

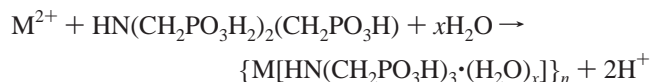
Alkaline Earth Metal Organotriphosphonates: Inorganic–Organic Polymeric Hybrids from Dication–Dianion Association

Konstantinos D. Demadis,^{*,†} Stella D. Katarachia,[†] Raphael G. Raptis,[§] Hong Zhao,[§] and Peter Baran[‡]*Department of Chemistry, University of Crete, 300 Leoforos Knossos, Heraklion GR-71409, Crete, Greece, Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico 00931-3346, and Department of Chemistry, Juniata College, 700 Moore Street, Huntingdon, Pennsylvania**Received November 30, 2005; Revised Manuscript Received February 21, 2006*

ABSTRACT: Mg²⁺ (**1**), Ca²⁺ (**2**), Sr²⁺ (**3**), or Ba²⁺ (**4**) salts react with amino-tris(methylenephosphonic acid) (H₆AMP) in a 1:1 ratio at low pH by replacing two of the six phosphonic acid protons, while the amino N maintains its proton, thus forming a zwitterion (H₄AMP²⁻). All four structures are polymeric and substantially different from one another. In all structures, each phosphonate group is singly deprotonated, whereas the N atom is protonated. **1** consists of {Mg[HN(CH₂PO₃H)₂(H₂O)]₃}_n units. Mg²⁺ ions form zigzag chains bridged by two of the three phosphonate groups. The third phosphonate group is noncoordinated and involved in hydrogen bonding. **3** is a three-dimensional (3D) polymer with the composition [Sr(H₄AMP)]_n. The Sr-atoms are seven-coordinate, with five monohapto and one chelating AMP ligands. In the 3D polymer **4**, {Ba(H₄AMP)(H₂O)]_n, the two crystallographically independent Ba²⁺ centers are 9- and 10-coordinated by phosphonate and H₂O oxygen atoms. All bridging oxygen atoms belong to phosphonate moieties that act as chelates for one Ba²⁺ and form 4-membered rings. The crystal structure of {Ba(H₄AMP)(H₂O)]_n is characterized by the complete absence of hydrogen bonds.

Polyphosphonic acids have attracted significant attention in recent years due to their utility in supramolecular chemistry and crystal engineering.¹ Polyphosphonates are also used extensively in an array of industrial applications such as chemical water treatment,² oilfield drilling,³ minerals processing,⁴ corrosion control,⁵ and metal complexation and sequestration.⁶ Metal phosphonates commonly form pillared-layered inorganic–organic hybrid materials and microporous solids.⁷ Their properties can be useful for intercalation, catalysis, sorption, and ion exchange. Hydrogen bonds are predominant in these architectures resulting in one-, two-, and three-dimensional (1D, 2D, and 3D) supramolecular networks. Although metal monophosphonates commonly create 2D structures, an increase in the number of ligand phosphonate groups results in a degree of unpredictability in the final solid-state structural architecture and a difficulty in isolating such materials in pure and crystalline form. It is not surprising that there are no structurally characterized metal phosphonate materials with more than four phosphonate groups.

In this communication, we describe the preparation and structural characterization of three new alkaline earth M–H₄AMP phosphonates (M = Mg, Sr, Ba; H₄AMP = amino-tris(methylenephosphonate) dianion) synthesized under identical conditions but of different crystal structures. These polymeric inorganic–organic hybrids have the formulae {Mg[(H₄AMP)(H₂O)]₃}_n, {Sr[(H₄AMP)]_n, and {Ba[(H₄AMP)(H₂O)]_n. The Ca²⁺ analogue has been reported previously and will not be discussed further.^{2a,8,9} Crystalline materials containing metal-coordinated H₄AMP²⁻ are obtained as products from reactions of H₆AMP and MCl₂ salts (M = Mg, **1**; Ca, **2**; Sr, **3**; Ba, **4**) in a 1:1 molar ratio under ambient conditions and low pH (1–2).¹⁰ A generalized reaction can be written as follows (proton content on the AMP ligand is also shown):



where M = Mg, $x = 3$ (**1**); Ca, $x = 3.5$, (**2**); Sr, $x = 0$, (**3**); Ba, $x = 1$, (**4**). The identity of **1**, **2**,^{2a,8,9} **3**, and **4** has been confirmed by single-crystal X-ray crystallography. At pH < 1, free H₆AMP exists as a “zwitterion” with two of the phosphonates fully protonated

(–PO₃H₂), the third monodeprotonated (–PO₃H⁻), and the amine N protonated.¹¹ The latter is deprotonated at pH > 13.¹² At pH 1–3, the ligand possesses a “2–” overall charge (H₄AMP²⁻). In principle, its association with M²⁺ cations leads to neutral, polymeric materials. **3** is 3D polymer consisting of [Sr(H₄AMP)]_n. The Sr-atoms are seven-coordinate, with five monohapto and one chelating AMP ligands and Sr–O bond distances ranging from 2.4426(17) to 2.9060(17) Å. Consequently, each H₄AMP²⁻ ligand is coordinated to six symmetry related Sr centers (Figure 1, left), with two oxygen atoms of each phosphate group acting as donors. The Sr atoms form layers separated by the H₄AMP²⁻ ligand, while each H₄AMP²⁻ bridges four Sr atoms in one layer and two in the next one; the best-fit planes of Sr layers are 8.069(2) Å apart. Within each layer, the Sr atoms form a distorted hexagonal honeycomb lattice with short (4.445(1) Å) and long (6.150(28) Å) distances (Figure 1, right).

4 has a 3D polymeric structure with the formula {Ba(H₄AMP)(H₂O)]_n (Figure 2). H₄AMP²⁻ maintains its “zwitterion” character in the crystal lattice of {Ba(H₄AMP)(H₂O)]_n. The coordination modes of both symmetry independent H₄AMP²⁻ octadentate ligands are identical. Metric features of the Ba-coordinated H₄AMP²⁻ ligand show insignificant variations from those in “free” H₆AMP.¹¹

Ba(1) is nine-coordinated, bound by nine oxygen atoms, eight originating from the phosphonate moieties and one from H₂O, whereas Ba(2) is 10-coordinated, linked by nine phosphonate and one H₂O oxygen atoms, Figure 3.

The geometry at Ba²⁺ does not approximate either of the idealized polyhedra, the bicapped square antiprism, or the bicapped dodecahedron; this observation is not surprising in view of the steric requirements of the triphosphonate ligand H₄AMP²⁻ in the structure. There are no lattice H₂O molecules of crystallization. The closest Ba···Ba contact is 4.3691(10) Å. This Ba···Ba close proximity has its origin in the three Ba(1)–μ-O–Ba(2) bridges by oxygen atoms from three different H₄AMP²⁻ ligands. The Ba–O(H₂O) bond distances are Ba(1)–O(51) 2.841(10) Å, and Ba(2)–O(52) 2.956(12) Å. Note that the longer Ba–O(H₂O) bond distance is associated with the 10-coordinate Ba²⁺ center. All bridging oxygen atoms belong to phosphonate moieties that act as chelates for one Ba²⁺ and form four-membered rings. This bridging motif has been observed in the structure of Ba-glyphosate, in which Ba is eight-coordinate.¹³ The structure of **4** can be compared with that of a recently reported barium amino-bis(methylenephosphonate), [Ba₃(O₃-PCH₂NH₂CH₂PO₃)₂(H₂O)₄]·3H₂O,^{7h} in which two crystallographically independent Ba centers are found (one is 8-coordinated, the

* Corresponding author. E-mail: demadis@chemistry.uoc.gr.

† University of Crete.

§ University of Puerto Rico at Rio Piedras.

‡ Juniata College, PA.

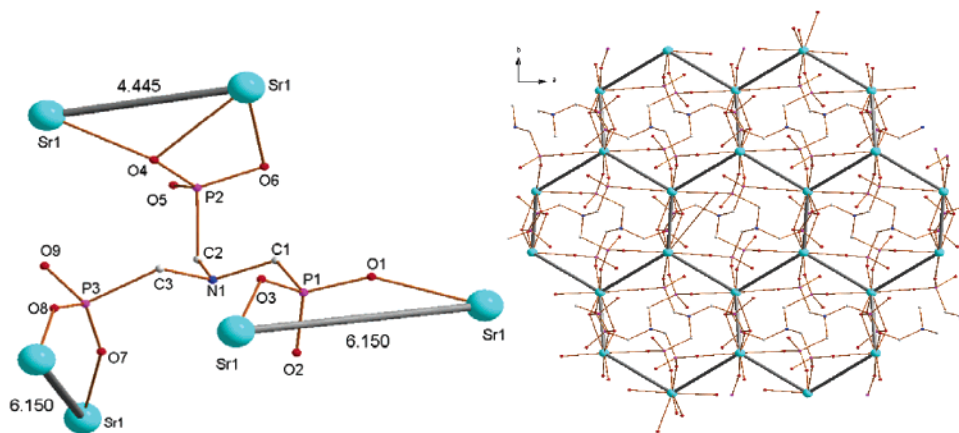


Figure 1. Coordination environment of one $\text{H}_4\text{AMP}^{2-}$ ligand chelating six Sr^{2+} ions in **3** (left). $\text{Sr}\cdots\text{Sr}$ distances are also shown. Distorted hexagons formed by Sr^{2+} centers (right).

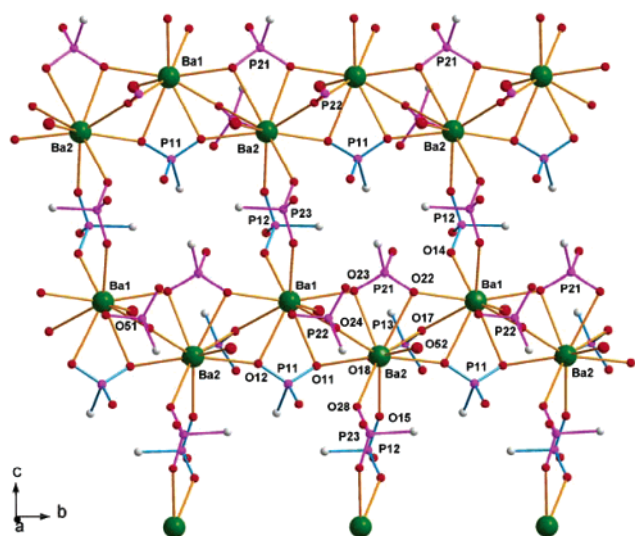


Figure 2. 3D structure of the $\{\text{Ba}(\text{H}_4\text{AMP})(\text{H}_2\text{O})\}_n$ polymer **4** that can be envisioned as a layer of Ba atoms lying in the bc plane interconnected via $\text{H}_4\text{AMP}^{2-}$ ligands in the a -direction. Only phosphonate groups of the $\text{H}_4\text{AMP}^{2-}$ ligand are shown for clarity.

other is 10-coordinated). The phosphonate groups are fully deprotonated due to the relatively high reaction pH of 5. The structure is microporous with removable H_2O molecules filling the pores. In contrast, the structure of **4** is nonporous and compact.

The 3D structure of **4** can be seen as a layer of Ba^{2+} centers lying in the bc plane interconnected via $\text{H}_4\text{AMP}^{2-}$ ligands in the a -

direction. $\text{Ba}\cdots\text{Ba}$ distances between the Ba^{2+} centers bridged by three oxygen bridges are 4.637(1) and 4.369(1) Å, while between doubly or singly μ -(O–P–O) bridged Ba^{2+} centers they are 7.163(1) or 7.687(1) Å apart (Figure 2).

Structural determination of compound **1** revealed that it is isostructural to the coordination polymers $\{\text{M}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]\}_n$ ($\text{M} = \text{Cd},^{14} \text{Mn},^{15} \text{Zn},^{16} \text{Cu}^{14}$) where M^{2+} is located in a slightly distorted octahedral environment of three phosphonate and three water oxygen atoms in a *mer* configuration (largest deviation from linearity being $169.75(8)^\circ$ for an O–Mg–O angle). $\text{H}_4\text{AMP}^{2-}$ forms an eight-membered chelate ring with Mg^{2+} , using its two phosphonate oxygen atoms. The third phosphonate arm is surprisingly *not* coordinated to Mg^{2+} but is exclusively involved in hydrogen bonding. Mg–O(P) bond distances range from 2.0213(15) to 2.1019(15) Å. A detailed description of $\{\text{Zn}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]\}_n$ (isostructural to **1**) can be found elsewhere.¹⁶

Structural aspects of a plethora of metal phosphonate materials have been reviewed extensively.¹⁷ On the other hand, structurally characterized M–AMP materials are limited, but a number of them have appeared in the literature and include metal ions such as Mn,¹⁵ Ca,^{2a} Pb,¹⁸ Na,¹⁹ Cd,¹⁴ Al,²⁰ and Zn¹⁶ that adopt diverse structural motifs.

Herein we report a series of conveniently synthesized alkaline earth metal polymeric materials with $\text{H}_4\text{AMP}^{2-}$. The four diverse M^{2+} – H_4AMP ($\text{M}^{2+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+},$ and Ba^{2+}) phosphonates exemplify the unpredictability in such 3D structural motifs, an observation undoubtedly related (at least in part) to differences in metal cation ionic radii. In contrast, there appears to be some regularity in the corresponding 3D structures of “simpler” phosphonates, such as $\text{M}(\text{HO}_3\text{PC}_6\text{H}_5)_2$, where all three $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+},$ and Ba^{2+} materials are isostructural (the Mg^{2+} analogue is not known).²¹ There, apparently other factors such as specific

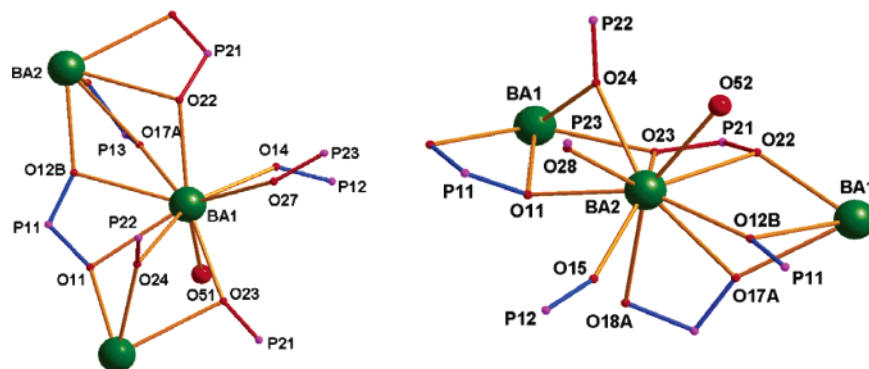


Figure 3. Coordination environments of the two Ba^{2+} centers in the structure of the $\{\text{Ba}(\text{H}_4\text{AMP})(\text{H}_2\text{O})\}_n$ polymer **4**: nine-coordinated Ba(1) (left) and 10-coordinated Ba(2) (right).

hydrogen bonding interactions and aromatic ring π - π stacking may overwhelm the cation size effect.

It is apparent that polyphosphonates are suitable ligands for the construction of metal-organic hybrids because of their versatility, multiple deprotonation processes, and ability to coordinate to virtually any metal cation.²² The intricacies of interactions between alkaline earth metal cations and phosphonates determine the crystal morphologies of minerals containing such cations, for example, calcite,²³ Barite,²⁴ hydroxyapatite,²⁵ and gypsum.²⁶

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Supporting Information Available: Various views of the structures, far- and mid-FT-IR spectra and XRD powder patterns for all compounds, crystallographic details (bond distances and angles) and cif files of **1**, **3**, and **4**.

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- Identical experimental procedures are followed for the synthesis of all four metal phosphonates. A quantity of hydrated metal chloride (25 mmol) is dissolved in deionized water (~90 mL) and AMP (11 mL of a 50% solution, 25 mmol) is added to it dropwise under vigorous stirring. Solution pH is below 1.5. The clear, colorless solution is stored at ambient temperature. All reaction solutions precipitate crystalline material within the first days, but crystallization is allowed to proceed over several days. The precipitates are isolated by filtration and air- or oven-dried. Yields range from 40 to 60% depending on crystallization time. Satisfactory elemental analyses were obtained for all products. FT-IR spectra of M-H₄AMP products display a multitude of bands in the region 1100–1270 cm⁻¹ assigned to the P=O stretch. Further details on synthesis and spectroscopic characterization are given in Supporting Information. X-ray diffraction data were collected on a SMART 1K CCD diffractometer at 298(2) K with Mo K α (λ = 0.71073 Å). Crystallographic details: Mg-AMP (**1**): rectangular plates (0.13 × 0.08 × 0.07 mm), monoclinic, space group *P2₁/c*, with *a* = 9.2172(7) Å, *b* = 16.0864(12) Å, *c* = 9.7392(7) Å, β = 115.688(1)°, *V* = 1301.33(17) Å³, and *Z* = 4, *d*_{calcd} (g/cm³) = 1.916, total reflections 8045, refined reflections (*I*_{net} > 2 σ *I*_{net}) 2380, number of parameters 209, *R* = 0.0285 (0.0366, all data), *R*_w = 0.0791 (0.0829, all data), GoF = 1.035. Sr-AMP (**3**): platelike crystals (0.17 × 0.15 × 0.06 mm), monoclinic, space group *P2₁/n*, with *a* = 8.0693(16) Å, *b* = 13.850(3) Å, *c* = 9.985(3) Å, β = 105.765(9)°, *V* = 1074.0(4) Å³, and *Z* = 4, *d*_{calcd} (g/cm³) = 2.379, total reflections 6738, refined reflections (*I*_{net} > 2 σ *I*_{net}) 2382, number of parameters 170, *R* = 0.0230 (0.0254, all data), *R*_w = 0.0617 (0.0626, all data), GoF = 1.075. Ba-AMP (**4**): rectangular crystals (0.12 × 0.08 × 0.03 mm). Crystals are monoclinic, space group *P2₁/c*, with *a* = 17.549(3) Å, *b* = 7.687(2) Å, *c* = 18.892(3) Å, β = 107.634(3)°, *V* = 2428.7(7) Å³, and *Z* = 4, *d*_{calcd} (g/cm³) = 2.474, total reflections 14 309, refined reflections (*I*_{net} > 2 σ *I*_{net}) 4809, number of parameters 353, *R* = 0.0688 (0.0785, all data), *R*_w = 0.1480 (0.1508, all data), GoF = 1.406. Copies of crystallographic data for the following structures may be obtained free of charge from CCDC: Mg-AMP (**1**) ref no. 268619, Ca-AMP (**2**) ref no. 237133, Sr-AMP (**3**) ref no. 275658, and Ba-AMP (**4**) ref no. 257969.
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