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$Co_5BP_3O_{14}$: The First Borophosphate with Planar BO_3 Groups Connected to PO_4 Tetrahedra

Ranko P. Bontchev[†] and Slavi C. Sevov*[,†]

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

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Most of the best known materials with optical and electro-optical applications are either *borates* or *phosphates*. Names such as **BBO** (β-BaB_2O_4),[1] **LBO** (LiB_3O_5),[2] **KTP** ($KTiOPO_4$),[3] and **KDP** (KH_2PO_4),[3] are well-known commercially and are heavily used industrially for making a range of different optical elements. In the last couple of years the first few compounds combining both borate *and* phosphate groups were synthesized and structurally characterized. High-temperature syntheses have produced handful of metal borophosphates, all of main group metals. These are the following: $MBPO_5$, where M = Ca or Sr,[4] $M_3BP_3O_{12}$, where M = Ba or Pb,[4,5] and $Na_5B_2P_3O_{13}$.[6] The main structural features in all of them is that boron is *tetrahedrally* coordinated by oxygen, and that the BO_4 and PO_4 tetrahedra share corners and build infinite chains. The lower temperature−higher pressure approach (hydrothermal synthesis) has been used by the nature to produce two minerals: $Mg_3B_2P_2O_8(OH)_6{\cdot}6H_2O$ with dimeric tetrahedral units of BPO_7^{6-},[7] and $Mn_3BPO_4(OH)_6$ with isolated BO_4 and PO_4 tetrahedra.[8] The same method in laboratory conditions has also yielded the first zeolite-like borophosphate, $CoB_2P_3O_{12}(OH){\cdot}C_2H_{10}N_2$, with an infinite framework of corner sharing BO_4- and PO_4-tetrahedra and CoO_6-octahedra.[9]

Here we report on the synthesis and structural characterization of the first transition metal borophosphate with *planar* BO_3 groups that are connected to tetrahedral PO_4 groups. The title compound was made in a flux of B_2O_3 (*ca.* 10-fold excess) from a stochiometric mixture of $CoCO_3{\cdot}xH_2O$ (Aldrich) and H_3PO_4 (Aldrich, crystals, 98+%). Heating the mixture at 950 °C for 12 h and then slow cooling it (1°/min) to room temperature provided relatively large (up to 3 mm) crystals with deep blue color and with no particular shape. The crystals were embedded in a light purple glassy matrix of B_2O_3 mixed with most likely cobalt phosphates. They were mechanically separated from the matrix since the latter could not be washed out (completely) and then cut to smaller pieces for structure determination. No other crystalline phase was detected.

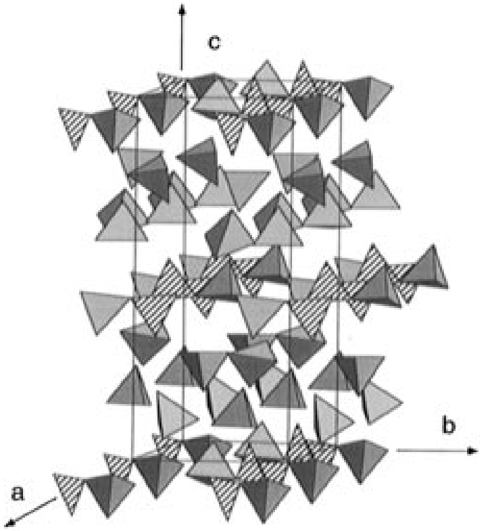

Figure 1. General view of the unit cell of $Co_5BP_3O_{14}$ with the cobalt atoms omitted for clarity. Planar BO_3 groups (striped triangles) share corners with PO_4 tetrahedra to form BPO_6^{4-} dimers. Layers of dimers run parallel to the *a,b* plane and are separated by double layers of isolated PO_4 tetrahedra.

Single-crystal studies[10] revealed a new type of B−O−P dimer in the structure. The dimer, BPO_6^{4-}, is a triangular BO_3 unit sharing an oxygen atom with a PO_4 tetrahedron (see Synopsis). In addition to the PO_4 tetrahedra in the dimers there are also twice as many isolated ones. There are no oxygen atoms coordinated only to cobalt atom(s); i.e., they are either part of PO_4 or BPO_6 units. Thus the formula can be written as $5Co^{2+} + BPO_6^{4-} + 2PO_4^{3-}$, and the compound should be considered a true phosphate−borophosphate. The dimers form layers perpendicular to the *c*-axis (Figure 1). The plane of the BO_3 groups is nearly perpendicular to the *a*-axis, and the B−P direction of the dimers is nearly along the *b*-axis. The layers of dimers are separated by double "layers" of PO_4 tetrahedra. The B−O−P angle in the dimers, 131.4(5)°, is within the expected range for a two-bonded oxygen atom. Although the BO_3 groups are not equilateral triangles, the angles around B, 125.5(7), 122.3(7), and 112.2(6)°, add up to 360(1)°, indicating that the group is indeed planar. The B−O and P−O separations range from 1.363(9) to 1.401(9) Å for B−O, and from 1.519(5) to 1.572(5) Å for P−O (for all PO_4 tetrahedra), and are well within the normal limits. The longest P−O and B−O distances are the ones to the shared oxygen atom, as expected.[11]

The IR spectrum of the compound shows strong but broad bands in the 1400−800 cm^{-1} region. This is consistent with P−O and B−O stretches for PO_4 and BO_3 groups.[12−14]

[†] E-mail addresses: R.P.B., ranko@nd.edu; S.C.S., ssevov@nd.edu.

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(10) The structure was solved by direct methods following data collection on a 0.20 × 0.15 × 0.15 mm single crystal (irregular piece of a larger deep-blue crystal) at 20°C on a CAD4 instrument with monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystal data: monoclinic, $P2_1/c$ (No. 14), $Z = 4$, a = 6.405(1) Å, b = 8.238(1) Å, c = 18.955(4) Å, β = 96.93(3)°, $R(F)/R_w(F^2)$ = 3.8/6.9% for 1388 independent observed reflections ($I \geq 2\sigma_I$; R_{ave} = 3.7%, 1905 total number of reflections; $2\theta \leq 50°$; $h,k,\pm l$ octants collected) and 224 variables, and with absorption (μ = 87.6 cm^{-1}) corrected with the aid of 4 ψ-scans at different θ angles (0.8902 < transmission < 0.9965). All atoms except boron were refined with anisotropic thermal parameters. Application of XABS for absorption correction did not lead to better results and was not used.

(11) For BO_3 groups connected similarly to BO_4 groups, the corresponding B−O distances for single bonded and shared oxygen atoms are 1.325(6) and 1.414(6) Å, respectively, in $CuTmB_5O_{10}$ (Schaefer, J.; Bluhm, K. *Z. Naturforsch.* **1995**, *50B*, 762) and 1.33(1) and 1.40(1) Å, respectively, in $CuTb_2B_8O_{16}$ (Schaefer, J.; Bluhm, K. *ibid.* **1995**, *50B*, 757).

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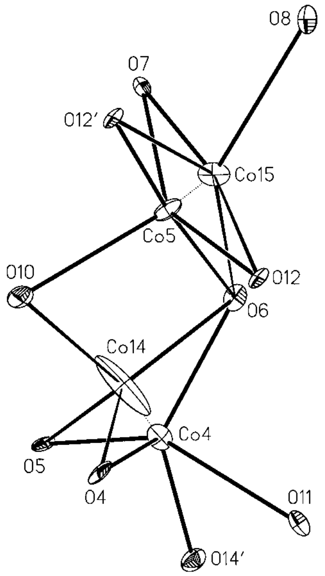

Figure 2. Shown are the two split cobalt positions, the Co4−Co14 and Co5−Co15 pairs (see the text). The atoms of the first pair are 5- and 4-coordinated by oxygen in a distorted trigonal bipyramid and in a face sharing tetrahedron, respectively. The second pair is in an octahedron that is elongated along O8−O10. The two cobalt atoms are thus 5-coordinated in two base-sharing square pyramids.

There are five crystallographically different cobalt atoms in the structure. Two of them, Co1 and Co3, are octahedrally coordinated with Co−O distances ranging from 2.010(5) to 2.187(5) Å. Another cobalt, Co2, is five-coordinated in a triangular bipyramid with distances to oxygen in the range 2.002(5)−2.123(5) Å. The remaining two cobalt atoms occupy two split positions, Co4−Co14 and Co5−Co15 (Figure 2). Initially the occupancies of these 4 sites were refined independently. The results were 90(1) and 10(1)% occupancies for Co4 and Co14, respectively, and 79(1) and 20(1)% occupancies for Co5 and Co15, respectively. Another set of X-ray data was later collected from a second crystal, and the corresponding numbers for these occupancies were 90(1) and 9(1)% for the Co4−Co14 pair, and 77(2) and 23(2)% for the Co5−Co15 pair.[15] This was a clear indication that each pair was fully occupied, and for the final refinement the sums of the occupancies were constrained to 100% for each pair. It can be seen from Figure 2 that Co5 and Co15 occupy the two halves of an octahedron (O6,7,8,10, 2 × O12) elongated along two opposite corners (O8 and O10). The coordination of the two cobalt sites, therefore, is nearly square pyramidal. The Co-O distances range from 1.933(5) to 2.223(5) Å for Co5, and from 2.042(9) to 2.30(2) Å for Co15.

The oxygen coordination around the Co4−Co14 pair is more difficult to describe as one polyhedron. Co4 is 5-coordinate and the corresponding polyhedron could be viewed as a heavily distorted trigonal bipyramid (for the lack of other way of describing it) with O4, O6, and O14 as the base and O5 and O11 as the opposite apices of the bipyramid (Figure 2). The "distortion" is expressed in moving the two apices away from the Co14 site and toward O14. The distances here range from 2.007(5) to 2.235(5) Å. The other site of this position, Co14, is more or less tetrahedrally coordinated (O4,5,6,10) with one face of the tetrahedron (O4,5,6) shared with the trigonal bipyramid around Co4. Naturally, the distances are shorter in this lower coordination, 1.82−2.34 Å. The tetrahedron is quite irregular, and most likely its distortion is the reason behind the irregular shape of the thermal ellipsoid of the central atom. The irregularity of the tetrahedron is due to the fact that one of its edges, O5−O10, is an edge of a much smaller PO$_4$ tetrahedron (around P1) at the same time. Thus this edge is much shorter, 2.44 Å, than the other edges, 3.49 Å (average). The result is a rather "flat" tetrahedron around Co14 and a thermal ellipsoid that is elongated perpendicularly to the "plane" of that flat tetrahedron. In addition to this, the two oxygen atoms that are directly in that plane, O6 and O4, are quite closer to Co14, 1.82 and 1.97 Å, respectively, than the other two oxygens, 2.06 and 2.34 Å. This brings the possibility of additional splitting of Co14 above and below the plane. Our attempts to refine the position as such were unsuccessful and proved that this was not the case. Similar results for the thermal ellipsoid of Co14 (elongation along the same direction) were observed from the refinement of the structure from the data taken on the second crystal (see above).

The cobalt polyhedra are quite heavily fused through edges and corners,[16] and form a three-dimensional "network". Each Co-polyhedron shares three edges and at least one corner with other Co-polyhedra.

Overall the structure of Co$_5$BP$_3$O$_{14}$ could be considered as built of packed but isolated BPO$_6^{4-}$ dimers and PO$_4$ tetrahedra with the Co^{2+} "countercations" surrounding these units and joining them together. The oxygen atom that is bridging in the BPO$_6^{4-}$ dimer is the only one with no cobalt neighbors. The others, except O8 and O10, have two such neighbors and therefore are 3-bonded. O8 and O10 are 4-bonded when the Co15 or Co14 positions, respectively, are occupied (Figure 2).

Apparently dimers such as BPO$_6$ and PO$_4$ tetrahedra can not pack well and leave "appropriate" holes for the cobalt atoms at the same time. This may be the explanation for the distorted cobalt polyhedra and also for the split positions. The fact that the structure forms despite the unfavorable Co-coordination suggests that the latter is not the primary driving force but is rather a consequence of the packing. The higher-energy positions, Co14 and Co15, are apparently not that unfavorable at the high temperature of the synthesis. They get partially occupied at these temperatures and can not get completely empty (equilibrated) upon cooling. Lower cooling rates are being tested to check if the compound can form with zero occupancies of these sites. Substitution of larger metals for the two cobalt atoms may also lead to full occupancies of one set of sites and leave the others empty.

The fact that BO$_3$ can connect to PO$_4$ is quite encouraging that compounds with infinite three-dimensional networks based on such or similar triangle-to-tetrahedron bonding may be accessible.

Acknowledgment. We thank the University of Notre Dame for the support of this work.

Supporting Information Available: Tables of data collection and refinement details, atomic coordinates and thermal parameters, anisotropic thermal parameters, and complete bond distances and angles and figures showing the fused cobalt polyhedra (8 pages). Ordering information is given on any current masthead page.

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(15) The second data set was refined to $R(F) = 4.5\%$. Boron could not be refined with anisotropic thermal parameters.

(16) The Co1-polyhedron shares edges with Co2-, Co3-, and Co4/14-polyhedra, and a corner with a second Co4/14-polyhedron. The Co2-polyhedron shares edges with Co1-, Co3-, and Co4/14-polyhedra, and a corner with a Co5/15-polyhedron. The Co3-polyhedron shares edges with Co1-, Co2-, and Co5/15-polyhedra, and corners with Co4/14- and an additional Co5/15-polyhedra. The Co4/14-polyhedron shares edges with Co1-, Co2-, and Co5/15-polyhedra, and a corner with a Co3-polyhedron. The Co5/15-polyhedron shares edges with Co3-, Co4/14-, and another Co5/15-polyhedra, and corners with Co2- and an additional Co3-polyhedra. Available as Supporting Information are three figures showing the way the cobalt polyhedra are fused.