

A Novel Borophosphate Coordination Polymer with Sandwich-type Supramolecular Architecture

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Abstract: A novel borophosphate $(\text{Hmel})_3\{\text{Co}_2[(\text{mel})_2(\text{HPO}_4)_2(\text{PO}_4)]\cdot\text{H}_3\text{BO}_3\cdot\text{H}_2\text{O}\}$ (mel = melamine) has been synthesized under mild solvothermal conditions. The structure of the compound exists a high ordered organic-inorganic sandwich-type supramolecular architecture *via* metal-coordination, hydrogen bonds and π - π stacking interactions.

Keywords: Borophosphate, coordination polymer, supramolecular architecture, solvothermal.

Self-assembly of two or more components into supramolecular architectures and coordination polymers is of considerable current interest by virtue of the diversity of the structures¹ and the potential applications of such materials to magnetism, optics, electronics^{2, 3} and catalysis⁴. Borophosphates have become another particularly fruitful area of investigation due to their potential use in catalysis⁵, especially in the nonlinear optical materials⁶. Today, the structural chemistry of borophosphate anions have already extended from isolated species, oligomers, rings, and infinite chains to two-dimensional layers as well as three-dimensional frameworks⁷. However, to the best of our knowledge, borophosphates with structural characteristic of coordination polymer and supramolecular architecture have not been reported yet. Aimed at new materials mentioned above, the synthesis was based on the following considerations: First, both hydrogen bonds and aromatic-aromatic (π - π stacking) interactions are important noncovalent intermolecular forces, they can contribute to self-assembly or molecular recognition process when extended structures are formed from building blocks with aromatic moieties⁸. Therefore, we used melamine as ligand or template agent to fulfill the construction of extended framework, since it has been shown that melamine is not only well-known to yield excellent complementary hydrogen-bonded structures⁹, but also forms structures with aromatic-aromatic stacking¹⁰ and metal-melamine coordination¹¹. Second, we have also used cobalt (II) chloride as the starting material expecting that introducing transition metal ions into such systems may offer new materials with interesting properties¹². Finally, the properties of the solvents are often vital to the success or failure of the attempted synthesis, and we have employed new solvothermal

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conditions with room temperature ionic liquids — BMIMCl (1-butyl-3-methylimidazolium chloride) as solvents. Ionic liquids are often non-coordinating solvents, as well as good solvents for a wide range of both inorganic and organic materials. They are less effective than water in hydrogen-bonding ability, and so there is a greater interaction between the framework particles and the templates. Additionally, they have higher viscosity than water and alcohols, and this may reduce convection currents and help produce large single crystals rather than polycrystalline product by sedimentation¹³. By employing the strategy above, we have obtained a novel compound with organic-inorganic sandwich-type supramolecular architecture. Here, we report the solvothermal synthesis and characterization of this compound.

The details of the synthesis of BMIMCl can be found in the reference¹⁴. The mixture of 0.062 g H₃BO₃, 0.137 g KH₂PO₄, 0.237 g CoCl₂·6H₂O, 0.126 g melamine and 0.70 mL BMIMCl was placed in a thick borosilicate glass tube. The tube was sealed and then kept at 120 °C for two days to give pure deep-blue single crystals. Anal. Calcd. for C₁₅H₄₀BCo₂N₃₀O₁₆P₃: (%) C 16.09, H 3.58, N 37.56; Found: C 15.85, H 3.55, N 36.05. IR (KBr, cm⁻¹): 3351 (m, ν_{N-H}), 3169 (s, ν_{O-H}), 1677 (vs, ν_{C=N}), 1534 (m, ν_{C=N}), 1380 (w, ν_{B-O}), 1336 (w, ν_{B-O}), 1164 (w, ν_{as PO4}), 1078 (m, ν_{as PO4}), 1010 (m, ν_{as PO4}), 926 (vw, ν_{as PO4}), 779 (w, ν_{s PO4}).

A single crystal with dimension of 0.50 × 0.05 × 0.05 mm was selected for the crystal structure analysis. Crystal data are: triclinic, *P*-1 (No.2), *a* = 1.07260(18) nm, *b* = 1.14995(19) nm, *c* = 1.7003(3) nm, α = 81.436(2)°, β = 72.442(2)°, γ = 87.187(2)°, *V* = 1.9772(6) nm³, *Z* = 2, *D*_{calc} = 1.879 g/cm³. The final *R* = 0.0577, *wR* = 0.1325 for 6870 unique reflections.

The structure of the compound contains melaminium cations, boric acid, water molecules, and the polyanion of Co₂[(mel)₂(HPO₄)₂(PO₄)]³⁻ which is made of five tetrahedra (two HPO₄-tetrahedra and two Co₂O₃N-tetrahedra form a four-membered ring,

Figure 1 View along the *ac*-plane (melamine molecules are omitted for clarity)

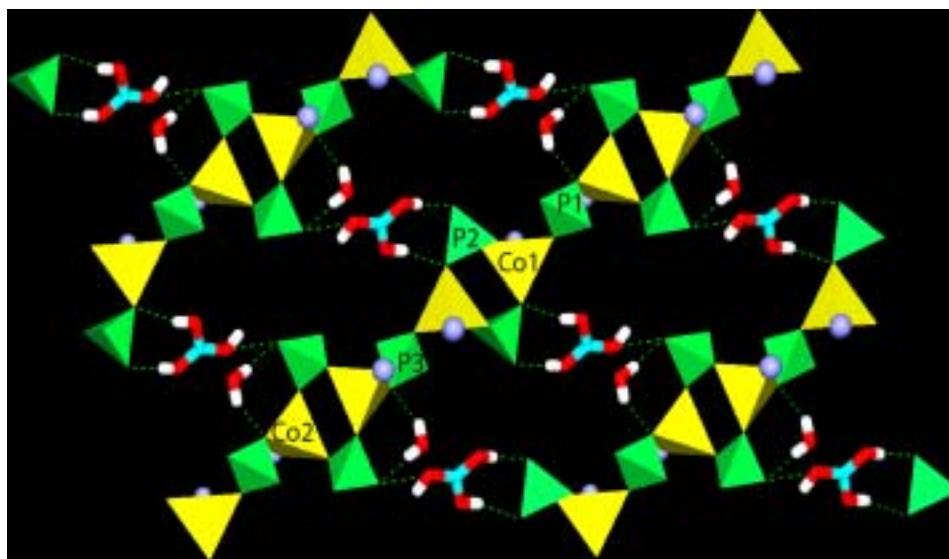
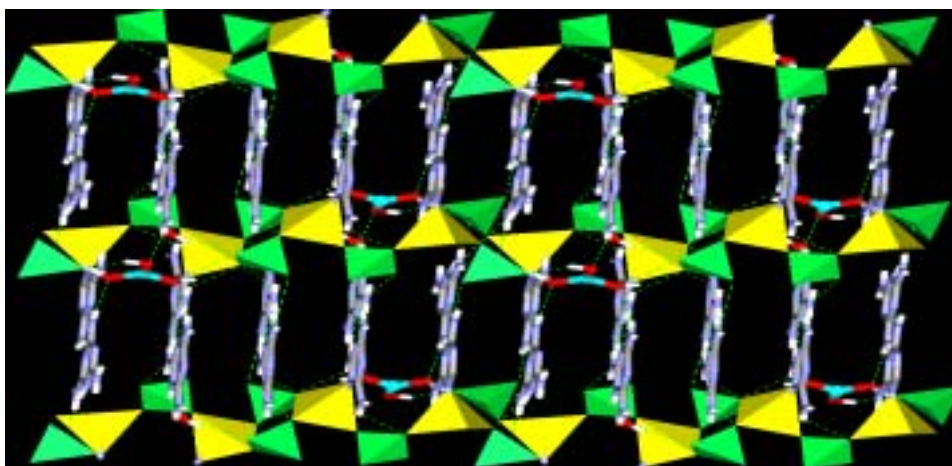


Figure 2 View along the *bc*-plane

followed by one PO_4 -tetrahedra) and linked together by corner-sharing O atoms to form infinite one-dimensional chains (**Figure 1**). In this coordination polymer, the melamine molecules bond to the Co atoms through the ring nitrogen by forming a Co–N bond (av. Co–N = 0.2059 nm). The free boric acid and water molecules located inter-chains can form strong hydrogen bonds with the distance of 0.2665–0.2769 nm. This connectivity gives rise to layer-like arrangement with 12-membered apertures of 0.627×1.407 nm within the *ac*-plane as shown in **Figure 1**. The two coordinated melamine molecules, along with another three protonated melaminium cations as templates, are stacked with the average face-to-face distance of 0.339 nm, and each linked to the neighbor pairs by the side-by-side double hydrogen bonds to form infinite zigzag molecule tapes in the *a* axis direction. The interesting feature is that these parallel tapes are bonded together to make infinite stacks along the *c* axis. Consequently, the π - π contacts and hydrogen bonds form a two-dimensional organic layer with a lattice structure (**Figure 2**). Thus the compound presented a well-organized organic-inorganic sandwich-type supramolecular architecture, which was assembled through the following organizing forces: (1) coordinate-covalent bond of cobalt and melamine; (2) π - π stacking of melamine and melamine; (3) DA-AD (D = hydrogen bond donor; A = hydrogen bond acceptor) complementary double hydrogen bonds between melamine molecules and the extensive hydrogen bonds among melamine, boric acid, water molecules and polyanions (**Figure 2**).

Further studies to establish the relationship between the novel structure and the potential excellent properties in catalysis, optics, magnetism and electrical conductivity are underway.

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