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A New Ion-exchangeable MOF with Reversible Dehydration and Dynamic Structural Behavior $(\text{NH}_4)_2[\text{Zn}_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{COO})_2]\cdot 5\text{H}_2\text{O}$ (BIRM-1)

Chao Zhao^{*[a, b]}, Louise Male^[a], Tzu-Yu Chen^[a, c], Joseph A. Barker^[a], Ian J. Shannon^[a] and Paul A. Anderson^{*[a]}

Abstract: $(\text{NH}_4)_2[\text{Zn}_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{COO})_2]\cdot 5\text{H}_2\text{O}$ (BIRM-1) is a new metal phosphonate material, synthesized through a simple hydrothermal reaction between zinc nitrate and 3-phosphonopropionic acid, using urea and tetraethylammonium bromide as the reaction medium. In common with other metal–organic framework materials, BIRM-1 has a large three-dimensional porous structure providing potential access to a high internal surface area. Unlike most others, it has the advantage of containing ammonium cations within the pores and has the ability to undergo cation exchange. Additionally, BIRM-1 also exhibits a reversible dehydration behavior involving an amorphization–recrystallization cycle. The ability to undergo ion exchange and dynamic structural behavior are of interest in their own right, but also increase the range of potential applications for this material. Here the crystal structure of this new metal phosphonate and its ion exchange behavior with K^+ as an exemplar are studied in detail, and its unusual structure-reviving property reported.

Metal–organic frameworks (MOFs) are highly crystalline porous materials constructed of single metal ions or polynuclear metal clusters linked by multidentate organic ligands, principally through coordinate bonds.^[1] This relatively new family of materials, which offers low density, huge surface to volume ratios, tunable pore structure and the flexibility to be functionalized, has developed into one of the most prolific new fields in chemistry and materials science,^[2] attracting attention from a wide spectrum of industrial and academic researchers for their interesting properties including catalysis,^[3] drug delivery,^[4] magnetic,^[5] sensing,^[6] proton conduction^[7] and, in particular, gas (water, hydrogen, carbon dioxide) adsorption^[8] and separation.^[9]

Many applications of existing porous framework materials, however, either depend upon, or are considerably enhanced by, the ability to undergo post-synthetic modification by ion exchange. This crucial property is of interest in its own right as it facilitates the removal and trapping of harmful toxic or radioactive cations

from waste solutions,^[10] and also enables the fine-tuning of properties such as gas adsorption where, for example, the hydrogen sorption properties of zeolites have been improved by varying the exchangeable cations.^[11] Of the several hundred different MOFs that have been reported, however, the number known to undergo ion exchange remains a tiny subset.^[12] Furthermore, in a significant proportion, the exchange observed involves anions or coordinatively saturated metal ions in the MOF secondary building units (framework nodes), and the effect on the desired properties is usually rather limited.^[13] Recent reviews have commented that anionic MOFs suitable for cation exchange have proven difficult to synthesize,^[14] and that the rarity of MOFs able to undergo cationic exchange severely limits their potential in important applications such as radionuclide or toxic ion removal.^[15]

Large amplitude flexibility is one of the more intriguing properties exhibited by MOF materials and their dynamic behavior has potential applications in many fields.^[16] In this context the combination of cation exchange and dynamic framework properties has attracted significant attention^[14] though the number of MOFs exhibiting both remains limited.

Phosphonate MOFs are rarer in the literature than their carboxylate counterparts, and crystalline cation-exchangeable phosphonates rarer still.^[12f, 17] Here we describe the synthesis of BIRM-1, a highly crystalline zinc phosphonate with a three-dimensional porous structure and a relatively lightweight framework, which could be advantageous in applications such as gas storage, where weight can be critical. Unusually, this material also contains extra-framework ammonium ions within the channels, which readily exchange with metal cations in aqueous solution, and also undergoes a reversible transformation from crystalline to amorphous upon dehydration/rehydration. Previous work by Bujoli et al. on the same metal-ligand pair yielded denser, layered phosphonate materials which did not exhibit large channels, ion-exchange behavior or dynamic structural behavior.^[18]

Needle-shaped, colorless crystals of BIRM-1 (Figure 1) were synthesized through the reaction of zinc nitrate and 3-phosphonopropionic acid, in the presence of urea as a pH controller and tetraethylammonium bromide as a mineralizer. Single crystal X-ray diffraction (XRD) revealed the material to have a three-dimensional coordination network in a tetragonal crystal system with $I4_1/acd$ space group. One ammonium cation per zinc atom is found to be disordered over five positions located in two main sites in the channels [Figure 2a, Supporting Information (SI) Figure S5 and Tables S1-S6 for full structural details]. The phosphorus atom is tetrahedrally bound to three oxygens and one carbon atom. The Zn atom is also tetrahedrally coordinated by four oxygens, one of which is from a carboxylate group of the $(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)^{3-}$ ligand and the other three from three

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different CPO_3 groups. The whole structure is constructed through the connection of helical inorganic double chains by the organic ligand $(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)^{3-}$ (Figure 2b). These double chains are built from ZnO_4 and CPO_3 tetrahedra. Rietveld refinement^[19] of the crystal structure against laboratory powder XRD data confirmed the structure and verified that the as-synthesized sample contained only one crystalline phase (SI, Figure S3).

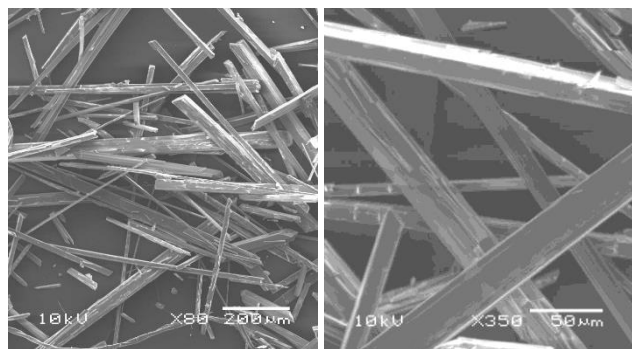


Figure 1. SEM images of as-synthesized BIRM-1 crystals.

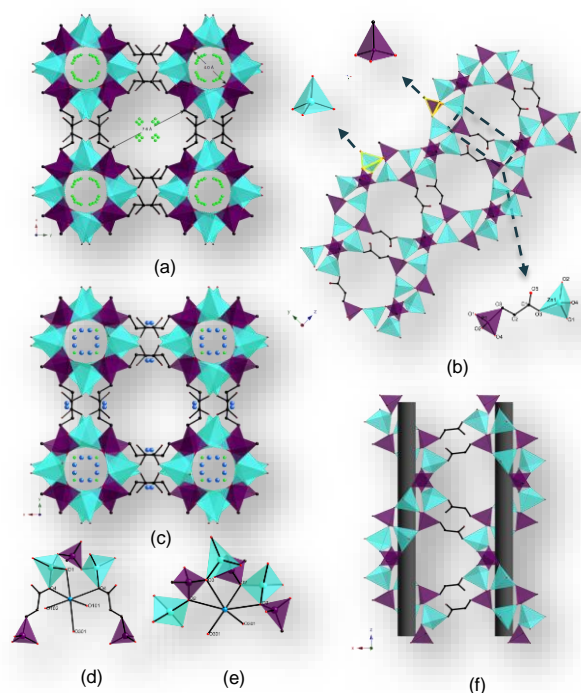


Figure 2. (a) Polyhedral view of the structure of BIRM-1 along the *c*-axis, showing a three-dimensional channel network with pores of diameter 7.6 Å and 4.0 Å; hydrogen atoms and channel water molecules have been omitted for clarity. (b) Representation of the connection of the inorganic chains showing the arrangement between ZnO_4 tetrahedra and CPO_3 tetrahedra; hydrogen atoms, nitrogen atoms and channel water molecules have been omitted for clarity. (c) Single crystal structure of K^+ -BIRM-1 viewed along the *c*-axis, showing the three dimensional channel network, potassium cations located in both the large and the small channels and residual NH_4^+ ions in the small channels; and (d) coordination spheres of potassium cations in the large channels and (e) in the small channels; hydrogen atoms, the minor component of the disordered water molecule $\text{O}(102)/\text{O}(12')$ and uncoordinated water molecules have been omitted for clarity. (f) View of the open channel of BIRM-1 along the *c*-axis, showing the helical construction of the inorganic chains which are arranged along the *c*-axis; the dark grey bar illustrates the void space inside the channel; hydrogen atoms,

internal solvent molecules have been omitted for clarity. Color scheme: ZnO_4 – turquoise tetrahedra, CPO_3 – purple tetrahedra, Zn – turquoise, K – blue, P – purple, O – red, N – green and C – black.

To investigate whether the NH_4^+ ions in the channels of BIRM-1 were exchangeable, ion exchange reactions were initially carried out with K^+ cations, which have a hydrated radius similar to NH_4^+ (2.13 Å)^[20] and smaller than both pore diameters. For the ion exchange experiment, the pH value of the ion exchange solution was adjusted to around 5.4 (that of the supernatant liquid after synthesis) through addition of 0.1 M HCl, in order to maintain the structure during the exchange procedure. After ion exchange, the powder XRD pattern of the exchanged product (K^+ -BIRM-1) was similar to that of as-synthesized BIRM-1 (Figure 3), indicating the structure remains unchanged. However, a noticeable change in relative intensities of certain peaks was observed owing to the replacement of ammonium cations with potassium inside the pores. The pattern of the exchanged compound was indexed with Crysfire^[21] and Chekcell^[22] to a tetragonal cell (space group $I4_1/acd$), which was validated through a Le Bail fit^[23] (SI, Figure S4).

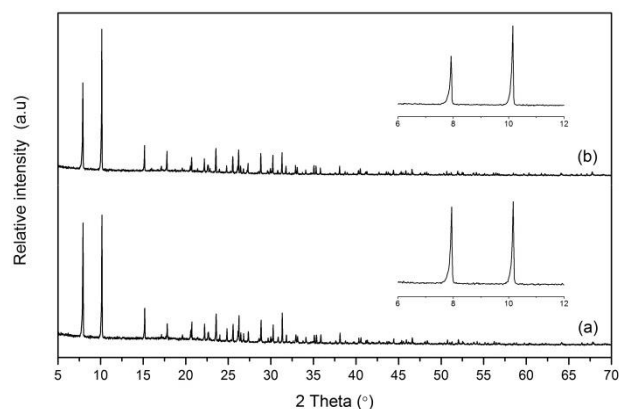


Figure 3. Powder XRD patterns of (a) K^+ -BIRM-1 and (b) BIRM-1.

SEM-EDX was employed to scan K^+ -BIRM-1 crystals to estimate the degree of ion exchange. From spot and area analysis on 28 different crystals, the results revealed that ion exchange was successfully achieved (SI, Table S7). The average molar ratios of Zn: P: K observed were 1.05: 1: 0.79. The molar ratio of Zn to P was very close to the theoretical value 1: 1, and the average molar ratio of K to P was 0.79: 1; the degree of ion exchange was therefore estimated to be 79%.

A complete structural model of K^+ -BIRM-1, derived from single crystal XRD (SI, Figure S6 and Tables S7-S13 for full structural details), confirmed that the ion exchange procedure was effective. The BIRM-1 framework was maintained with tetragonal symmetry, and potassium cations were successfully exchanged into both the large and the small channels of the structure (Figure 2c). In the large channel, potassium cations are located close to the organic ligands in a six-fold coordination environment with three framework oxygen atoms and three water oxygen atoms, one of which is disordered over two positions (Figure 2d). In the smaller channel (Figure 2e), potassium cations are found close to the

ZnO₄/CPO₃ inorganic chain in a six-fold coordination environment of four framework oxygen atoms and two water oxygen atoms. Residual NH₄⁺ ions are also distributed inside the smaller channels.

From crystallographic occupancies the structure contained 0.76 moles of potassium ions per mole of zinc atoms, consistent with the value obtained from EDX data, with the remaining charge on the framework balanced by the presence of 0.24 moles of ammonium ions per mole of zinc located in the small channels.

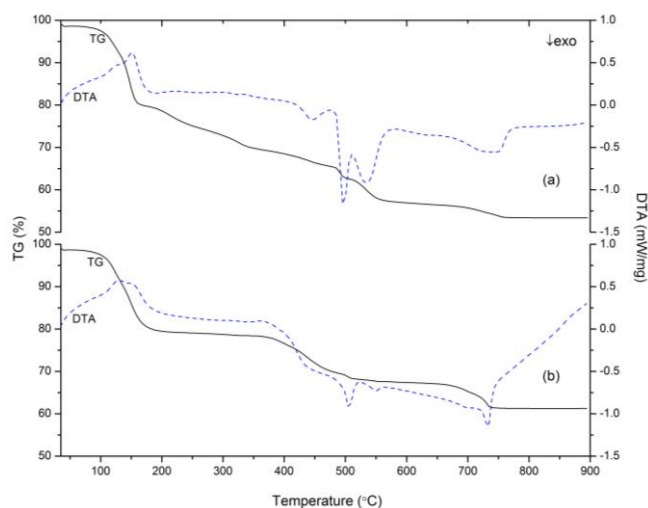


Figure 4. TGA (black trace) and DTA (blue dotted trace) of (a) BIRM-1 and (b) K⁺-BIRM-1.

The TGA and DTA curves of K⁺-BIRM-1 (Figure 4b) were significantly different from those of BIRM-1. After losing coordinated water and ammonia at around 130 °C, there followed a prolonged plateau up to around 350 °C in the TGA trace, which was not seen in that of BIRM-1 and suggests that the K⁺-exchanged product formed a stable dehydrated phase. This enhanced stability of K⁺-BIRM-1 could be exploited for use in applications which may require elevated temperatures, such as catalysis. Overall K⁺-BIRM-1 suffered a weight loss of 38.5 % on heating up to 900 °C. The product left in the crucible was identified by powder XRD as a mixture of KZn₄(PO₄)₃ and KZnPO₄ (SI, Figure S12 and Table S15).

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of BIRM-1 (Figure 4a) show three weight loss steps in the range 150 °C to 330 °C, which can be attributed to the removal of physisorbed and coordinated water, possibly accompanied by the release of a small amount of ammonia. The broad exothermic peaks at around 500 °C mark the decomposition of the coordination network. The solid residue was identified through powder XRD as zinc pyrophosphate Zn₂P₂O₇. The total weight change on heating up to 900 °C (45.70 %) was in excellent agreement with the theoretical value of 45.50 %.

Another key feature of BIRM-1 is its dynamic structural behavior. When the internal solvent was removed from the structure either by heating or evacuation, its long-range order completely disappeared (Figure 5b) and the compound did not retain any porosity. Rather than being an irreversible collapse of the framework, it was found that when the sample was rehydrated,

the structure was able to recover with a slight loss of crystallinity (Figure 5c). This feature was also observed in K⁺-BIRM-1 (SI, Figure S14). Such behavior has the potential to be exploited in various applications such as chemical sensing^[24], drug delivery^[16a] and gas or liquid separations^[16b].

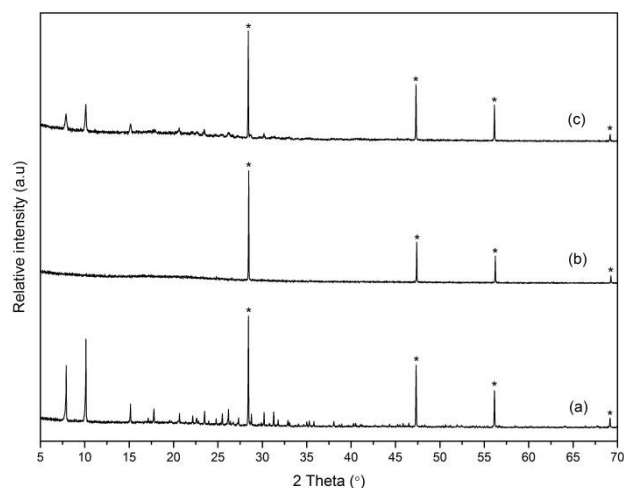


Figure 5. Powder XRD patterns of (a) BIRM-1, (b) dehydrated BIRM-1 and (c) rehydrated BIRM-1; Bragg peak positions marked with (*) originated from silicon (used as a reference).

There are a number of structural features of BIRM-1 that may be responsible for this dynamic behavior: (i) absence of an inflexible organic ligand to help preserve the framework rigidity; (ii) single bond connections of the carboxylate groups with the zinc of the ZnO₄ clusters, and of the carbon chain with the phosphorus of the CPO₃ cluster, which provide free rotation to relax the structure; and (iii) the helical shape of the inorganic chains (Figure 2f), which can act as springs that are compressed in the dehydrated form and recovered on rehydration. Further details of this process will be published elsewhere.

In this work, a new three-dimensional porous zinc carboxethylphosphonate material BIRM-1 has been synthesized, a large cation exchange capacity demonstrated for potassium, and the structure determined for both unexchanged and ion-exchanged forms. Detailed ion exchange studies on a range of mono- and divalent cations including Li⁺, Na⁺, Mg²⁺, Mn²⁺ and Co²⁺ are underway with early indications suggesting that exchange with a range of different metal cations is possible. Dehydration and rehydration investigations on both BIRM-1 and K⁺-BIRM-1 revealed interesting structural flexibility. The discovery of this dynamic property offers the potential to develop a new family of tunable MOFs in which the relationship between ion-exchange behavior and other applications dependent on control of the dehydration/rehydration characteristics of the framework can be exploited.

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