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NEW COPPER FLUOROCOMPOUNDS AND THEIR CRYSTAL STRUCTURES

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The compounds Na_2CuCrF_7, Na_2CuFeF_7, $Cu_3M_2F_{12}\cdot 12\ H_2O$ (M^{3+} = V, Cr, Fe) and $Ba_2Cs_2Cu_3F_{12}$ were prepared in the form of single crystals and their structures determined by X-ray methods. The resulting average distances, Cu - F and Cu - O, respectively, for the Jahn-Teller distorted elongated CuX_6 octahedra are listed in Table 1 along with further crystal data. The structural relations of Na_2CuCrF_7 and Na_2CuFeF_7 to the weberite types [1-3] were discussed. The hydrates and the barium compound, on the other hand, are both related to the structure types of chiolite and perovskite [3], as illustrated in Figures 1-3 [4].

Table 1: Crystal data and results of X-ray structure determinations

Compound R_g (number of reflections)	S.G. Z	a(pm) α(°)	b(pm) β(°)	c(pm) γ(°)	Cu - F Cu - O	(pm) (pm)
Na_2CuCrF_7	Pmnb	710.0	1033.8	751.8	212.4	2x
0.028(1545)	4				192.5	4x
Na_2CuFeF_7	A2/n	2468.7	734.7	1245.2	207.4	2x
0.089(2805)	16		80.71		194.5	4x
$Cu_3V_2F_{12}\cdot 12H_2O$	$P\bar{1}$	750.8	760.7	812.2	231.0	2x
0.025(2485)	1	91.01	89.80	92.84	196.4	4x
$Cu_3Cr_2F_{12}\cdot 12H_2O$	$P\bar{1}$	746.8	759.5	809.2	231.9	2x
0.024(2547)	1	90.69	89.90	92.84	196.1	4x
$Cu_3Fe_2F_{12}\cdot 12H_2O$	$P\bar{1}$	750.4	761.2	812.4	231.4	2x
0.027(2052)	1	90.81	89.82	92.99	196.4	4x
$Ba_2Cs_2Cu_3F_{12}$	$I4_1/amd$	854.1		1704.1	233.3	2x
0.032(459)	4				190.6	4x

1 A. Byström, Ark. Kemi, 18 (1944) 10.
2 W. Verscharen, D. Babel, J. Solid State Chem. 24 (1978) 405.
3 D. Babel, A. Tressaud, in Inorganic Solid Fluorides, Chemistry and Physics, P. Hagenmuller, ed., Academic Press Inc., chap. 3, 1985, p. 77.
4 S. Kummer, Thesis, Marburg, 1986.

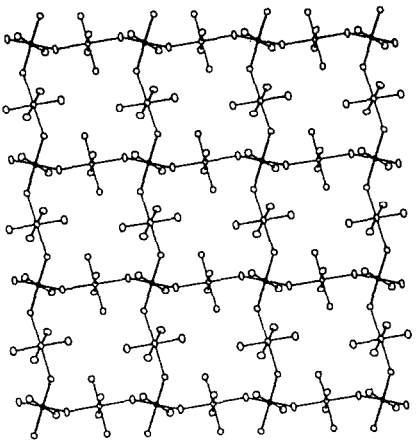

Fig.1. Linking of Octahedra in the triclinic $Cu_3Cr_2F_{12}\cdot 12H_2O$ Structure.

a,c section through nine pseudocubic unit cells.

The CrF_6^{3-} octahedra interconnected by tetra-hydrated $Cu(H_2O)_4^{2+}$ ions form CHIOLITE-like square meshes.

Average bridge angles and distances:

Cr - F - Cu = 131.7°

Cr - F = 190.7 pm

Cu - F = 231.9 pm

Cu - O = 196.1 pm

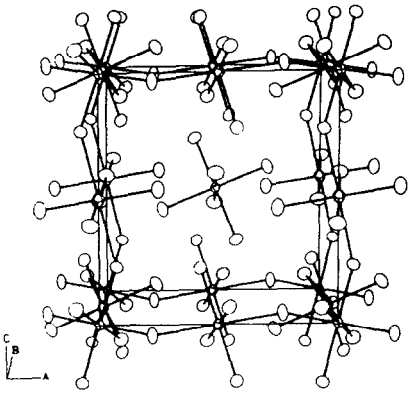

Fig. 2.

The Structure of Hydrated Fluorides $Cu_3M_2F_{12}\cdot 12\ H_2O$ (M^{3+} = V, Cr, Fe) interpreted as ANTI - PEROVSKITE

$MF_6MF_6\ [Cu(H_2O)_4]_3$

A M X_3

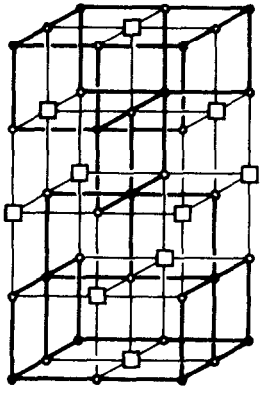

Fig.3.

The Order of Octahedral Vacancies □ in the Cation - deficient PEROVSKITE Structure of

$Ba_2Cs_2Cu_3F_{12} = ACu_{3/4}F_3$ a = 854.1 pm

c = 1704.1 pm

$I4_1/amd$, Z = 4

Cu2: long axes ⊥c

Cu1: long axes ∥c strong lines:

linear Cu1- F -Cu2 bridges