atoms, which ensure the electroneutrality and the cohesion of the crystal, are inserted between the chains as shown on the projection of the structure perpendicular to *c* (Fig. 6). Information about bond lengths, coupled to a bond valence analysis (8), is given in Table 7. The barium atoms exhibit 12- and 13-coordination, for a Ba–F interatomic distance shorter than 3.53 Å.

TABLE 5
Bond Angles (°) in the Triangular and Rectangular Faces of the [Cu(4)F_6] Trigonal Prism

Triangular face	F5-F68-F21	F68-F21-F5	F21-F5-F68	
Angles				
($\sum = 180.0$)	59.2	68.5	52.3	
Triangular face	F60-F44-F17	F44-F17-F60	F17-F60-F44	
Angles				
($\sum = 180.0$)	59.3	58.3	62.4	
Rectangular face	F17-F5-F-68	F5-F68-F60	F68-F60-F17	F60-F17-F5
Angles				
($\sum = 359.9$)	101.7	74.7	100.8	82.7
Rectangular face	F60-F68-F21	F68-F21-F44	F21-F44-F60	F44-F60-F68
Angles				
($\sum = 359.7$)	75.7	108.2	72.8	103.0
Rectangular face	F5-F21-F44	F21-F44-F17	F44-F17-F5	F17-F5-F21
Angles				
($\sum = 359.7$)	92.0	82.5	95.8	89.4

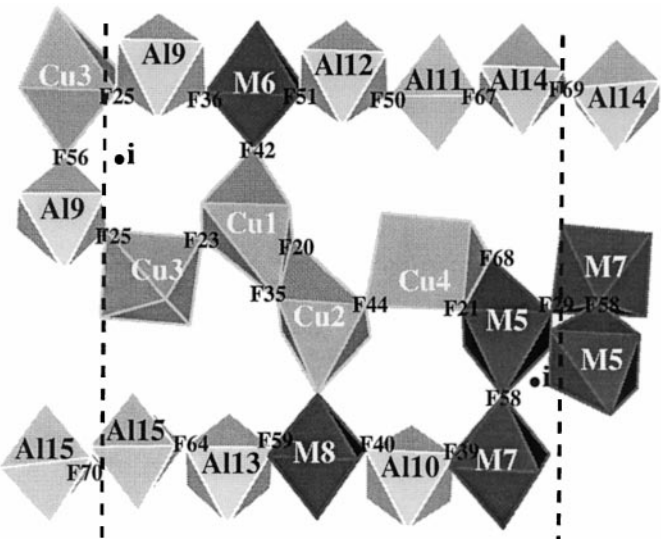

FIG. 5. Modes of linkage between the polyhedra in the structure of $Ba_5Cu_2Al_3F_{23}$ (motif between the hatched lines).

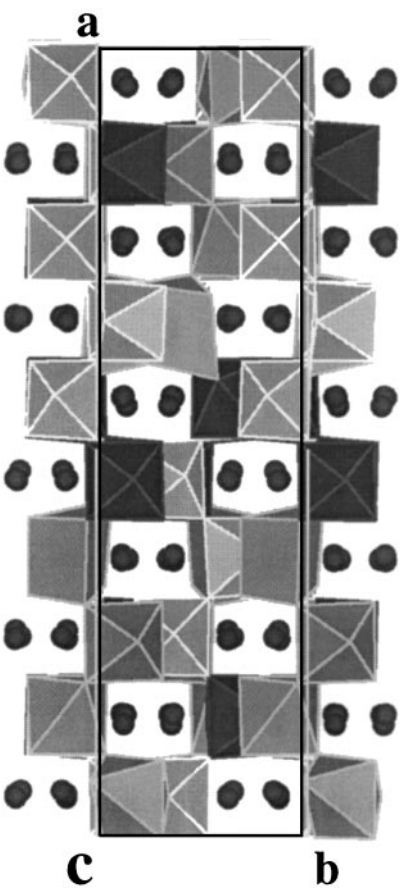

FIG. 6. Projection of the crystal structure of $Ba_5Cu_2Al_3F_{23}$ perpendicular to the *c* direction. Barium atoms are black circles.

TABLE 6
Interatomic Distances (Å) in the 6-Coordinated Polyhedra and Bond Valence Analysis: $v_{ij} = \exp[(R_{ij} - d_{ij})/b]$, with $b = 0.37$ Å (8)

Central atom M_i	F_j $dM_i - F_j$ (esd)	F_j $dM_i - F_j$ (esd)	F_j $dM_i - F_j$ (esd)	F_j $dM_i - F_j$ (esd)	F_j $dM_i - F_j$ (esd)	F_j $dM_i - F_j$ (esd)	Mean bond length $dM_i - F_j$	R_{ij} (Å)	$V_i = \sum v_{ij}$ (theory)
Cu(1)	F9	F8	F23	F20	F35	F42			
	1.874	1.876	1.909	1.951	2.329	2.476	2.069	1.600	2.01
	(13)	(12)	(13)	(13)	(10)	(11)			(2.0)
Cu(2)	F6	F44	F14	F35	F20	F31			
	1.864	1.879	1.927	1.930	2.377	2.538	2.086	1.600	1.98
	(11)	(12)	(12)	(11)	(13)	(11)			(2.0)
Cu(3)	F12	F10	F66	F25	F23	F56			
	1.834	1.890	1.906	2.018	2.076	2.547	2.045	1.600	2.10
	(11)	(11)	(14)	(12)	(12)	(14)			(2.0)
Cu(4)	F5	F17	F60	F21	F44	F68			
	1.849	1.850	1.879	2.139	2.444	2.589	2.125	1.600	1.89
	(13)	(13)	(12)	(11)	(10)	(25)			(2.0)
M(5)	F15	F1	F21	F29	F68	F58			
	1.843	1.863	1.873	1.911	2.074	2.250	1.969	1.573	2.20
	(13)	(11)	(11)	(12)	(26)	(18)			(2.5)
M(6)	F47	F28	F7	F42	F51	F36			
	1.797	1.830	1.831	1.868	1.915	2.024	1.878	1.573	2.69
	(12)	(10)	(11)	(12)	(15)	(13)			(2.5)
M(7)	F63	F16	F30	F39	F29	F58			
	1.801	1.852	1.861	1.932	2.031	2.110	1.931	1.573	2.37
	(14)	(12)	(11)	(13)	(12)	(16)			(2.5)
M(8)	F45	F31	F41	F4	F59	F40			
	1.808	1.809	1.815	1.824	1.858	1.972	1.848	1.573	2.89
	(10)	(12)	(12)	(13)	(13)	(12)			(2.5)
Al(9)	F11	F53	F2	F25	F36	F56			
	1.786	1.809	1.818	1.855	1.879	1.942	1.848	1.545	2.67
	(13)	(16)	(14)	(13)	(14)	(16)			(3.0)
Al(10)	F13	F38	F3	F37	F39	F40			
	1.789	1.793	1.793	1.833	1.883	1.907	1.833	1.545	2.78
	(13)	(12)	(13)	(12)	(14)	(13)			(3.0)
Al(11)	F49	F46	F22	F52	F67	F50			
	1.727	1.745	1.775	1.795	1.866	1.958	1.811	1.545	2.99
	(11)	(14)	(14)	(11)	(17)	(15)			(3.0)
Al(12)	F33	F18	F19	F24	F51	F50			
	1.745	1.763	1.784	1.815	1.861	1.863	1.805	1.545	2.99
	(12)	(14)	(10)	(10)	(16)	(16)			(3.0)
Al(13)	F34	F26	F43	F48	F64	F59			
	1.738	1.750	1.792	1.818	1.859	1.888	1.808	1.545	2.98
	(13)	(14)	(12)	(12)	(14)	(12)			(3.0)
Al(14)	F54	F65	F32	F67	F61	F69			
	1.685	1.718	1.770	1.780	1.823	1.889	1.778	1.545	3.25
	(12)	(14)	(12)	(17)	(15)	(6)			(3.0)
Al(15)	F55	F27	F62	F57	F70	F64			
	1.750	1.780	1.784	1.786	1.794	1.946	1.807	1.545	3.00
	(14)	(14)	(12)	(11)	(6)	(16)			(3.0)

$Ba_5Cu_2Al_3F_{23}$ represents a new structural type in barium, copper (II), aluminum fluoride crystal chemistry. Some structural particularities of other related compounds already reported in previous papers are also observed in this new structure. For instance, it presents an original kind of linkage between the polyhedra which involves simultaneously edges and vertices, as it has been observed in $Ba_2Cu_2AlF_{11}$ (1) and $Ba_4Cu_2Al_3F_{21}$ (2). Some sites show a mixed occupation rate (50% Cu^{2+}/50% Al^{3+}), as already observed in Ba_2CuAlF_9 (3) and $Ba_2CuAl_2F_{12}$ (10). Moreover, in $Ba_5Cu_2Al_3F_{23}$ is evidenced an original and rare kind of 6-coordination in fluoride chemistry: copper (II) is located at the center of a fluorinated trigonal prism. It is the first example encountered until now.

TABLE 7

Mean Interatomic Ba–F Distances (Å) and Bond Valence Analysis in the Barium Coordination Polyhedra: $v_{ij} = \exp[(R_{ij} - d_{ij})/b]$, with $b = 0.37$ Å (8)

Atom	C.N.	Mean bond length	$V_{ij} = \sum v_{ij}$	Min. bond length	Max. bond length
Ba(1)	12	2.832	2.18	2.741(9)	3.021(12)
Ba(2)	12	2.845	2.15	2.681(12)	3.132(12)
Ba(3)	12	2.834	2.18	2.674(11)	3.009(11)
Ba(4)	12	2.845	2.15	2.620(12)	3.039(14)
Ba(5)	12	2.852	2.16	2.662(10)	3.194(12)
Ba(6)	12	2.875	2.07	2.671(11)	3.212(12)
Ba(7)	12	2.867	2.04	2.621(11)	3.107(10)
Ba(8)	13	2.932	2.12	2.573(7)	3.448(6)
Ba(9)	13	2.941	2.02	2.540(13)	3.320(3)
Ba(10)	13	2.973	1.96	2.610(6)	3.483(4)
Ba(11)	12	2.929	1.86	2.711(12)	3.497(3)
Ba(12)	12	2.925	1.88	2.740(10)	3.502(19)
Ba(13)	12	2.925	1.89	2.686(10)	3.466(3)
Ba(14)	12	2.918	1.92	2.674(13)	3.522(19)
Ba(15)	12	2.924	1.82	2.728(12)	3.297(13)

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