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Preparation and Intercalation Properties of Novel Layered Zinc 1,3,5-Benzenetriphosphonates Composed of Anionic Hybrid Layers

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Zinc 1,3,5-benzenetriphosphonates (ZBP) prepared in the presence of organic cations contain unique layers composed of inorganic 1D chains bridged with benzene rings. ZBP showed intercalation and cation-exchange properties while retaining the layer structure, resembling layered metal phosphates rather than conventional layered phosphonates.

The crystal structures of inorganic–organic hybrid solids have considerable importance in designing properties and applications. Recently open-framework materials composed of both inorganic and organic components have been extensively explored to produce a number of unique microporous and layered materials. Especially metal organophosphonates have attracted wide attention for potential design of chain, layered, and open-framework materials with numerous combinations of metal sources and organophosphonate units.[1] Monophosphonic acids without other linkable functional groups generally tend to form layered structures with various metals in a similar fashion to layered metal phosphates[2] except several open-framework and nanotube structures.[3] Since each layer is covered with inert organic groups in these layered monophosphonates, they give generally poor reactivities. Similarly diphosphonic acids tend to form dense pillared layer structures, composed of inorganic metal phosphonate layers and interlayer organic pillars covalently connected to the inorganic layers. Use of rigid multifunctional phosphonates, therefore, has been recently explored to avoid formation of such conventional dense layered structures and to favor formation of more open structures.[4–7] Kong et al. reported preparation of open-framework copper compounds using 1,3,5-benzenetriphosphonic acid (BTP) as the building block.[4] BTP was also found to form a variety of self-assembly networks in the presence of organic amines[8,9] or without such additives[10] via ionic and hydrogen bonds. In spite of these reports, still a limited number of BTP-containing open-framework materials are known; therefore, no general features for formed structure have been established. We here report an unprecedented type of isomorphic layered phosphonates ZBP–bpy and ZBP–TMA, hydrothermally prepared from BTP and zinc sources in the presence of 4,4′-bipyridyl (bpy) or tetramethylammonium (TMA) hydroxide as interlayer cations, respectively. Their intercalation and ion-exchange behaviors are also discussed.

The compositions of ZBP–bpy and ZBP–TMA considering the charge balances were determined to be $Zn_2[C_6H_3(PO_3)_2PO_3H]\cdot 0.5H_2bpy\cdot H_2O$ and $Zn_2[C_6H_3(PO_3)_{1+x}(PO_3H)_{2-x}]\cdot x\mathrm{TMA}\cdot H_2O$ ($x = 0.5$–1), respectively, according to CHN elemental analysis and ICP-AES. The CHN analysis for several ZBP–TMA samples revealed the deficiency of TMA cations. Part of the TMA cations may be lost during washing of the as-prepared sample with water. Since no single crystals were obtained for both the compounds, the ab initio crystal structure determination was attempted using powder diffraction data. Finally isomorphous layered structures were revealed by successful Rietveld refinement.[11,12,18] As shown in Figure 1, both the solved structures contain isomorphous layers composed of BTP and zinc as well as interlayer organic and water molecules. Kong et al. reported a material with layers composed of copper and BTP that are bridged with bpy pillars by coordination to Cu atoms.[4] However, bpy is not coordinated to zinc atoms but exists as a cation in ZBP–bpy. Four-coordinated zinc atoms are bridged with phosphonate groups forming one-dimensional chains along the *b* axis. These chains are linked with benzene rings of BTP forming hybrid layers perpendicularly to the *c* axis. There are three independent phosphorus sites within a BTP molecule while two zinc sites exist in the structure. Four-coordinated zinc atoms are linked with three different phosphonate groups via oxygen atoms, and two ZnO_4 tetrahedra form a dimer by sharing an O5 oxygen atom. The O5 oxygen is three-connected with P3 and two zinc atoms. Although all three oxygen atoms included in the P3-centered phosphonate group are bound with zinc atoms, two oxygen sites O8 and O9, connected with P1 and P2 respectively, are bound with no zinc atoms. Thus, the surface of each sheet is covered with electronegative and reactive phosphonate oxygen atoms. If it is assumed that all the O8/O9 oxygen atoms are not protonated at all, the negative charge per unit cell should be 8−. In ZBP–bpy, however, the positive charge from the two interlayer biprotonated H_2bpy^{2+} in a unit cell is 4+. To elucidate the charge balance, it

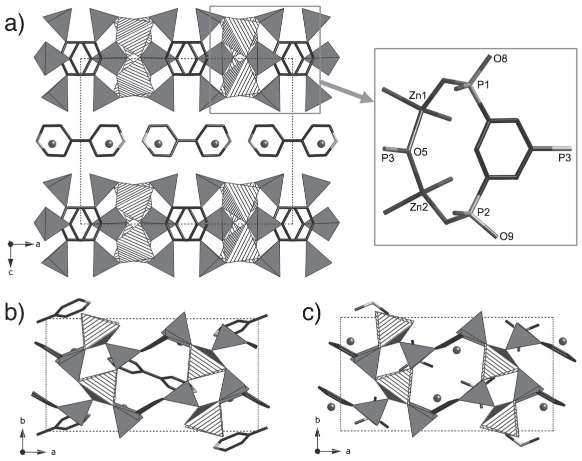

Figure 1. Crystal structures of ZBP–bpy (a,b) and ZBP–TMA (c) viewed along [010] (a) and [001] (b, c) direction. The ZnO_4 and PO_3C units are indicated as hatched and gray tetrahedra, and the interlayer water molecules are displayed as gray spheres.

is reasonable to assume that half of the O8/O9 oxygen atoms are protonated to form an intralayer hydrogen bond with the adjacent unprotonated O8/O9 atom. This hypothesis is supported by the distances between the nearest adjacent terminal oxygen atoms within the same layer, 2.47 (O8–O8) and 2.46 Å (O9–O9) for ZBP–bpy. These distances are close to those of the shortest hydrogen bonds (2.41–2.48 Å for P–O$^-$···H–OP) found in the crystal composed of BTP and bipyridyl.[9a] As for ZBP–TMA the positive charge from the TMA molecules in a unit cell was estimated to be 3.4+ according to the refined population parameters regarding the TMA units, because the crystallographic site of TMA is not fully occupied. This should result in increasing number of protonated O8/O9 atoms. Observed longer distances for the intralayer hydrogen bonds in ZBP–TMA, 2.63 (O8–O8) and 2.68 Å (O9–O9), are probably related to increasing contribution of hydrogen bonds between adjacent terminal oxygens, both of which are protonated (P–O(H)···H–OP). The topology of ZBP layers proved to be related to that of $Zn_3[C_6H_3(PO_3)_3]\cdot 4H_2O$,[7] which was reported recently during the preparation of this paper. In this compound the neighboring terminal phosphonate oxygen atoms in the ZBP layer are bridged with another zinc atom on the layer surface, making the charge of the layer neutral.

The model with the three phosphorus sites in ZBP–bpy was also supported by ^{31}P MAS NMR[18] giving two resonances at $\delta = 18.9$ and 16.1, which are assigned to P3 and P1/P2, respectively. If the proton contained in the hydrogen bond can be exchanged relatively quickly between both O8/O9 oxygen atoms through the hydrogen bond, it explains the absence of discrimination in the latter peak. The ^{31}P MAS NMR of ZBP–TMA gave three distinct peaks at $\delta = 18.6$, 16.4, and 13.0. Although the former two peaks can be assigned in a similar manner to ZBP–bpy, the last one, which does not appear in ZBP–bpy, can be assigned to protonated phosphonate groups with the adjacent protonated phosphonate group owing to the deficiency of the TMA cations.

The cationic sites, i.e., nitrogen atoms, of the interlayer biprotonated 4,4′-bipyridyl molecules are located between the P3-centered PO_4 tetrahedra belonging to different layers. Also in ZBP–TMA the determined positions of the TMA cations in the *ab* plane are close to those of the cationic sites in ZBP–bpy. Since the ZBP phase can be obtained readily with bpy, a structure-directing role of bpy is suggested in the formation of the specific hybrid layer structure in a manner related to zeolite synthesis. Interlayer water molecules (O_w) were also found in both ZBP–bpy and ZBP–TMA, and they are hydrogen-bonded with terminal phosphonate oxygen atoms (2.5–2.9 Å for O8/O9–O_w in both the compounds) and also with pyridinium cations (2.6 Å for N_c–O_w) in ZBP–bpy. The interlayer water molecules can be removed on heating under 100 °C without loss of crystallinity. ZBP–bpy was stable up to 350 °C though it started to collapse on heating at 400 °C with decomposition of the interlayer bpy. ZBP–TMA was stable up to 300 °C.

Cheetham et al. classified inorganic–organic hybrid frameworks according to the dimensionality of both inorganic (I^n: $n = 0$–3) and metal–organic–metal (O^m: $m = 0$–3, $n + m \leq 3$) connectivities.[13] Compared with I^2O^0 type layers, typically observed in most of the conventional layered metal phosphonate compounds, and I^0O^2 type layers, included in many MOF-type layered compounds, I^1O^1 type layers, found in the ZBP materials, are unprecedented for metal organophosphonates as far as we know. Rather than conventional layered metal phosphonates, in which the layers are covered with organic functionalities, similarities could be found in layered phosphates, represented by α-zirconium phosphate (α-ZrP),[14] in view of the existence of surface-covering terminal phosphorus-bound oxygens. Consequently, various structural transformation such as intercalation, cation exchange, exfoliation, and pillaring, which are known for layered phosphates, should be potentially possible also for ZBP materials. Although intercalation reactions with alkylamines and alkanols were reported for several conventional simple layered metal phosphonates,[15] introduction of the intercalants is mainly driven by coordination of the functional groups of an intercalant molecule with a metal center in the layer.

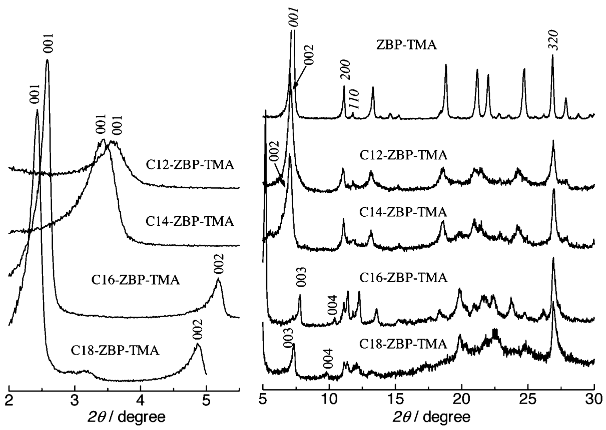

Figure 2. XRD patterns of ZBP–TMA intercalated with long chain alkyltrimethylammonium cations. The Miller indices of the cation-intercalated species are indicated in normal letters. The Miller indices of the original ZBP–TMA are indicated in italics for comparison.

Intercalation of organic cations was first examined, and the XRD patterns of the solids when long-chain alkyltrimethylammonium (C12 to C18) bromides were reacted with ZBP–TMA (C*n*–ZBP–TMA) are shown in Figure 2. The 00*l* reflections of the products shifted to lower angles, while *hk*0, especially 200, 110, 320, which were clearly observed in the original ZBP–TMA, remained almost unchanged with a slight broadening of peaks, supporting the intercalation with the retained layer structure. According to TG-DTA and CHN analysis, approximately 1.4 molecules of C18 cations are estimated to be intercalated per $Zn_2[C_6H_3(PO_3)_3]$.[18] Longer-chain intercalant gave a larger interlayer distance. The intercalants are probably introduced in interdigitated monolayers judging from the interlayer distances. The C16 and C18 cations were readily intercalated at an ambient temperature within 12 h without remaining original ZBP–TMA. Meanwhile, considerable portions of ZBP–TMA remained intact on intercalation of C12 and C14 under the same reaction conditions even after 2 d. The difference in intercalation behavior is probably due to difference in packing of intercalant molecules between C12/14 and C16/18.[18] ZBP–bpy also showed similar intercalation behavior, though it generally needed longer reaction time than ZBP–TMA.

ZBP–TMA was reacted with aqueous solutions of alkali metal chlorides to investigate ion-exchange properties. The nitrogen contents of the solids recovered after dispersing in sodium and potassium chloride solutions were 0.36 and 0.05%,

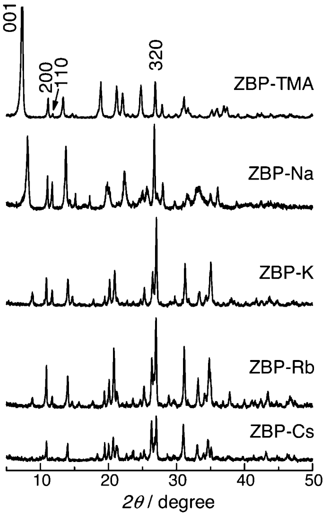

Figure 3. XRD patterns of alkali cation-exchanged ZBP–TMA.

respectively, whereas that of the original ZBP–TMA was 1.66% according to the CHN elemental analysis,[18] revealing that most of the interlayer TMA cations were lost. The elemental analysis and TG-DTA showed that the loss of the TMA cations was caused by the ion-exchange reaction with alkali metal cations. Figure 3 shows the XRD patterns of alkali metal cation-intercalated ZBP–TMA samples. The positions of the *hk*0 reflections, 200, 110, 320, seems to remain almost unchanged irrespective of the exchanged cation, supporting the proposal that the original phosphonate layers remain almost intact after the ion exchange. Meanwhile, the original basal reflection (d_{001} = 12.1 Å) of ZBP–TMA is shifted to higher angles, d = 10.9 (Na), 9.9 (K), and 10.0 Å (Rb) after the reactions, while the basal reflection of Cs-exchanged sample is almost extinct. Especially the XRD patterns of K-, Rb-, and Cs-exchanged ZBP–TMA resemble each other in spite of different cation sizes, suggesting isomorphous crystal structures. All of them are successfully indexed with orthorhombic unit cells with *a* and *b* dimensions close to those of the original ZBP phases.[18] The higher angle shifts of the basal reflection, which are indexed as 002 after the reactions, are consistent with shrinkage of the interlayer distance on ion exchange with smaller cations. These results provide strong evidence that the interlayer cations are exchanged while retaining the layer. The lower intensity of the basal reflection with the heavier cation should not be caused by loss of crystallinity but change in distribution of electron density. The larger basal spacing of Na-exchanged ZBP–TMA is probably due to intercalation of the as-hydrated form of the sodium cations.

Attempts to exfoliate the sheets with several additives in aqueous media so far resulted in no dispersion of ZBP particles in the solvent. However, C18–ZBP–TMA was successfully dispersed in toluene at ambient temperature to give an apparently transparent solution. The XRD pattern of the white solid reprecipitated on standing the solution at ambient temperature was identical to that of C18–ZBP–TMA. For the apparently transparent solution after filtrating the precipitate, the Tyndall effect was observed on irradiation of laser light. This revealed that the solution is colloidal. Accordingly, the sheet structure is assumed to be unchanged during the dispersion–reprecipitation process. Further characterization using AFM to confirm formation of nanosheets[16] on exfoliation of ZBP layers will be published elsewhere.

In conclusion, a novel type of layered phosphonates ZBP–TMA and ZBP–bpy were prepared, and their crystal structures were solved from powder diffraction data. The anionic layer containing organic moieties within a layer is unprecedented as metal phosphonates. Intercalation of long-chain alkylammonium cations and ion exchange with alkali metal cations occurred while retaining the layer structure. If a single I^1O^1 layer can be exfoliated, such nanosheets should attract attention because they can be utilized as nanoparts, namely, 2D building units, to construct ordered nanostructures.[17]

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