

Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>MOF<sub>5</sub>·2H<sub>2</sub>O (M = Nb, Ta): Aligned [MOF<sub>5</sub>]<sup>2-</sup> Oxide Fluoride Anions

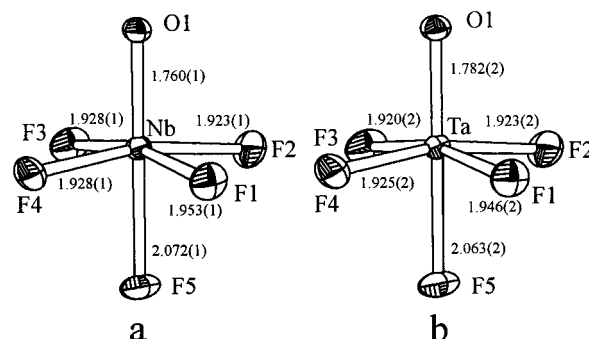
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The polar distortion in the [NbO<sub>6</sub>]<sup>2-</sup> octahedra of LiNbO<sub>3</sub><sup>1</sup> has been postulated to be the origin of the large nonlinear optical (NLO) response of this inorganic oxide.<sup>2,3</sup> This out of center tetragonal distortion is mimicked by oxide fluoride anions, MOF<sub>5</sub><sup>2-</sup> (M = V,<sup>4,5</sup> Nb,<sup>6–8</sup> Ta) (Figure 1). Unlike the distortions in [NbO<sub>6</sub>]<sup>2-</sup>, however, those in the oxide fluorides are inherent to the anion and not a product of a phase transition. Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>NbOF<sub>5</sub>·2H<sub>2</sub>O and Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>TaOF<sub>5</sub>·2H<sub>2</sub>O, which were prepared hydro(solvato)thermally,<sup>9,10</sup> contain the oxide fluoride anions [NbOF<sub>5</sub>]<sup>2-</sup> and [TaOF<sub>5</sub>]<sup>2-</sup>, respectively. Compounds containing the [MOF<sub>5</sub>]<sup>2-</sup> (M = Nb, Ta) anion seldom crystallize without internal disorder, and when they do the distortions in the octahedra align in an antiparallel fashion. In order to design a polar structure containing [MOF<sub>5</sub>]<sup>2-</sup> anions the structure-directing properties of the anions and cations need to be considered.

In order for one-dimensional chain structures to be engineered into an NLO material two conditions must be achieved. First, the octahedra should crystallize without disorder, because orientational disorder introduces an internal center of symmetry. Much work has been done to understand the factors which govern the



**Figure 1.** ORTEP diagrams (50% probability) of the complex anions (a) [NbOF<sub>5</sub>]<sup>2-</sup> and (b) [TaOF<sub>5</sub>]<sup>2-</sup>. Selected bond lengths are included (Å).

crystallization of ordered [MOF<sub>5</sub>]<sup>2-</sup> octahedra.<sup>11</sup> Second, the anions need to crystallize in a non-centrosymmetric fashion with respect to one another. In this communication we report how the first condition has been met by using the chelating ligand 2,2'-dipyridylamine (dpa) to complex the Cu<sup>2+</sup> cation.

Two dpa ligands coordinate to the Cu<sup>2+</sup> cation in a cis fashion, the structure-directing cation, [Cu(dpa)<sub>2</sub>]<sup>2+</sup>, forms a 1:1 complex with the [MOF<sub>5</sub>]<sup>2-</sup> anion, and this motif repeats along one direction in the crystal with the oxide ion bound to one of the two remaining coordination sites on copper and the trans fluoride ion hydrogen bonded to the acidic hydrogen of a dpa ligand. Thus the anions and cations (as a 1:1 complex) form one-dimensional chains in which the out of center distortions of the [MOF<sub>5</sub>]<sup>2-</sup> anion are aligned (Figure 2).

The nucleophilicity of the ligands around the metal atom in the [NbOF<sub>5</sub>]<sup>2-</sup> anion has been studied with the use of bond valence calculations.<sup>12</sup> The Nb is strongly distorted toward the oxide ligand (see Table 1). The short Nb=O1 bond, with a valence of 1.54, results in a long trans Nb–F5 bond and a high negative charge on the fluoride ligand F5. The four equatorial fluoride ligands each have significantly less negative charge. The most negatively charged oxide and trans fluoride ligands are the most nucleophilic, and so coordination is preferential to those sites.

The crystallographic ordering of the [TaOF<sub>5</sub>]<sup>2-</sup> anion in the title compound has been rarely observed, so bond valence calculations are especially revealing. The ligands with the most negative charge are the most nucleophilic and either coordinate to Cu<sup>2+</sup> or become hydrogen bond acceptors for dpa (See Table 1). The bond valence calculations of the [TaOF<sub>5</sub>]<sup>2-</sup> anion yield results similar to those of the [NbOF<sub>5</sub>]<sup>2-</sup> anion. The oxide and trans fluoride ligands are the most nucleophilic and influence the directional packing.

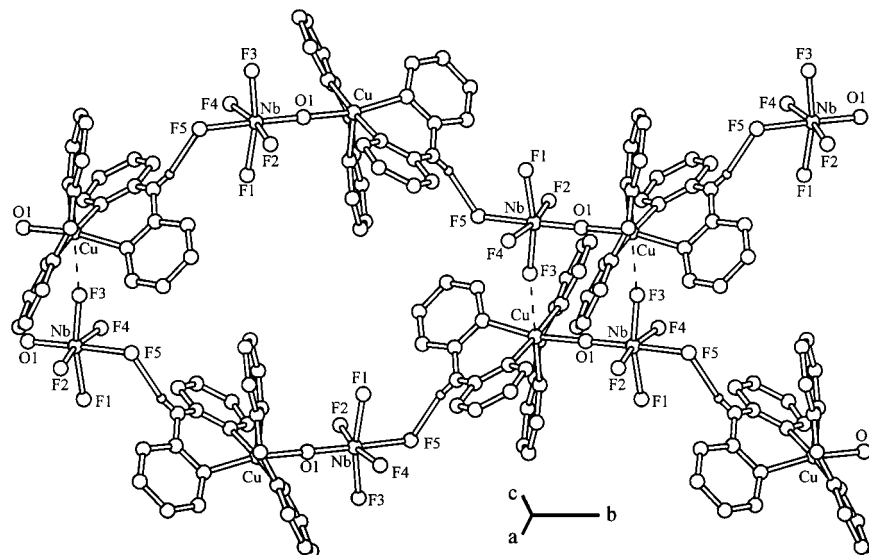
Because the anions direct coordination in a trans fashion, they can crystallize with an appropriate cation and form a one-dimensional chain where trans coordination is essential. The

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- (1) Mattias, B. T.; Remeika, J. P. *Phys. Rev.* **1949**, *76*, 1886.
- (2) DiDomenico, M.; Wemple, S. H. *J. Appl. Phys.* **1969**, *20*, 720.
- (3) Chen, C.; Liu, G. *Annu. Rev. Mater. Sci.* **1986**, *16*, 203.
- (4) Rieskamp, H.; Mattes, R. Z. *Naturforsch. B* **1976**, *31*, 1453.
- (5) Stomberg, R. *Acta Chem. Scand. A* **1986**, *40*, 325.
- (6) Sarin, V. A.; Dudarev, V. Y.; Fykin, L. E.; Gorbunova, Y. E.; Il'in, E. G.; Buslaev, Y. B. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 393.
- (7) Halasyamani, P.; Willis, M. J.; Stern, C. L.; Lundquist, P. M.; Wong, G. K.; Poeppelmeier, K. R. *Inorg. Chem.* **1996**, *35*, 1367.
- (8) Halasyamani, P.; Heier, K. R.; Willis, M. J.; Stern, C. L.; Poeppelmeier, K. R. *Z. Anorg. Allg. Chem.* **1996**, *622*, 479.
- (9) Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>NbOF<sub>5</sub>·2H<sub>2</sub>O was synthesized by adding 5.89 × 10<sup>-2</sup> g (7.41 × 10<sup>-3</sup> mol) of CuO, 9.84 × 10<sup>-2</sup> g (3.71 × 10<sup>-3</sup> mol) of Nb<sub>2</sub>O<sub>5</sub>, 1.95 × 10<sup>-1</sup> g (7.42 × 10<sup>-3</sup> mol) of (HF)<sub>x</sub>·pyridine, 1.03 × 10<sup>-1</sup> g (5.71 × 10<sup>-2</sup> mol) of H<sub>2</sub>O, 6.45 × 10<sup>-1</sup> g (3.77 × 10<sup>-3</sup> mol) of 2,2'-dipyridylamine, and 8.05 × 10<sup>-1</sup> g (1.02 × 10<sup>-2</sup> mol) of pyridine to a FEP Teflon "pouch". Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>TaOF<sub>5</sub>·2H<sub>2</sub>O was synthesized by adding 2.92 × 10<sup>-2</sup> g (3.67 × 10<sup>-3</sup> mol) of CuO, 8.12 × 10<sup>-2</sup> g (1.84 × 10<sup>-3</sup> mol) of Ta<sub>2</sub>O<sub>5</sub>, 2.02 × 10<sup>-1</sup> g (7.65 × 10<sup>-3</sup> mol) of (HF)<sub>x</sub>·pyridine, 1.19 × 10<sup>-1</sup> g (6.61 × 10<sup>-2</sup> mol) of H<sub>2</sub>O, 5.83 × 10<sup>-1</sup> g (3.41 × 10<sup>-3</sup> mol) of 2,2'-dipyridylamine, and 2.01 × 10<sup>-1</sup> g (2.55 × 10<sup>-2</sup> mol) of pyridine to a FEP Teflon "pouch". These pouches were sealed and placed in a 2000 mL autoclave (Parr) filled with 600 mL of water. The autoclave was sealed, heated to 150 °C for 24 h, and then slow cooled to 25 °C over an additional 24 h. Green blocks were recovered. Crystal dimensions: for Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>NbOF<sub>5</sub>·2H<sub>2</sub>O, 0.218 × 0.214 × 0.154 mm; for Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>TaOF<sub>5</sub>·2H<sub>2</sub>O, 0.200 × 0.178 × 0.108 mm.
- (10) Single-crystal X-ray analyses were performed on a Bruker Smart CCD diffractometer. In both cases an analytical absorption correction was applied. Crystal data: for Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>NbOF<sub>5</sub>·2H<sub>2</sub>O, monoclinic, space group P2<sub>1</sub>/n (No. 14) with a = 9.4720(4) Å, b = 19.3027(8) Å, c = 13.0634(5) Å, β = 91.155(1)°, and Z = 4, V = 2388.0(1) Å<sup>3</sup>, T = -120(1) °C, ρ(calc) = 1.796 g/cm<sup>3</sup>, ρ(obsd) = 1.779(2) g/cm<sup>3</sup>, μ = 14.451 cm<sup>-1</sup>, λ = 0.710 69 Å, 2θ<sub>max</sub> = 56.6°, total data 15 390, unique data 5806 (R<sub>int</sub> = 0.021), observations (I > 3σ(I)) 4708, number of variables 414, final R/R<sub>w</sub> 0.023/0.025; for Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>TaOF<sub>5</sub>·2H<sub>2</sub>O, monoclinic, space group P2<sub>1</sub>/n (No. 14) with a = 9.4890(4) Å, b = 19.3320(8) Å, c = 13.1053(6) Å, β = 91.253(1)°, and Z = 4, V = 2403.5(2) Å<sup>3</sup>, T = -120(1) °C, ρ(calc) = 2.028 g/cm<sup>3</sup>, ρ(obsd) = 2.003(1) g/cm<sup>3</sup>, μ = 55.02 cm<sup>-1</sup>, λ = 0.710 69 Å, 2θ<sub>max</sub> = 56.5°, total data 21 649, unique data 5893 (R<sub>int</sub> = 0.041), observations (I > 3σ(I)) 4922, number of variables 326, final R/R<sub>w</sub> 0.019/0.022. IR data: for Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>MOF<sub>5</sub>, ν(Nb=O) 921 (2) cm<sup>-1</sup>; for Cu(C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>)<sub>2</sub>TaOF<sub>5</sub>, ν(Ta=O) 928 (2) cm<sup>-1</sup>.

(11) Heier, K. R.; Norquist, A. J.; Wilson, C. G.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **1998**, *37*, 76.

(12) Kunz, M.; Brown, I. D. *J. Solid State Chem.* **1995**, *115*, 395.



**Figure 2.** One-dimensional chains of  $\text{Cu}(\text{C}_{10}\text{H}_9\text{N}_3)_2\text{MOF}_5 \cdot 2\text{H}_2\text{O}$  ( $M = \text{Nb}, \text{Ta}$ ) showing the oriented distortions of the  $\text{MOF}_5^{2-}$  octahedra. N3–F5 distances are 2.714(2) and 2.721(3) Å, respectively. The sixth coordination site of the Cu is occupied by F3 through long 2.845(1) and 2.877(2) Å bonds, respectively. Dashed lines represent these long Cu–F3 interactions. Water molecules have been removed for clarity.

**Table 1.** Bond Valence Sums<sup>a,b</sup> for  $[\text{NbOF}_5]^{2-}$  and  $[\text{TaOF}_5]^{2-}$

	$R_i$ , Å	$S_i$	$\Sigma S_M$	$V_i - S_i$
$[\text{NbOF}_5]^{2-}$				
			5.01	
Nb=O1	1.760(1)	1.54		0.46 <sup>c</sup>
Nb–F1	1.953(1)	0.70		0.30
Nb–F2	1.923(1)	0.76		0.24
Nb–F3	1.928(1)	0.75		0.25
Nb–F4	1.928(1)	0.75		0.25
Nb–F5	2.072(1)	0.51		0.49 <sup>d</sup>
$[\text{TaOF}_5]^{2-}$				
			4.80	
Ta=O1	1.782(2)	1.45		0.55 <sup>c</sup>
Ta–F1	1.946(2)	0.68		0.32
Ta–F2	1.923(2)	0.72		0.28
Ta–F3	1.920(2)	0.73		0.27
Ta–F4	1.925(2)	0.72		0.28
Ta–F5	2.063(2)	0.50		0.50 <sup>d</sup>

<sup>a</sup> Bond valence calculated with the program Bond Valence Calculator versus 2.00, C. Hormillosa, S. Healy, and T. Stephen, McMaster University (1993). <sup>b</sup> Valence sums calculated with the formula  $S_i = \exp[(R_0 - R_i)/B]$ , where  $S_i$  = bond valence of bond “ $i$ ”,  $R_0$  = constant dependent on the bonded elements,  $R_i$  = bond length of bond “ $i$ ”, and  $B = 0.370$ .  $\Sigma S_M$  = bond valence sum for the metal.  $V_i - S_i$  = calculated charge of the ligand.  $R_0(\text{Nb}-\text{O}) = 1.911$ ,  $R_0(\text{Nb}-\text{F}) = 1.822$ ,  $R_0(\text{Ta}-\text{O}) = 1.920$ ,  $R_0(\text{Ta}-\text{F}) = 1.803$ . <sup>c</sup> Bound to  $\text{Cu}^{2+}$ . <sup>d</sup> H bond acceptor.

complex cation  $[\text{Cu}(\text{dpa})_2]^{2+}$  consists of a  $\text{Cu}^{2+}$  atom coordinated by two dpa chelating ligands. In previous one-dimensional or “linear chain” compounds studied by this group<sup>7,13</sup> the copper cation was coordinated by monodentate ligands such as pyridine, pyrazine, or water, with two additional trans coordination sites,

in a square planar arrangement. This geometry has higher symmetry,  $D_{4h}$  or  $D_{2h}$ , compared to the  $[\text{Cu}(\text{dpa})_2]^{2+}$  cation, where the two dpa ligands coordinate in a cis arrangement. The remaining sites for coordination on the copper center are then cis to one another, and the point symmetry of the copper center is reduced to  $C_1$ . No direct trans coordination of the copper atom by the  $[\text{MOF}_5]^{2-}$  anions is possible so the potential for copper to crystallize on an inversion center is eliminated. Steric considerations and anion–anion repulsion prevent the coordination of two  $[\text{MOF}_5]^{2-}$  anions in a cis geometry to form an anionic cluster. A linear chain structure of a 1:1 complex of  $[\text{Cu}(\text{dpa})_2]^{2+}$  cations and  $[\text{MOF}_5]^{2-}$  anions is possible because dpa introduces a hydrogen-bonding donor site through which the trans fluoride ligand (F5) of the anion is linked. The chelating ligand 2,2'-dipyridylamine has been shown to lower the symmetry of the cation through cis coordination, yet maintain a one-dimensional structure of  $[\text{Cu}(\text{dpa})_2]^{2+}$  cations and  $[\text{MOF}_5]^{2-}$  anions in which the polar distortions present in the  $[\text{MOF}_5]^{2-}$  anions are aligned within the centrosymmetric structure.

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**Supporting Information Available:** ORTEP plots (50% probability) of the title compounds and stereoscopic views of the crystal packing. Two X-ray crystallographic files, in CIF format, including tables of crystallographic details, atomic coordinates, anisotropic thermal parameters, and interatomic distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(13) Halasyamani, P. S.; Heier, K. R.; Norquist, A. J.; Stern, C. L.; Poepfelmeier, K. R. *Inorg. Chem.* **1998**, *37*, 369.