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# The Layered Compound $Tl_2NbO_2PO_4$: Synthesis and Crystal Structure

M. FAKHFAKH,* M. F. ZID,* N. JOUINI,†‡ AND M. TOURNOUX‡

*Laboratoire de Chimie Minérale, Faculté des Sciences, Campus Universitaire, Le Belvédère, 1060 Tunis, Tunisia; †Ecole Normale Supérieure de l'Enseignement Technique, B.P. 56, 1008 Tunis, Tunisia; and ‡Institut des Matériaux de Nantes, Laboratoire de Chimie des Solides, 2 rue de la Houssinière, 44072 Nantes Cedex 03, France

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A new layered compound, $Tl_2NbO_2PO_4$, has been isolated. It crystallizes in the rhombohedral system, space group $R\bar{3}$. The cell parameters are $a$ = 8.746(2)Å, $c$ = 44.753(7)Å, $Z$ = 18. Its structure has been determined from 990 independent reflections, with $I \geq 3\sigma(I)$, collected on a CAD4 automated diffractometer. The final $R$ index and weighted $R_\omega$ index are 0.034 and 0.032, respectively. This structure is built up from layers of $NbO_6$ octahedra and $PO_4$ tetrahedra sharing corners. The Tl ions are located in the interlayer spaces.

## Introduction

As part of a search for new materials likely to exhibit ion-exchange properties, several systems $A^I$–$M$–$M'$–O ($M$ = Nb, Ta, Sb; $M'$ = P, As) have been investigated. Some years ago, starting with alkali phosphatoantimonates (*1, 2*) synthesized at high temperatures and using ion exchange in an acidic medium at 50°C, two layered phosphatoantimonic acids, $HSb(PO_4)_2 \cdot xH_2O$ and $H_3Sb_3O_6(PO_4)_2 \cdot xH_2O$, were prepared (*3, 4*). The former has a structure closely related to that of $Zr(HPO_4)_2 \cdot H_2O$ (*5*) but exhibits stronger acidic properties, as expected from the higher covalency of its 2-D framework.

We report here on the synthesis and crystal structure of a new layered compound, $Tl_2NbO_2PO_4$, identified during the investigation of the Tl–Nb–P–O system.

## Experimental

Single-phase powder was prepared from a stochiometric mixture of $Tl_2CO_3$, $Nb_2O_5$, and $NH_4H_2PO_4$. The starting materials were heated in air, in a platinium crucible, at 300°C for 12 hr to decompose $NH_4H_2PO_4$ and were then fired up to 570°C for 2 days. However, to obtain single crystals of $Tl_2NbO_2PO_4$, a large excess of $Tl_2CO_3$ and $NH_4H_2PO_4$, corresponding to a mixture of the chemicals in a molecular ratio 5 : 1 : 4, was needed. These crystals are colorless thin hexagonal platelets with large (001) faces.

Single-crystal X-ray study indicated a rhombohedral symmetry. The possible space groups are $R32$, $R3m$, $R\bar{3}m$, $R3$, and $R\bar{3}$. However, according to the intensity data and to the results of the structure solution, the latter space group was retained unambiguously.

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TABLE I

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

| | |
|---|---|
| Formula weight ($g mol^{-1}$) | 628.62 |
| Space group | $R\bar{3}$ |
| a (Å) | 8.746(2) |
| c (Å) | 44.753(6) |
| V ($Å^3$) | 2964.6(7) |
| Z | 18 |
| ρcalc ($g\ cm^{-3}$) | 6.337 |
| Crystal size(mm) | 0.04 X 0.04 X 0.015 |
| Radiation(Å) | $MoK\bar{\alpha}$, $\lambda = 0.71069$ |
| Scan mode | $\omega$ |
| Scan angle (°) | $\Delta\omega = 1.3 + 0.35tg\theta$ |
| Recording angular range θ(°) | 1.5 - 30.0 |
| Number of independent data observed with $\sigma(I)/I \geq 0.33$ used in refinement | 990 |
| Number of variables (isotropic temperature factors) | 46 |
| $R = \Sigma([\|Fo\| - \|Fc\|)2/\Sigma\omega Fo^2]^{1/2}$ | 0.066 |
| $R_\omega = [\Sigma\omega(\|Fo\| - \|Fc\|)^2 / \Sigma\omega Fo^2]^{1/2}$ | 0.064 |
| Number of variables (anisotropic temperature factors for Tl, Nb and P atoms) | 64 |
| R | 0.034 |
| $R_\omega$ | 0.032 |
| Extinction parameter refined | 3.3(2) $10^{-8}$ |
| Absorption coefficient ($cm^{-1}$) | 514.3 |

The cell parameters (Table I) were least-squares refined from powder diffraction data collected with an INEL curved multidetector using Cu $K\alpha$ radiation. The powder pattern (Table II) includes observed and calculated $d(hkl)$ along with intensities calculated with the Lazy-pulverix program (*6*).

Diffraction intensities for structure determination were measured with a Nonius CAD4 diffractometer using graphite monochromated Mo $K\alpha$ radiation. The data collection was carried out under the conditions given in Table I. On account of the crystal dimensions and of the calculated linear absorption coefficient, an absorption correction was applied. For data reduction, structure solution, and refinements, the MoLEN program chain from Enraf–Nonius (*7*) was used.

### Refinement of the Structure

Refinement was carried out by the full matrix least-squares method. The starting positional parameters for Tl atoms were deduced from the Patterson map. Successive refinements and Fourier difference maps then gave the positions of the other atoms. In a first stage of refinement, the atomic coordinates and isotropic temperature factors were refined to $R = 0.066$ and $R_\omega = 0.064$. The final refinement carried out with anisotropic thermal factors for Tl Nb, and P atoms and isotropic ones for oxygen atoms, including secondary extinction and anomalous dispersion, led to $R = 0.034$ and $R_\omega = 0.032$. The main results of the final refinement are indicated in Table I. The final Fourier difference map is featureless, with maxima and minima in the range ± 1.0 $e^-$ $Å^{-3}$. Tables III and IV present the final atomic coordinates and thermal parameters (structure factor tables will be sent on request).

### Description and Discussion of the Structure

This structure is two-dimensional, which is its most striking feature. Six identical $(NbO_2PO_4)^{2-}$ anionic layers related to each other by inversion centers are stacked per-

TABLE II

$Tl_2NbO_2PO_4$ X-RAY POWDER DIFFRACTION DATA

| h k l | $d_{obs}$ (Å) | $d_{calc}$ (Å) | $I/I_o$ | h k l | $d_{obs}$ (Å) | $d_{calc}$ (Å) | $I/I_o$ |
|---|---|---|---|---|---|---|---|
| 1 1 0 | 4.368 | 4.369 | 25 | 0 1 17 | 2.483 | 2.484 | 17 |
| 1 1 3 | 4.193 | 4.193 | 9 | 3 0 6 | 2.389 | 2.389 | 3 |
| 1 1 6 | 3.767 | 3.769 | 9 | 1 1 18 | 2.160 | 2.159 | 10 |
| 0 0 12 | 3.725 | 3.725 | 4 | 2 2 6 | 2.097 | 2.096 | 14 |
| 1 1 9 | 3.279 | 3.280 | 100 | 0 2 19 | 1.999 | 1.998 | 7 |
| 1 0 13 | 3.129 | 3.130 | 8 | 3 0 18 | 1.769 | 1.769 | 7 |
| 2 1 1 | 2.856 | 2.855 | 44 | 1 1 27 | 1.548 | 1.548 | 7 |
| 1 1 12 | 2.837 | 2.835 | 8 | 4 1 12 | 1.509 | 1.510 | 4 |
| 0 3 0 | 2.523 | 2.523 | 22 | | | | |

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

| Atom | x | y | z | B(Å²) |
|---|---|---|---|---|
| Tl(1) | 0.64040(7) | 0.71840(7) | 0.02869(2) | 1.70(1) |
| Tl(2) | 0.67530(9) | 0.72594(8) | 0.13956(2) | 2.49(1) |
| Nb | 0.6693 (1) | 0.0915 (1) | 0.08670(3) | 0.69(2) |
| P(1) | 1/3 | 2/3 | 0.0842 (2) | 0.73(9) |
| P(2) | 2/3 | 1/3 | 0.0273 (2) | 0.77(9) |
| P(3) | 0 | 0 | 0.0831 (2) | 0.90(9) |
| O(1) | 1/3 | 2/3 | 0.0068 (4) | 1.2 (3)* |
| O(2) | 0 | 0 | 0.1167 (4) | 1.2 (3)* |
| O(3) | 1/3 | 2/3 | 0.1176 (4) | 1.2 (3)* |
| O(4) | 0.478 (1) | 0.146 (1) | 0.0911 (2) | 0.7 (2)* |
| O(5) | 0.670 (1) | 0.023 (1) | 0.1231 (2) | 1.2 (2)* |
| O(6) | 0.157 (1) | 0.638 (1) | 0.0705 (2) | 1.0 (2)* |
| O(7) | 0.174 (1) | 0.151 (1) | 0.0700 (2) | 1.0 (2)* |
| O(8) | 0.659 (1) | 0.163 (1) | 0.0390 (2) | 0.9 (2)* |

*Note*. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

pendicular to the $c$ axis of the hexagonal cell (Fig. 1). These layers can be described as being built up from triangular $Nb_3O_{15}$ units sharing corners with $PO_4$ tetrahedra (Fig. 2). The same type of triangular units resulting from the association of three $MO_6$ octahedra appears in hexagonal tungsten bronze (HTB) and in tetragonal tungsten bronze (TTB) frameworks (*8, 9*). In order to simplify the description, one can distinguish in each octahedron equatorial oxygens approximately in a plane parallel to the sheet and axial oxygens. On one side of the layer, each octahedron of the $Nb_3O_{15}$ unit shares one of its two axial oxygens with the same $P(2)O_4$ tetrahedron. The unshared $P(2)O_4$ vertex points into the interlayer space. Two of the equatorial oxygens of an octahedron are used to form the $Nb_3O_{15}$ unit. The two others are shared with $P(1)O_4$ and $P(3)O_4$ respectively. Each of these tetrahedra is linked to three octahedra belonging to three

TABLE IV

GENERAL DISPLACEMENT PARAMETER EXPRESSIONS BETAS(×10⁴)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | Beq (Å²) |
|---|---|---|---|---|---|---|---|
| Tl(1) | 68.2(6) | 79.3(6) | 2.2(1) | 76.6(9) | 1.9(3) | 1.2(3) | 1.70(1) |
| Tl(2) | 169.6(9) | 104.4(7) | 2.0(1) | 161(1) | 5.0(3) | 3.5(3) | 2.49(1) |
| Nb | 29(5) | 20(1) | 1.2(1) | 28(2) | 0.2(5) | -0.3(5) | 0.69(2) |
| P(1) | 31(5) | 31(5) | 0.9(3) | 31(5) | 0 | 0 | 0.73(9) |
| P(2) | 31(5) | 31(5) | 1.1(3) | 31(5) | 0 | 0 | 0.77(9) |
| P(3) | 33(6) | 31(5) | 1.5(3) | 31(5) | 0 | 0 | 0.90(9) |

*Note*. The form of the anisotropic displacement parameter is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13}\ kl\beta_{23})]$.

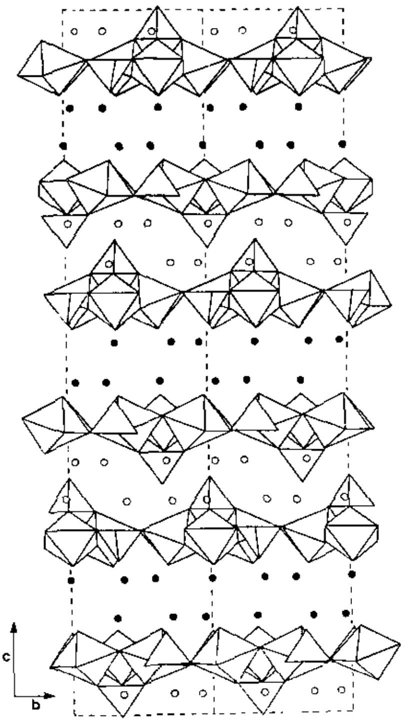

FIG. 1. Structure view along [1 0 0]. Thallium (1) and thallium (2) are represented by open and dark circles, respectively.

different $Nb_3O_{15}$ units. The fourth tetrahedron vertex is unshared and points, just like the unshared axial oxygen of each octahedron, into the interlayer space in a direction opposed to that of the unshared $P(2)O_4$ vertex. This results into two types of interlayer space. Into the first, points the unshared vertex of $P(2)O_4$ and into the second points each unshared vertex of the $P(1)O_4$, $P(3)O_4$, and $NbO_6$ polyhedra. This way of linking $Nb_3O_{15}$ units and tetrahedra ($P(1)O_4$, $P(3)O_4$) results in layers similar to those observed in $A_3M_6Si_4O_{26}$ (*10, 11*), which are also formed by $Nb_3O_{15}$ units but held together by $SiO_4$ tetrahedra. The main difference between the two structures is their dimensionality. Adding a $P(2)O_4$ tetrahedron to the layer leads to the 2-D anionic network of the title compound. The 3-D anionic framework of $A_3M_6Si_4O_{26}$ results from the association of these layers by corner sharing, in a mirror plane of all the polyhedra.

In both structures, one recognizes pentagonal windows reminiscent of the TTB ones. In TTB, these windows are delimited by five edges of octahedra instead of two edges of tetrahedra and three edges of octahedra as in the title compound and in $A_3M_6Si_4O_{26}$. Composite pentagonal windows are also observed in $KNb_3O_3(PO_4)_3$ (*12*): in that case they are delimited by four octahedra and one tetrahedron. It should be noted that the association of $P(2)O_4$ and $Nb_3O_{15}$ units leads to $Nb_3PO_{16}$ groups similar to those observed in the layered compound $K_3Sb_3O_6(PO_4)_2 \cdot xH_2O$. In this oxophosphate, the windows are hexagonal and quite similar to those of HTB.

In front of the pentagonal windows which provide a possible pathway between two adjacent anionic sheets, Tl(1) and Tl(2) cations are located in space I and space II, respectively, and ensure the cohesion of the structure along *c*. It should be pointed out that for each interanionic-sheet space the corresponding thallium cations are located in such a way that they form a double-cationic layer.

Examination of Tl–O distances (Table V) allows us to discuss bonding along *c*. Only Tl–O distances of less than 3.25 Å have been considered. The nearest oxygen neighbors (7 and 5 oxygens for Tl(1) and Tl(2), respec-

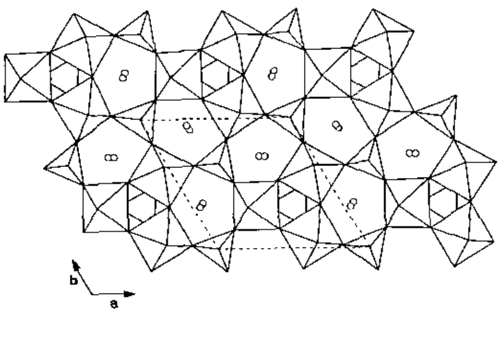

FIG. 2. Anionic sheet projection along [0 0 1].

TABLE V

PRINCIPAL INTERATOMIC DISTANCES (Å) AND COORDINATION ANGLES (°) RELATED TO THE STRUCTURE OF $Tl_2NbO_2PO_4$

| Nb | O(4$^{i}$) | O(4$^{iv}$) | O(5) | O(6) | O(7) | O(8) |
|---|---|---|---|---|---|---|
| O(4$^{i}$) | 1.959(9) | 2.85(2) | 2.79(1) | 2.81(1) |  | 2.79(1) |
| O(4$^{iv}$) | 94.4(5) | 1.914(9) | 2.75(1) |  | 2.83(1) | 2.83(1) |
| O(5) | 97.9(4) | 97.8(5) | 1.73(1) | 2.85(2) | 2.84(2) |  |
| O(6) | 88.0(4) | 165.6(4) | 95.9(4) | 2.09(1) | 2.79(1) | 2.80(1) |
| O(7) | 164.5(4) | 90.5(4) | 96.1(4) | 83.8(4) | 2.07(1) | 2.86(1) |
| O(8) | 82.6(4) | 85.5(4) | 176.6(4) | 80.8(4) | 83.0(4) | 2.24(1) |

| P(1) | O(3) | O(6$^{ii}$) | O(6$^{v}$) | O(6$^{viii}$) |
|---|---|---|---|---|
| O(3) | 1.49(2) | 2.52(2) | 2.55(2) | 2.55(2) |
| O(6$^{ii}$) | 113.1(5) | 1.56(1) | 2.48(2) | 2.48(2) |
| O(6$^{v}$) | 113.1(5) | 105.8(6) | 1.56(1) | 2.48(2) |
| O(6$^{viii}$) | 113.1(5) | 105.8(6) | 105.8(6) | 1.56(1) |

| P(2) | O(1) | O(8$^{i}$) | O(8$^{iv}$) | O(8$^{vii}$) |
|---|---|---|---|---|
| O(1) | 1.52(2) | 2.52(2) | 2.52(2) | 2.52(2) |
| O(8$^{i}$) | 109.9(5) | 1.55(1) | 2.52(2) | 2.52(2) |
| O(8$^{iv}$) | 109.9(5) | 109.1(5) | 1.55(1) | 2.52(2) |
| O(8$^{vii}$) | 109.9(5) | 109.1(5) | 109.1(5) | 1.55(1) |

| P(3) | O(2) | O(7$^{vi}$) | O(7$^{x}$) | O(7$^{iii}$) |
|---|---|---|---|---|
| O(2) | 1.50(2) | 2.52(2) | 2.52(2) | 2.52(2) |
| O(7$^{vi}$) | 112.2(5) | 1.54(1) | 2.47(2) | 2.47(2) |
| O(7$^{x}$) | 112.2(5) | 106.7(5) | 1.54(1) | 2.47(2) |
| O(7$^{iii}$) | 112.2(5) | 106.7(5) | 106.7(5) | 1.54(1) |

| | | | |
|---|---|---|---|
| Tl(1)-O(1$^{i}$) | 2.67(1) | Tl(1)-0(7$^{vii}$) | 3.18(1) |
| Tl(1)-O(6$^{iv}$) | 2.86(1) | Tl(1)-O(8$^{iv}$) | 3.20(1) |
| Tl(1)-O(6$^{vii}$) | 2.85(1) | Tl(1)-O(8$^{vii}$) | 2.93(1) |
| Tl(1)-O(7$^{iv}$) | 2.99(1) | Tl(1)-O(8$^{ix}$) | 3.22(1) |

| | | | |
|---|---|---|---|
| Tl(2)-O(2$^{i}$) | 2.837(8) | Tl(2)-O(5$^{i}$) | 2.71(1) |
| Tl(2)-O(3$^{i}$) | 2.927(7) | Tl(2)-O(5$^{iv}$) | 3.12(1) |
| Tl(2)-O(4$^{vii}$) | 2.78(1) | Tl(2)-O(5$^{vi}$) | 3.19(1) |

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

tively) are situated on the same side with respect to thallium position and belong to the same anionic sheet (Fig. 3). There exists, however, a weaker bond with the adjacent layer (Tl(1)–O, 3.22 Å; Tl(2)–O, 3.19 Å). Thus it appears that bonding along *c* is rather weak.

The structure may indeed be described in terms of neutral sandwich-stacked along *c*. Each sandwich is formed by an anionic sheet between two cationic monolayers containing Tl(1) and Tl(2), respectively.

It should also be noted that the dissymmetrical environments of the two thalliums

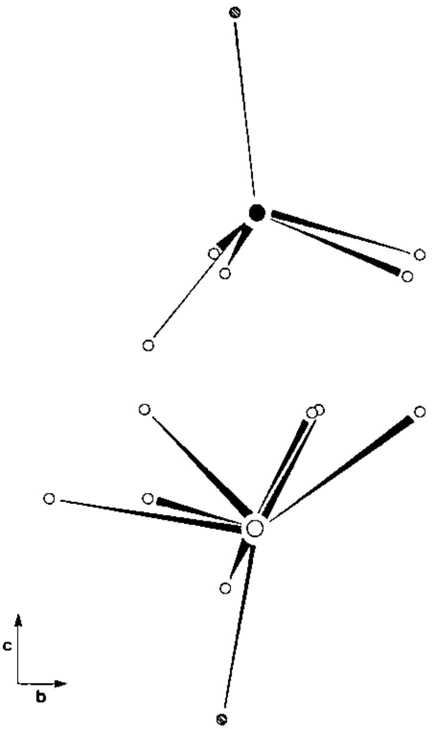

FIG. 3. Environment of Tl(1) and Tl(2) ions. Oxygens belonging to the same anionic sheet are represented by small open circles.

reveal a stereochemical activity of the lone pair $6s^2$ of this cation. Calculation of the lone pair position and measurement of the NMR chemical shift are presently in progress.

Looking at the Nb coordination, one observes only a weak distortion of the $NbO_6$ octahedron with O–O distances ranging from 2.75 to 2.86 Å. The Nb atom is off centered within this octahedron, thus leading to a long Nb–O distance (Nb–O(8) : 2.24 Å) and a short one (Nb–O(5) : 1.73 Å) corresponding to the unshared oxygen. The four remaining Nb–O distances range from 1.92 to 2.09 Å with two short (1.92 and 1.96 Å) and two longer (2.07 and 2.09 Å) distances corresponding to Nb–O–Nb and Nb–O–(P(1) or P(3)) bonds, respectively. The coordination polyhedron around the Nb atom could then be considered as a tetragonal pyramid similar to those observed for Mo(V) in $K_4Mo_8P_{12}O_{52}$ (*13*) and for Nb(V) in $CsNbOP_2O_7$ (*14*), $KNbOP_2O_7$ (*15*), $RbNbOP_2O_7$ (*16*), $\alpha$–$NbOPO_4$ (*17*), $K_3NbO(AsO_4)_2$ (*18*), and $Cs_4(NbO)_2Si_8O_{21}$ (*19*). This off-centered position of Nb enables the title compound to be considered as a thallium niobyl oxophosphate $Tl_2(NbO)O(PO_4)$. Correlatively the $P(2)O_4$, bonded to three $NbO_6$ octahedra by sharing O(8) which corresponds to the longest Nb–O distances, exhibits four P–O distances ranging from 1.52 to 1.55 Å. This tetrahedron is almost regular. The two other tetrahedra $P(1)O_4$ and $P(3)O_4$ characterized by O–O and P–O distances ranging from 2.47 to 2.55 Å and from 1.49 to 1.56 Å, respectively, appear weakly distorted. The unshared oxygen forms one P–O bond that is significantly shorter, namely 1.49 and 1.50 Å for P(1) and P(3), respectively.

The 2-D character of the structure and the possible diffusion pathway through the layers using the pentagonal windows favor ion mobility. A study of the ionic conductivity and ion exchange properties of this compound is presently in progress.

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