

Communications to the Editor

Deprotonation of Phosphonic Acids with M^{2+} Cations for the Design of Neutral Isostructural Organic–Inorganic Hybrids

C. V. Krishnamohan Sharma and Abraham Clearfield*

Department of Chemistry, Texas A&M University
College Station, Texas 77843-3255

Aurelio Cabeza, Miguel A. G. Aranda, and Sebastian Bruque

Departamento de Química Inorganica,
Cristalografía y Mineralogía
Universidad de Malaga, 29071 Malaga, Spain

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Organic–inorganic hybrids constitute an important class of compounds in the exploratory research area of advanced materials design, because these materials can be reliably designed by integrating highly predictable structural features of pure organic and inorganic solids.^{1–3} For example, in inorganic materials, variations in the nature of the metal cation or counterion or reaction conditions cause drastic structural changes; likewise in organic compounds, the interplay of strong and weak intermolecular interactions pose problems in structure prediction.^{2,3} However, by carefully choosing anionic ligands with strong affinity for metal cations and the ability to form robust complementary hydrogen-bonding motifs one can reliably design hybrid materials. When a ligand(s) functions as an anion and balances the charge of a metal cation, the entry of counteranions into the crystal lattice can be avoided and predictable neutral coordination networks will be formed irrespective of the nature of the counteranion. Further, the robust hydrogen bonds between ligands in hybrids exist in consonance with the coordination bonds (in other words, these bonds are insulated from each other) and form preordained network topologies.^{3a} In this context, our experience with the molecular and metal complexes of organophosphonates suggests that phosphonates are among the best candidates for attempting the design of novel organic–inorganic hybrid materials.^{4–6}

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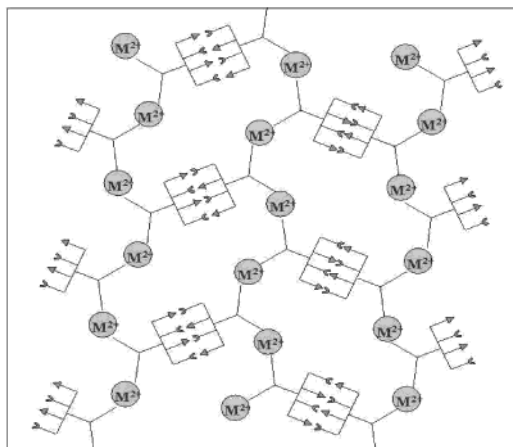


Figure 1. Oversimplified schematic representation of coordinate and hydrogen bonds in isostructural complexes **2–3**. The arrows and grooves represent hydrogen bond donors and acceptors, respectively (Motif X).

Recently, we have demonstrated that mono-deprotonation of nitrilotri(methylphosphonic acid), $[N(CH_2PO_3H_2)_3]H_6$, with organic amines results in predictable three-dimensional (3D) hexagonal structures through very short ionic hydrogen bonds, and double deprotonation of the acid **1H₆** leads to the formation of hydrogen-bonded dimers stabilized by as many as four ionic hydrogen bonds.^{5a,7} Therefore, it occurred to us that if we can doubly deprotonate the acid **1H₆** with M^{2+} metal cations, we could not only form a rigid neutral coordination network but also trigger a self-assembly process among the phosphonate anions of **1H₄** through motif X (Figure 1).⁵ The metallo deprotonated networks are expected to be isomorphous irrespective of M^{2+} metal salt type.

The doubly deprotonated salts of the acid **1H₆** were synthesized by reacting the acid with a single or a mixture of metal salts under mild hydrothermal conditions or by using layering techniques. When the acid **1H₆** was reacted with more than one metal salt and the ligand-to-metal salts ratio was kept constant at 1:1, the triphosphonic acid became doubly deprotonated, and isostructural metal complexes were formed. For example, when the acid **1H₆** (75.0 mg, 0.025 mmol), dissolved in a water–ethanol mixture (10 mL), was layered on top of an ethanolic solution of $Co(ClO_4)_2 \cdot 6H_2O$ (92.0 mg, 0.025 mmol, 15 mL), a doubly deprotonated complex $[Co(1H_4)(H_2O)_3]$ **2b** was formed. The Mn analogue of **2b** was synthesized by dissolving $MnSO_4 \cdot xH_2O$ (151.0 mg, 1 mmol) and acid **1H₆** (300.0 mg, 1 mmol) together in deionized water and by placing the reaction mixture in a high-pressure bomb at 120–130 °C for 24 h. The single crystals that resulted from mild (120 °C) hydrothermal synthesis, $[Mn(1)(H_2O)_3]$ **2a** were identical in structure to that of the metal complex synthesized using $Mn(O_2CCH_3)_2 \cdot 4H_2O$ and layering techniques. By more severe hydrothermal treatment and increasing the ratio of acid to metal, an anhydrous complex and an as yet unknown phase were also obtained. These compounds will be reported upon, subsequently.

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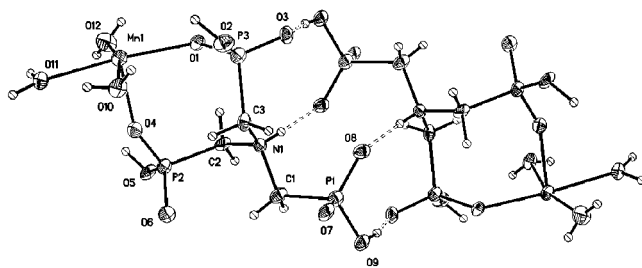


Figure 2. ORTEP diagram of two units of $\text{Mn}(\text{H}_2\text{O})_3[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3]$ showing the H-bonding as double dashed lines. The metal atoms are chelated by two of the phosphonate groups forming eight-membered rings. O6 fills out the metal coordination to form the infinite chains shown in Figure 3.

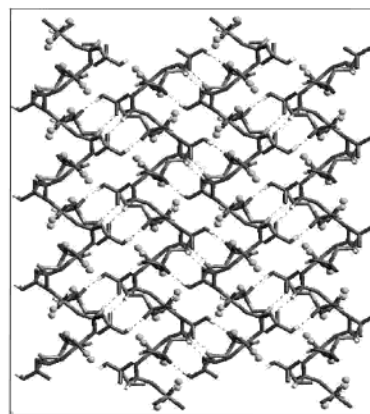
Complexes of the type $[\text{M}(\mathbf{1H}_4)(\text{H}_2\text{O})_3]$ were formed with $\text{M} = \text{Mn}$, **2a**; Co , **2b**; Ni , **2c**; Zn , **2d**; Cu , **2e**; and Cd , **2f**. The mixed-metal complex crystals of acid $\mathbf{1H}_6$, $[(\text{M1})_x(\text{M2})_{1-x}(\mathbf{1H}_4)(\text{H}_2\text{O})_3]$, (Zn (23.5%) and Cd (76.5%), **3a**; Ni (7.2%) and Cd (92.8%), **3b**; Ni (15.2%) and Zn (84.8%), **3c**; Ni (20.0%) and Mn (80.0%), **3d**) were obtained when the above metal salts were reacted (mixed-metal ratio of 50%:50%, **3b**, **3c** or 25%:75% **3a**, **3d**) with the acid $\mathbf{1H}_6$ using layering techniques. The percentage of metal ions in mixed-metal complexes of **3a–3d** was measured by direct-coupled plasma-atomic emission (DCP-AE) spectroscopy. The unit-cell parameters of all the mono- and mixed-metal complexes of **2a–2f** and **3a–3d** are similar and they are isostructural. Crystallographic details of only **3a** are presented here.⁸

Three water molecules and three O atoms from two phosphonate anions of $\mathbf{1H}_4$ octahedrally coordinate to the metal centers in the isomorphous complexes. The phosphonate anions chelate to the metal center to form an eight-membered ring and one of them additionally interconnects the neighboring metal centers to form a one-dimensional (1D) helical coordination polymer. The hydrogen-bonding sites of the triphosphonate anions, $\mathbf{1H}_4$, on the 1D polymer are oriented at an angle, $\sim 73^\circ$, as the presence of three-coordinate water molecules demands such a configuration. Consequently, the complementary hydrogen-bonding recognition sites (X) of the 1D helical polymer, form a 2D corrugated sheet structure through divergent hydrogen bonds, instead of a double helix through convergent hydrogen bonds, $\text{O}\cdots\text{O}$, 2.588(3) Å, $\text{N}\cdots\text{O}$, 2.723(3) Å, (Figures 2 and 3).

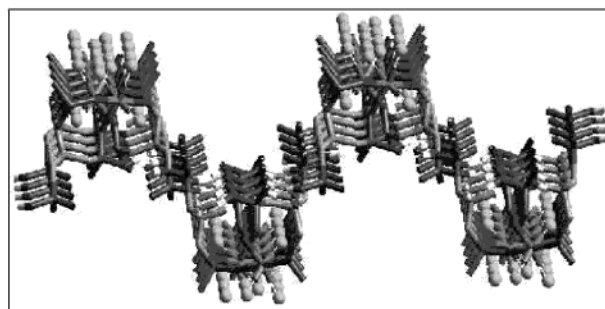
The three-coordinate water molecules play a crucial role in the formation of predictable hybrid structures. If the metal centers were not coordinated with the water molecules, additional O atoms from the phosphonate anions of $\mathbf{1H}_4$ would be required to bond to the metals so as to complete the coordination sphere. In this case, the hydrogen bond donor:acceptor complementarity of $\mathbf{1H}_4$ would be affected, and the formation of motif X in these complexes would have been unpredictable. The coordinate water molecules form both intra- and intermolecular hydrogen bonds that are lost completely upon heating anywhere between 200 and 250 °C, depending upon the metal cation(s) they are bonded to.

In recent years, several discrete examples of coordination polymers with interesting structural features have been reported,

(8) **Crystal Data 3a:** $[(\text{Zn})_{0.25}(\text{Cd})_{0.75}(\mathbf{1H}_4)(\text{H}_2\text{O})_3]$ $M = 451.72$, Monoclinic, $P2_1/c$, $a = 9.3067(6)$ Å, $b = 16.035(1)$ Å, $c = 9.7666(6)$ Å, $\beta = 114.892(1)^\circ$, $V = 1322.1(1)$ Å³, $Z = 4$, $D_c = 2.269$ Mg m⁻³, $\text{GOF} = 1.081$. X-ray data on a single crystal of **3a** ($0.30 \times 0.24 \times 0.20$ mm) were collected at -110 °C on a Bruker CCD diffractometer ($4 < \theta < 56$). 3099 absorption corrected reflections out of 8307 reflections measured on convergence gave final values of $R = 0.029$, $R_w = 0.065$. Identical fractional coordinates with different metal site occupancies were used to refine the Cd and Zn atoms. The metal composition evaluated from X-ray studies closely matches with the DCP-AE results. The OH and NH protons were determined via difference Fourier maps and the H atoms bonded to C atoms were fixed ($d_{\text{C-H}} = 0.95$ Å). All non-H atoms were anisotropically refined.



(a)



(b)

Figure 3. (a) Neutral corrugated layered structure of 10 isomorphous complexes **2a–2f**, **3a–3d**. The water molecules are shown as gray color balls. The 1D helical coordination polymers are held together through motif X (compare with Figure 2). (b) A perpendicular view of the hydrogen-bonded corrugated sheet.

but unfortunately none of these systems successfully carry over the network topology from one structure to the other irrespective of metal cations (of any given oxidation state series). The isomorphous complex series reported here provides a highly useful and successful strategy for the design of novel hybrid materials using M^{2+} cations across the periodic table.

In summary, the results presented here suggest a unique neutral organic–inorganic hybrid system, which can be synthesized irrespective of the M^{2+} salt type by doubly deprotonating the acid $\mathbf{1H}_6$. Although we have reported mixed-metal complexes considering only two different types of metal cations, one can, in principle, synthesize crystalline materials of this system using virtually all possible combinations of M^{2+} cations. The strategy/concept reported here is not specific to the current system alone; one can use a variety of phosphonates (or other appropriate ligands) and systematically deprotonate them with complementary metal cations to obtain neutral isomorphous organic–inorganic hybrid materials for structure–property correlation studies.

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Supporting Information Available: Crystallographic data of **3a** (crystallographic information, atomic coordinates, bond lengths and angles, and temperature factors), ORTEP and packing diagrams of **3a**, TGA (**2a–2f**, **3a–3c**), X-ray powder diffraction spectra of a dehydrated sample of **2b** and magnetic susceptibility measurements of **2a** and **2c**, powder pattern of **2e** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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