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$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$: Synthesis and Crystal Structure

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Single crystals of $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$ were grown by hydrothermal synthesis in HF aqueous solutions. The structure is established from single crystal X-ray diffraction data: S.G. $Cmc2_1$, $Z = 4$, $a = 22.633(3)$ Å, $b = 7.804(1)$ Å, and $c = 7.748(1)$ Å ($R = 0.0310$, $R_w = 0.0331$ for 2619 independent reflections and 99 parameters). The tridimensional network is built up from $NbOF_6$ pentagonal bipyramids connected by Ba^{2+} ions (in 9- and 11-fold coordination). The location of anions and water molecules is discussed from bond valence calculations. © 1993 Academic Press, Inc.

Introduction

In the course of a general study of barium complex oxide fluorides of transition metals (*1–3*), we report the synthesis and the crystal structure of $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$, a new acentric hydrated oxide fluoride presenting isolated $NbOF_6$ pentagonal bipyramids.

Preparation

Single crystals of the title compound were prepared by hydrothermal synthesis (*4*) from BaF_2 and NbO_2F. Typical preparation conditions are listed in Table I. It was also possible to obtain $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$ at 200°C when BaF_2 and Nb_2O_5 (ratio 3 : 1) were mixed in 5 cm^3 of 20% HF solutions in closed Teflon vessels, heated for 2 days, and then allowed to cool slowly to room temperature (cooling rate 7.5°/hr). In both cases, small colorless needle-shaped crystals were filtered off, rapidly washed with a dilute HF solution, and air dried. The chemical analysis of fluoride ($F_{exp} = 23.0 \pm 2.5\%$, $F_{theo} = 25.5\%$), conducted by pyrohydrolysis, and TGA experiments on washed crystals, revealed a 3.4% weight loss starting at 95°C ($\Delta m_{theo} = 4.0\%$), thus confirming the formulation.

X-Ray Data Collection

A small crystal, of approximate size $0.06 \times 0.12 \times 0.1$ mm^3, with boundary faces $\pm$ <100>, <010>, and <001>, was chosen for the structural study. Standard photographic methods revealed an orthorhombic symmetry ($a \approx 22.6$ Å, $b \approx 7.80$ Å, and $c \approx 7.75$ Å). The experimental conditions of the X-ray data collection are listed in Table II. The lattice parameters were refined by the double scan technique from the positions of 37 reflections in the vicinity of 30° (2θ). The intensity data showed the systematic absences characteristic of *Cmcm*, $Cmc2_1$, and *C2cm* space groups ($hkl: h + k = 2n + 1$, $h0l: h, l = 2n + 1$, $00l: l = 2n + 1$).

Determination of the Structure

All the calculations were made with the SHELX-76 program (*5*). Atomic scattering factors for Ba^{2+}, Nb^{5+}, and F^- ions, $\Delta f'$ and $\Delta f''$, were taken from "International Tables for X-ray Crystallography" (*6*) and from (*7*) for O^{2-}. Direct and Patterson methods were unable to give any clear proposition in the *Cmcm* and *C2cm* space groups, whereas a starting model, two Ba positions, one for

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TABLE I

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$: OPERATING CONDITIONS OF CRYSTAL GROWTH

Volume of platinum tube	2.62 cm^3	P_{init} (RT)	1000 bars
Filling rate	55%	Heating rate	200°C/hr
H_2O, volume	1.8 cm^3	Temp. max. (T_f)	590°C
Ba/Nb molar ratio	$\frac{1}{1}$	Stay at T_f	50 hr
BaF_2 mass	1.947 g	P_{final} at T_f	2010 bars
NbO_2F mass	1.598 g	Natural cooling rate	

Nb, and nine other sites, was obtained by the Patterson method using the acentric $Cmc2_1$ space group. Successive refinements and Fourier difference synthesis made it possible to refine the structure. However, as in $BaTiOF_4$ (*1*), Ba_2TiOF_6 (*2*) and $Ba_4Nb_2O_3F_{12}$ (*3*), it was impossible to determine, from X-ray diffraction data, the relative positions of O^{2-} and F^- ions and those of the water molecules. The bond valence

TABLE II

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$: OPERATING CONDITIONS OF THE INTENSITY DATA COLLECTION (SIEMENS AED 2 FOUR-CIRCLE DIFFRACTOMETER)

Symmetry	Orthorhombic
Space group	$Cmc2_1$
a (Å)	22.633(3)
b (Å)	7.804(1)
c (Å)	7.748 (1)
V (Å^3)	1368.5
Z	4
Formula weight (g)	893.83
D_{calc} (g/cm^3)	4.34
Temperature (°C)	20
Radiation	MoK_α (graphite monochromatized)
Crystal volume (10^{-4} mm^3)	6.59
Scanning mode	$\omega/2\theta$
Aperture (mm)	3.5 × 3.5
Range registered:	
θ_{max} (°)	35
h, k, l_{max}	36, 12, 12
Absorption coefficient (cm^{-1})	μ = 101.76
Absorption correction	Gaussian method
Transmission factors:	
T_{max}, T_{min}	0.5757, 0.3918
R_{int}	0.0135
Reflections measured:	two independent sets—250 standards
total	4057
independent	3040
used in refinement ($I > 3\sigma(I)$)	2619
Number of refined parameters	99
Weighting scheme	$w = 1.89/(\sigma^2(F) + 4.38\ 10^{-4}\ F^2)$
Electron density in final Fourier difference map: maximum, minimum (e^-/Å^3)	3.0, −3.2
R, R_w	0.0310, 0.0331

TABLE III

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$: CALCULATED VALENCE V FOR THE ANIONIC SITES ($V_i = \Sigma_j \nu_{ij}$ WITH $\nu_{ij} = \exp[(R_{ij} - d_{ij})/b]$) (8)

		Ba1	Ba2	Nb	Σs
Site 1	O^{2-}		0.31–0.21–0.18	0.66	1.36
	F^-		0.24–0.16–0.13	0.60	1.13
Site 2	O^{2-}	0.32	0.25	0.71	1.28
	F^-	0.25	0.19	0.63	1.07
Site 3	O^{2-}	0.35–0.33		0.77	1.45
	F^-	0.27–0.25		0.69	1.21
Site 4	O^{2-}	0.03	0.28	0.80	1.11
	F^-	0.02	0.22	0.72	0.96
Site 5	O^{2-}		0.30–0.24–0.17	0.66	1.37
	F^-		0.23–0.18–0.13	0.59	1.13
Site 6	O^{2-}		0.30	0.87	1.17
	F^-		0.23	0.78	1.01
Site 7	O^{2-}		0.30–0.20	1.18	1.68
	F^-		0.23–0.15	1.05	1.43
Site 8	O^{2-}	0.28–0.23			0.51
	F^-	0.21–0.18			0.39
Site 9	O^{2-}	0.24			0.24
	F^-	0.18			0.18

method (8) made it possible to clear up this problem and showed unambiguously the O^{2-}, F^-, and H_2O positions. Table III presents the calculated valence for the nine noncationic sites : site 7 is found to be occupied by O^{2-}, while water molecules are located at sites 8 and 9 (positions quoted hereafter OW1 and OW2). It is worthy of note that it was impossible to locate the hydrogen positions of water molecules even if the data collection was limited to lower values of 2θ.

With the absorption correction, anisotropic thermal parameters, and weighting scheme, the final stage of refinement converged to $R = 0.0310$ and $R_w = 0.0331$. In these conditions, the Fourier difference synthesis final result was featureless with maxima and minima in the range ± 3 $e^-/\text{Å}^3$. Calculations in the other absolute configuration, in the same conditions, led to higher discrepancy factors ($R = 0.039$ and $R_w = 0.043$). Tables IVa and IVb present the final atomic coordinates and thermal parameters, while the main interatomic distances and angles are given in Table V (F_o and F_c tables will be sent upon request).

Description of the Structure

The structure contains isolated $NbOF_6$ pentagonal bipyramids. Figures 1a and 1b show the location of the eight $NbOF_6$ bipyramids in the unit cell. As shown in Table V, the shortest Nb–X distance, 1.851(4) Å, is found for Nb–O as in $Ba_4Nb_2O_3F_{12}$ (3), where it was even shorter, 1.704(4) Å. In both compounds, the mean distance Nb–X is very close to the sum of the ionic radii (9). Several distances X–X (F5–F1 = 2.342(7) Å, F3–F4 = 2.390(7) Å, F2–F3 =

TABLE IVa

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$: FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

	x	y	z	B_{eq} [Å^2]
Ba1	0	0.1050(1)	0	1.15(2)
Ba2	0.1951(1)	0.3097(1)	0.7887(1)	0.89(1)
Nb	0.8600(1)	0.7676(1)	0.7907(1)	1.26(2)
F1	0.2970(2)	0.1532(6)	0.6368(6)	1.2(1)
F2	0.3867(2)	0.2905(7)	0.5405(6)	1.4(2)
F3	0.4362(2)	0.3993(5)	0.7915(6)	1.6(1)
F4	0.3830(2)	0.2971(7)	0.0373(5)	1.6(2)
F5	0.2950(2)	0.1550(6)	0.9390(6)	1.2(1)
F6	0.3964(2)	0.0398(5)	0.7947(8)	1.8(1)
O	0.3120(2)	0.4595(5)	0.7848(10)	1.4(1)
OW1	0.5	0.7197(12)	0.6630(13)	3.4(5)
OW2	0.5	0.0350(11)	0.4777(15)	2.6(4)

2.400(7) Å, F5–F4 = 2.403(7) Å, and F1–F2 = 2.414(7) Å) are smaller than the usual values which can be explained by the Nb–X distances observed, very close to those found in an octahedral environment. It is worthy of note that such distances have already been observed in compounds with sevenfold coordinated Ta^{5+} and Nb^{5+} (*3, 10, 11*).

There is a clear break for the Ba–X distances near 3.0 Å, so Ba1 and Ba2 are respectively in a 9- and 11-fold environment.

In the Ba1 polyhedron, a trigonal prism Ba1 $(F3)_4(F2)_2$ tricapped by water molecules (Fig. 2), the longest distances Ba1–X are those relative to the water molecules. Each Ba1 polyhedron connects four $NbOF_6$ bipyramids: a Ba1 polyhedron, with Ba1 at

TABLE IVb

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$ ANISOTROPIC THERMAL PARAMETERS U_{ij} (Å^2 × 10^4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba1	137(2)	188(2)	112(2)	−18(2)	0	0
Ba2	119(1)	120(1)	100(1)	2(2)	1(1)	10(1)
Nb	143(2)	240(2)	96(2)	4(3)	−1(2)	−101(2)
F1	147(17)	211(21)	106(17)	−19(16)	−23(14)	−74(16)
F2	149(17)	227(20)	158(20)	−21(14)	22(15)	−38(16)
F3	151(15)	284(19)	182(16)	−21(27)	−4(16)	−105(13)
F4	215(20)	309(24)	94(18)	−40(14)	−14(15)	−104(19)
F5	147(16)	170(19)	127(18)	3(15)	9(15)	−35(15)
F6	205(16)	175(16)	317(21)	22(20)	6(22)	58(13)
O	210(18)	84(15)	244(21)	13(23)	−11(24)	19(13)
OW1	888(88)	202(39)	218(43)	44(33)	0	0
OW2	318(40)	256(40)	410(59)	39(39)	0	0

Note. The form of the anisotropic thermal parameter is $T = \exp - [2\pi^2(h^2 a^{*2}U_{11} + k^2 b^{*2}U_{22} + l^2 c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

TABLE V

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

NbOF$_6$ pentagonal bipyramid

Nb	O	F6	F4	F3	F2	F1	F5
O	**1.851(4)**	3.793(9)	2.831(7)	2.850(6)	2.860(7)	2.673(7)	2.688(7)
F6	168.9(6)	**1.960(4)**	2.767(7)	2.947(5)	2.785(7)	2.709(6)	2.707(6)
F4	94.8(8)	88.8(4)	**1.994(4)**	2.390(7)	3.850(8)	3.831(5)	2.403(7)
F3	95.2(4)	95.9(4)	73.4(4)	**2.008(4)**	2.400(7)	3.880(5)	3.893(5)
F2	94.6(4)	88.3(4)	145.5(4)	72.7(5)	**2.038(4)**	2.414(7)	3.868(5)
F1	86.0(4)	84.7(4)	141.7(3)	144.8(3)	72.1(5)	**2.062(4)**	2.342(7)
F5	86.6(4)	84.5(4)	72.6(5)	146.0(3)	141.1(3)	69.2(5)	**2.063(4)**

⟨Nb–X⟩ = 1.997 Å

Ba1 polyhedron

2 × Ba1–F3	2.681(5)	Ba1–OW1	2.760(10)
2 × Ba1–F3	2.697(4)	Ba1–OW2	2.815(9)
2 × Ba1–F2	2.709(5)	Ba1–OW1	2.831(9)

⟨Ba1–X⟩ = 2.731 Å

Ba2 polyhedron

Ba2–F1	2.718(5)	Ba2–F5	2.815(5)
Ba2–F5	2.732(5)	Ba2–F1	2.863(5)
Ba2–O	2.738(4)	Ba2–O	2.893(5)
Ba2–F6	2.742(5)	Ba2–F1	2.933(5)
Ba2–F4	2.759(5)	Ba2–F5	2.944(5)
Ba2–F2	2.801(5)		

⟨Ba2–X⟩ = 2.813 Å

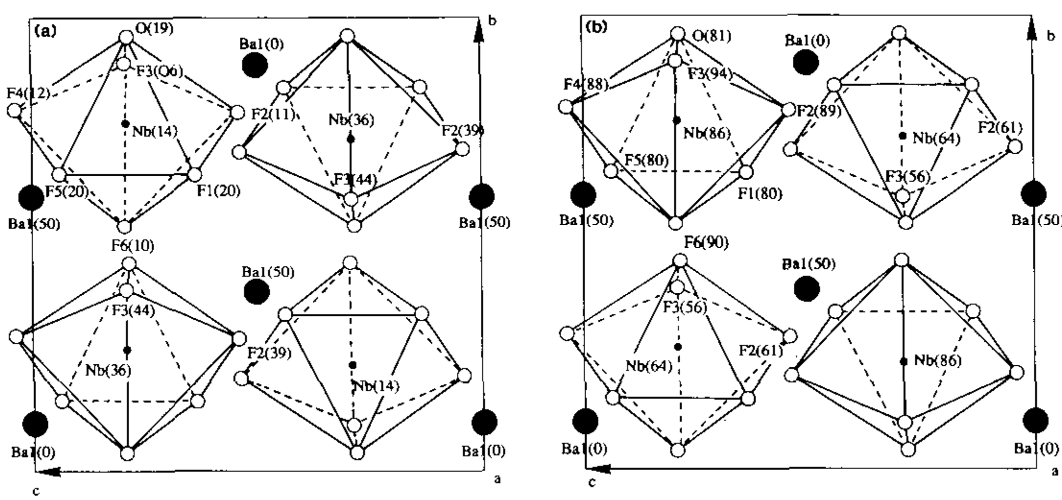

FIG. 1. $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$—Partial projection on the (100) plane showing the location of the eight isolated NbOF$_6$ pentagonal bipyramids in the unit cell for $x < \frac{1}{2}$ (a) and $x > \frac{1}{2}$ (b), and the positions of Ba1 cations (numbers indicate the x coordinate (×100) of the atoms).

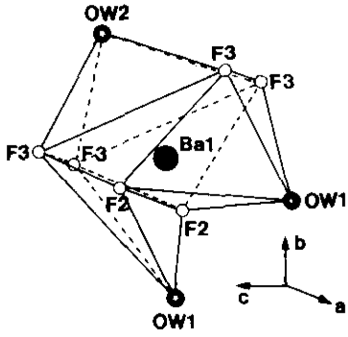

FIG. 2. $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$—Ba1 polyhedron constituted by a trigonal prism $Ba1(F3)_4(F2)_2$ tricapped by water molecules (one OW2 and two OW1).

$x = 0.5$, shares two vertices F3–F2 with two $NbOF_6$ groups (with Nb at $x = 0.36$ and 0.64) and two corners F3 with the other two $NbOF_6$ bipyramids (with Nb at $x = 0.36$ and 0.64), forming zigzag chains (Fig. 3). These chains are running parallel to the c axis. The same situation is observed between the polyhedra centered at Ba1, at $x = 0$, and the $NbOF_6$ groups with Nb at $x = \pm 0.14$.

The Ba2 polyhedron presents a pentagonal basis (2 × F1, 2 × F5, and O) in the same (100) plane as Ba2. The six other anions form two triangular faces (F2–F4–F6 and F5–F1–O) which are located above and under the pentagonal basis with the same orientation (Fig. 4). Each Ba2 polyhedron ensures the tridimensional connection of the two kinds of zigzag chains by linking five $NbOF_6$ bipyramids: the Ba2 polyhedron, centered at $x = 0.19$, shares one face F5–F1–O with the $NbOF_6$ group centered at $x = 0.36$, one other face F5–F6–F1 with the bipyramid centered at $x = 0.14$, two edges F2–F1 and F4–F5 respectively with two bipyramids centered at $x = 0.14$, and last, one O^{2-} anion with a fifth $NbOF_6$ group centered at $x = 0.14$ (Fig. 5). So each Ba2 polyhedron links together three chains.

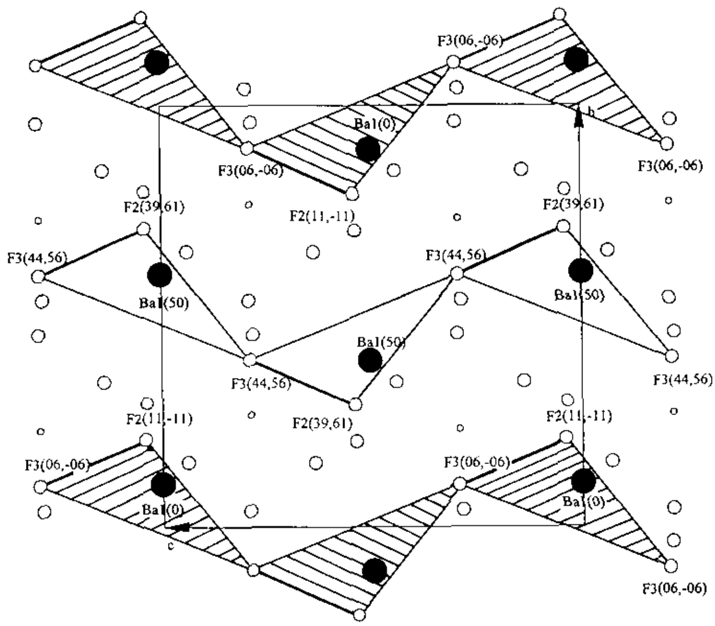

FIG. 3. $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$—Partial projection on the (100) plane showing the zigzag chains constituted by the association of the trigonal prisms $Ba1(F3)_4(F2)_2$. These chains are running parallel to c axis and are at $x = 0$ (shaded) and $x = \frac{1}{2}$ (numbers indicate the x coordinate (×100) of the atoms).

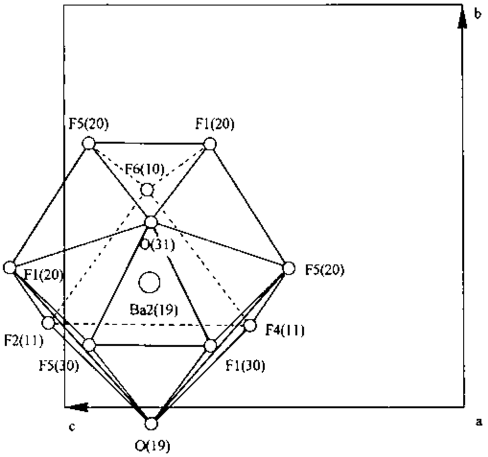

FIG. 4. $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$—Ba2 polyhedron projection on the (100) plane, showing the pentagonal basis (2 × F1, 2 × F5, and O) and the two triangular faces (F2–F4–F6 and F5–F1–O).

Conclusion

$Ba_3Nb_2O_2F_{12} \cdot 2H_2O$ is a new acentric hydrated niobium oxide fluoride. Its structure is built from isolated $NbOF_6$ pentagonal bipyramids, linked together by Ba1 cations, in 9-fold coordination forming zigzag chains along [001]. Ba2 cations, in 11-fold coordination, ensure the tridimensional connection of the chains. Further studies on the dehydration and the physical properties related to the noncentrosymmetry of the title compound are now in progress.

Acknowledgments

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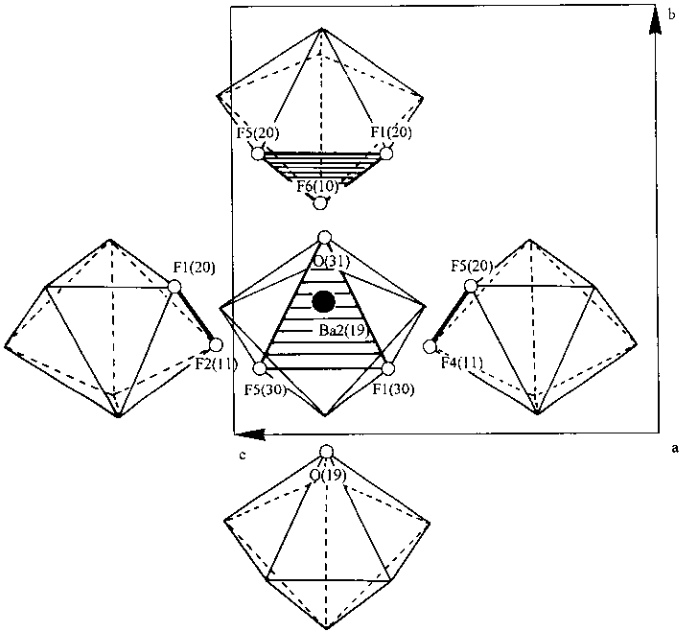

FIG. 5. $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$—Projection on the (100) plane of a Ba2 polyhedron which links together five $NbOF_6$ pentagonal bipyramids by sharing two triangular faces (shaded), two edges and one vertex (numbers indicate the x coordinate (×100) of the atoms).

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