

Crystal growth and characterization of zinc–(amino-*tris*-(methylenephosphonate)) organic–inorganic hybrid networks and their inhibiting effect on metallic corrosion

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Abstract

Amino-*tris*-(methylenephosphonate) (AMP, $\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3$) forms various organic–inorganic hybrids with divalent metal cations. Zn^{2+} reacts with AMP at a 1:1 ratio by replacing two of the six phosphonic acid protons, while amino N maintains its proton, thus forming a zwitter ion. The product is a polymeric material, $\text{Zn}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]$. Its crystal is monoclinic, space group $P2_1/c$, with $a = 9.1908(7) \text{ \AA}$, $b = 16.0054(12) \text{ \AA}$, $c = 9.6791(7) \text{ \AA}$, $\beta = 115.2890(10)^\circ$, $V = 1287.37(17) \text{ \AA}^3$, and $Z = 4$. The Zn^{2+} ions form zig-zag chains bridged by two of the three phosphonate groups. The third phosphonate group is non-coordinating and involved in hydrogen bonding. The Zn^{2+} centers are located in a slightly distorted octahedral environment and are coordinated by three H_2O molecules in a *mer* fashion, two phosphonate oxygens from the same AMP ligand forming an eight-member chelate and another phosphonate oxygen from a neighboring AMP. Adjacent chains are hydrogen-bonded to each other through P–O–H and H–N donors, and the additional participation of all H_2O hydrogens in H-bonding results in a corrugated sheet-like structure. Zn^{2+} and AMP form a synergistic combination of additives that acts as corrosion inhibitor for carbon steel surfaces. The composition of this protective layer is a Zn–AMP material based on spectroscopic comparisons (FT-IR, XRF and EDS) with authentically prepared Zn–AMP.

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Phosphonic acids have attracted significant attention due to their utility in supramolecular chemistry and crystal engineering [1]. Metal-phosphonates commonly form pillared-layered inorganic–organic hybrid materials and microporous solids [2]. Their properties can be useful for intercalation, catalysis, sorption, and ion exchange [3]. In these architectures, hydrogen bonds are

predominant resulting in one-, two-, and three-dimensional supramolecular networks. Phosphonates are also used extensively in chemical water treatment [4], oil drilling applications [5] and corrosion control [6].

Zn^{2+} is used extensively as an anodic inhibitor for metallic corrosion protection [7]. Literature reports point to a synergistic action of Zn^{2+} and polyphosphonates that is explained on the basis of metal-phosphonate inhibiting films on the metallic surface [8]. Accurate description of these protective materials is lacking at the molecular level. In this paper, we describe the preparation, crystal growth and crystal and molecular structure of a polymeric inorganic–organic hybrid $\text{Zn}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]_x$ (Zn–AMP,

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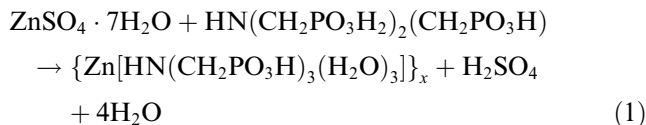
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AMP = amino-*tris*-(methylenephosphonate)) and its application as an inhibitor for the corrosion of steel.

Reaction of AMP and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at $\text{pH} \sim 1$ in a 1:1 molar ratio under ambient conditions gives $\{\text{Zn}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]\}_x$ (Zn-AMP), Eq. (1) (proton content on AMP also shown) [9]

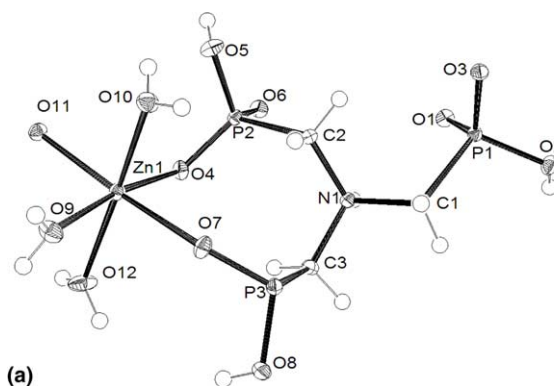


The crystalline Zn-AMP polymeric product is conveniently crystallized from acidic water and isolated by filtration. Free AMP in low pH regions (<1) exists as a “zwitter ion” with two of the phosphonates fully protonated ($-\text{PO}_3\text{H}_2$), the third monodeprotonated ($-\text{PO}_3\text{H}^-$) and the amine N protonated [10]. The latter is deprotonated at $\text{pH} > 13$ [11]. Nitrilotriacetic acid exhibits similar behavior [12]. In the presence of Zn^{2+} , single deprotonation of two phosphonate groups occurs, rendering the AMP ligand possessing a “2-” overall charge.

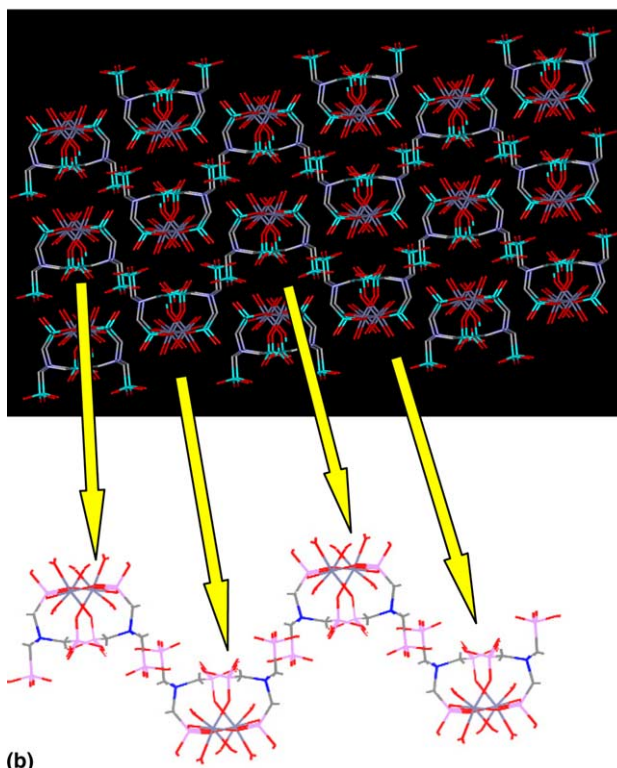
In the structure of Zn-AMP [13], each phosphonate group is singly deprotonated, whereas the N atom is protonated. Therefore, AMP maintains its “zwitter ion” character in the crystal lattice. Zn^{2+} is coordinated by three phosphonate O's and three H_2O molecules. Notably, there are no lattice H_2O molecules. The asymmetric unit is shown in Fig. 1(a). AMP forms an eight-member chelate ring with Zn^{2+} . Zn–O(P) bond distances range from 2.0459(13) to 2.1218(13) Å. Bond angles point to a slightly distorted octahedral geometry, with the largest deviation being $166.90(6)^\circ$ for the O12–Zn–O10 angle. The third phosphonate arm is surprisingly *not* coordinated to Zn^{2+} , but is exclusively involved in H-bonding through O1, O2, and O3 (*vide infra*).

A zig-zag chain parallel to the *c*-axis is formed by Zn^{2+} , Fig. 1(b). The Zn^{2+} centers are located at the corners of the zig-zag chain, whereas the “linear” portion of the zig-zag is made of the non-coordinating, hydrogen bonded phosphonate groups. Besides the three metal-bonded phosphonate oxygens (O4, O7 and O11), three additional oxygens (O5, O8 and O2) are protonated and the remaining three O atoms serve as hydrogen bond acceptors.

There is only one long intramolecular H-bonding interaction (2.469 Å) between O5 (from a Zn-coordinated phosphonate) and O10 from the water located at a *cis* position to it. The presence of a non-coordinated, singly deprotonated phosphonate group in the lattice is somewhat surprising. This phosphonate moiety participates in a complicated H-bonding network that presumably “relieves” the presence of the negative charge. Based on the bond distances of P1–O1 (1.4998 Å) and P1–O3 (1.5202 Å), the P=O and P–O[−] bonds cannot be unequivocally distinguished. These



(a)



(b)

Fig. 1. ORTEP of the asymmetric unit of the $\text{Zn}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]_x$ polymer (a), 50% probability ellipsoids). Packing diagram of the Zn-AMP lattice showing the corrugated structure and an isolated zig-zag chain (b).

bond distances point to delocalization of the negative charge over the two P–O bonds. The non-coordinating $-\text{PO}_3\text{H}^-$ moiety participates in six “short” and two “long” hydrogen bonding interactions. The $-\text{P1}-\text{O2}-\text{H9}$ proton forms a H-bond (1.875 Å) with the O of the P=O moiety that belongs to a phosphonate coordinated to a neighboring Zn^{2+} center. The O3 oxygen of the same moiety interacts via three short interactions with the H of a neighboring free $-\text{P}-\text{O}-\text{H}$ group (1.914 Å), with the H the H–O–P group of a neighboring Zn-coordinated phosphonate (1.891 Å) and with the H (1.963 Å) of a neighboring Zn-coordinated water, O12. O3 also forms two “long” interactions with a Zn-bound

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