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$Na_3Pb^{II}[B(O_3POH)_4]$: An Alkali-Metal Lead Borophosphate with Heterocubane-like Units Na_3PbO_4

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$Na_3Pb^{II}[B(O_3POH)_4]$ was synthesized under hydrothermal conditions. The crystal structure determination from single-crystal X-ray diffraction data ($I4_1/a$, $Z = 4$, $a = 6.9182(8)$ Å, $c = 27.309$ (3) Å, $V = 1307.0(3)$ Å^3) revealed the presence of $[B(O_3POH)_4]^{5-}$ oligomers and heterocubane-like units Na_3PbO_4 with mixed-occupied metal cation sites.

Recent research in the field of borophosphates[1] has led to the discovery of exciting structures such as chiral helices[2,3] as well as novel oligomers,[4] which are currently unknown for pure phosphates or borates. In search of new borophosphates, we investigated the use of heavy group 14 elements (Sn and Pb), which might show stereochemically active free electron pairs,[5] leading to noncentrosymmetric crystal structures.[6] The successful synthesis of the zinc/cobalt−lead compounds $Pb^{II}M^{II}[BP_2O_8(OH)]$[7] proved that the hydrothermal synthesis at moderate temperatures is suitable for obtaining lead(II)-containing borophosphates.

In this paper, we report on the synthesis and crystal structure of the first alkali-metal lead borophosphate $Na_3Pb^{II}[B(O_3POH)_4]$ exhibiting a "propeller" borophosphate anion[8] and a heterocubane-like arrangement of cation sites, which are mixed occupied by Na^+ and Pb^{2+} cations.

The title compound was obtained by hydrothermal treatment of the appropriate educts.[9] A selected single crystal was subjected to X-ray diffraction, revealing the atomic structure of the new borophosphate.[10]

The complex anion of $Na_3Pb^{II}[B(O_3POH)_4]$ consists of one central BO_4 tetrahedron, which is connected via O atoms to four PO_4 tetrahedra, resulting in a pentameric fundamental building unit (Figure 1a). The four equal B−O distances in the tetrahedron are 1.472(3) Å, and the P−O distances range from 1.504(3) to 1.571(3) Å. The P−O distance to the bridging O atom between B and P amounts to 1.571(3) Å, and the included angle is 127.1(2)°. The shortest bond is observed for the terminal O2 atom, which has three short contacts to the surrounding Na/Pb cations and is part of a heterocubane-like atomic arrangement consisting of alternating O atoms and metal cations (Figure 1b). According to the single-crystal X-ray diffraction data and subsequent energy-dispersive X-ray analysis of the crystal under inves-

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(9) A total of 0.5 g of $PbB_2O_4 \cdot H_2O$ (Alfa Aesar) and 1.145 g of $Na_2HPO_4 \cdot 2H_2O$ (99.5% Riedel de Haën) were dissolved in 8 mL of deionized water together with 1 mL of H_3PO_4 (85%, Merck KGaA) and stirred at 353 K for 1 h. The pH of the solution was found to be 2. The white gel was transferred into a 10 mL Teflon autoclave (filling degree 35%) and heated at 443 K for 5 days. The colorless crystals were separated from the mother liquor by vacuum filtration, washed with water/acetone, and dried in air at 333 K. The powder X-ray diffraction pattern of the product shows only weak reflections of unknown impurities. The chemical bulk analyses gave (in wt %) Na 10.0(2), Pb 30.3(6), B 1.53(3), and P 17.7(3), which is in good agreement with the calculated values for $Na_3Pb^{II}[B(O_3POH)_4]$ (Na 10.28, Pb 30.88, B 1.61, and P 18.46). The IR spectrum exhibits four broad absorption bands in the range from 4000 to 1450 cm^{-1} (3420, 2774, 2361, and 1633 cm^{-1}), which are assigned to OH groups.

(10) (a) X-ray diffraction data were collected on a Rigaku AFC7 four-circle diffractometer equipped with a Mercury CCD detector (Mo Ka radiation, graphite monochromator). The structure was solved by direct methods (space group $I4_1/a$) and refined by full-matrix least-squares methods by using *SHELXS*[10b] and *SHELXL*[10c] included in the program package *WinGX*.[10d] The free refinement of the occupation factor of the Na/Pb site led to 0.758(2)/0.242, which was fixed to 0.75/0.25 for the final refinement cycle. The H positions could not be located in the difference Fourier map (for further details, see the text). The final data for the refinement are $Na_3Pb^{II}[B(O_3POH)_4]$, $M = 666.9$ g/mol, tetragonal, $I4_1/a$ (No. 88), $a = 6.9182(8)$ Å, $c = 27.309(3)$ Å, $V = 1307.0(3)$ Å^3, $Z = 4$, 4613 measured reflections, 877 independent reflections, $R1 = 0.037$, $wR2 = 0.086$ for all data. (b) Sheldrick, G. M. *SHELXS-97: A program for automatic solution of crystal structures*; University of Goettingen: Goettingen, Germany, 1997. (c) Sheldrick, G. M. *SHELXL-97: A program for crystal structure refinement*; University of Goettingen: Goettingen, Germany, 1997. (d) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

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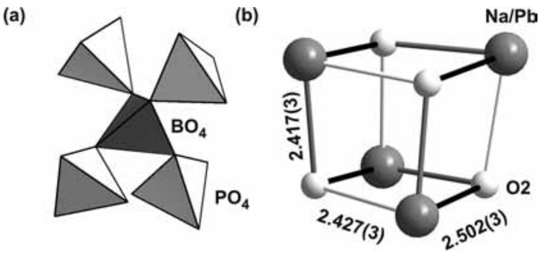

Figure 1. Structural units of $Na_3Pb^{II}[B(O_3POH)_4]$: (a) borophosphate anion $[B(O_3POH)_4]^{5-}$ consisting of a central borate tetrahedron, which is connected to four PO_4 tetrahedra (H atoms are not shown); (b) heterocubane-like arrangement of metal cations and O anions. The cation sites are mixed occupied by Na and Pb in the ratio 3:1. The Na/Pb−O distances (in Å) are shown in different gray shades.

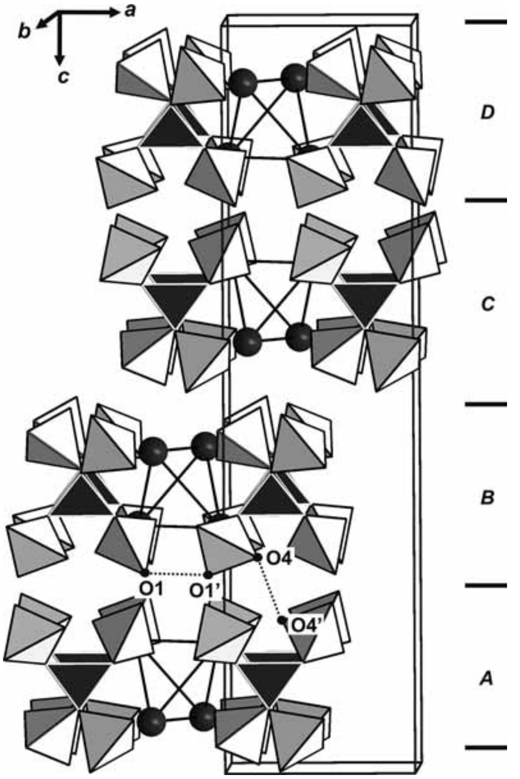

Figure 2. Crystal structure of $Na_3Pb^{II}[B(O_3POH)_4]$ with outlined unit cell: The borophosphate anions $[B(O_3POH)_4]^{5-}$ and metal cations are packed in layers parallel to *ab* and are stacked along *c* in the sequence ...*ABCD*.... Two of the shortest O···O distances between the anions are shown as dotted lines [d(O1···O1′) = 2.492(6) Å and d(O4···O4′) = 2.523(6) Å] and resemble strong O−H···O bridges. The Na/Pb atoms of each heterocubane-like unit are highlighted as dark-gray balls.

tigation, the cationic site is mixed occupied by Na and Pb in the atomic ratio 3:1. Three distinct Na/Pb−O distances are found for the 12 edges of the distorted cube (Figure 1b).

The two different structural units in the crystal structure of $Na_3Pb^{II}[B(O_3POH)_4]$ form layers perpendicular to the [001] direction, as shown in Figure 2. The layers are stacked with the sequence...*ABCD*..., resulting in the long *c* axis of 27.309 (3) Å. Short O···O distances [d(O1···O1′) = 2.492(6) Å and d(O4···O4′) = 2.523(6) Å] between the oligomeric borophosphate units are found within and between the layers (dotted lines in Figure 2). In addition, the same two crystallographically distinct O atoms have a significantly lower partial charge according to valence bond calculations.[11] We therefore conclude that protons are located between these O atoms close to the Wyckoff positions 8*d* (origin choice 2: 0, 0, $^1/_2$) and 8*e* (0, $^1/_4$, 0.265), giving the charge-balanced chemical formula $Na_3Pb^{II}[B(O_3POH)_4]$. Similar bonding situations were found in other borophosphates or in hydrogenphosphates and discussed in detail for the crystal structure of $Li_2Fe[(PO_4)(O_3POH)]$.[12]

The title compound enriches the family of borophosphates in two regards: Chemically, it is the first example with alkali metal and Pb^{II} ions compensating for the negative charge of a borophosphate complex and, structurally, it displays the first compound containing the oligomeric unit $[B(O_3POH)_4]^{5-}$. In the case of pure sodium borophosphates, only chains or layers are observed in the crystal structures of $Na_5[B_2P_3O_{13}]$[13] and $Na_2[BP_2O_7(OH)]$,[14] respectively. Three different examples are known for pure lead borophosphates ($Pb_3[BP_3O_{12}]$,[15] $Pb[BPO_5]$,[16] and $Pb_2[BP_2O_8(OH)]$[17]), which contain different types of complex chain anions. The only examples with a related oligomeric borophosphate unit are reported for $M_6[B(PO_4)_4][PO_4]$ (M^{II} = Pb, Sr)[18,19] containing additional isolated phosphate ions, and no protonation of the oligomer was observed.

The "propeller"-like anion consisting of five tetrahedra (Figure 1a) can be thought of as a cutout of a 3D tetrahedral network. Such a kind of network is encountered in the polymorphs of SiO_2 or in the parent crystal structure of BPO_4.[20] The first and most prominent example of the isolated tetrahedral pentamer in the solid state is given by $[Si(SiO_4)_4]^{12-}$, which was discovered in the mineral zunyite $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$ and exhibits a straight Si−O−Si angle.[21] Later on, the existence of pentameric ions, e.g., $[B(SO_4)_4]^{-}$[22] and $[Hg(SO_3Cl)_4]^{2-}$,[23] was also discovered in solution. Further examples with a central BO_4 tetrahedron are $K[B(SO_3Cl)_4]$[24] and $Pb_6[B(AsO_4)_4][AsO_4]$.[25]

The heterocubane-like arrangement of metal cations together with oxygen (Figure 1b) represents a well-known structural motif in the chemistry of sodium and lead. Representative examples for sodium are the metal−organic compounds $[Na_4(OSiPh_3)_4(H_2O)_3]$[26] or $[Na_4(OPh)_4(TMU)_4]$

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(Ph = phenyl, TMU = *N*,*N*,*N*′,*N*′-tetramethylurea).[27] The preferred formation of clusters with varying numbers of metal atoms is characteristic for lead[28] and is already observed in acidic solutions of Pb^{II} ions proved by the precipitation of $[Pb_4(OH)_4][NO_3]_4$.[29] These examples show the relationships in coordination geometry requirements of the differently charged cations, and the observed mixed occupation becomes plausible, which is further supported by other examples exhibiting the same phenomenon: $PbNa_4[P_3O_9]$[30] and $NaPb_4[PO_4]_3$[31] as representatives for phosphates or $Na_8Pb_2[Ge_2S_6]$, $Na_8Pb_2[Si_2Se_6]$,[32] and $Na_{0.5}Pb_{1.75}GeX_4$ (X = S, Se)[33,34] as examples for chalogenides.

In the complex anion $[B(O_3POH)_4]^{5-}$, all of the corners of the central tetrahedron are connected to neighboring PO_4 tetrahedra, and in the case of 4-fold-coordinated boron, no higher P:B ratio can be attained because a direct connection of PO_4 tetrahedra is omitted for borophosphates.[35] However, the OH groups at the PO_4 tetrahedra, in principle, open the way to further condensation. Therefore, the title compound was subjected to controlled thermal decomposition in a thermobalance (Figure 3) with subsequent analysis of the products by powder X-ray diffraction.

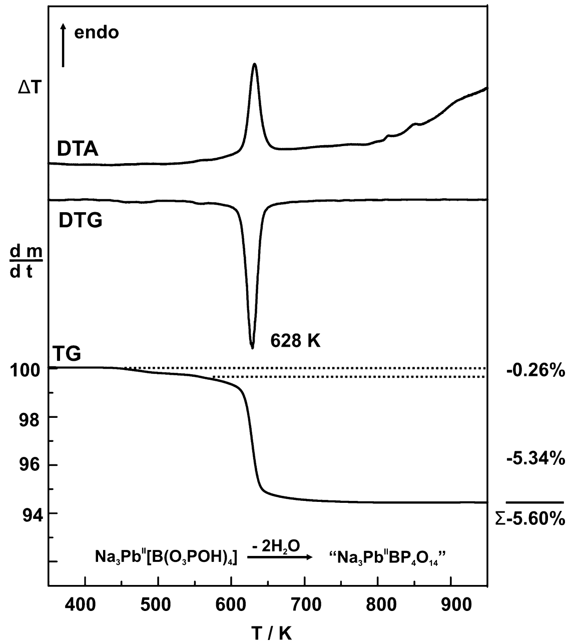

Figure 3. DTA, differential thermogravimetry, and TG curves for the thermal decomposition of $Na_3Pb^{II}[B(O_3POH)_4]$ (heating rate, 5 K/min; purge gas, argon). At 628 K, a strong mass loss is observed, which is endothermic and close to the expected mass loss of 2 mol of water per formula unit (5.37 wt %).

The thermogravimetric (TG) curve shows two steps under the chosen experimental conditions. Between 418 and 506 K, the sample weight is decreased by 0.26 wt % followed by a pronounced mass loss of 5.34 wt % having its highest rate of mass loss at 628 K, which is, according to the difference thermal analysis (DTA) trace, endothermic. The overall mass loss of 5.60 wt % is close to the calculated mass loss of 5.37 wt % (2 mol of water) assuming the chemical formula $Na_3Pb^{II}[B(O_3POH)_4]$ for the single-phase educt and "$Na_3Pb^{II}BP_4O_{14}$" for the bulk reaction product. The powder pattern of the decomposition product shows sharp reflections up to $2\theta = 40°$ (Cu $K\alpha_1$ radiation), which, however, could not be assigned to known phases. The quality of the pattern was not sufficient to gain structural information about the newly formed crystalline phases. Investigations are underway to obtain samples of better quality or even single crystals.

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Supporting Information Available: Crystallographic data in CIF format, tables of atomic coordinates, anisotropic displacement parameters, and selected interatomic distances, and an IR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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