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Structures of Cesium Containing Fluorides, VI: The Pyrochlore-Related Layer Structures of $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18+x}$

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The crystal structures of the hexagonal compounds $Cs_4CoCr_4F_{18}$ (a = 720.3, c = 1076.1 pm) and $Cs_4Cr_5F_{18.24}$ (a = 720.0, c = 1067.9 pm), both crystallizing in space group $P\bar{3}m1$, Z = 1, have been determined (R_g = 0.041 and 0.045, respectively). They exhibit a new triple layer arrangement of octahedra, which has the composition M_5F_{18} and derives from the $RbNiCrF_6$-type pyrochlore structure. The overall average distances are M–F = 192.9 and 192.0 pm for the Co(II) and the Cr(II) compound, respectively, the smaller value of the latter being mainly due to the higher Cr(III) portion in it. The compensating anion excess is located and its influence discussed, as well as the evidence on the distribution of M(II) and M(III) ions on the lattice sites, including some hints on the presence of a Jahn–Teller distortion in the Cr(II) compound.

Introduction

In the course of our studies to grow single crystals of $CsCrF_4$ (*2, 3*) we used chloride fluxes $CsCl/CoCl_2$ (*3*), as similar systems have been successfully applied (*4, 5*) to get single crystals of the modified pyrochlores $A^IM^{II}M^{III}F_6$ (A^I = Rb, Cs; M^{II}, M^{III} = 3d transition metal ions) (*6, 7*). In the present case, in addition to the octahedral crystals of the cubic pyrochlore $CsCoCrF_6$, the formation of platelike crystals of another, hexagonal species was observed. Their composition $Cs_4CoCr_4F_{18}$ with $M:F$ = 5 : 18 was new for a fluoride and lies just between that of pyrochlores or perovskites (6 : 18 = 1 : 3) and that of binuclear $Cs_3Fe_2F_9$ (*8*) (4 : 18 = 2 : 9). Our interest in the structure of this new compound was stimulated when we found crystals of a nearly isodimensional and obviously isostructural phase, which formed in slowly cooled melts of pure $CsCrF_4$ and which had a slightly fluoride excessive composition $Cs_4Cr_5F_{18+x}$ (*3*). In this paper we report the results of our single crystal structure determinations of both compounds $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18+x}$ (x = 0.24).

Experimental

Preparation

Crystals of $Cs_4CoCr_4F_{18}$ were grown from a flux of 3 $CoCl_2$ + 18 CsCl + 2 CsF + 2 CoF_2 + 4 CrF_3, which was heated at 850°C during 12 hr and slowly (8°C/hr)

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TABLE 1

CELL DIMENSIONS OF THE TRIGONAL COMPOUNDS $Cs_4M^{II}Cr_4F_{18(+x)}$ (M^{II} = Cr, Co: FROM SINGLE CRYSTALS; M^{II} = Ni, Mg: FROM POWDER DATA) AND OF CUBIC[a] PYROCHLORES $CsM^{II}CrF_6$

	$Cs_4Cr_5F_{18.24}$	$Cs_4CoCr_4F_{18}$	$Cs_4NiCr_4F_{18}$	$Cs_4MgCr_4F_{18}$
a(pm)	720.0	720.3	718.1	716.9
c(pm)	1067.9	1076.1	1072.5	1074.4
c/a	1.483	1.494	1.494	1.499
$V(10^{-30}\ m^3)$	479.4	483.5	479.0	478.2
$d(g\ cm^{-3})$ calculated for $Z = 1$	3.944	3.917	3.953	3.840
$d(g\ cm^{-3})$ measured		3.87		
$r_{M^{II}}$(pm) (*17*)	74.3	72.6	69.0 (*18*)	68.2
a(pm) (*17*) $CsM^{II}CrF_6$	1040.5 (*19*)	1036.6	1028.8	1027.0

[a] From the cell volume of the orthorhombic pyrochlore $CsCr_2F_6$ (*19*) a pseudocubic lattice constant is calculated. It agrees well with cubic a = 1039.5 pm found in multiphase mixtures of the compound (*3*).

cooled then to 300°C. Together with small amounts of dark $CsCoCrF_6$ octahedra, greenish plates of cleavable crystals were found in the mass. The chemical analysis of the plates fitted the composition $Cs_4CoCr_4F_{18}$: Cs 46.4 (46.61 calculated), Co 5.1 (5.17), Cr 18.1 (18.24), F 29.9 (29.98)%.

Polycrystalline samples of this compound and its homologs $Cs_4M^{II}Cr_4F_{18}$ with M^{II} = Mg, Ni could also be obtained by prolonged heating (920°C) of stoichiometric mixtures of the binary component fluorides. However, our efforts to vary the Cr(III) ions by substitution with M^{III} = Al, V, Fe or to prepare rubidium compounds were unsuccessful. In all these cases only pyrochlore $AM^{II}M^{III}F_6$ and $AM^{III}F_4$ phases could be identified.

Some bottle green crystals of $Cs_4Cr_5F_{18+x}$ were found in the partly decomposed mass which had formed after slow cooling (4–5°C/hr) of melts of $CsCrF_4$ (or CsF + CrF_3 mixtures) in sealed platinum tubes from 1000 to 600°C (*3*). The composition $Cs_4Cr_5F_{18.24}$, derived from the structure determination, may get its Cr(II) content from the disproportionation $3\ CrF_3 \rightarrow 2\ CrF_2 + CrF_5$, which is quantitative at 1100°C (*9, 10*), but noticeable already at 850°C (*11*). However, powder preparations using CrF_2 to get $Cs_4Cr_5F_{18}$ always resulted in multiphase mixtures (*3*). Obviously the formation of small amounts of CrF_2 during heating near the incongruent melting point of $CsCrF_4$ (936°C) (*12*), followed by prolonged cooling, is essential for the growth of $Cs_4Cr_5F_{18+x}$ phase crystals within the main product of $CsCrF_4$, containing also some Cs_3CrF_6.

Crystal Studies and Data Collection

Selected crystals of $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18+x}$ were of trigonal symmetry and mainly bounded by faces {001}, {100}, {010}, {110}, and $\{1\bar{1}0\}$. Precession photographs, which showed no systematic absences, were in accordance with Laue group $\bar{3}m$. From the possible space groups $P\bar{3}m1$, $P3m1$, and $P321$ (*13*) the centrosymmetric one, $P\bar{3}m1$, was selected, as no evidence of acentricity could be obtained from nonlinear optical measurements on $Cs_4CoCr_4F_{18}$.

The lattice constants of the crystals and those refined of powder samples of isostructural $Cs_4MgCr_4F_{18}$ and $Cs_4NiCr_4F_{18}$ are shown in Table 1. The cell dimensions a_c of the corresponding cubic pyrochlores $CsM^{II}CrF_6$ are given for comparison; the relation $a \approx a_c/\sqrt{2}$, $c \approx a_c$ is obvious.

The conditions of data collection using automatic 4 circle diffractometers CAD4 (ENRAF–NONIUS) are listed in Table 2, which also shows the final reliability factors and the computers and programs used. The atomic form factors used were those of the ions given in parametric form (*14, 15*). Anomalous dispersion corrections have been applied (*14, 16*).

Structure Determination

From Patterson syntheses it became evident that the four cesium atoms in the unit cell of the basic $Cs_4M_5F_{18}$ structure are situated in two different twofold positions, Cs1 in 2*c* (0,0,*z*) and Cs2 in 2*d* ($\frac{1}{3}$,$\frac{2}{3}$,*z*) of space group $P\bar{3}m1$ (*13*), with $z \approx 0.23$ and 0.37, respectively. These atoms are centered by a layer containing three of the five transition metal ions (*M*1), which could be localized in the fixed threefold position 3*e* ($\frac{1}{2}$,0,0). Regarding the metric relations to the pyrochlore structure the octahedrally coordinating ligands F1 and F2, both in sixfold positions 6*i* ($x,\bar{x},z$) near the layer, could

TABLE 2

CONDITIONS OF DATA COLLECTION AND TREATMENT

	$Cs_4CoCr_4F_{18}$	$Cs_4Cr_5F_{18.24}$
Radiation	Mo*K*α-graphite monochromatized	— Mo*K*α
Crystal size (mm)/volume (10^{-3} mm³)	0.14 × 0.42 × 0.06	0.16 × 0.27 × 0.07/2.53
Absorption coefficient μ(cm^{-1}) for Mo*K*α	104.8	98.3
Transmission factors: minimum, maximum	0.238, 0.550	0.238, 0.534
Scanning:		
Mode	$\omega/2\theta$	$\omega/2\theta$
Aperture (°)	$(1.6 + 0.45 \tan\theta)$	$(1.5 + 0.3 \tan\theta)$
Time (sec)	variable, max. 50	variable, max. 45
Range registered:		
θ_{min}, θ_{max}(°)	1, 35	2, 45
h k l (min)	−11, 0, −17	−14, 0, 0
h k l (max)	11, 11, 17	14, 14, 21
Reflections measured		
Total	3414	4303
Suppressed	all $I \leqq 3\sigma(I)$	—
Independent ($R_{average}$)	770 (0.0207)	1535 (0.0326)
Used in refinement	671 ($F_o > 6\sigma(F_o)$)	834 ($F_o > 2\sigma(F_o)$)
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0449	0.0413
$R_g = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_o^2]^{1/2}$	0.0411	0.0451
Weight w =	$k/(\sigma^2(F_o) + 5 \cdot 10^{-6} F_o^2)$	$k/\sigma^2(F_o)$
k refined	15.761	0.5001
Extinction correction ε in F_c(corr.) = $F_c(1 - \varepsilon F_c^2/\sin\theta)$	$4.51 \cdot 10^{-6}$	—
Computer	IBM 370/168 CIRCE (Orsay)	TR440, Rechenzentrum der Philipps-Universität Marburg
Programs	SHELX (*22*)	System STRUX (*20*) including CADLP (*21*), SHELX (*22*)

TABLE 3

ATOM PARAMETERS FOR $Cs_4CoCr_4F_{18}$ (UPPER LINE; $M = Co^{II}_{0.33}Cr^{III}_{0.67}$) AND $Cs_4Cr_5F_{18.24}$ (LOWER LINE; $M = Cr^{II}_{0.25}Cr^{III}_{0.75}$) IN SPACE GROUP $P\bar{3}m1$ (THE ANISOTROPIC TEMPERATURE FACTORS U_{ij} REFERRING TO THE EXPRESSION $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^*)]$ ARE MULTIPLIED BY 10^4)

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	2*c*	0	0	0.22510(11)	415(3)	U_{11}	741(7)	0	0	208(2)
				0.22765(9)	328(2)		574(5)			164(1)
Cs2	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	0.37383(8)	690(4)	U_{11}	256(4)	0	0	345(2)
				0.37306(7)	578(4)		212(3)			289(2)
Cr	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	0.71764(13)	157(4)	U_{11}	114(6)	0	0	78(2)
				0.71642(11)	170(3)		118(4)			85(2)
M	3*e*	$\frac{1}{2}$	0	0	104(3)	75(4)	167(5)	−10(4)	−21(8)	37(2)
					162(3)	100(4)	164(3)	−9(3)	−5(2)	50(2)
F1	6*i*	0.20494(27)	$-x$	0.03863(33)	185(10)	U_{11}	332(17)	−43(8)	$-U_{23}$	48(12)
		0.20391(37)		0.03982(38)	302(12)		442(19)	−74(10)		47(16)
F2	6*i*	0.54091(25)	$-x$	0.17336(31)	337(13)	U_{11}	221(15)	9(7)	$-U_{23}$	272(15)
		0.54121(27)		0.17326(28)	445(16)		214(12)	8(6)		359(18)
F3	6*i*	0.79331(30)	$-x$	0.37813(35)	466(15)	U_{11}	303(18)	−5(8)	$-U_{23}$	329(17)
		0.79060(32)		0.37818(32)	568(21)		268(15)	29(7)		457(23)
F4	1*b*	0	0	$\frac{1}{2}$	400 (fixed), 0.24(3) occupancy, leading to $Cs_4Cr_5F_{18.24}$*					

**Note added in proof.* Final simultaneous refinement of temperature factor and multiplier for F4 lead to $U = 616(180) \cdot 10^{-4}$ and 0.29(5) occupancy, both correlating with a factor of 0.74.

be found around the atoms *M*1. Finally, on both sides of this layer, the remaining two atoms *M*2 could be detected in a 2*d* position ($z \approx 0.72$) just opposite to that of the cesium atoms Cs2 and occupying octahedral sites between the ligands F2 and F3. The additional anions F3 are positioned once more in 6*i*, where they have about the *z* height of Cs2 and nearly the same *x*,*y* coordinates as the F1 ligands (*3*).

The resulting model of composition $Cs_4M_5F_{18}$ could be refined for both compounds to about $R = 0.1$ using isotropic temperature factors. Anisotropic refinement of the cobalt compound $Cs_4CoCr_4F_{18}$ was performed then with mixed atoms $M = (Co + nCr)/(1 + n)$ in (1) only 2*d* positions, (2) only 3*e* positions, (3) both positions. The resulting R_g factors were 0.060, 0.041, and 0.044, respectively, favoring version 2. The final atomic coordinates, listed in Table 3, refer to an atom mixing $M = Co^{II}_{0.33}Cr^{III}_{0.67}$, in which all Co(II) ions are distributed on 3*e* positions and 2*d* positions consist only of Cr(III) ions.

The analogous distribution of Cr(II) ions was assumed to be valid for the mixed-valent chromium compound $Cs_4Cr_5F_{18}$. In the final difference Fourier map, however, the strongest peak, corresponding to the special position 1*b* (0,0,½), indicated the presence of some electron density at this site, which is just midway between the Cs1 atoms and 291 pm away from them. For an additional fluorine atom F4 in this position multiplicity and isotropic temperature factors could be successfully refined. The resulting temperature factor was the same as the mean value of the other anions within its standard deviation. With the temperature factor fixed at this value, the atom multiplier refined to 0.0198(24), corresponding to 0.24(3) occupancy, also noted in Table 3. An improvement of R_g from 0.047 to 0.045 accompanied this change of composition despite its small contribution of only about 0.4% to the total scattering power. In the resulting formula $Cs_4Cr_5F_{18.24}$ the chromium(II) content is therefore only 0.76 instead of 1 Cr(II) ion per unit cell. Under the

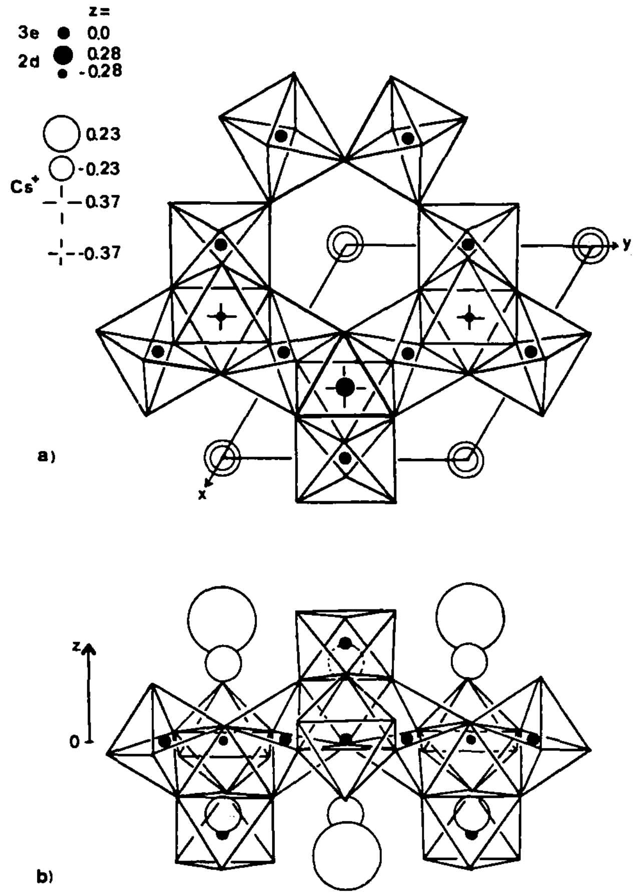

FIG. 1. Octahedral network in the structure of the compounds $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18.24}$. (a) Projection [001]; (b) projection [210].

assumption mentioned this corresponds to 0.76 Cr(II) + 2.24 Cr(III) in the $3e$ position, or $M = Cr^{II}_{0.25}Cr^{III}_{0.75}$ for the mixed atom, as also stated in Table 3.

Another indication of lowered Cr(II) and increased Cr(III) content may be seen in the smaller cell volume of $Cs_4Cr_5F_{18.24}$ compared to $Cs_4CoCr_4F_{18}$, as $r_{Cr^{3+}} < r_{Co^{2+}} < r_{Cr^{2+}}$ (17, 18) (see Table 1). Still more convincing seems the significant contraction of the c axis and consequently c/a in the mixed-valent chromium compound, quite in accordance with lowered repulsion of the Cs1 ions by some additional fluoride ions between them. On the other hand, arguments based on the Jahn–Teller effect of the Cr(II) ion could equally well account for some distortion. This will be discussed later.

The anisotropic thermal parameters of the atoms in the structures of $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18.24}$ are also listed in Table 3. Tables of the structure factors F_o and F_c are omitted here, but are available from the authors upon request.

Results and Discussion

The structure of the $Cs_4M_5F_{18(+x)}$ compounds determined is shown in projections [001] and [210] in Figs. 1a and b, respectively. The triple layer arrangement of octahedra found in the structure is just a section

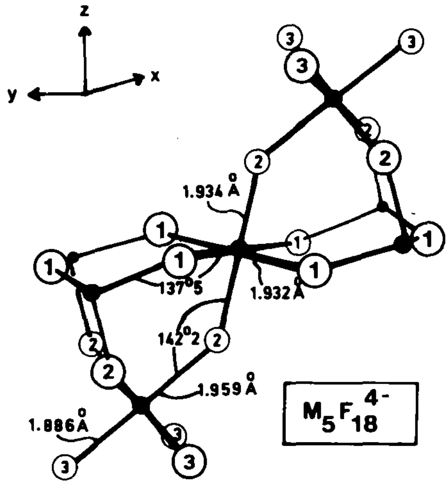

FIG. 2. The $M_5F_{18}^{4-}$ content of one unit cell of $Cs_4CoCr_4F_{18}$. The central cation is situated in ½,½,0 of position 3e in space group $P\bar{3}m1$.

of the framework of the cubic pyrochlores $A^{I}M^{II}M^{III}F_6$, where layers of exactly the same kind extend along the (111) planes (*7*). But in the pyrochlores these layers are further connected to identical ones, so as to make all ligands bridge in the same way; this results in a composition $M_2F_6^-$. The different composition $M_5F_{18}^{4-}$ is illustrated in Fig. 2, showing just the content of 18 ligands within one hexagonal unit cell of $Cs_4CoCr_4F_{18}$. In this compound only the ligands F1 and F2 bridge; the F3 species, contrary to the pyrochlores, are terminal. This is also reflected by the distances Cr–F3 being the shortest in the network of octahedra of $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18.24}$ (see Fig. 2 and Table 4).

The pyrochlore-related layer structure shown in the figures consists of a central puckered sheet, where the *M* ions in position (3*e*) form triangles and hexagons, as also found in sections of the hexagonal tungsten bronze (*1*, *23*) and weberite structures (*24–26*). However, an identical central single layer is known in the compound $Cs_2NaAl_3F_{12} = Cs_{0.67}Na_{0.33}AlF_4$ (*27*). But, as the other varieties of $AAlF_4$ layer structures do (*28*, *29*), it exhibits four longer bridging bonds within and two shorter terminal ones normal to the layers. The new and special feature of the $Cs_4M_5F_{18(+x)}$ structure is that such an isolated single layer becomes triple by condensing to it additional transition metal centered octahedra, which are located in turn at the upper and the lower sides of the triangles mentioned (see Fig. 1). The tetrahedra of cations formed this way are but slightly elongated to trigonal pyramids, as may be seen from the distances Cr–*M* > *M*–*M* (see Table 4). Undistorted cation tetrahedra with similar distances, e.g., *M*–*M* = 366.5 pm in $CsCoCrF_6$, are found in the pyrochlores (*7*).

One half of the cesium atoms (Cs2) of the $Cs_4M_5F_{18(+x)}$ structure is inserted between the triple layers just at the opposite side of the central triangles of cations, in face of the additional octahedra. The other half (Cs1) is arranged above and below the hexagons mentioned. This corresponds once more to the cubic pyrochlore structure, where the cesium atoms are positioned in a distance of $a\sqrt{3}/8$ away from the central layer and twice this value, Cs–Cs = 448.9 pm in $CsCoCrF_6$, away from each other. In the $Cs_4M_5F_{18(+x)}$ structures, where the layers are separate, a considerably enlarged distance of about Cs1–Cs1 = 485 pm is found (see Table 4). Still larger is the corresponding distance between Cs1 atoms situated at neighboring layers. It is large enough to make insertion of additional anions possible, as found in the fluoride excessive compound $Cs_4Cr_5F_{18.24}$. Not only the shorter *c* axis of this compound, as already mentioned before, but also the still more contracted Cs1–Cs1 distance of 581.7 pm, compared to 591.6 pm in $Cs_4CoCr_4F_{18}$, demonstrate the presence of some excessive anions (F4) in it. They lower the repulsion by some Cs1–F4–Cs1 insertion. Perhaps the resulting short distances F4–Cs1 prevent the F4 position, which is just halfway between the layers and surrounded by

TABLE 4

INTERATOMIC DISTANCES AND ANGLES OF $Cs_4CoCr_4F_{18}$ (M = $Co^{II}_{0.33}Cr^{III}_{0.67}$) AND $Cs_4Cr_5F_{18.24}$ (M = $Cr^{II}_{0.25}Cr^{III}_{0.75}$) (STANDARD DEVIATIONS IN PARANTHESES. IN THE CASE OF ANGLES, THESE ARE 0.1° OR LESS, IF NOT OTHERWISE STATED)

		Co(II) compound		Cr(II) compound				Co(II) compound	Cr(II) compound
		Distance (pm)	Angle at center (°)	Distance (pm)	Angle at center (°)			Distance (pm)	Distance (pm)
M–F2	2×	193.4(2)		192.0(3)		Cs1–F3	3×	306.0(4)	306.6(3)
–F1	4×	193.2(1)		193.7(2)		–F1	3×	324.9(3)	323.9(3)
M–F	av	193.3		193.1		–F2	6×	368.0(4)	368.3(2)
						Cs1–F	av	341.7	341.8
F1–F1	2×	268.9(5)	88.2	268.1(4)	87.6				
–F1	2×	277.5(6)	91.8	279.6(3)	92.4	Cs1–Cs1		484.5/ 591.6	486.2/581.7
–F2	4×	268.8(4)	88.1	267.8(4)	88.0	F4–Cs1	2×		290.8(1)
–F2	4×	277.8(5)	91.9	277.6(4)	92.0	F4–F3	6×		291.7(2)
F1–F1	2×		180.0		180.0				
F2–F2			180.0		180.0	Cs2–F3	3×	310.2(4)	307.3(3)
F–F	av	273.3		273.1		–F2	3×	337.0(3)	335.8(2)
						–F3	6×	363.6(3)	364.0(2)
Cr–F3	3×	188.6(2)		184.6(3)		Cs2–F	av	343.6	342.8
–F2	3×	195.9(2)		195.9(2)					
Cr–F	av	192.2		190.2		Cs2–Cr		370.0(2)	366.7(1)
						Cr–M		368.2(2)	367.3(1)
F2–F2	3×	271.8(5)	87.8	271.0(2)	87.6	M–M	*a*/2	360.1	360.0
F3–F3	3×	273.6(7)	93.0	267.7(3)	92.9				
F2–F3	6×	270.8(4)	89.5	268.5(4)	89.7			angle (°)	
F2–F3	3×		179.3		176.2				
F–F	av	271.7		268.7		M–F1–M		137.5	136.7(2)
						M–F2–Cr		142.2	142.5

a puckered ring of six anions, from being fully occupied. This would result in isostructural compounds $Cs_4M_5F_{19}$, which to our knowledge have never been observed in 4 CsF : 5 MF_3 systems.

Neglecting the possible presence of excessive anions, the cesium ions in both positions and structures are similarly coordinated by 12 anions in strongly distorted cuboctahedral arrangements. The average distances Cs–F of more than 340 pm are untypically high for 12-coordination. In fact the average distances of the six nearest anions are close to 320 pm, similar to the conditions observed in the pyrochlores within their 6 + 12 = 18 coordination around the alkali ions (*6, 7*). In the $Cs_4M_5F_{18(+x)}$ structures there are also three additional anions at each cesium atom, which may or may not be counted to enlarge their coordination sphere to 15. However, these distances in the range Cs–F = 387 ± 5 pm exceed the shortest cation separation of about 370 pm for the cesium atoms, and are not listed in Table 4.

At first sight the interatomic distances and angles within the triple layers of distorted octahedra are very much the same in $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18.24}$. The average anion bridging angles of nearly 140° agree well with 141° for undistorted octahedra in ideal pyrochlores (*7*). One larger discrepancy concerns the distances Cr–F3 of the terminal ligands and hence the mean values Cr–F, which are in the compound $Cs_4Cr_5F_{18.24}$ in significantly better agreement with Cr–F = 190.5 ± 0.5 pm found in many Cr(III) fluorides (*2, 30–35*). It seems possible therefore, that the greater distance in the cobalt compound is caused by some Co(II) mixing with Cr(III) ions in the 2*d* position, contrary to the assumption based solely on the *R* factor criterion. From the chemical point of view, however, this assumption of only higher valent cations in this site, offering better charge balance by its terminal ligands, also seemed well justified.

One smaller discrepancy between $Cs_4CoCr_4F_{18}$ and $Cs_4Cr_5F_{18.24}$ is the splitting of distances *M*–F of the presumably mixed cations *M* in the latter compound. The mean values 193.3 and 193.1 pm, respectively, are close to expectation from the ionic radii listed in Table 1. These radii, as well as $r_{Cr^{III}} = 61.4$ pm, were derived from pyrochlore dimensions (*17*). Taking Shannon's radius of 2-coordinated fluoride ions, $r_F = 128.5$ pm (*18*), and considering the atom mixing ($Co^{II} + 2\ Cr^{III}$)/3 and ($0.76\ Cr^{II} + 2.24\ Cr^{III}$)/3, *M*–F values of 193.6 and 193.2 pm, respectively, are calculated. But to account for the splitting in the chromium(II) compound, the Jahn–Teller effect (*36*) may be claimed.

The difference of 1.7 pm between the two shorter *M*–F2 and the four longer *M*–F1 bonds seems small, but the Cr(II) content which is believed to cause it is also small. However, compression of octahedra like this is rarely found in Jahn–Teller systems (*37*). It should be interpreted therefore as simulated by a disorder of longer and shorter axes within the *M*–F1 plane of long average bonds or by a planar dynamic Jahn–Teller effect. These models, which have been used to explain the much more marked pseudo-compression of octahedra in $CsMnF_4$ (*38*) [Mn(III) being isoelectronic with Cr(II)] are based on the assumption of essentially elongated octahedra. An indication of their presence may be found by comparing the individual atomic temperature factors of the Cr(II) and the Co(II) compound (see Table 3).

In fact just the U_{11} components of the concerned atoms *M* and F1 in the chromium(II) compound are at least 20% more enhanced than is true for all other atoms and main temperature factors compared to the cobalt compound. In addition, the standard deviations of coordinates, being very much the same in corresponding pairs of the other atoms, are significantly higher for the F1 atoms only in $Cs_4Cr_5F_{18.24}$. Therefore, regarding the low Cr(II) content in this compound, the evidence seems sufficient that there is a Jahn–Teller distortion towards elongated octahedra, static or dynamic, effective in it and responsible for its small deviations from the cobalt compound.

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