$K_5[W_4O_8(H_2BO_4)(HPO_4)_2(PO_4)_2]\cdot 0.5H_2O$: A Tungsten Borophosphate with a Novel Sandwich-like Layered Structure

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The first tungsten borophosphate compound, $K_5[W_4O_8(H_2BO_4)(HPO_4)_2(PO_4)_2]\cdot 0.5H_2O$, has been synthesized under mild hydrothermal conditions, and the crystal structure with a new stoichiometry (B:P ratio 1:4) exhibits a novel sandwich-like layered structure.

Borophosphates as a relative young research field have drawn much attention during the past few years because of their potential for novel structures and, correspondingly, catalytic applications.[1,2] Although systematic investigations on borophosphates began only a few years ago, a broad spectrum of compounds has already been characterized with various anionic partial structures such as oligometric units, chains, ribbons, layers, and three-dimensional frameworks.[3–11] The possibility of creating more open structure by using organic templates was also demonstrated.[12–20] However, surprisingly, despite the numerous cluster anions known for molybdenum and tungsten phosphates, not much attention has been paid to such borophosphate compounds. To our best knowledge, known are only two molybdenum borophosphates, $(C_3N_2H_5)_8[Mo^{V}{}_5Mo^{VI}{}_7O_{22}(BO_4)_2(PO_4)_5(HPO_4)_3]\cdot nH_2O(n \approx 4)$ and $(C_3N_2H_5)_5[Mo_5{}^{V}Mo_7{}^{VI}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]\cdot H_2O$ prepared by Sevov's group.[21,22] Their structures are quite interesting as they resemble Dawson anions but where the two pole caps of three edge sharing MoO_6 octahedra in the latter are replaced by tetrahedral borate sharing corners with three phosphonic groups. Here, we report the hydrothermal synthesis and characterizations of $K_5[W_4O_8(H_2BO_4)(HPO_4)_2(PO_4)_2]\cdot 0.5H_2O$ (**1**), the first tungsten borophosphate with a novel layered structure of new stoichiometry (B:P = 1:4).

The synthesis of $K_5[W_4O_8(H_2BO_4)(HPO_4)_2(PO_4)_2]\cdot 0.5H_2O$ can be successfully carried out under mild hydrothermal conditions. $Na_2WO_4\cdot 2H_2O$ (1.652 g), KH_2PO_4 (4.080 g), H_3BO_3 (1.850 g) were mixed in molar ratios of 1:6:6, and then 3 mL H_2O and 4.631 g of KCl were added. The resulting solution was transfered into a Teflon-lined autoclove and heated at 397 K for 6 days. Colorless crystals of **1** remained after filtration. The crystals were washed with water and air dried. No sodium was detected in the compound using EDX analysis although used in the starting materials. The yield is 50% based on Na_2WO_4.

The crystal structure of the new compound was determined by single-crystal X-ray diffraction.[23] The structure of compound **1** can be best described as made of novel sandwich-like layers (Figure 1), stacked along the *c* axis, which are built from bioctahedral W_2O_{11} units and PO_4, BO_4 tetrahedra. Tungsten share one oxygen atoms with the neighboring WO_6 octahedron to constitute the bioctahedral W_2O_{11}(W–O3 = 1.898 Å), and three O-atoms with three PO_4 tetrahedra units (W–O = 1.968–2.169 Å). Additionally, each W atom of W_2O_{11} units has two terminal oxygen on one side of the layers (W–O = 1.728 and 1.746 Å), which is considered as the reason for the low dimensionality of the structure. Each of phosphate tetrahedra, in turn, share three corners with WO_6 octahedra, and the remaining vertex is shared with a BO_4 tetrahedron. The BO_4 tetrahedra bridge pairs of PO_4 goups by sharing two corners, and has two poronated oxygen atoms (B–O = 1.437 Å).

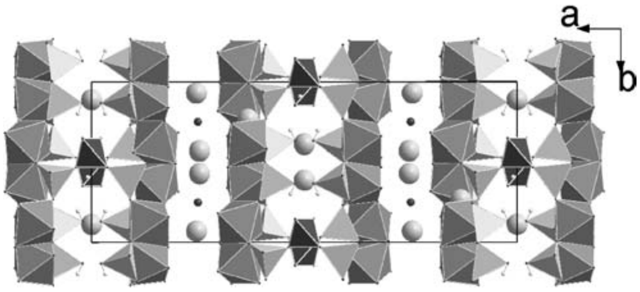

Figure 1. View of the crystal structure of **1** along the *c* axis, showing the novel sandwich-like layers and the K^+ ions located in the cavities and interspace of these layers (WO_6 octahedron, medium grey; PO_4 tetrahedron, light grey; BO_4 tetrahedron, dark grey; K atom, grey sphere; O atom, dark sphere; H atom, small light grey sphere).

Such layer could also be considered as consisting of two sublayers, each one being constructed from only corner-sharing W_2O_{11} and PO_4 units. In each sublayer, the bioctahedral W_2O_{11} groups are corner-connected, through four of its oxygen atoms, with two PO_4 groups to form $W_2P_2O_{15}{}^{8-}$ anions groups with two 3-membered polyhedral rings. Each $W_2P_2O_{15}{}^{8-}$ group is also corner-connected with four neighboring groups to form a novel 8-membered polyhedral rings, making the layer microporous (Figure 2), where the potassium ions are located. The framework of **1** examined here, therefore, can also be characterized by the presence of infinite number of 4- and 8-membered polyhedral rings. These sublayers are staggered and pillared with borate tetrahedra through P–O–B bridges, which leads to a sandwich-like layered structure. It is worth noting that there are different types of intersecting channels within the double-layer slabs. One is formed from eight polyhedra sharing corners in the following sequence: $-WO_6-PO_4-BO_4-PO_4-WO_6-PO_4-BO_4-PO_4-$ along the *b* axis (Figure 3a). The channels are not exactly straight and round but rather wavelike and oblong. The short axis of the opening is about 3.311 Å, and the long one is about 5.789 Å (O–O distances). There is no charge balance cations blocking this channel. The other opening is made up from twelve corner-sharing polyhedra runing along the *c* axis (Figure 3b). The shape of the channel is close to ellipse with the long radius of around 10.6 Å and the short one of 5.0 Å. The guest K^+ ions

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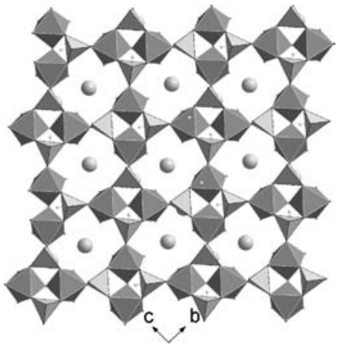

Figure 2. Polyhedral view of the sublayer along the *a* axis, showing the numerous 3-, 4-, and 8-membered polyhedral rings made from corner-shared WO_6 and PO_4. The K^+ ions are located in the centers of the 8-membered rings (WO_6 octahedron, medium grey; PO_4 tetrahedron, light grey; K atom, grey sphere).

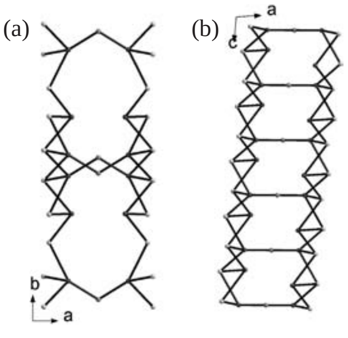

Figure 3. Wires view of the layer of **1**, showing the intersecting channel systems. (a) View of the 12-membered ring channel running along *c* axis, (b) view of the 8-membered ring channel running along *b* axis.

and water molecules, occupy the opening space, channels, and the interlayer space of layers to keep the structural stability and satisfy the charge balance. Such, $K(1)^+$ ions fill in the center of the eight-membered rings within sublayers, and $K(2)^+$ ions are located in the twelve-membered ring channels, while $K(3)^+$ ions and water molecules occupy alternately the interlayer spaces to separate the open-framework into layers.

Difference-thermoanalytical and thermogravimetric studies on the title compound up to temperatures of 1273 K were carried out on a STA-409PC/4/H LUXX DSC-TGA analyzer (heating rate 10 K/min, system open to air, corundum crucible). The compound is stable in air up to about 650 K and then has a continuous weight loss of total 4% to 1273 K, corresponding to the releasing of free H_2O, water through condensation of –OH groups and B_2O_3. The metal ratio measuremed with ICP is W:P:K:B = 4:4.54:4.98:0.93.

$K_5[W_4O_8(H_2BO_4)(HPO_4)_2(PO_4)_2]\cdot 0.5H_2O$ is the first tungsten borophosphate. It presents a novel sandwich-like layered structure, which is unique in the sense that it has not previously been observed in a large collection of borophosphates. Furthermore, it also is the first example of a borophosphate compound with a B:P ratio of 1:4. Interestingly, the X-ray excitation spectra of the title compound at room temperature shows a broad emission band between 500 and 650 nm with the maximum at around 550 nm. Therefore, the successful synthesis of $K_5[W_4O_8(H_2BO_4)(HPO_4)_2(PO_4)_2]\cdot 0.5H_2O$ indicates that tungsten borophosphates exist and it may be possible to prepare compounds with more complex structures having useful properties.

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23 Crystal data: M = 6102.49, monoclinic, space group $C2/c$, $a = 26.987(5)$ Å, $b = 9.794(2)$ Å, $c = 9.5407(19)$ Å, $\beta = 99.98(3)^\circ$, $V = 2483.6(9)$ Å^3, $Z = 1$, $D = 4.108$ Mg m^{-3}, $3.80^\circ < \theta < 29.99^\circ$, λ (Mo Kα) = 0.71073 Å, $\mu = 19.819$ cm^{-1}, $F(000) = 2752$, $T = 293(2)$ K. The sample ($0.06 \times 0.03 \times 0.035$ mm^3) is studied on a Nonius Kappa CCD with graphite monochromatized Mo Kα radiation. 330 unique reflectiongs ($R_{\text{int}} = 0.0399$) and 203 parameters were used for the full-matrix, least-squares refinement of F^2 using the program package SHELXL,[24] $R1 = 0.0527$ [$I > 2\sigma(I)$], $R1 = 0.0617$ (all data); $wR2 = 0.0933$ [$I > 2\sigma(I)$], $wR2 = 0.0963$ (all data).
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