[Co(en)3][B2P3O11(OH)2]: A Novel Borophosphate Templated by a Transition-Metal Complex

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The interest in borophosphates has been steadily growing after the discovery of the first borophosphate with an open-framework structure, the ethylene-diamine-templated CoIIB2P3O11(OH)2enH2.1 Since then, a number of purely inorganic compounds of alkalimetal (or ammonium)—borate—phosphate with or without transition metal and of all dimensionalities have been made.2–5 In addition to these, a few organically templated borophosphates, all based on vanadium and mostly low-dimensional, are known.6 We have now taken one step further in complexity and have made the first borophosphate compound templated by a transition-metal complex, [Co(en)3][B2P3O11(OH)2]. The view is approximately along the a axis, and c is horizontal. Lighter and darker polyhedra in part b denote borate and phosphate, respectively.

Compounds with extended structures that are templated by transition-metal complexes are very rare. Known are only a very few aluminophosphates of this kind. They are all 1- and 2-dimensional compounds, most templated with Co(III) complexes and a few with Ir(III) complexes such as Co(en)3,7 Co(tn)3,8 Co(dien)3,9 Co(NH3)6,10 Ir(III) complexes such as Co(en)3,7 Co(tn)3,8 Co(dien)3,9 Co(NH3)6,10 Ir(en)3,11 and Ir− or Co(1,2-diaminocyclohexane),11 There seems to be only one compound, a gallium phosphate, that is templated by a transition-metal complex and is 3-dimensional, Co(en)3[Ga2P4O13(OH)3] with an open-framework structure, the ethylenediamine-templated CoII B2P3O12(OH)2. The discovery of the first borophosphate with an open-framework templated compounds is the first such borophosphate, [Co(en)3][B2P3O11(OH)2]. The corresponding mixture was made very acidic, pH ~ 1.5, and was heated at 155 °C for 7 days in Teflon-lined stainless-steel autoclaves. Later, the compound was made at 150 °C and at pH as high as 7. We have tried many reactions (more than 50) keeping the conditions as similar as possible to those given above but without the 1,3-diaminopropane. All of these attempts failed. We also tried different diamines and amines instead of the diaminopropane, but the only other amine that was successful was DABCO. The corresponding mixture was made very acidic, pH = 1.5, and was heated at 155 °C for 4 days. The product contained very large crystals of [Co(en)3][B2P3O11(OH)2].

The compound is made hydrothermally at 130 °C from [Co(en)3]Cl2·2H2O, boron phosphate (or boric and phosphoric acids), and dianminophosphate or DABCO as an additive.12 Often found, in addition to the yellow-orange crystals of [Co(en)3][B2P3O11(OH)2], were purple crystals of the known Co(II) borophosphate with very similar composition, Co[B2P3O11(H)2(en)2](2).7 The valence state of the cobalt atoms was confirmed by the negative and temperature independent magnetic susceptibility measured for the compound.13 This is in agreement with the yellow-orange color of the crystals and the overall stoichiometry. The structure of [Co(en)3][B2P3O11(OH)2] is made of chains of borophosphate with a repeating unit of B2P3O11(OH)2 (Figure 1) that are separated by stacks of the octahedral cobalt complex [Co(en)3]2+ (Figure 2). The chains are made of corner-

Figure 1. (a) ORTEP (50% probability thermal ellipsoids) and (b) polyhedral views of the chain of [B2P3O11(OH)2] in the compound [Co(en)3][B2P3O11(OH)2]. The view is approximately along the a axis, and c is horizontal. Lighter and darker polyhedra in part b denote borate and phosphate, respectively.
sharing tetrahedra centered by boron and/or phosphorus. There are two alternating motifs in the chains, a three-membered ring of two boron- and one phosphorus-centered tetrahedra and a four-membered ring of two boron- and two phosphorus-centered tetrahedra (Figure 1). Two oxygen atoms at the phosphorus in the smaller ring and one oxygen atom at each phosphorus atom in the larger ring are terminal. The distances to these atoms, 1.511(2) and 1.484(2) Å for P2 and P1, respectively, are clearly shorter than those to the shared oxygen atoms, 1.569(2) Å to P2 and 1.533(2) and 1.539(2) Å to P1. Each of the two phosphorus atoms in the larger ring has also a terminal hydroxyl group with a P–O distance that is somewhat longer, as it should be, 1.556(2) Å. There is also one oxygen atom in the smaller ring that is bonded to two boron atoms only, and is naturally with the shortest B–O distance, 1.417(4) Å, compared to the other three distances 1.474(4), 1.480(4), and 1.504(4) Å. These distances agree with the corresponding B–O distances in 2, 1.433 and 1.477 Å for the averaged distances from boron to the oxygen atom shared by boron atoms (and cobalt) only and to the oxygen atoms shared with phosphorus, respectively.1

The octahedral coordination symmetry of the “templates” [Co(en)(NH2CH2CH2NH2)3]3+ is very close to ideal with three pairs of identical (within 0.05 Å) Co–N distances of 1.960(3), 1.961(3), and 1.969(3) Å, and angles within the range 85.6(1)–92.7(1)°. The distances agree well with those in the same Co(III) complex of various alumino- and gallophosphates such as [Co(en)3][Al2P2O7]·3H2O, [Co(en)3][AlP2O7]2− and [Co(en)3(Ga2P2O7)(OH)2]1− with average Co–N distances of 1.95, 1.969, and 1.974 Å, respectively. There is extensive hydrogen bonding in the structure. Each terminal oxygen atom at P2 has a nitrogen atom at a distance of 2.984(3) Å, the terminal oxygen atom at P1 has two nitrogen atoms at distances of 2.861(3) and 2.921(3) Å, and the OH group at P1 has one terminal oxygen at P2 and one nitrogen at distances of 2.483(3) and 2.926(3) Å, respectively.

The formulas of the borophosphate moieties in 1 and 2 are very similar, [B2P2O7(OH)]2− and [B2P2O7(OH)]4−, respectively. The charge in the latter is balanced by Co(II) and the diprotonated ethylenediamine templates [enH2]2+, while counterions in the former are the trisethylenediamine–cobalt(III) templates. The structures of the moieties are also very closely related. That in compound 2 is made of layers (Scheme 1a) that contain the same three-membered rings of two boron and one phosphorus atoms as in 1. However, instead of alternating with four-membered rings as in the chains of 1 these rings in 2 are connected by only one phosphate group (P” in Scheme 1a) which has two terminal oxygen atoms while another phosphate group with one hydroxyl group and two terminal oxygen atoms is an end group (boxed in Scheme 1a). The second dimension is achieved by connecting a boron atom to the phosphorus atom of another three-membered ring (B′–O–P′ in Scheme 1a). The chain in 1 (Scheme 1b) can be viewed as derived from the layer in 2 by taking the following steps: (1) break the B′–O bond that provides the second dimension and leave the oxygen atom as terminal to P”; (2) replace the bond at B’ with a bond from a terminal oxygen atom of the dangling phosphate group (arrows in Scheme 1b); (3) protonate a terminal oxygen atom of the phosphate group connecting the three-membered rings. This process preserves the number of bonds while the charge is reduced from 4− to 3− only due to the protonation of one otherwise terminal oxygen.

The IR spectrum of 1 contains the characteristic bands of the phosphate and borate groups in the region 980−1200 cm−1. This part of the spectrum is nearly identical with that of 2.1 The stretching bands of the OH, NH2, and CH2 groups are observed at ca. 3500, 3150−3300, and 2900−3050 cm−1, respectively. Also present are bands for the bending in NH2 and CH2 at around 1600 and 1470 cm−1, respectively, and a C–N stretching band at 1280 cm−1. The compound is stable up to about 300 °C, above which temperature it starts to lose weight in a very broad temperature range, and by 900 °C it loses about 35.8 wt % of its weight (calcd 35.2 wt % for water and ethylenediamine). The product of this heating is amorphous (same is the result of heating 2 at that temperature).

In conclusion, it should be pointed out that the fact that borophosphates can be “templated” with transition-metal complexes is yet another similarity of this class of compounds with the much larger class of aluminoo- and gallophosphates. It is very encouraging, therefore, that despite the hydrolytic instability of BPO4 itself (in contrast with the rock-stable AlPO4 and GaPO4), we should keep looking for other molecular-sieve-like compounds based on B–P–O bonding. Moreover, even more diverse structural chemistry is expected for such borophosphates due to the potential of boron for trigonal-planar coordination and to the possibility for B–O–B connections (as observed here).

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Scheme 1

Figure 2. A polyhedral view of the cell of [Co(en)3][B2P2O7(OH)2] along the c axis (b is vertical) with the unit cell shown. The borophosphate chains of darker and lighter tetrahedra of PO4 and BO4, respectively, are separated by the stacks of [Co(en)3]3+ octahedra.