

seventh water molecule is uncoordinated and lies between the $\text{Mg}(\text{H}_2\text{O})_6$ and ZnBr_4 groups. The structure can be described (Fig. 2) as formed by sheets containing two kinds of parallel chains extended along the b axis: one formed by the alternation of $[\text{Mg}(1)(\text{H}_2\text{O})_6]$ and $[\text{Mg}(2)(\text{H}_2\text{O})_6]$ octahedra, the other of $[\text{ZnBr}_4]$ and uncoordinated H_2O molecules.

An extensive network of $\text{O}-\text{H}\cdots\text{Br}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds holds the different groups together. Although there are 14 H atoms in the asymmetric unit, they participate in 16 hydrogen bonds (Table 2) since two of the H atoms form bifurcated $\text{O}-\text{H}\begin{matrix} \nearrow \text{Br} \\ \searrow \text{Br} \end{matrix}$ bonds.

The environment around O(7), the oxygen of the uncoordinated water molecule, is tetrahedral, with angles varying between 90 and 122° (ave. 108.6°). O(7) participates in two donor hydrogen bonds, to Br(1') and Br(4), and in two acceptor ones, from O(3) and O(6).

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A Mixed-Valence Niobium Phosphate with an Empty Nasicon Structure: $\text{Nb}_2(\text{PO}_4)_3$

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Abstract. Niobium(IV) niobium(V) phosphate, $M_r = 470.73$, trigonal, $R\bar{3}c$, $a = 8.6974$ (7), $c = 22.123$ (2) Å, $V = 1449.3$ (3) Å³, $Z = 6$, $D_x = 3.24$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.824$ mm⁻¹, $T = 294$ K, $F(000) = 223$, $R = 0.0347$ and $wR = 0.03706$ for 435 observed reflections. The niobium has a mixed valence (IV)–(V). The framework is built up from NbO_6 octahedra sharing corners with PO_4 tetrahedra and belongs to the empty Nasicon-type structure.

Introduction. The introduction of mixed-valence transition elements in oxides characterized by a mixed framework of octahedra and tetrahedra can be used to generate particular physical properties. Two classes of materials can be distinguished according to whether the octahedra share their corners forming infinite chains or layers, or whether they are only linked to the tetrahedra. The crystal chemistry of phosphates which

shows the great ability of PO_4 tetrahedra and MO_6 octahedra to adapt to each other allows both families to be synthesized. The first class of oxides, which is represented by the large family of phosphate tungsten bronzes (Raveau, 1986), allows anisotropic metallic or semi-metallic conductivity to be generated owing to the delocalization of electrons along the octahedral chains or layers. Conversely, the second class in which the MO_6 octahedra are isolated from each other does not present such electron-transport properties but is of interest for the study by local structural methods of the environment of such ions in the crystalline matrix and for the study of their distribution, ordered or not, in the lattice; it also raises the question of the possible electron transfer between two centers which each have a different oxidation state. Few compounds corresponding to this latter family have been isolated up to now. Those that have include the molybdenum phosphates $\text{AMo}_3\text{P}_6\text{Si}_2\text{O}_{25}$ ($A = \text{K, Rb, Tl, Cs}$) (Leclaire, Monier &

Table 1. Positional parameters and their estimated standard deviations

	x	y	z	B(Å ²)*
Nb	0.000	0.000	0.14131 (3)	0.377 (4)
P	0.2821 (2)	0.000	0.250	0.51 (2)
O(1)	0.1692 (5)	-0.0289 (6)	0.1943 (2)	1.56 (7)
O(2)	0.2012 (6)	0.1704 (6)	0.0916 (2)	1.38 (8)

* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Raveau, 1984; Leclaire, Borel, Grandin & Raveau, 1985; Leclaire, Monier & Raveau, 1985), and Na_{0.3}-MoP₂O₇ (Leclaire, Borel, Grandin & Raveau, 1988) in which one observes the simultaneous presence of molybdenum(III) and -(IV), the titanium phosphates Na_xTi₂P₃O₁₂ with the Nasicon structure (Nadiri, 1986) and K_{2-x}Ti₂P₃O₁₂ with the langbeinite structure (Leclaire, Benmoussa, Borel, Grandin & Raveau, 1989) in which titanium exhibits the two valence states (III) and (IV). Also, Masse, Durif, Guitel & Tordjman (1972) have isolated the empty Nasicon phosphate NbTiP₃O₁₂ characterized by the classical *a*⁰ configuration of Nb^V and Ti^{IV}. Moreover, they have incorporated alkali ions in the cavity of this framework, leading to a partial reduction of Nb^V and/or Ti^{IV} so that the question of the existence of the different species Nb^V, Nb^{IV}, Ti^{IV} and Ti^{III} and their distribution in the structure is raised. In order to study the behavior of niobium as a possible mixed-valence cation in this latter structure, the investigation of the systems A-Nb-P-O and Nb-P-O (A = alkali ion) was undertaken. We report here the structure of a mixed phosphate, Nb₂P₃O₁₂, with an empty Nasicon structure.

Experimental. The preparation was performed in two steps. First, (NH₄)₂HPO₄ and Nb₂O₅ were mixed in an agate mortar in the molecular ratio needed to obtain stoichiometric Nb_{1.8}(PO₄)₃, and heated at 600 K to decompose the ammonium phosphate. The resulting mixture was then added to the required amount of niobium and placed in an evacuated silica ampoule. This mixture was heated for several days at 1473 K. Black crystals of Nb₂(PO₄)₃ were obtained. The composition was confirmed by microprobe analysis.

Dark crystal 0.096 × 0.048 × 0.008 mm. *3m* symmetry with systematic absences *hkl* for $-h + k + l \neq 3n$ and *hh0l* for *l* odd. Space group *R* $\bar{3}c$. Enraf-Nonius CAD-4 diffractometer. Mo *K* α radiation. Unit cell: least squares on 25 reflections $\pm 2\theta$: $36 \leq 2\theta \leq 44^\circ$. Intensity: measurement by ω - 2θ scan of $(0.8 + 0.35\tan\theta)^\circ$ and with a $(1 + \tan\theta)$ mm counter slit; determined by a study of some reflections in the $\omega\theta$ plane. Scanning speed adjusted to obtain $\sigma(I)/I \leq 0.018$ or to approach it in a time limited to 60 s. Three standards: for count, every 2000 s, and for orientation,

every 600 reflections; no appreciable trends. 435 reflections ($h_{\max} = 17$, $k_{\max} = 17$, $l_{\max} = 44$) $2 \leq \theta \leq 45^\circ$, with $I/\sigma(I) \geq 3$, used to solve and refine the structure. No correction made for extinction and absorption. All subsequent calculations on a MicroVAXII with the SDP system (B. A. Frenz & Associates Inc., 1982). $(\Delta/\sigma)_{\max} = 0.01$, $\Delta\rho \leq 0.8 \text{ e \AA}^{-3}$, $R = 0.035$, $wR = 0.037$, $S = 1.1$. Atomic parameters are given in Table 1.* Structure solved by heavy-atom methods. Refinement by full-matrix least squares using *F*'s. Weighting scheme $w = F(\sin\theta/\lambda)$ adjusted using the program *POND* (Leclaire, unpublished). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The structural study of this oxide shows that the Nb₂P₃O₁₂ framework, built up from corner-sharing NbO₆ octahedra and PO₄ tetrahedra (Fig. 1), belongs to the Nasicon-type structure. One indeed recognizes the [Nb₂P₃O₁₈] units formed by two octahedra and three tetrahedra, already observed in the Nasicon-type titanium phosphate Na_xTi₂P₃O₁₂ and in the langbeinite-type structure K_{2-x}Ti₂P₃O₁₂. These units, which share their free corners in such a way that their ternary axes are all parallel, form rather spacious cages, which here are empty. This confirms the particular stability of this structural type in the absence of invited cations, a phenomenon which is rather rare in cage and tunnel structures.

The PO₄ tetrahedra have the classical geometry observed in the monophosphates, *i.e.* four equal P-O distances of 1.52 Å and O-P-O angles close to 109°.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51617 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

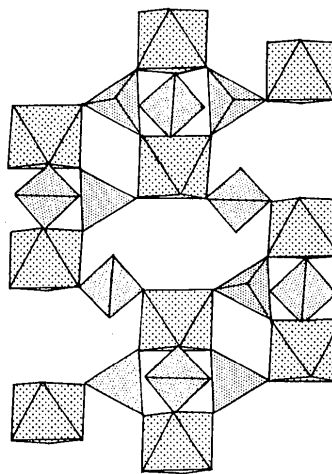


Fig. 1. Projection of a [210] layer showing the Nb₂P₃O₁₈ units.

Table 2. Distances (Å) and angles (°) in the NbO₆ octahedron and in the PO₄ tetrahedron

Nb	O(1)	O(1 ⁱ)	O(1 ⁱⁱ)	O(2)	O(2 ⁱ)	O(2 ⁱⁱ)
O(1)	1.994 (4)	2.792 (8)	2.792 (8)	2.786 (7)	3.961 (9)	2.798 (7)
O(1 ⁱ)	88.9 (2)	1.994 (4)	2.792 (8)	2.798 (7)	2.786 (7)	3.961 (9)
O(1 ⁱⁱ)	88.9 (2)	88.9 (2)	1.994 (4)	3.961 (9)	2.798 (7)	2.786 (7)
O(2)	89.4 (2)	89.9 (2)	177.9 (2)	1.968 (4)	2.828 (9)	2.828 (9)
O(2 ⁱ)	177.9 (2)	89.4 (2)	89.9 (2)	91.8 (2)	1.968 (4)	2.828 (9)
O(2 ⁱⁱ)	89.9 (2)	177.9 (2)	89.4 (2)	91.8 (2)	91.8 (2)	1.968 (4)

P	O(1)	O(1 ⁱⁱⁱ)	O(2 ^{iv})	O(2 ^v)
O(1)	1.516 (4)	2.501 (9)	2.494 (6)	2.461 (5)
O(1 ⁱⁱⁱ)	111.2 (4)	1.516 (4)	2.461 (5)	2.494 (6)
O(2 ^{iv})	110.3 (3)	108.1 (3)	1.525 (4)	2.481 (9)
O(2 ^v)	108.1 (3)	110.3 (3)	108.9 (4)	1.525 (4)

Symmetry code: (i) $-x, x-y, z$; (ii) $y-x, -x, z$; (iii) $x-y, -y, \frac{1}{2}-z$; (iv) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$; (v) $\frac{1}{3}-x+y, y-\frac{1}{3}, \frac{1}{3}+z$.

The NbO₆ octahedra are regular as shown from the O—O distances (Table 2) but the niobium atom is off-center in its octahedron by about 0.04 Å along *c*, leading to two sets of Nb—O distances significantly different at 3σ.

Since only one independent site is available for niobium, a statistical distribution of Nb^v and Nb^{iv} on the octahedral sites can be proposed. This oxide, which is the first Nasicon phosphate involving the lone

mixed-valence Nb^v—Nb^{iv}, is characterized by a high Nb^{iv} content, *i.e.* 50%. The possibility of introducing alkali ions or alkaline-earth ions in the cages in order to increase the Nb^v/Nb^{iv} ratio will be investigated. The study of the local environment of niobium by EPR is in progress.

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The Structures of Thallous Perbromate at 294 and 169 K

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Abstract. TlBrO₄, *M_r* = 348.28, orthorhombic, *Pnma*, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, *Z* = 4, *F*(000) = 592; *T* = 294 K, *a* = 9.182 (2), *b* = 6.095 (2), *c* = 7.649 (2) Å, *V* = 428.1 (2) Å³, *D_x* = 5.40 g cm⁻³, $\mu = 472.21 \text{ cm}^{-1}$, 764 unique reflections with *I* > 0, *R* = 0.073, *wR* = 0.050; *T* = 169 K, *a* = 9.140 (1), *b* = 6.049 (1), *c* = 7.612 (1) Å, *V* = 420.9 (1) Å³, *D_x* = 5.50 g cm⁻³, $\mu = 480.31 \text{ cm}^{-1}$, 628 unique reflections with *I* > 0, *R* = 0.072, *wR* = 0.071. These structures are of the BaSO₄ type and consist of nearly regular tetrahedral perbromate ions and monovalent thallium ions coordinated in an irregular geometry by ten O atoms from seven perbromate groups. The mean Br—O bond lengths were found to be 1.603 (6) Å at 294 K and

1.609 (9) Å at 169 K and are in good agreement with previous values; the mean O—Br—O bond angles were 109.4 (2)° at 294 K and 109.4 (3)° at 169 K. The principal departure of the perbromate ions from regular tetrahedral geometry is angular. Attempted refinement in the potential alternative space group *Pna*2₁ failed.

Introduction. Through an initial interest in crystalline lanthanide perbromates, we have become interested in the structures of other simple perbromates. We have previously reported on the structure of barium perbromate trihydrate (Gerkin, Reppart & Appelman, 1988) and of nickel perbromate hexahydrate (Gallucci, Gerkin & Reppart, 1988). We here report structural studies of monovalent thallium perbromate.

Experimental. Crystals of thallous perbromate were produced by slow evaporation at room temperature

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