A (4,2)-connected niobium phosphate $Na_{13}Nb_3P_6O_{28}F_2$ with a unique 6.12-net layer: Synthesis, structure and ion exchange properties†

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A severely interrupted (4,2)-connected niobium phosphate, $Na_{13}Nb_3P_6O_{28}F_2$, with a unique 6.12-net topology sheet and novel structure type has been synthesized under mild hydrothermal conditions, and its ion exchange properties preliminarily investigated.

Open-framework phosphates have received considerable interest in past decades due to their rich structural diversity and very interesting properties, which can be observed in a variety of different compositional domains.[1] One promising area for the discovery of structures with novel topologies and properties is the synthesis of frameworks by combining tetrahedral and octahedral coordination geometries.[2] The presence of local geometric interruptions surrounding individual polyhedral centers plays a vital role in the overall framework topology, and has been recognized as being prone to forming large pore sizes and a low framework density (*e.g.*, CLO[3] and JDF-20[4]). However, few open crystalline niobium phosphates have been reported hitherto.[5] An inherent difficulty faced in making niobium phosphates is the very low solubility of niobium sources obtained from typical commercial suppliers. Conversely, vanadium analogues have been intensively investigated. Generally, niobium phosphates were made by solid-state reactions or by reactions in fluxes.[6]

Layered compounds are promising materials for ion exchange, ion storage and intercalation reactions due to their chemically manipulable features within the interlamellar region.[7] Niobium phosphates form a series of layered hydrates, with the composition $NbOPO_4{\cdot}nH_2O$ showing a wide range of intercalation reactions.[8] The dense niobyl phosphate (Nb–P–O) layer can be conceptually deduced from anhydrous $NbOPO_4$ by cleaving the 3-D network of NbO_6 octahedra and PO_4 tetrahedra perpendicular to the c-axis.[9] The structural features and intercalation properties of $NbOPO_4{\cdot}nH_2O$ are closely similar to those first observed in $VOPO_4{\cdot}2H_2O$.[8c] Recently, Jacobson *et al.*[5d] reported an open layered niobium phosphate based on the dense Nb–P–O layer, corresponding to one-half of the niobium octahedra removed from the dense layer, giving rise to 8-membered ring (MR) bifurcated apertures within the layer. Herein we describe the synthesis, crystal structure and ion exchange properties of a novel layered niobium phosphate, $Na_{13}Nb_3P_6O_{28}F_2$ (**1**), with a unique 6.12-net sheet that has never previously been seen in metal phosphate systems.

1 was synthesized using a two-step hydrothermal process in a 30 mL Teflon lined autoclave.‡ The asymmetric unit contains one unique octahedral Nb atom, located at an inversion center, and one unique tetrahedral P atom, located in a general position (Fig. 1).§ Each Nb atom bonds to four equatorially bridging O atoms (Nb–O 1.962(8)–2.022(8) Å) and two terminal O/F atoms located at the apical positions of the octahedron (Nb–O/F 1.932(7) Å). The P atoms are only 2-connected into the layers, and link two bridging O and two terminal O atoms ($P{-}O_{bridging}$ 1.551(7)–1.569(8) Å and P=O 1.472(8)–1.485 (9) Å).

The framework structure of **1** consists of alternating linkages of 4-connected Nb octahedral and 2-connected P tetrahedral units *via* corner sharing, forming an unusual layered architecture in the ab-plane (Fig. 2a). The 2-D layer is built only of 6- and 12-MRs, arranged in such way that each 12-MR is surrounded by six 6-MRs and six 12-MRs. Conversely, each 6-MR is surrounded by three 6-MRs and three 12-MRs (Fig. 2a). The Nb/P stoichiometry within the layers is 1 : 2, which conforms to the limitation rule in strictly alternating systems that says the composition is inversely proportional to the ratio of the attachable coordination numbers of the individual cationic sites. Within each layer, each Nb octahedron is located in the middle of the layer and related to two 6-MRs and two 12-MRs, whereas each P tetrahedron is situated on each side of the octahedra and associated with one 6-MR and one 12-MR. One of the two terminal P=O in each P tetrahedron protrudes into the center of the 12-MR and the other P=O, as well as the two terminal Nb–F/O, point towards the interlayer. It is noteworthy that this kind of layer topology, with the unique 6.12-net, is unlike that of any previously reported metal phosphates, where 4.6-, 4.8- and 4.12-nets are ubiquitous;[1b] while similar (4,2)-connected layer topologies have only been observed in a small number of compounds, such as $(C_5NH_6)[M(HPO_4)_2(H_2O)_2]$ (M = Al or Ga).[10]

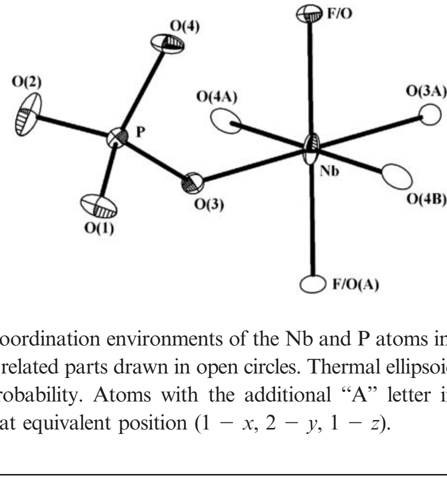

Fig. 1 Coordination environments of the Nb and P atoms in **1**, with the symmetry related parts drawn in open circles. Thermal ellipsoids are given at 30% probability. Atoms with the additional "A" letter in the atom labels are at equivalent position (1 − *x*, 2 − *y*, 1 − *z*).

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† Electronic supplementary information (ESI) available: Additional figure of the structure of **1**. See DOI: 10.1039/b614265f

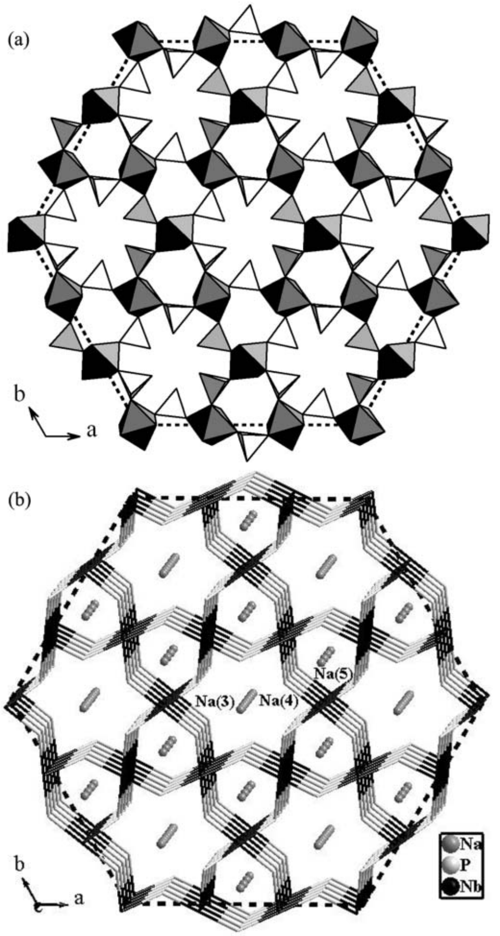

Fig. 2 (a) A layer of 6- and 12-MRs constructed by strict alternation of $Nb(O,F)_6$ octahedra (black) and PO_4 tetrahedra (white). (b): Topological view of the packing of layers in **1**, showing the Na^+ cations situated in the channels of 6-MRs and 12-MRs along the c-direction.

Adjacent layers stack in an –AAAA– sequence along the c-axis, resulting in a unidimensional 6-MR and 12-MR channel system parallel to this direction (Fig. 2b). There exist five unique extra-framework Na^+ cations in order to fulfil the requirement of charge-balance in the anionic framework. Na(1), occupying a general position, exhibits a squashed trigonal-prismatic configuration (Na(1)–O/F 2.387(10)–2.693(11) Å). Na(2), Na(3) and Na(4) are located at the remaining inversion centers unoccupied by Nb atoms, while Na(5) lies on a C_3 axis. These guest cations are all six-coordinate to framework anions in distorted octahedral geometric configurations, with Na–O/F contacts in the range 2.306(8)–2.695(11) Å. Of the five cations, Na(3) is located at the center of the 12-MRs, and the remaining cations are situated between the interlayer, with Na(4) and Na(5) in the 12-MR and 6-MR channels, respectively (Fig. 2b).

1 has a high charge density, with a 1.44 Na^+ ion/polyhedral center that corresponds to an ion exchange capacity of 10.40 mmol g^{-1}, as described by Zou *et al.*[11] The layering perpendicular to the 6- and 12-MRs gives a very open structure, well suited to ion exchange. We found that the Na^+ in $Na_{13}Nb_3P_6O_{28}F_2$ could be partially exchanged by NH_4^+ and Ag^+, respectively, in solution.¶

For the sample treated with NH_4Cl, about 87% of NH_4^+ was exchanged for Na^+, giving $(NH_4)_{11.3}Na_{1.7}Nb_3P_6O_{28}F_2$ as the product on the basis of chemical analysis and energy dispersive spectroscopy,[12] which was further confirmed by thermogravimetric analysis (TGA). The TGA data for the NH_4^+-exchanged sample showed that a sharp weight loss of 22.8% occurred between about 160 and 325 °C, followed by a further weight loss of 2.9% between 325 and 600 °C, corresponding to combustion of the NH_4^+ ions and dehydration of the framework (calc. NH_3/H_2O 16.1/7.0%), as well as loss of HF (calc. 3.2%), respectively. The IR spectrum of the NH_4^+-exchanged product (Fig. 3) showed a peak at 1400 cm^{-1}, which is characteristic of N–H bending, and peaks at 3016 and 3160 cm^{-1}, which correspond to N–H stretching frequencies.

Upon treating sample **1** with $AgNO_3$, it slowly darkened when exposed to light and about 71% exchange of Ag^+ for Na^+ was completed. The identity of the exchanged product was formulated as $Ag_{9.3}Na_{3.7}Nb_3P_6O_{28}F_2$ by energy dispersive spectroscopy.[13] TGA revealed that there was no significant weight loss up to 600 °C for both **1** and the Ag^+-exchanged sample.

The structures of the ion exchanged $Na_{13}Nb_3P_6O_{28}F_2$ were maintained, as demonstrated by IR spectroscopy (Fig. 3) and X-ray diffraction patterns (Fig. 4). The slight difference in the IR spectra, as well as the PXRD patterns, of $Ag_{9.3}Na_{3.7}Nb_3P_6O_{28}F_2$ and $Na_{13}Nb_3P_6O_{28}F_2$ are probably due to the strong guest Ag^+-framework anion bonding interaction.[5c] Preliminary studies show that **1** readily undergoes ion exchange with a wide variety of mono- and di-cations, such as K^+ and Ba^{2+}. Further studies on the ion conduction behavior of this material are in progress.

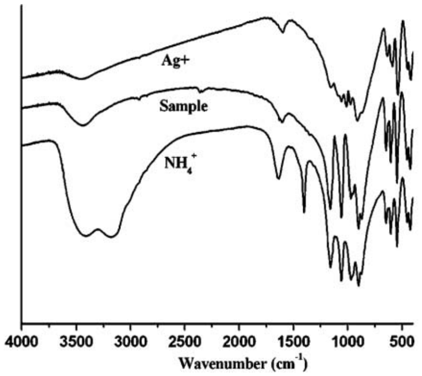

Fig. 3 IR spectrum of sample **1** and various corresponding ion exchanged phases.

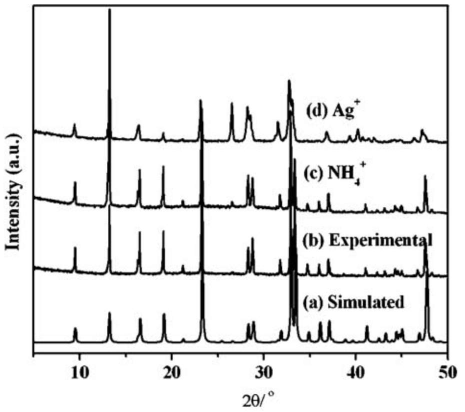

Fig. 4 X-ray powder diffraction pattern of sample **1** and various corresponding ion exchanged phases.

In summary, a severely interrupted, layered niobium phosphate, $Na_{13}Nb_3P_6O_{28}F_2$, with well-defined ion exchange properties, has been successfully made in good yield using a two-step hydrothermal process. The structure consists of very open niobyl phosphate layers, with 6- and 12-MRs constructed from the strict alternation of 4-connected niobium octahedra and 2-connected phosphorus tetrahedra, and with sodium cations occupying the extra-framework sites. Our preliminary data show that zeolitic Nb-containing phosphates incorporating organic species can also be obtained by using a procedure similar to that reported here.

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Notes and references

‡ Synthesis of **1**: Typically, 0.134 g Nb_2O_5 was first dissolved in 0.268 g HF (40 wt%) and heated to 110 °C for 24 h. After cooling, this clear solution was dispersed into a mixture of 4 mL H_2O and 3 mL ethylene glycol (EG) with constant stirring, followed by the addition of 0.968 g $Na_2HPO_4 \cdot 10H_2O$. The resulting mixture, with a molar composition of $0.5Nb_2O_5 : 3Na_2HPO_4 \cdot 10H_2O : 222H_2O : 53EG : 6.4HF$, was stirred until it was homogeneous and then heated under autogenous pressure at 180 °C for 7 d. Colorless prism-like crystals of title compound were recovered as the sole product of the reaction by filtration; these were washed with water and allowed to dry in air. The yield was greater than 90% based on Nb_2O_5.

§ Crystal data for **1**: $F_2Na_{13}Nb_3O_{28}P_6$, $M_r = 1249.42$, trigonal, space group $P\text{-}3$, $a = 10.6887(9)$, $c = 6.6917(11)$ Å, $V = 662.09(13)$ Å^3, $Z = 1$, $\rho = 3.134$ g cm^{-3}, $\mu = 1.989$ mm^{-1}, $F(000) = 598$, GOF = 1.047. A total of 5090 reflections were collected, 1010 of which were unique ($R_{\text{int}} = 0.0443$). $R1$ (w$R2$) = 0.0676 (0.1308) for 88 parameters and 994 reflections ($I > 2\sigma(I)$). ICSD 417073. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program package. Energy dispersive spectroscopy gives the Nb : P : F ratio as 1.0 : 2.0 : 0.8, which unambiguously shows that fluorine occurs in **1**. Due to the small difference in the form factors of O and F, the location of the fluorine atom could not be determined from the X-ray data. However, by comparison with the large number of known metal oxyfluorides, it is highly likely that the fluorine atom is located at one of the two terminal positions on the niobium atom. Since both terminal atoms are located on the same crystallographic site, this site is split, with a ⅔ O occupancy and ⅓ F occupancy based on charge balance and chemical analysis considerations, which is not uncommon in niobium-containing compounds.[5b,14] For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b614265f

¶ The ion exchange reactions were performed by stirring a sample of as-synthesized product (150 mg) in 10 mL of $AgNO_3$ or MCl_x salt (1 M) (where M = NH_4^+, K^+, $x = 1$; or M = Ba^{2+}, $x = 2$) at room temperature for 3 d, respectively. The exchanged samples were first washed repeatedly with copious amounts of de-ionized water, then ethanol, and followed by air drying. The Ag^+-exchanged sample slowly darkened when exposed to light.

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13 Anal. calc. for $Ag_{9.3}Na_{3.7}Nb_3P_6O_{28}F_2$: Ag, 49.2; Na, 4.17. Found: Ag, 49.2; Na, 4.28%.

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