

The synthesis and single crystal structure of an amino acid intercalated layered niobium phosphate: $[(\text{NbOPO}_4)_4 \cdot (\text{H}_3\text{NCH}_2\text{CO}_2\text{H})_2][\text{H}_2\text{PO}_4][\text{OH}, \text{F}]$

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Niobium phosphate containing interlayer glycine phosphate has been synthesized hydrothermally and its structure determined from single crystal X-ray diffraction data.

The structure of anhydrous niobium phosphate NbOPO_4 contains layers of NbO_6 distorted octahedra connected in their equatorial planes by PO_4 tetrahedra *via* sharing of corners.¹ Adjacent layers are connected through corner-sharing the remaining unshared oxygen atoms in the NbO_6 octahedra. Niobium phosphate forms a series of hydrates with composition $\text{NbOPO}_4 \cdot n\text{H}_2\text{O}$ that have been characterized by powder diffraction and infrared spectroscopy.^{2–5} No single crystal structural data are available but the hydrates most probably contain layers similar to those found in the anhydrous phase with the bridging oxygen atoms replaced by H_2O molecules to give layers of composition $\text{NbO}(\text{H}_2\text{O})\text{PO}_4$. The presence of the interlayer coordinated water molecules permits intercalation of various types of amines and alcohols between the formally electroneutral layers. The coordination intercalation chemistry is similar to that first observed in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.^{4,6} The niobium phosphate layers are stable at high temperature, with respect to radiation damage and in most organic environments. Consequently they are suitable hosts for building composite materials.⁷

We are interested in direct incorporation of organic templates into layered compounds by using hydrothermal synthesis. Here, we report an unusual compound resulting from these studies, $[(\text{NbOPO}_4)_4 \cdot (\text{H}_3\text{NCH}_2\text{CO}_2\text{H})_2][\text{H}_2\text{PO}_4][\text{OH}, \text{F}]$ **1** and, to the best of our knowledge, the first single crystal structure of a NbOPO_4 intercalation compound.

In a typical synthesis of compound **1**, a solution was prepared by dissolving 0.1 g glycine, 0.12 ml phosphoric acid and 28 mg NH_4HF_2 in 2.1 ml H_2O . The solution (pH = 2.5) was then sealed together with 20 mg niobium metal in a Teflon bag in air. The bag was subsequently sealed in a steel reaction vessel filled with water to about 60% volume, and heated at 165 °C for 38 h. After cooling to room temperature for 3 h, the products were filtered off, washed with water, and dried in air. Colorless square-like plates of **1** with rather uniform sizes of *ca.* 0.1 × 0.1 × 0.01 mm were recovered together with residual niobium metal. The solution pH was 2.7 at the end of the reaction. Incorporation of glycine into the structure was confirmed by the crystal structure refinement[†] and the IR spectrum.[‡]

The crystal structure of **1** consists of NbOPO_4 layers bridged by the carboxylic groups of the glycine $\text{H}_3\text{NCH}_2\text{CO}_2\text{H}$ cations with H_2PO_4 , F and OH anions located in the interlayer spaces. The layers are structurally equivalent to those of NbOPO_4 , and are formed from alternating NbO_6 octahedra and PO_4 tetrahedra interconnected through Nb–O–P bonds. The four equatorial oxygen atoms of each NbO_6 octahedron with Nb–O bond lengths of 2.028–2.033 Å are shared by four phosphate tetrahedra. The two apical positions of the NbO_6 octahedron are completed by a terminal Nb=O bond of 1.708 and a weak Nb–O bond (2.219 Å) to an oxygen atom of the interlayer glycine cation (Fig. 1). The layers are parallel to the (100) plane and stacked in ABAB... sequences. Neighboring layers are shifted relative to each other along [010] by exactly 0.5*b* and along [001] by *ca.* 0.43*c*. The shifts are

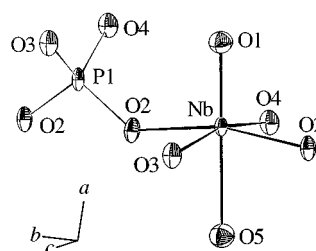


Fig. 1 Coordination environments of the Nb and P atoms in the layers. Thermal ellipsoids are drawn at the 50% probability level. Bond lengths (Å): Nb–O(1) 1.708(5), Nb–O(4) 2.028(4), Nb–O(2) 2.029(3)(×2), Nb–O(3) 2.033(4), Nb–O(5) 2.219(5), P(1)–O(4) 1.535(4), P(1)–O(3) 1.536(4), P(1)–O(2) 1.539(3)(×2).

required by the glycine cations that bridge neighboring layers through Nb–O–C–O–Nb bonds (Fig. 2). While the oxygen atoms of the glycine cations are ordered, the C–N chain is disordered randomly over four symmetry equivalent positions inside the large interlayer cavities. Although the two oxygen atoms of the carboxyl group are symmetry equivalent, there are two C–O bond lengths, 1.35 and 1.41 Å. The latter corresponds to C–OH–Nb bonds and confirms the protonation of the glycine molecule as expected from the highly acidic synthesis conditions. Because of the C–O–Nb bonding, the C–O distances are longer than those typically found in isolated glycine molecules. The charge balancing $(\text{H}_2\text{PO}_4)^-$ anions are disordered and were located from difference maps, but not unambiguously, at two

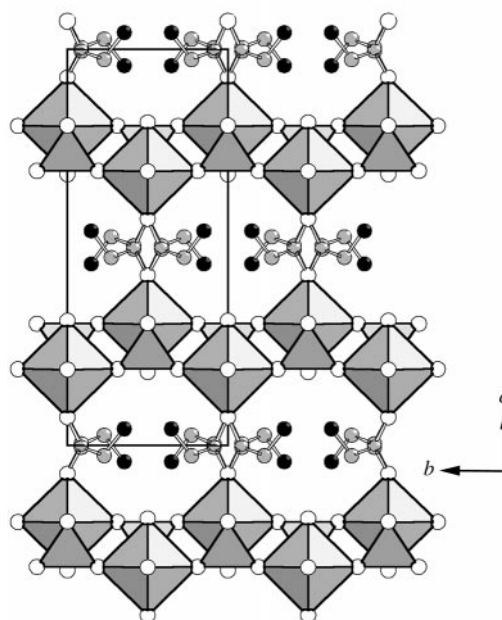


Fig. 2 Projection of the structure along [001]. Open, hatched and solid circles represent O, C and N atoms, respectively. The $\text{H}_3\text{NCH}_2\text{CO}_2\text{H}$ cations are disordered randomly over four orientations. The disordered interlayer anions are omitted for clarity.

non-equivalent positions in the interlayer cavities. Both positions can be included in the refinements as rigid groups with a fixed occupancy of 6.3% in agreement with the electron microprobe analysis[§] that gave the atomic ratios: Nb:P:F = 4:5.0:0.4. The charge balancing F⁻ and probably also OH⁻ anions could not be located because of electron density overlapping caused by the disorder. Thermogravimetric analysis measured in air up to 900 °C shows two continuous weight loss stages separated by *ca.* 300 °C. The total observed weight loss of 17.8% agrees well with the given formula assuming the residue to be Nb₄P₅O_{22.3}F_{0.4} (calc. 17.7%).

The structure of **1** is closely related to the structure model proposed for NaNb₂(OH)₂(PO₄)₃•*n*H₂O based on powder X-ray diffraction data. In the model, neighboring niobyl phosphate layers are bridged by PO₄ tetrahedra.⁶ There are several precedents for NbOPO₄ intercalation compounds in which the layers are bridged by anionic groups. (VOSO₄)₂•H₂SO₄ is generally considered to be the archetype but there are several other examples.^{8,9} Compound **1** is unusual because the bridging carboxylate group is cationic and consequently the interlayer charge is compensated for by interlayer anions. All of the other examples in this family contain interlayer cations. [(NbOPO₄)₄•(H₃NCH₂CO₂H)₂][H₂PO₄][OH,F] is a rare example of a layered inorganic anion exchanger and is analogous to the hydrotalcites.

In summary, we have synthesized single crystals of a novel layered niobium phosphate containing glycinium cross-linking adjacent NbOPO₄ layers. Our preliminary data also show that layered niobium phosphates incorporating other organic species can also be obtained in single crystal form through hydrothermal reactions.

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Notes and references

† *Crystal data*: C₄N₂H_{14.6}O_{28.6}F_{0.4}Nb₄P₅, *M* = 1082.3, crystal system: monoclinic, space group *C2/m*, *a* = 17.020(2), *b* = 6.4973(7), *c* = 6.4992(7) Å, β = 109.304(2)°, *V* = 678.3(1) Å³, *Z* = 1, *T* = 223 K, μ = 1.99 mm⁻¹, *R*(*F*) = 0.036. Measured/independent reflections: 2117/850, *R*_{int} = 0.033, refined variables: 74. CCDC 182/1477. See <http://www.rsc.org/suppdata/cc/1999/2531/> for crystallographic files in .cif format.

‡ IR data (cm⁻¹): 3464m, 3217m, 1618m, 1501m, 1468m, 1416m, 1352w, 1115s, 1015vs, 692m, 581w, 525m, 463w. The peaks between 1352 and 1618 cm⁻¹ are characteristic of amino acetic acid.

§ Electron microprobe analysis was carried out with a JEOL 8600 electron microprobe operating at 15 keV with a 10 μm beam diameter and a beam current of 30 nA.

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