

Bi₃(PO₄)O₃, the Simplest Bismuth(III) Oxophosphate: Synthesis, IR Spectroscopy, Crystal Structure, and Structural Complexity

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Supporting Information

ABSTRACT: The bismuth(III) oxophosphate Bi₃(PO₄)O₃ was obtained by hydrothermal synthesis. The unit cell has $a = 5.6840(6)$ Å, $b = 7.0334(7)$ Å, $c = 9.1578(9)$ Å, $\alpha = 78.958(2)^\circ$, $\beta = 77.858(2)^\circ$, $\gamma = 68.992(2)^\circ$, $V = 331.41(6)$ Å³, space group $P\bar{1}$, and $Z = 2$. The crystal chemical formula that reflects the presence of oxo-centered tetrahedra and triangles is $^{2D}[O^{III}O^{IV}_2Bi_3](PO_4)$. The crystal structure contains $[O_3Bi_3]^{3+}$ -heteropolyhedral corrugated layers parallel to (001), which alternate along [001] with isolated (PO₄) tetrahedra. The structural complexity parameters are $\nu = 22$ atoms, $I_G = 3.459$ bits/atoms, and $I_{G,\text{total}} = 76.107$ bits/unit cell, and thus Bi₃(PO₄)O₃ is the simplest pure bismuth(III) oxophosphate.

Bismuth oxides, bismuth-based oxosalts of inorganic acids, and their derivatives with transition-metal ions are well-known classes of inorganic compounds that attract interest because of their wide range of physical and chemical properties, such as luminescence, selective oxidation catalysts, and multi-ferroic behavior.^{1–4} The ionic conductivity properties, induced by vacancies at oxygen-atom positions in fluorite-related structures, are established in α , β , γ , δ , and ϵ modifications of Bi₂O₃,^{5,6} in the family of bismuth isomorphous mixed oxophosphates–oxovanadates with the general formula Bi₂₃V_{4–4x}P_{4x}O_{44.5} ($0 \leq x \leq 1$),^{7,8} as well as in Bi₁₄(PO₄)₄O₁₅⁹ and Bi₄₆(PO₄)₈O₅₇.¹⁰ Bismuth-based oxosalts of transition metals attract interest because of their low-dimensional magnetic properties. Most belong to the Bi₂O₃–MO–X₂O₅ ternary system ($M = \text{divalent metal}$; $X = \text{P, As, V}$).¹¹

Bismuth oxosalts are characterized by the presence of “additional” oxygen atoms¹² that do not belong to tetrahedral polyanions. These oxygen atoms are typically tetrahedral or, more rarely, are 3-fold-coordinated by bismuth cations. The positively charged anion-centered OBi₄ tetrahedra [OBi₃ triangles or mixed O(Bi₄M²⁺)₄ tetrahedra], with oxygen atoms at the centers of the polyhedra and bismuth atoms at the vertexes, are dominant building units in the structures. Such cation-centered units manifest a wide structural diversity associated with

edge-sharing OBi₄ tetrahedra, forming 0D, 1D, 2D, and 3D polycationic frameworks.¹²

Compounds with different ratios of Bi₂O₃–P₂O₅ belonging to the Bi₂O₃–BiPO₄ system have been reported previously.¹³ It was shown that the phase with the chemical composition Bi₃PO₇ [=Bi₃(PO₄)O₃] is stable up to 1193 K and appears in both equilibrium and metastable phase diagrams.¹⁴ The same compound was also obtained as a side product in the system Bi₂O₃–H₃BO₃–NH₄H₂PO₄.¹⁵ Despite having the simplest stoichiometry among bismuth oxophosphates, Bi₃(PO₄)O₃ has been characterized only by powder X-ray diffraction (XRD) analysis,^{13–15} and its crystal structure is unknown.

The only pure bismuth oxophosphates are structurally characterized Bi_{4.25}(PO₄)₂O_{3.375},¹⁶ Bi₅(PO₄)₂O_{4.5},¹⁶ Bi_{6.67}(PO₄)₄O₄,¹⁷ Bi₁₄(PO₄)₄O₁₅,⁹ Bi₂₃(PO₄)₄O_{28.5},⁷ and Bi₄₆(PO₄)₈O₅₇,¹⁰ as well as the minerals smrkovicite Bi₂(PO₄)O(OH)¹⁸ and petitjeanite Bi₃(PO₄)₂O(OH),¹⁹ which also contain hydroxyl groups.

Here we report the synthesis of the bismuth oxophosphate Bi₃(PO₄)O₃ and its investigation by powder XRD and single-crystal X-ray analysis and IR spectroscopy. A crystal chemical discussion and a comparison of all bismuth(III) oxophosphates are provided.

Single crystals of Bi₃(PO₄)O₃ were synthesized as a side product by a hydrothermal method in the system Bi(OH)₃–NiCO₃–K₂CO₃–K₃PO₄. The synthesis was carried out with a Bi₂O₃–NiO–K₂O–P₂O₅ ratio of 1:1:1:1 at pH = 6–7 in a copper-lined stainless steel autoclave. The reaction was done at a constant pressure of 480–500 atm in the temperature range of 690–700 K. The reaction went to completion during heating for 20 days, followed by cooling to room temperature for over 24 h. The precipitate was separated by filtration, washed several times with hot distilled water, and finally dried at room temperature for 12 h. The reaction products consisted of several phases: ~30 vol % small yellow crystals of the Bi₃(PO₄)O₃ phase (Figure S1), green crystals of Bi₂Ni(PO₄)O₂(OH),²⁰ yellow-green needles of KBi₄Ni₂(PO₄)₃O₄,²¹ and colorless crystals of Bi_{6.67}(PO₄)₄O₄.

Crystals of Bi₃(PO₄)O₃ were selected manually for further studies.^{22–24} Powder XRD (Figure S3) data match those

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previously reported for $\text{Bi}_3(\text{PO}_4)_3$.¹³ The IR absorption spectrum is shown in Figure 1. The number of bands in the mid-IR spectrum exactly corresponds to those predicted by theoretical-group analysis (see the Supporting Information, SI).

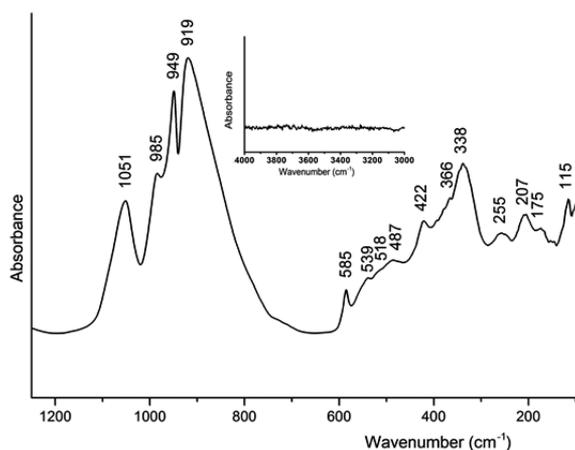


Figure 1. IR spectrum of $\text{Bi}_3(\text{PO}_4)_3$. The region 1200–4000 cm^{-1} is featureless, which excludes the presence of OH groups and H_2O molecules.

The crystal structure of $\text{Bi}_3(\text{PO}_4)_3$ was studied by single-crystal X-ray analysis.²⁵ The experimental details of the data collection and refinement results are listed in Tables S1–S4. Bond-valence-sum calculations were done using bond-valence parameters for $\text{Bi}^{3+}-\text{O}^{26}$ and $\text{P}^{5+}-\text{O}^{27}$ bonds and are presented in Table S5.

Following the tradition of describing structures emphasizing cation-centered polyhedra, in the crystal structure of $\text{Bi}_3(\text{PO}_4)_3$, bismuth cations are coordinated to produce distorted $\text{Bi}(1,2)\text{O}_8$ and Bi3O_7 polyhedra. The bond strengths scatter considerably in these polyhedra, with strong bonds in one coordination hemisphere and longer weak bonds in the other, because of the stereoactivity of the lone electron pair (LEP) on the Bi^{3+} cations. The distortion of the BiO_n polyhedra can be described by the eccentricity parameter Φ_i (see the SI),²⁸ for which the absolute value measures the deformation density of the LEP [the $|\Phi|$ values for Bi(1–3) are 5.32×10^{-5} , 5.79×10^{-5} , and 6.17×10^{-5} , respectively]. BiO_n polyhedra are linked via common edges, forming layers that are parallel to (001). Isolated (PO_4) tetrahedra link the layers, forming a heteropolyhedral framework (Figure 2a).

When the principles of anion-centered crystal chemistry are emphasized,¹² the crystal chemical formula of the compound studied here can be written as ($Z = 2$): ${}^{2\text{D}}[\text{O}^{\text{IV}}_2\text{O}^{\text{III}}\text{Bi}_3](\text{PO}_4)$, where square brackets denote a layered structural unit consisting of anion-centered polycations, with Roman numerals denoting the coordination numbers of the oxygen atoms. Atoms O1 and O2 are tetrahedrally coordinated by Bi^{3+} cations with mean distances O1–Bi = 2.429 Å and O2–Bi = 2.420 Å. The O3 atom is characterized by planar 3-fold coordination with O3–Bi = 2.206 Å. $[\text{OBi}_4]$ tetrahedra are linked via common trans edges to form $[\text{O}_2\text{Bi}_3]^{5+}$ double chains of the type C8,¹² which is common in inorganic compounds,^{12,29} extending along [100]. Adjacent chains are linked by $[\text{OBi}_3]$ triangles, forming positively charged $[\text{O}_3\text{Bi}_3]^{3+}$ heteropolyhedral corrugated layers parallel to (001). Along [001], these layers alternate with isolated (PO_4) tetrahedra (Figure 2b).

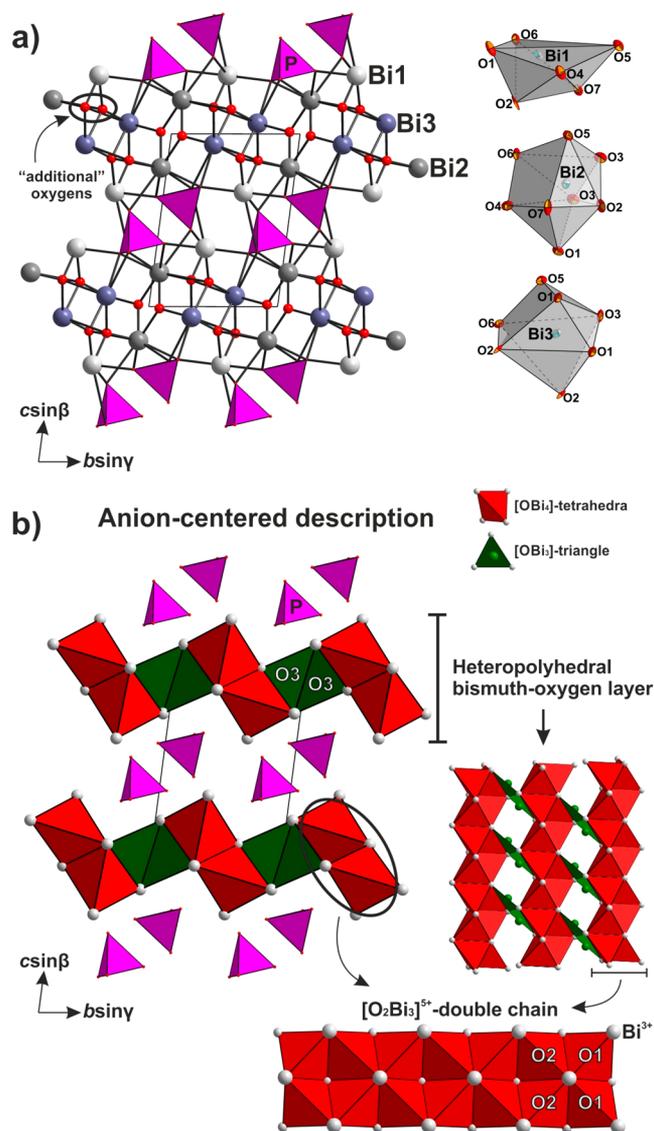


Figure 2. General view of the crystal structure of $\text{Bi}_3(\text{PO}_4)_3$ as cation-centered (a) and anion-centered (b) polyhedra.

Similar double chains of anion-centered polyhedra with mixed cationic composition were found in the structures of $\text{K}[\text{O}_4\text{Bi}_4\text{Ni}_2](\text{PO}_4)_3$ ²¹ and oxosalts with the general formula $[\text{O}_2\text{Bi}_m\text{T}](\text{TO}_4)$ (where $M = \text{Zn}, \text{Cd}, \text{Ca}, \text{Cu}, \text{Mn}, \text{Mg}, \text{Pb}$; $T = \text{P}, \text{V}, \text{As}$).¹² In the structure of ${}^{2\text{D}}[(\text{O}_4\text{Bi}_5)\text{O}_{0.5}](\text{PO}_4)_2$,¹⁶ similar $[\text{O}_2\text{Bi}_3]^{5+}$ double chains of the type C8 are linked via common bismuth edges, forming an $[\text{O}_4\text{Bi}_5]^{7+}$ layer of the type L5 (“cresnel”-type).¹² The positive charge of the chain is compensated for by (PO_4) tetrahedra and O7 atoms, which statistically (25%) occupy large windows of the layer.

The compound $[\text{O}_3\text{Bi}_3](\text{PO}_4)$ belongs to a group of pure bismuth oxophosphates (Table 1) with structures based on polycations of anion-centered $[\text{OBi}_4]$ tetrahedra and $[\text{OBi}_3]$ triangles. In the structure of ${}^{2\text{D}}[\text{O}^{\text{III}}_2\text{O}^{\text{IV}}_{13}\text{Bi}_{14}](\text{PO}_4)_4$ ⁹ fluorite-like complexes of edge-sharing $[\text{OBi}_4]$ tetrahedra and $[\text{OBi}_3]$ triangles form heteropolyhedral layers, which alternate with isolated (PO_4) tetrahedra. Heteropolyhedral cation frameworks are present in the crystal structure of ${}^{3\text{D}}[\text{O}^{\text{IV}}_{18.62}\text{O}^{\text{III}}_{0.6}\text{Bi}_{18.71}\text{Cr}_{0.27}](\text{PO}_4)_6$,³⁰ where $[\text{O}_{18.62}\text{Bi}_{17.98}]^{16.7+}$ layers of edge-sharing $[\text{OBi}_4]$ tetrahedra are linked by two disordered $[\text{OBi}_2(\text{Bi},\text{Cr})]$ triangles, and in the

Table 1. Crystallographic Data and Complexity Parameters for Bismuth(III) Oxyphosphates Containing Oxo-Centered Tetrahedra and Triangles

compound/mineral	space group, <i>Z</i>	unit cell parameters			<i>V</i> (Å ³)	<i>v</i> (atoms)	<i>I_G</i> (bits/atoms)	<i>I_{G,total}</i> (bits/unit cell)
		<i>a</i> (Å), <i>α</i> (deg)	<i>b</i> (Å), <i>β</i> (deg)	<i>c</i> (Å), <i>γ</i> (deg)				
Bi ₃ (PO ₄) ₃ O ₃	$\bar{P}1$, 2	5.684, 78.96	7.033, 77.86	9.158, 68.99	331.41	22	3.459	76.107
smrkovicite Bi ₂ (PO ₄) ₂ O(OH) ¹⁸	<i>P2</i> ₁ / <i>c</i> , 4	6.954	7.494, 107.00	10.809	538.68	36	3.170	114.117
petitjeanite Bi ₃ (PO ₄) ₂ O(OH) ¹⁹	$\bar{P}1$, 2	9.798, 88.28	7.250, 115.27	6.866, 110.70	408.35	30	3.907	117.207
Bi _{6,67} (PO ₄) ₄ O ₄ ¹⁷	$\bar{P}1$, 2	9.195, 112.2	7.552, 93.9	6.933, 106.9	417.81	31	3.986	123.850
Bi ₅ (PO ₄) ₂ O _{4.5} ¹⁶	<i>C2</i> / <i>c</i> , 4	13.093	5.707, 98.240	15.293	1130.92	40	3.422	136.877
Bi _{4,25} (PO ₄) ₂ O _{3.375} ¹⁶	$\bar{P}1$, 4	7.048, 77.604	9.863, 84.556	15.365, 70.152	980.93	71	5.164	366.632
Bi ₄₆ (PO ₄) ₈ O ₅₇ ¹⁰	<i>C2</i> / <i>m</i> , 2	19.607	11.418, 112.14	21.112	4377.99	142	5.502	781.264
Bi ₂₃ (PO ₄) ₄ O _{28.5} ⁷	$\bar{P}1$, 2	11.366, 77.535	11.369, 86.214	20.453, 119.565	2197.83	162	6.340	1027.059
Bi ₁₄ (PO ₄) ₄ O ₁₅ ⁹	<i>C2</i> / <i>c</i> , 16	19.275	11.370, 93.63	52.408	11462.07	392	3.615	2592.966

structure of ^{3D}[O^{III}₂O^{IV}₅₅Bi₄₆](PO₄)₈,¹⁰ in which the framework is formed by fluorite-like complexes of [OBi₄] tetrahedra decorated by [OBi₃] triangles.

The presence of hydroxyl groups in the crystal structures of smrkovicite ^{2D}[O(OH)Bi₂](PO₄)₂¹⁸ and petitjeanite ^{1D}[O(OH)Bi₃](PO₄)₂¹⁹ leads to the formation of [(OH)Bi₃]⁸⁺ triangles. The structure of smrkovicite is based on heteropolyhedral layers of the type **L21**¹² formed by pairs of edge-sharing [OBi₄] tetrahedra, connected by common bismuth vertexes into a layer with windows that are occupied by [(OH)Bi₃] triangles. In the structure of petitjeanite, edge-shared [O₂Bi₄] dimers of the type **I4**¹² are linked by [(OH)Bi₃] triangles, forming heteropolyhedral chains.

Calculation of the structural complexity parameters³¹ was done using information-based complexity measures (see the SI). All calculations were performed using the *ToposPro* software,³² and the results are given in Table 1. The structural complexity parameters for Bi₃(PO₄)₃O₃ are *v* = 22 atoms, *I_G* = 3.459 bits/atoms, and *I_{G,total}* = 76.107 bits/unit cell (herein *v* is the number of atoms per reduced unit cell, and *I_G* and *I_{G,total}* are the amounts of structural information per atom and per reduced unit cell, respectively). Bi₃(PO₄)₃O₃ is the simplest pure bismuth(III) oxyphosphate. The most complex compound is Bi₁₄(PO₄)₄O₁₅,⁹ which has *I_{G,total}* = 2592.966 bits/unit cell.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01195.

Photograph of the crystals, SEM image, EDS spectra, chemical composition, powder XRD data, description of IR spectra based on factor-group analysis, results of the crystal structure refinement, eccentricity parameter calculations, and structural complexity calculations (PDF)

Accession Codes

CCDC 1824125 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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- (22) The element contents were determined using a JEOL JSM6480LV scanning electron microscope equipped with an INCA Wave 500 wavelength spectrometer and using the following conditions: accelerating voltage, 20 kV; current, 20 nA; beam diameter, 3 μm (Figure S2 and Table S1).
- (23) Powder XRD analysis was performed on a STOE-STADI MP diffractometer equipped with a curved $\text{Ge}(111)$ monochromator that yields strictly monochromatic $\text{Co K}\alpha_1$ radiation. Data were collected using a regime of sequential overlapping of scanned regions using a linear position-sensitive detector with an angle coverage of 5° at 2θ with a channel width of 0.02° . Determination of the phase composition was made using a software package *WinXPow* and associated PDF-2 powder database.
- (24) The middle- and far-IR regions were registered using a Bruker IFS 125HR Fourier transform infrared spectrometer equipped with an attenuated-total-reflectance module.
- (25) Structural data for $\text{Bi}_3(\text{PO}_4)_3\text{O}_3$: A total of 4455 reflections were collected representing a full reciprocal sphere from a yellow irregular grain with dimensions $0.10 \times 0.11 \times 0.12 \text{ mm}^3$, triclinic, $\bar{P}1$ (No. 2), $a = 5.6840(6) \text{ \AA}$, $b = 7.0334(7) \text{ \AA}$, $c = 9.1578(9) \text{ \AA}$, $\alpha = 78.958(2)^\circ$, $\beta = 77.858(2)^\circ$, $\gamma = 68.992(2)^\circ$, $V = 331.41(6) \text{ \AA}^3$, $Z = 2$, $\rho = 7.715 \text{ g cm}^{-3}$, and $\mu(\text{Mo K}\alpha) = 79.682 \text{ mm}^{-1}$ measured on a Bruker Apex II diffractometer at 120 K. An empirical adsorption correction based on symmetry-equivalent reflections was applied. The structure was solved by the “charge-flipping” method and refined using the *Jana2006* software. The final refinement cycles converged with $R_1 = 4.41$, $wR_2 = 5.34$, $\text{GOF} = 1.02$, 1445 for $I > 2\sigma(I)$, and $\Delta\rho_{\text{max,min}} = +1.94/-1.71 \text{ e \AA}^{-3}$.
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