

Hence one may conclude that the formula units are connected by Cu—S bonds within the asymmetric units and by weak Cu—N bonds between adjacent asymmetric units. Thus the two Cu coordination tetrahedra are connected to adjacent tetrahedra by some of the C—N triple bonds. The result is a network comprising two sorts of tetrahedra forming a layer parallel to (100). The gaps within the network are filled by the *N,N*-dimethylthioformamide residues (Fig. 3). The layers are puckered with an overall thickness of $a/2$ (Fig. 4). Closest distances between atoms of adjacent layers are N(2)—Sⁱⁱⁱ, 3.651 (9) Å. Hence the cohesion between the layers is due solely to van der Waals forces.



Fig. 3. A stereoscopic view of a layer of molecules in projection parallel to [100].

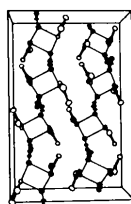


Fig. 4. A stereoscopic view of the molecular arrangement viewed along *c*.

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Refinement of the PbFCl Types BaFI, BaFBr and CaFCI

BY BERNARD W. LIEBICH

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève, Switzerland

AND DANIEL NICOLLIN

Département de Chimie-Physique, Université de Genève, 30 quai Ernest Ansermet, CH-1211 Genève, Switzerland

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BaFI, BaFBr and CaFCI are of the PbFCl structure type with tetragonal space group $P4/nmm$: $a = 4.654$ (3), $c = 7.962$ (12) Å for BaFI; $a = 4.508$ (4), $c = 7.441$ (15) Å for BaFBr and $a = 3.894$ (3), $c = 6.818$ (20) Å for CaFCI. Least-squares refinement based on 348, 325 and 114 independent reflexions led to R values of 7.7% ($R_w = 5.0\%$), 8.0% ($R_w = 5.4\%$) and 8.1% ($R_w = 6.7\%$) for BaFI, BaFBr and CaFCI respectively. The observed variations of interatomic distances and angles are discussed.

Introduction

The structures of BaFI, BaFBr and CaFCI refined in this work are of the tetragonal PbFCl ($E0_1$) structure type, a ternary derivative of the Cu_3Sb or Fe_3As type (C38). The structure and cell parameters of CaFCI and BaFI were first determined from powder diffraction data (Frevel, Rinn & Anderson, 1946). These values

have recently been remeasured, by the same technique, including those for BaFBr (Beck, 1976). However, it was thought useful to obtain more accurate information on the bond distances and angles of the title compounds from the refinement of single-crystal data. Further, it is of interest to compare these results with those from the refined structures of SrFCl and BaFCI (Sauvage, 1974), who also confirmed the preliminary results of

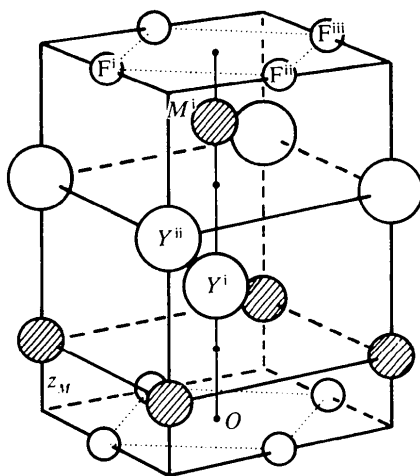


Fig. 1. Unit cell of the compounds MXY . Origin (O), displaced by $(\frac{1}{4}, \frac{1}{4}, 0)$ from second setting.

Nicklaus & Fischer (1972) for $BaFCl$. Thus, structural information is provided for $BaFI$, $BaFBr$, $BaFCl$, $SrFCl$ and $CaFCl$, which compounds can be divided into two groups: those with halogen varying and those with varying alkaline-earth metals. These isotypes are characterized by the packing of layers along c (Fig. 1). The stacking of these layers is of the type: $X-M-Y-Y-M$, where $X = F^-$, $M = Ca^{2+}$, Sr^{2+} , Ba^{2+} and $Y = Cl^-$, Br^- , I^- .

Experimental

Crystals were grown by the Kyropoulos–Czochralski and Bridgman techniques.

For all three compounds the XRAY system (1976) was used for absorption correction, data reduction and least-squares refinement. Absorption corrections were made with *ABSCOR*, programmed by Alcock, according to the analytical method of de Meulenaer & Tompa (1965). This method was most suitable because it proved easy to determine the shape and size of these crystals, which have a plate-like form parallel to (001).

Table 1. Crystal data for the title compounds

	BaFI	BaFBr	CaFCl
Space group	$P4/nmm$	$P4/nmm$	$P4/nmm$
a	4.654 (3) Å	4.508 (4) Å	3.894 (3) Å
c	7.962 (12)	7.441 (15)	6.818 (20)
Z	2	2	2
U	172.45 Å ³	151.22 Å ³	103.38 Å ³
FW	283.24	236.25	94.53
$F(000)$	236	200	92
D_x	5.45 g cm ⁻³	5.19 g cm ⁻³	3.04 g cm ⁻³
μ	206.8 cm ⁻¹	272.6 cm ⁻¹	37.6 cm ⁻¹
λ (Mo $K\alpha$)	0.7107 Å	0.7107 Å	0.7107 Å
R	7.7% ($R_w = 5.0\%$)	8.0% ($R_w = 5.4\%$)	8.1% ($R_w = 6.7\%$)

Anisotropic temperature factors were refined for all atoms: $\exp\{-2\pi^2[a^{*2}U_{11}(h^2 + k^2) + c^{*2}U_{33}l^2]\}$, as well as an isotropic extinction factor. Ion scattering factors were from Cromer & Mann (1968). Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1974). The crystal data are shown in Table 1.

BaFI, BaFBr

For BaFI a single crystal $0.064 \times 0.012 \times 0.080$ mm was used for intensity measurements on a Philips PW 1100 automatic diffractometer. 446 intensities were collected (ω - 2θ scans, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, graphite monochromator).

The final atomic parameters are listed in Table 2, corresponding to $R = 7.7\%$ ($R_w = 5.0\%$) for 348 reflexions with $F \geq 3\sigma(F)$.

For BaFBr the same procedure was used with a crystal $0.032 \times 0.018 \times 0.080$ mm. 405 reflexions were collected of which 325 with $F \geq 3\sigma(F)$ were used in the refinement. The final atomic parameters (Table 2) correspond to $R = 8.0\%$ ($R_w = 5.4\%$).

CaFCl

A crystal $0.352 \times 0.176 \times 0.096$ mm was used. However, a decrease in intensity of the reference

Table 2. Atomic positional and thermal parameters of BaFI and BaFBr

Second setting, with symmetry centre at origin, was used.

	x	y	z	U_{11} (Å ² × 10 ²)	U_{33} (Å ² × 10 ²)
BaFI					
Ba (2c)	0.25	0.25	0.1704 (3)	1.09 (9)	1.60 (11)
F (2a)	0.75	0.25	0	0.44 (41)	1.32 (76)
I (2c)	0.25	0.25	0.6522 (3)	1.63 (12)	1.57 (12)
BaFBr					
Ba (2c)	0.25	0.25	0.1911 (4)	0.94 (6)	1.88 (12)
F (2a)	0.75	0.25	0	1.00 (49)	4.5 (1.3)
Br (2c)	0.25	0.25	0.6497 (5)	1.55 (12)	2.22 (22)

Table 3. Atomic positional parameters and thermal parameters of CaFCl

Second setting, with symmetry centre at origin, was used.

	x	y	z	U (Å ² × 10 ³)
Ca (2c)	0.25	0.25	0.1962 (12)	0.34 (12)
F (2a)	0.75	0.25	0	0.34 (35)
Cl (2c)	0.25	0.25	0.6432 (14)	0.70 (17)

reflexions, probably due to hydration, was observed. Because of this, only the first 120 measured intensities were considered, of which 114 had $F \geq 4\sigma(F)$. These were used in the final refinement to the isotropic level, with temperature factors expressed as $\exp[-8\pi^2 U(\sin^2/\lambda)^2]$.* The final atomic parameters (Table 3) correspond to $R = 8.1\%$ ($R_w = 6.7\%$).

Discussion

The results should allow a better interpretation of the EPR, ENDOR, Raman and luminescence spectra (Bill, Moret & Lacroix, 1969; Cevey & Lacroix, 1970; de Siebenthal, Bill & Lacroix, 1974; Nicollin & Bill, 1976, 1977).

Flahaut (1974) showed that the PbFCl-type compounds can be divided into a real PbFCl type and a ternary variant of the anti-Fe₂As type, according to the c/a ratio as a function of the z_M coordinate of the metal (Fig. 2). The distinguishability of one type from the other seems to depend on whether the interactions between the X atoms within the corresponding layer are mainly ionic, like F in PbFCl, or mainly covalent, like Si in NbSiAs. The dependence of the c/a ratio on the nature of the intralayer bonding has been noted by

* Lists of structure factors for BaFI, BaFBr and CaFCl have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32572 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

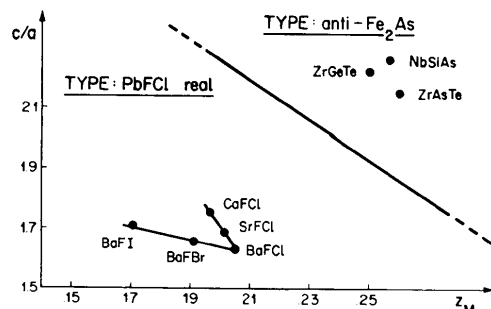


Fig. 2. The c/a cell-parameter ratio as a function of the z_M metal coordinate for MXY compounds including those presently examined. The boundary line (Flahaut, 1974) separates the PbFCl structure type into two variants: the real PbFCl type and the ternary variant of the anti-Fe₂As type.

Johnson & Jeitschko (1973). Fig. 2 shows that the ionic MXY compounds of the present study are real PbFCl type structures, and that their c/a ratios as a function of z_M form two straight lines intersecting at a minimum on BaFCl.

Fig. 3 shows that, as the cell volume of the compounds increases, the ratios $(r_Y + r_X)/r_M$ and c/a go through a minimum, indicating for the two series of values the same trend.

The variations of interatomic distances and angles as well as the distances between the parallel monatomic layers are now examined. The values found for BaFI, BaFBr and CaFCl are given in Tables 4, 5 and 6; the latter two tables also include the values for BaFCl and SrFCl.

The section of the unit cell along c composed of a layer of metal atoms and a layer of F atoms is first considered. As shown in Fig. 4, the distance M^i-F^j as a function of the cell volume varies rapidly from CaFCl to BaFCl and then slowly from BaFCl to BaFI, thus showing a similar variation with the size of the cations.

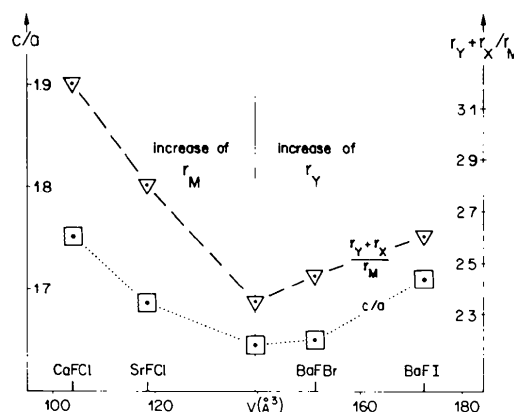


Fig. 3. The ratios c/a of the cell parameters and $(r_Y + r_X)/r_M$ as a function of the cell volume (Å³), where r_M , r_Y , r_X are the ionic radii according to Pauling (1960) for the MXY compounds examined. E.s.d.'s are within the sides of the box around experimental points.

Table 4. Interatomic distances (Å) and angles (°) for title compounds MXY with $X = F$

	BaFI	BaFBr	CaFCl
M^i-F^i	2.694 (2)	2.665 (3)	2.362 (5)
M^i-Y^i	3.836 (7)	3.412 (8)	3.048 (16)
M^i-Y^{ii}	3.581 (2)	3.401 (3)	2.963 (5)
F^i-F^{ii}	3.291 (2)	3.188 (2)	2.753 (2)
F^i-Y^{ii}	3.617 (4)	3.446 (5)	3.116 (9)
Y^i-Y^{ii}	4.087 (3)	3.889 (4)	3.376 (9)
$F^i-M^i-F^{ii}$	119.5 (1)	115.5 (2)	111.0 (4)
$F^i-M^i-Y^i$	75.30 (5)	73.46 (7)	71.3 (2)
$F^i-M^i-Y^{ii}$	120.25 (6)	122.25 (8)	124.5 (2)
$Y^i-M^i-Y^{ii}$	66.78 (6)	69.61 (8)	68.3 (2)
$Y^{ii}-Y^i-M^i$	53.62 (6)	55.05 (9)	54.7 (2)

Table 5. *Interlayer distances (Å) along c*

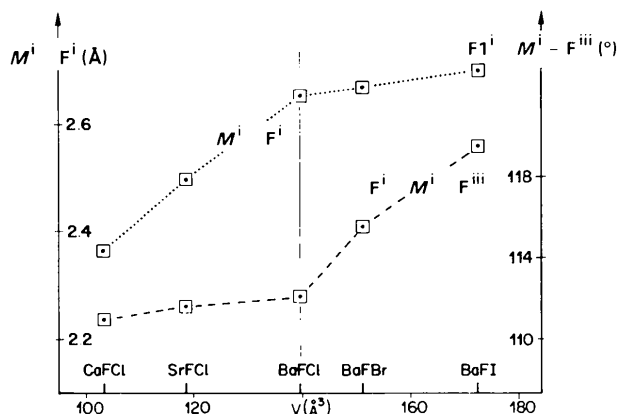
	BaFI	BaFBr	BaFCl*	SrFCl*	CaFCl
Plane (M^i)—Plane (F)	1.357	1.422	1.480	1.402	1.338
Plane (M^i)—Plane (Y^{ii})	1.412	1.185	1.069	1.083	1.095
Plane (Y^{ii})—Plane (Y^i)	2.424	2.228	2.127	1.989	1.953

* Values from Sauvage (1974).

Table 6. *Selected interatomic distances (Å) and angles (°)*

	BaFI	BaFBr	BaFCl*	SrFCl*	CaFCl
F^i — F^{ii}	3.291	3.188	3.107	2.918	2.753
Y^i — Y^{ii}	4.087	3.889	3.765	3.531	3.376
M^i — Y^i	3.836	3.412	3.196	3.072	3.048
M^i — Y^{ii}	3.581	3.401	3.286	3.112	2.963
M^i — F^i	2.694	2.665	2.649	2.494	2.362
Y^i — M^i — Y^{ii}	66.8	69.6	71.0	69.6	68.3
Y^{ii} — Y^i — M^i	53.6	55.1	55.6	55.7	54.7
F^i — M^i — F^{iii}	119.5	115.5	112.1	111.6	111.0

* Values from Sauvage (1974).

Fig. 4. Distance M^i — F^i (Å) and angle F^i — M^i — F^{iii} (°) as a function of the cell volume (Å^3).

These M^i — F^i distances (Table 6) lie near the sum of their ionic radii (Pauling, 1960) with, however, a slight negative deviation decreasing from BaFCl to BaFI. The distances F^i — F^{ii} (Table 6) increase from CaFCl (2.753) to BaFI (3.291 Å) with an increasing deviation from the sum of ionic radii from 0.03 to 0.57 Å. It has been noticed here that the volumes, defined by the product $z_V ca^2$, of this cell section vary in a comparable way with the distances M^i — F^i . Fig. 4 also illustrates the variation of angle F^i — M^i — F^{iii} with cell volume. In contrast to the other plot on this figure, the variation is less pronounced going from CaFCl to BaFCl than from BaFCl to BaFI. It can be observed that this angle, as well as the angle F^i — M^i — M^{ii} , is more affected by the variation of the type of the remote anions than by the variation of the cation type.

The difference in the electronegativities ($\phi_Y - \phi_M$) (Pauling, 1960) as a function of the cell volume varies little from CaFCl to BaFCl (values of 2.0, 2.0 and 2.1 respectively) but then decreases in a more pronounced way in BaFBr and BaFI (values of 1.9 and 1.6). Therefore the variation of ($\phi_Y - \phi_M$) shows a changing trend at BaFCl such as is also observed on Fig. 4 for the angle F^i — M^i — F^{iii} , but in the opposite direction.

The section containing one layer of metal atoms and two layers of halogens (Y) is considered next. The deviation from the sum of the ionic radii is positive for all M — Y distances. The angle Y^i — M^i — Y^{ii} goes through a maximum at BaFCl, and the angle Y^{ii} — Y^i — M^i presents a much smaller variation with a maximum at SrFCl. In Fig. 5 the variation of distance Y^i — Y^{ii} , increasing regularly from CaFCl to BaFI with the cell volume, is shown, together with the corresponding variation of the sum of the ionic radii ($2r_Y$). Negative deviations of about 0.2 Å are observed for CaFCl as well as for BaFI in contrast to the positive deviation for BaFCl.

EPR studies on V_K centres, Cl_2^- , in SrFCl and BaFCl (Bill, Moret & Lacroix, 1969; Yuste, Taurel & Rahmani, 1975) led respectively to the values of 52.5 and 53.0° for angles Y^{ii} — Y^i — M^i between (Cl—Cl) and c . These values lie near the corresponding angles obtained by X-ray analysis for this group of MX_Y compounds. Other EPR measurements with Mn^{2+} substituting Sr^{2+} in SrFCl have been reported (Cevey & Lacroix, 1970; Zevenhuijzen, van Winsum & den Hartog, 1976). These results show greater interaction of Mn^{2+} with the four F than with the five Cl atoms and furnish a larger value for angle F^i — M^i — F^{iii} than that found from X-ray data.

Recently, EPR results of Gd^{3+} and Eu^{2+} -doped

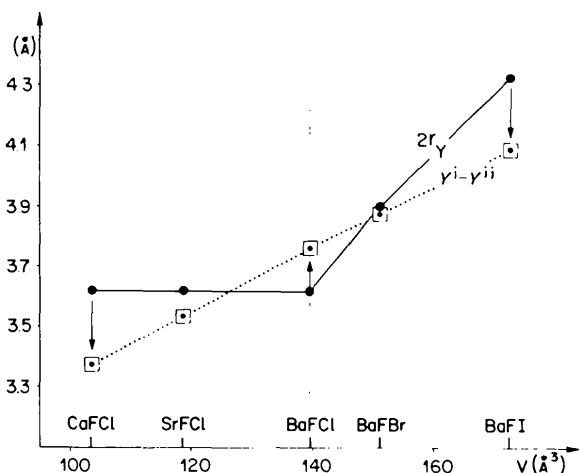


Fig. 5. Distance Y^i-Y^{ii} (\AA) and $2r_Y$ [ionic radii according to Pauling (1960)] as a function of the cell volume (\AA^3).

SrFCI and BaFCI were published (Nicollin & Bill, 1976) in which the precise crystallographic data were needed for use with the theoretical model of Newman (1971). These calculations can now be extended to BaFI, BaFBr and CaFCI (Nicollin & Bill, 1977). Furthermore, the values obtained by Nicollin & Bill (1977) for the EPR (b_2^0) parameter, measured on Gd^{3+} and Eu^{2+} -doped CaFCI, SrFCI, BaFCI, BaFBr and BaFI, can be correlated with structural parameters such as $z_Y c/a$ or angle $F^i-M^I-F^{iii}$. This correlation is almost linear from CaFCI to BaFCI and then, with a different slope, from BaFCI to BaFI.

With ENDOR measurements on doped BaFCI and SrFCI, the same authors have obtained information on angle $F^i-M^I-F^{iii}$ as well as on the interaction of the S -state ions with the F atoms. These results together with the structural data show the strong interaction between the F and metal layers in this group of ionic compounds.

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