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About the Crystal Structure of $CuNb(OH, F)_7 \cdot 3H_2O$

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Single crystals of $CuNb(OH, F)_7 \cdot 3H_2O$ have been grown from aqueous HF solutions. Their crystal structure is isotypic with that of $CuTiF_6 \cdot 4H_2O$ and consists of bent chains of *trans-F*-linked alternate $Cu(H_2O, OH, F)_6$ and $Nb(OH, F)_6$ octahedra, running along the [101] direction of the monoclinic unit cell ($P2_1/c$, a = 5.590(1) Å, b = 9.978(4) Å, c = 7.544(1) Å, and β = 103.36(1)°; R = 0.0272 and R_w = 0.0272 for 459 reflections and 58 parameters). Bond valence calculations reveal a partial disorder between OH^-, F^-, and water molecules on all the nonbridging anionic sites. The CuX_6 octahedra are classically distorted by the Jahn–Teller effect. A network of O–H . . . F hydrogen bonds ensures the tridimensional cohesion of the structure.

INTRODUCTION

In the course of our general study of complex oxide fluorides of transition metals, the $CuNbOF_5 \cdot 4H_2O$ compound, already mentioned in the literature (1, 2), has been synthesized. According to Fischer *et al.* (1), this oxide fluoride, isostructural with $CuTiF_6 \cdot 4H_2O$ (2), belongs to a series with the general formula $CuMX_6$. $4H_2O$(M = Si, Ti, Zr, Sn, Nb, W, Hf and X = O, F). We report here the synthesis and the crystal structure of the niobium compound and point out that the formula suggested by Fischer *et al.* (1) is probably not correct, based on bond valence calculations and fluorine chemical analysis. We propose the formula: $CuNb(OH)_xF_{7-x}$. $3H_2O$ with x close to 3.

PREPARATION

Crystals of this oxide fluoride were prepared from CuO and Nb_2O_5 (stoichiometric ratio) in acid solution HF (4.6 N) at 150°C in a PTFE beaker. The solution was evaporated and acid re-added a further two times: beautiful light blue crystals were obtained and were only air dried. The chemical analysis of the F content was conducted by pyrohydrolysis (F = 26.3 ± 2.0%) and led to the proposed formula, $CuNb(OH)_xF_{7-x} \cdot 3H_2O$, with x close to 3.

X-RAY DATA COLLECTION AND DETERMINATION OF THE STRUCTURE

A small crystal of approximate size 0.02 × 0.06 × 0.09 mm^3, with natural boundary faces $\pm\langle 111\rangle$, $\langle 11\bar{1}\rangle$, $\langle 010\rangle$, was chosen for the structural determination after standard X-ray photographic studies. The experimental conditions of the X-ray data collection are listed in Table 1; the lattice parameters were refined by the double scan technique from the positions of 34 reflections near 2θ = 30°. The space group proposed by Fischer *et al.* (1, 2), $P2_1/c$(No. 14), is confirmed. All the calculations were made with the SHELX-76 program (3). Atomic scattering factors for Cu^{2+}, Nb^{5+} and F^- ions, $\Delta f'$ and $\Delta f''$ were taken from "International Tables for X-ray Crystallography" (4) and from (5) for O^{2-}.

Direct methods gave the starting model: one Cu and one Nb position. Successive refinements and Fourier difference synthesis showed five anionic sites in agreement with the previous model (2). However, as in such compounds, it was impossible to distinguish O^{2-} and F^-. So, bond valence calculations (6) were made to clear up this question: Table 2 gathers the results. A careful examination of the different values observed shows unambiguously that there are no O^{2-} sites (no bond valence values equal to 2). Water molecules are located in sites 1 and 2 based on the bond valence values of these two sites (0.4). This suggests a new formula with only OH^-, F^- anions (bond valence values are close to 1 for the three other sites), and H_2O molecules, which involves only six water molecules. The chemical analysis of the F content requires: $Cu_2Nb_2(OH)_{2x}F_{14-2x} \cdot 6H_2O$ with x close to 3.

Different attempts to locate the hydrogen atoms of OH^- anions and H_2O molecules were unsuccessful even if the data collection was limited to lower values of 2θ. So, we cannot distinguish OH^- and F^-. Therefore, three quarters of the two sites 1 and 2 are occupied by water molecules (quoted OW1 and OW2). Six OH^- and four F^- anions are statistically disordered on the two sites 3 and 4 (quoted $X1$ and $X2$) and on the last quarter of the sites 1 and 2 (quoted OW1 and OW2), while site 5 (quoted F), linking together CuX_6 and NbX_6 octahedra, is probably only occu-

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TABLE 1

$CuNb(OH)_xF_{7-x}\cdot 3H_2O$: Operating Conditions of the Intensity Data Collection

Symmetry	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	5.590 (1) Å, *5.576(5) Å*
b (Å)	9.978 (4) Å, *9.96(1) Å*
c (Å)	7.544(1) Å, *7.537(7) Å*
β (°)	103.36(1), *103.32(10)°*
V (Å^3)	409.40
Z	2
Formula weight (g)	337.51 (for $x = 3.0$)
D_{calc} (g/cm^3)	2.74 (for $x = 3.0$)
Temperature (°C)	20
Radiation	Mo$K\alpha$ (graphite monochromatized)
Crystal volume (10^{-4} mm^3)	9.31
Scanning mode	$\omega/2\theta$
Aperture (mm)	3.0 × 3.0
Range registered	
θ_{max} (°)	60
h, k, l max	7, 14, 10
Absorption coefficient (cm^{-1})	$\mu = 40.73$
Absorption correction	
Transmission factors	
T_{max}, T_{min}	0.8637, 0.6207
R_{int}	0.0204
Reflections measured	two independent sets −96 standards
Total	1890
Independent	973
Used in refinement ($I > 3\sigma(I)$)	459
Number of refined parameters	58
Electron density in final Fourier difference map maximum, minimum ($e^-/Å^3$)	0.8, −0.5
R, R_w	0.0272, 0.0272

Note. Data calculated on a Siemens AED2 Four-Circle Diffractometer. Italicized values are from Fischer *et al.* (1).

pied by F^- anions. This distribution led to the valence values of the cationic sites for Nb and Cu: 5.44 and 2.11 respectively.

With absorption correction, anisotropic thermal parameters and unit weights, the final stage of refinement converged to $R = 0.0272$ and $R_W = 0.0272$. The Fourier difference synthesis in these conditions was featureless with maxima and minima in the range ± 0.7 $e^-/Å^3$. Tables 3a and 3b present the final atomic coordinates and thermal parameters while the main interatomic distances and angles are given in Table 4 (F_0 and F_c tables will be sent upon request).

DESCRIPTION OF THE STRUCTURE

As described by Fischer *et al.* (1, 2), the framework is built from alternate $Cu(H_2O, F, OH)_6$ and $Nb(F, OH)_6$

TABLE 2

$CuNb(OH)_xF_{7-x}\cdot 3H_2O$: Calculated Valence S for the Anionic Sites[a]

		Cu	Nb	ΣS
Site 1	O^{2-}	0.46		0.46
	F^-	0.37		0.37
Site 2	O^{2-}	0.47		0.47
	F−	0.38		0.38
Site 3	O^{2-}		0.98	0.98
	F^-		0.87	0.87
Site 4	O^{2-}		0.93	0.93
	F−		0.83	0.83
Site 5	O^{2-}	0.18	1.00	1.18
	F^-	0.15	0.90	1.05

[a] For the sites i, $S_i = \Sigma_j \exp[R_{ij} - d_{ij})/b]$ with $b = 0.37$ and R_{ij} for oxygen and fluorine are respectively 1.679 and 1.60 for Cu^{2+} and 1.911 and 1.87 for Nb^{5+} (6).

TABLE 3a

$CuNb(OH)_xF_{7-x}\cdot 3H_2O$: Fractional Atomic Coordinates and Thermal Parameters

	x	y	z	B_{eq} (Å^2)
Nb	$\frac{1}{2}$	0	$\frac{1}{2}$	1.6(7)
Cu	0	0	0	1.6(8)
OW1	0.2287(16)	0.3748(8)	0.4232(9)	4.0(4)
OW2	0.1335(19)	0.6541(10)	0.3937(11)	4.8(5)
$X1$	0.2749(15)	0.1243(8)	0.5682(8)	3.3(3)
$X2$	0.3628(14)	0.6451(7)	0.1159(8)	2.6(3)
F	0.7351(16)	0.4613(6)	0.2212(8)	2.8(2)

TABLE 3b

$CuNb(OH)_xF_{7-x}\cdot 3H_2O$: Anisotropic Thermal Parameters U_{ij} (Å^2 × 10^4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb	241(7)	222(8)	166(8)	−61(8)	1(6)	−71(11)
Cu	230(9)	211(11)	146(10)	−1(11)	64(8)	−109(15)
OW1	592(61)	358(47)	471(44)	−18(37)	274(40)	325(45)
OW2	686(73)	560(60)	526(48)	−68(50)	119(45)	47(56)
$X1$	479(52)	446(50)	278(32)	81(35)	150(33)	−66(41)
$X2$	470(47)	198(33)	239(28)	−51(29)	232(29)	131(34)
F	448(34)	488(34)	182(47)	7(22)	−82(33)	25(32)

TABLE 4
$CuNb(OH)_xF_{7-x} \cdot 3H_2O$: Selected Interatomic Distances (Å) and Angles (°)

			Nb octahedron			
Nb	F	F	*X*1	*X*1	*X*2	*X*2
F	**1.910(6)**	3.820(9)	2.713(9)	2.703(11)	2.693(8)	2.750(10)
F	180.0(2)	**1.910(6)**	2.703(11)	2.713(9)	2.750(10)	2.693(8)
X1	90.2(3)	89.8(3)	**1.920(8)**	3.839(9)	2.741(10)	2.715(11)
X1	89.8(3)	90.2(3)	180.0(2)	**1.920(8)**	2.715(11)	2.741(10)
X2	88.8(3)	91.2(3)	90.5(3)	89.5(3)	**1.939(7)**	3.877(5)
X2	91.2(3)	88.8(3)	89.5(3)	90.5(3)	180.0(2)	**1.939(7)**
			Cu octahedron			
Cu	OW2	OW2	OW1	OW1	F	F
OW2	**1.960(10)**	3.920(8)	2.836(13)	2.717(14)	3.003(12)	3.053(10)
OW2	180.0(3)	**1.960(10)**	2.717(14)	2.836(13)	3.053(10)	3.003(12)
OW1	92.5(4)	87.5(4)	**1.968(9)**	3.936(9)	2.956(11)	3.108(9)
OW1	87.5(4)	92.5(4)	180.0(3)	**1.968(9)**	3.108(9)	2.956(11)
F	89.0(3)	91.0(3)	87.1(3)	92.9(3)	**2.308(6)**	4.616(9)
F	91.0(3)	89.0(3)	92.9(3)	87.1(3)	180.0(3)	**2.308(6)**

octahedra linked together via corner-sharing (F) to form bent chains running along the [101] direction (Cu–F–Nb = 158.4(3)°) (see Fig. 1). The $Nb(F, OH)_6$ octahedra are almost regular, the distances Nb-*X* ranging from 1.910(6) to 1.939(7) Å, with the two $Nb–F_{bridg}$ distances being the shortest. As in the case of many Cu^{II} compounds, a Jahn-Teller effect is observed, leading to four short $Cu–(H_2O, OH, F)$ distances, 1.960(10) to 1.968(9) Å, and two long $Cu–F_{bridg}$ distances, 2.308(6) Å. The water molecules are located in equatorial sites of the CuX_6 octahedral chains. Each chain, $–Cu(H_2O, F, OH)_6 –Nb(F, OH)_6–$, is surrounded by six other chains in such a way that each $Cu(H_2O, F, OH)_6$ octahedron is surrounded by six $Nb(F, OH)_6$ octahedra. The cohesion of the structure is probably realized via O–H . . . F hydrogen bonds, which could explain the relatively high values found for all the temperature factors. The geometry of the O–H . . . F hydrogen bond has been summarized by Simonov and Bukvetsky from their analysis of structures of metal fluoride hydrates (7). They had shown that the O . . . F distances between atoms involved in a hydrogen bond range from 2.56 to 2.86 Å, with an average equal to 2.68 Å. In the case of $CuNb(OH)_xF_{7-x}$. $3H_2O$, four distances are in good agreement with these observations, two OW1–*X*1 distances at 2.717(11) Å and 2.749(10) Å and two OW2–*X*2 distances at 2.699(12) Å and 2.734(11) Å. It follows that a water molecule located on the site OW1 of a chain could exchange two hydrogen bonds with two F^- anions located on sites *X*1 belonging to two different chains; the angle *X*1–OW1–*X*1 being equal to 111.9(3)°. In the case of OW2, the angle *X*2–OW2–*X*2 observed is equal to 105.1(4)°.

In the case of $CuTiF_6 \cdot 4H_2O$, the structure consists of infinite-$TiF_6–Cu(H_2O)_4F_2$-bent chains (Cu–F–Ti = 149.6°) running along [101] direction and connected via hydrogen

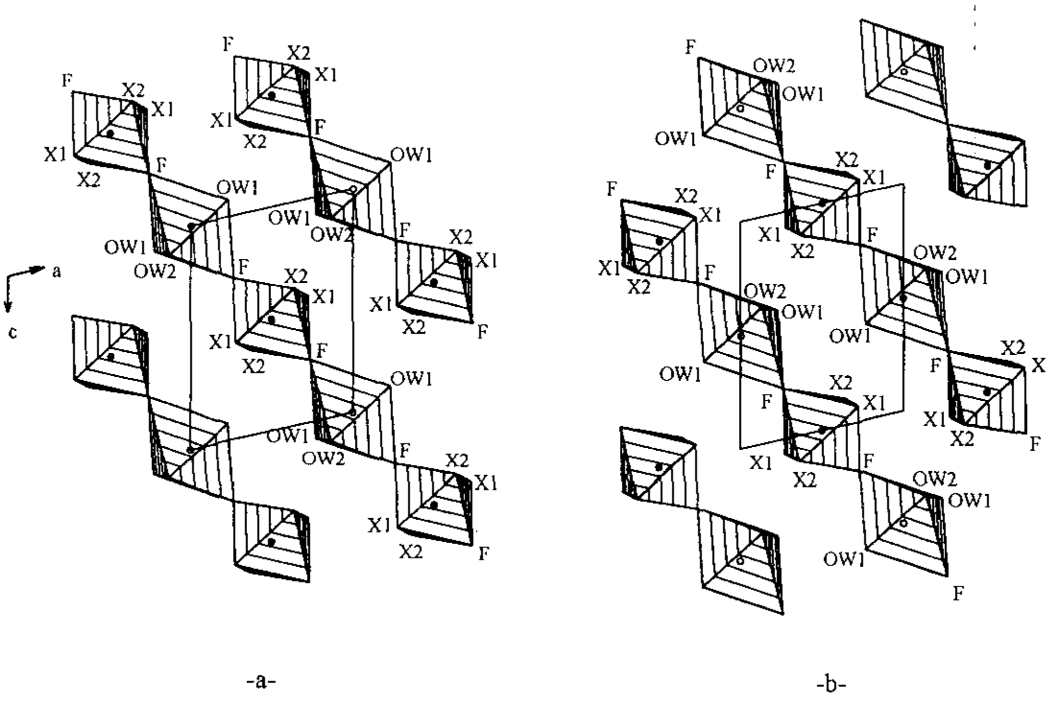

FIG. 1. $CuNb(OH)_xF_{7-x} \cdot 3H_2O$: Projection of the structure on the (010) plane, showing the *F-trans*-linked chains of octahedra for $-\frac{1}{4} < y < \frac{1}{4}$ (a) and $\frac{1}{4} < y < \frac{3}{4}$ (b) (black and open circles correspond to Nb and Cu atoms respectively).

bonds. The TiF_6 octahedra are almost regular whereas a strong Jahn-Teller effect is observed for the Cu^{II} octahedra. As in $CuNb(OH, F)_7 \cdot 3H_2O$, the water molecules are located around the Cu^{II} in equatorial sites of the Cu^{II} octahedral chains.

CONCLUSION

As described by Fischer *et al.* (1, 2), the structural type $CuMX_6 \cdot 4H_2O$ consists of bent chains of *trans*-F-linked alternate CuX_6 and MX_6 octahedra running along the [101] direction. However, in the case of the present compound, where M = Nb, a partial disorder between OH^-, F^-, and water molecules is observed on all the nonbridging anionic sites. A Jahn-Teller effect distorts classically the $Cu(H_2O, OH, F)_6$ octahedra. The tridimensional character of the structure is explained by a network of O–H . . . F hydrogen bonds.

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