

The Crystal Structure of NbOPO₄

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The crystal structure of NbOPO₄ has been accurately determined on the basis of three-dimensional X-ray data using a crystal grown at high pressure under hydrothermal conditions. The symmetry is tetragonal, space group No. 85, *P4/n*, and the unit cell contains two formula units and has the following dimensions:

$$\begin{aligned} a &= 6.3873 \pm 0.0010 \text{ \AA} \\ c &= 4.1037 \pm 0.0008 \text{ \AA} \\ V &= 167.4 \text{ \AA}^3 \end{aligned}$$

The structure contains chains of corner-shared NbO₆ octahedra running parallel to the *c* axis. Tetrahedra of PO₄ link the chains together to give a three-dimensional network. The structure is discussed and compared to structurally related compounds.

The investigation of NbOPO₄ is part of research program at this Institute concerned with the determination of accurate structural data for discussion of bonding in transition metal compounds of simple stoichiometry. In connection with this project, the structures of MoOPO₄¹ and VOSO₄² have recently been completed.

The preparation and chemical analysis of NbOPO₄ was first accomplished by Hahn³ who studied this compound along with TaOPO₄ by means of X-ray powder diffraction. Latter workers^{4,5} have studied NbOPO₄ and recently Haider has established the tetragonal unit cell.

EXPERIMENTAL

Preparation of crystals. NbOPO₄ may be prepared by many methods. Hahn's³ process, which involves precipitation from an acidic potassium hexaniobate solution with 85 % phosphoric acid and subsequent ignition yielded good results but no single crystals. The powder obtained in this manner was sealed in platinum tubes and heated for 8 days at 1200°C. The sample was well sintered and gave very sharp X-ray diffraction patterns but no single crystals of NbOPO₄ could be found. Preparation of single crystals did not succeed when sodium chloride was used as a flux at 900°C followed by very slow cooling. The use of PbO as a flux at 900° also did not give any crystals of the desired phase.

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Table 1. Observed X-ray powder data for NbOPO₄. CuK α ₁ radiation.
 $\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$.

| <i>h k l</i> | 10 ⁵ sin ² θ obs | 10 ⁵ sin ² θ calc | <i>I</i> obs | <i>h k l</i> | 10 ⁵ sin ² θ obs | 10 ⁵ sin ² θ calc | <i>I</i> obs |
|--------------|--|---|-----------------|--------------|--|---|-----------------|
| 1 1 0 | 2 917 | 2 908 | m- | 4 2 0 | 29 067 | 29 084 | m+ |
| 1 0 1 | 4 981 | 4 977 | s | 3 3 1 | 29 706 | 29 699 | w= |
| 2 0 0 | 5 821 | 5 817 | s+ | 0 0 3 | 31 744 | 31 707 | w(d) |
| 1 1 1 | 6 427 | 6 431 | m | 3 2 2 | 32 980 | 32 997 | w(d) |
| 2 1 1 | 10 794 | 10 794 | m- | 1 0 3 | 33 186 | 33 161 | w- |
| 2 2 0 | 11 635 | 11 634 | m | 1 1 3 | 34 644 | 34 615 | w= |
| 0 0 2 | 14 092 | 14 092 | m- | 4 0 2 | 37 354 | 37 359 | w |
| 3 1 0 | 14 526 | 14 542 | m+ | 2 0 3 | 37 536 | 37 524 | w |
| 3 0 1 | 16 618 | 16 611 | m+ | 5 1 0 | 37 796 | 37 810 | w |
| 1 1 2 | 17 011 | 17 000 | m- | 4 1 2 | 38 807 | 38 814 | w- |
| 3 1 1 | 18 058 | 18 065 | m- | 2 1 3 | 38 971 | 38 978 | w- |
| 2 0 2 | 19 919 | 19 909 | w+ | 5 0 1 | 39 883 | 39 878 | m+ |
| 2 1 2 | 21 363 | 21 363 | w | 4 3 1 | | | |
| 3 2 1 | 22 408 | 22 428 | m+ | 3 3 2 | 40 276 | 40 268 | m |
| 4 0 0 | 23 270 | 23 267 | s- | 5 1 1 | 41 346 | 41 332 | m- |
| 2 2 2 | 25 730 | 25 726 | *w(d) | 4 2 2 | 43 176 | 43 176 | m- |
| 3 3 0 | 26 169 | 26 176 | m- | 2 2 3 | 43 338 | 43 340 | m- |
| 4 1 1 | 28 241 | 28 245 | m- | 3 0 3 | 44 805 | 44 795 | m- |
| 3 1 2 | 28 631 | 28 634 | m+ | 5 2 1 | 45 683 | 45 695 | m- |
| | | | | 4 4 0 | 46 538 | 46 535 | m |

* d = diffuse

Single crystals could be made, however, by hydrothermal techniques. A sample consisting of a mixture of 80 mg of 50 % phosphoric acid and 13 mg of Nb₂O₅ was sealed in a gold capsule. The sample was placed in a pressure bomb and subjected to 1800 atmospheres of pressure at 600°C for 3 days. The resulting white crystalline mass contained many very thin transparent square plates of NbOPO₄.

X-Ray diffraction data and computing methods. The powder pattern of a well sintered sample could be completely indexed on the basis of a tetragonal unit cell of dimensions similar to those reported by Haider. Values for the cell dimensions were calculated from a photograph taken with a Guinier type focusing camera using monochromatized CuK α ₁ radiation. Potassium chloride ($a = 6.29228 \text{ \AA}$)⁷ was used as an internal standard and the sin² θ values were refined using least-squares methods. Table 1 gives a comparison of observed and calculated data. The unit-cell dimensions with standard deviations at 25°C are:

$$\begin{aligned} a &= 6.3873 \pm 0.0010 \text{ \AA} \\ c &= 4.1037 \pm 0.0008 \text{ \AA} \\ V &= 167.4 \text{ \AA}^3 \end{aligned}$$

A thin crystal of NbOPO₄ whose dimensions are 0.040 mm (*a*) \times 0.056 mm (*b*) \times 0.003 mm (*c*) was mounted along the *c* axis. From rotation and Weissenberg photographs (*hk0*–*hk3*) of this crystal it was established that NbOPO₄ has the Laue symmetry *4/m*. Since only the *hk0* reflections with *h*+*k* = odd are systematically absent, the space group No. 85, *P4/n* was indicated.

The reflections were recorded photographically with the multiple-film technique using CuK α radiation and the relative intensities were estimated visually by comparison to an intensity scale obtained by photographing a single reflection [200] of the same crystal for varying lengths of time. A total of 269 reflections were assigned an intensity with 151 of them being independent. The use of MoK α radiation did not significantly increase the total number of reflections observed.

Table 2. The structure of NbOPO₄.Space group: No. 85, *P4/n*Unit-cell dimensions: *a* = 6.3873 ± 0.0010 Å*c* = 4.1037 ± 0.0008 Å*V* = 167.4 Å³Cell contents: 2 NbOPO₄2 Nb, 2 O₁ in 2 × 2 (*c*): ±(½, ½, *z*)2 P in 2 (*b*): ±(½, ½, ½)8 O₂ in 8 (*g*): ±(*x*, *y*, *z*) ±(½ - *x*, ½ - *y*, *z*)
±(½ - *y*, *x*, *z*) ±(*y*, ½ - *x*, *z*)

| Atom | <i>x</i> ± σ(<i>x</i>) | <i>y</i> ± σ(<i>y</i>) | <i>z</i> ± σ(<i>z</i>) | <i>B</i> ± σ(<i>B</i>) Å ² |
|----------------|--------------------------|--------------------------|--------------------------|---|
| Nb | ¼ | ¼ | 0.7828 ± 0.0004 | 0.75 ± 0.02 |
| P | ¼ | ¾ | ¼ | 1.08 ± 0.06 |
| O ₁ | ¼ | ¼ | 0.2172 ± 0.0028 | 0.89 ± 0.16 |
| O ₂ | 0.7737 ± 0.0014 | 0.4462 ± 0.0014 | 0.2902 ± 0.0024 | 1.76 ± 0.14 |

Practically all of the computational work involved in this study, including refinement of lattice constants (Program No. 6018), absorption correction (No. 6019), Lorentz-polarization correction (No. 6024), least-squares refinement (No. 6023), calculation of interatomic distances (No. 6016) and calculation of standard deviations in bond lengths were performed on the electronic computers FACIT EDB and BESK. The program numbers refer to the *World List of Crystallographic Computer Programs*.⁸

The intensity material has been corrected for absorption using the linear absorption coefficient, $\mu = 345.3 \text{ cm}^{-1}$, derived from the mass absorption coefficients given in the *International Tables*.⁹ The absorption factor (*A**) ranged in value from 0.30 for the 0 level to 0.83 for the 3rd level in the formula $I = I_{\text{obs}}/A^*$. The numerical value of *A** for each reflection is included in a document¹⁰ which is available from this Institute.

A comparison of the X-ray data for MoOPO₄ and NbOPO₄ indicated that the two compounds were isostructural. The atoms of the two formula units of NbOPO₄ occupy the point positions of space group *P4/n* as shown in Table 2. A least-squares refinement of the structure was run using the parameters of MoOPO₄ as the initial ones for NbOPO₄. Hughes' weighting function $w = 1/h^2 |F_{\text{obs-min}}|^2$ for $|F_{\text{obs}}| \leq h |F_{\text{obs-min}}|$ and $w = 1/|F_{\text{obs}}|^2$ for $|F_{\text{obs}}| > |F_{\text{obs-min}}|$ with *h* equal to 4 was used in the refinement. Atomic scattering factors for un-ionized atoms were used with the real part of the anomalous dispersion correction¹¹ being applied to the scattering curves.¹² Initially all 269 reflections were used but after a few cycles four strong low-angle reflections (020, 200, 011, 101) were removed since they were suffering from extinction. The refinement was then continued until the parameter shifts were less than five per cent of the standard deviations. The final discrepancy index

$$R = \sum | |F_{\text{obs}}(hkl)| - |F_{\text{calc}}(hkl)| | : \sum |F_{\text{obs}}(hkl)|$$

was then down to 0.058.

The final parameters including isotropic temperature factors are included in Table 2. The weight analysis at the last cycle of refinement is given in Table 3. A comparison of the observed structure factors and final calculated structure factors forms a part of an available document.¹⁰

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of NbOPO₄ may be described as consisting of chains of corner-shared NbO₆ octahedra running parallel to the *c* axis. The chains are coupled together by tetrahedra of PO₄, so that every NbO₆ octahedron shares

Table 3. Normalized weight analysis obtained in the final cycle of the least-squares refinement of NbOPO₄. $w =$ weighting factor, $\Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$.

| Interval $\sin \theta$ | Number of reflections | $\overline{w \Delta^2}$ | Interval F_{obs} | Number of reflections | $\overline{w \Delta^2}$ |
|---------------------------|--------------------------|-------------------------|------------------------------|--------------------------|-------------------------|
| 0.00—0.46 | 32 | 0.80 | 0—7 | 5 | 0.72 |
| 0.46—0.58 | 30 | 1.04 | 7—15 | 28 | 0.56 |
| 0.58—0.67 | 36 | 0.77 | 15—23 | 63 | 0.98 |
| 0.67—0.74 | 33 | 1.14 | 23—30 | 62 | 1.00 |
| 0.74—0.79 | 24 | 1.55 | 30—38 | 35 | 1.12 |
| 0.79—0.84 | 26 | 0.83 | 38—45 | 34 | 1.34 |
| 0.84—0.89 | 31 | 1.01 | 45—53 | 10 | 0.89 |
| 0.89—0.93 | 17 | 0.88 | 53—60 | 11 | 1.17 |
| 0.93—0.97 | 38 | 1.05 | 60—68 | 6 | 0.71 |
| 0.97—1.00 | | | 68—75 | 11 | 1.06 |

corners with four phosphate tetrahedra, each of which shares corners with four octahedra giving a three-dimensional network. The schematic drawings of Figs. 1 and 2 show the linking of octahedra and tetrahedra.

The interatomic distances and standard deviations (σ) of neighbouring atoms are given in Table 4. A complete list of all distances less than 3.5 Å

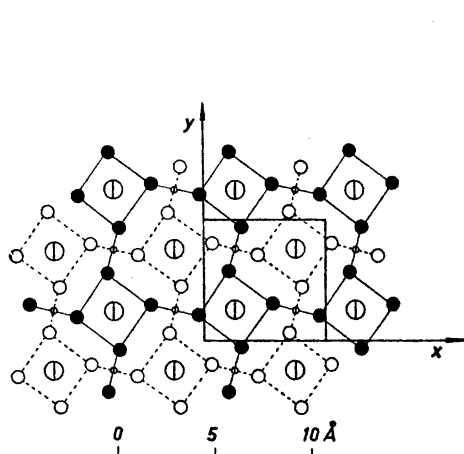


Fig. 1. Schematic drawing showing the links between PO₄ tetrahedra and NbO₆ octahedra viewed along [001] in the structure of NbOPO₄. Open and full large circles denote oxygen atoms in two separate planes, 1.72 Å apart. Lined open circles denote oxygen atoms shared between NbO₆ octahedra as shown in Fig. 2. Small lined circles denote phosphorus atoms. The niobium atoms have not been indicated.

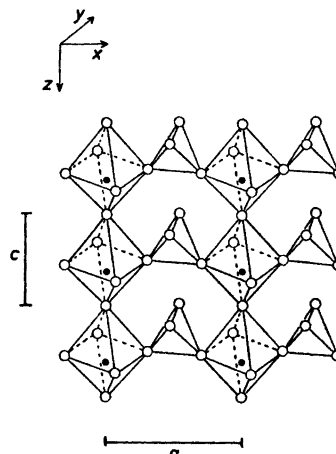


Fig. 2. The structure of NbOPO₄. Schematic drawing showing the chains formed by NbO₆ octahedra linked together by sharing corners and also showing the links between PO₄ tetrahedra and NbO₆ octahedra. Full circles denote niobium atoms and open ones oxygen atoms. The phosphorus atoms have not been indicated. The two remaining oxygens in each PO₄ tetrahedron are shared — as shown in Fig. 1 — with two further NbO₆ octahedra which have not been indicated.

Table 4. Interatomic distances and standard deviations (σ in Å) for NbOPO₄.

| | |
|------|---|
| Nb—O | Nb—2 O ₁ (O ₁ —2 Nb) = 1.783 ± 0.012; 2.321 ± 0.012 Nb—4 O ₂ (O ₂ —Nb) = 1.969 ± 0.009 |
| P—O | P—4 O ₂ (O ₂ —P) = 1.528 ± 0.009 |
| O—O | O ₁ —12O ₂ = 4 × (2.806 ± 0.013) 4 × (2.850 ± 0.013) 4 × (3.304 ± 0.009) (O ₂ —3 O ₁) = (2.806; 2.850; 3.304) O ₂ —8 O ₂ = 2 × (2.480 ± 0.013) * 2.525 ± 0.013 * 2 × (2.976 ± 0.013) 2 × (2.753 ± 0.012) 3.434 ± 0.013 |

* Denotes O—O distances within PO₄ group.

and significant bond angles are given in the previously described document.¹⁰ It can be seen from the table that all distances are reasonable and in good agreement with previous knowledge of Nb(V) and phosphate structural chemistry. The table also indicates that the structure is well stabilized by the rather close packing of oxygen atoms. Each oxygen is surrounded by eleven or twelve other oxygens at distances of from 2.5 to 3.4 Å. The oxygen volume (unit-cell volume/number of oxygens in unit cell) is 16.7 Å³ which also indicates a closepacking of oxygens.

The phosphate group is a regular tetrahedron with P—O distances being 1.528 ± 0.009 Å while O—O distances are 2.52 ± 0.01 Å (four values) and 2.48 ± 0.01 Å (two values). These values give an average O—P—O angle within the tetrahedra of 109.5°. The distances and angles of the PO₄ tetrahedra are almost identical with those of MoOPO₄ and in good agreement with those found by Furberg¹³ in H₃PO₄ (average values 1.56 Å and 109.9°) and those reported in the *International Tables*¹⁴ for normal orthophosphates, 1.53 Å.

The niobium is essentially octahedrally coordinated with four oxygens at 1.969 ± 0.009 Å, one at 1.78 ± 0.01 Å and the last at 2.32 ± 0.01 Å. The niobium has moved out the plane of the four atoms along the *c* axis toward one of the corner shared oxygens. This one dimensional distortion of the octahedral coordination has been found in other niobium compounds. In the Nb—P—O system the new phase P₂O₅·9Nb₂O₅ has been reported¹⁵ and its crystal structure determined. One group of niobium octahedra are distorted with the following Nb—O distances (4 at an average of 2.00 ± 0.06 Å, 1 at 1.76 ± 0.08 Å and 1 at 2.30 ± 0.05 Å). The structure of Nb₂O₇F has been completed¹⁶ and shows for a group of octahedra the following Nb—O distances (4 at an average of 1.98 ± 0.01 Å, one at 1.86 ± 0.03 Å and the last at 2.20 ± 0.03 Å).

The niobium octahedron is less distorted than the octahedra in the isomorphous compounds MoOPO₄ and VOMoO₄¹⁷ where the long and short bonds are 1.66 Å, 2.63 Å, and 1.68 Å, 2.59 Å, respectively. The niobium has no unpaired electrons associated with it as do Mo⁵⁺ or V⁴⁺ to account for

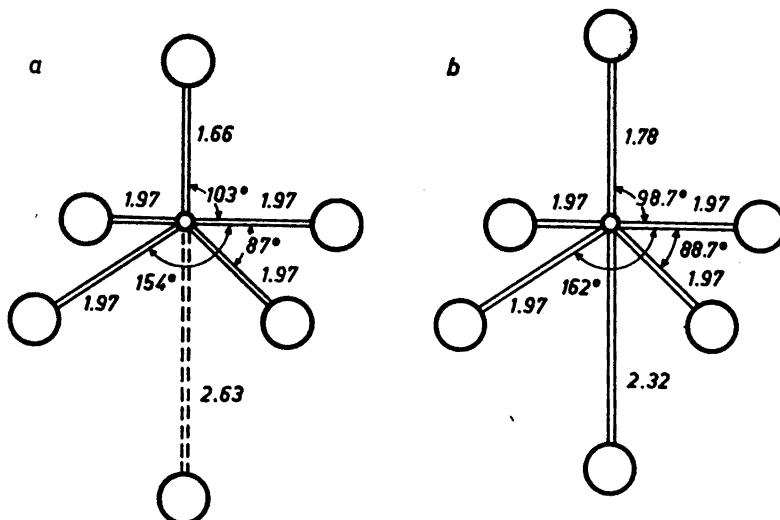


Fig. 3. The coordination of oxygen atoms (large circles) around the molybdenum or niobium atom (small circle) in MoOPO₄ (Fig. 3a) and NbOPO₄ (Fig. 3b). Angles related to the others by symmetry have not been indicated.

the short metal oxygen distance. Orgel¹⁸ has suggested that metal ions such as Nb⁵⁺ are too small to form regular octahedral coordination. The usual distortion which results is for the metal ion to move within a regular octahedron of oxygens to achieve a coordination of between five and six oxygens.

A comparison of the octahedra of NbOPO₄ and MoOPO₄ is given in Fig. 3. The rather large difference between the unit cell dimensions (MoOPO₄ has $a = 6.177$, $c = 4.293$) of these two compounds is due to the degree of distortion of the octahedra and not to difference in size of the metal ions.

Acknowledgements. This investigation has received financial support from the *Swedish Natural Science Research Council* and from the *Malmfonden - Swedish Foundation for Scientific Research and Industrial Development*. Permission for the use of the computers FACIT EDB and BESK was granted by the *Computer Division of the National Swedish Rationalization Agency*.

The authors wish to thank Professor Arne Magnéli for his perfunctorily encouraging and stimulating interest and for all facilities placed at their disposal. They are also indebted to Dr. Sten Andersson for his willing help in the hydrothermal synthesis of single crystals of NbOPO₄.

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Received September 30, 1965.