

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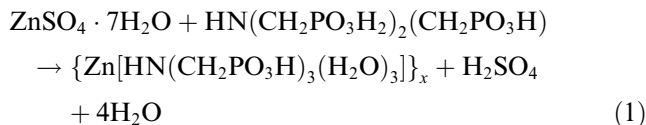
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AMP = amino-*tris*-(methylenephosphonate)) and its application as an inhibitor for the corrosion of steel.

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]

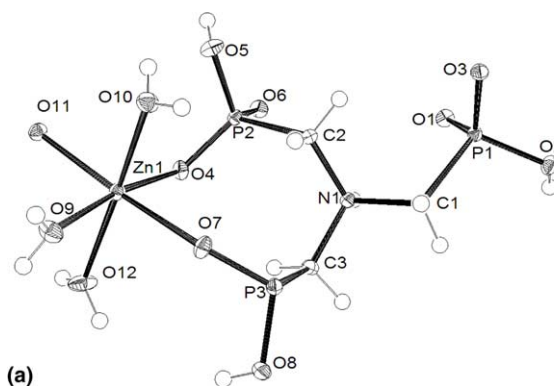


The crystalline Zn-AMP polymeric product is conveniently crystallized from acidic water and isolated by filtration. Free AMP in low pH regions (<1) exists as a “zwitter ion” with two of the phosphonates fully protonated ($-\text{PO}_3\text{H}_2$), the third monodeprotonated ($-\text{PO}_3\text{H}^-$) 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.

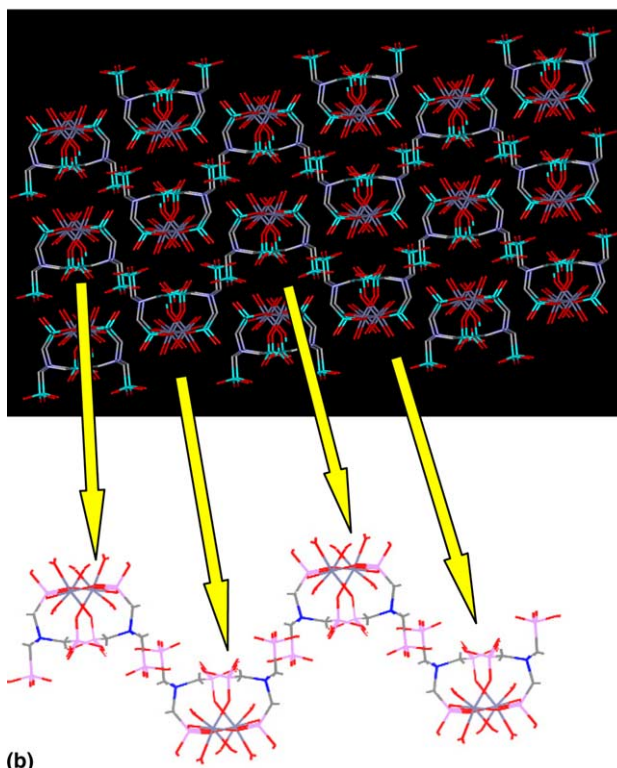
In the structure of Zn-AMP [13], each phosphonate group is singly deprotonated, whereas the N atom is protonated. Therefore, AMP maintains its “zwitter ion” character in the crystal lattice. Zn^{2+} is coordinated by three phosphonate O's and three H_2O molecules. Notably, there are no lattice H_2O molecules. 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

water (2.569 Å) and the H of a neighboring phosphonate (2.843 Å) that participates in the eight-member chelate. The third O (O1) of the uncoordinated phosphonate interacts with the N–H group (1.843 Å) of a neighboring AMP ligand and with the O=P (1.937 Å) of a Zn-coordinated water. The H-bonding network that involves the uncoordinated phosphonate group is shown in Fig. 2.

The H₂O molecule (O9) located *trans* to a coordinated phosphonate (P2) participates in two H-bonds with O6 (1.961 Å) of a Zn-bound phosphonate (P2) and O1 (1.937 Å) of a free phosphonate (P1). Of the other two water molecules that are *trans* to each other, O12–H15 interacts with O7 that belongs to phosphonate P3 that bridges two Zn²⁺ centers and O12–H16 interacts with O3 (1.963 Å) that belongs to a non-coordinated phosphonate. The remaining water (O10) forms an interaction with O4 (2.168 Å) of a neighboring Zn-bound phosphonate group.

The three H₂O molecules form their hydrogen bonds, mostly in the *a*-axis direction. The H-bonds create a 3D network of H-bonded linear chains. The overall effect is the formation of 2D corrugated sheets that nest within each other running along the *ab* diagonal. However, these sheets are made up of individual chains where the non-coordinated phosphonate groups overlap.

Structural aspects of metal-phosphonate chemistry have been reviewed extensively [14]. Structurally characterized metal-AMP materials reported in the literature include Mn-AMP (that is isostructural to Zn-AMP reported herein) [15,16], Ca-AMP, [4a,17], Pb-AMP [18], Na-AMP [19], and Al-AMP [20].

Synergistic combinations of 1:1 molar ratio Zn²⁺ and AMP are reported to exhibit superior inhibition performance than either Zn²⁺ or AMP alone [8b–d]. However, no mention is made regarding the identity of the inhibitor species involved in corrosion inhibition. Therefore, a corrosion experiment is designed [21] in order to verify the literature results and prove that the protective material acting as a corrosion barrier is an organic–inorganic hybrid composed of Zn and AMP. A synergistic combination of Zn²⁺ and AMP

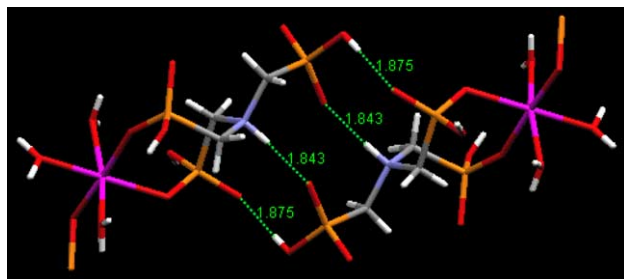


Fig. 2. Hydrogen bonding network that connects two Zn-AMP units through the non-coordinated phosphonate group.

in a 1:1 ratio (under identical conditions used to prepare crystalline Zn-AMP) offers excellent corrosion protection for carbon steel (see Fig. 3). Although differentiation between the “control” and “Zn-AMP protected” specimens is evident within the first hours, the corrosion experiment is left to proceed over a 3-day period. Based on mass loss measurements, the corrosion rate for the “control” sample is 2.5 mm/year, whereas for the Zn-AMP protected sample 0.9 mm/year, a 270% reduction in corrosion rate. The filming material is collected and subjected to FT-IR, XRF and EDS studies [22].

These show that the inhibiting film is a material containing Zn (from added Zn²⁺) and P (from added AMP) in an approximately 1:3 ratio. Fe was also present apparently originating from the steel specimen. FT-IR showed multiple bands associated with the phosphonate groups that closely resemble those of an authentically prepared Zn-AMP material. For comparison, EDS and XRF spectra of a “protected” and an “unprotected” region show the presence of Zn and P in the former, but complete absence in the latter [22].

Herein, a conveniently synthesized and structurally characterized Zn-AMP organic–inorganic hybrid polymeric material is presented. Its structure is composed of 2D corrugated sheets that nest within each other. This material, when generated in situ, acts as a corrosion inhibitor for steel surfaces. It is apparent that polyphosphonates are ideal candidates as ligands for the construction of metal-organic hybrids because of their versatility, multiple deprotonation processes and ability to coordinate to virtually any metal cation [23].

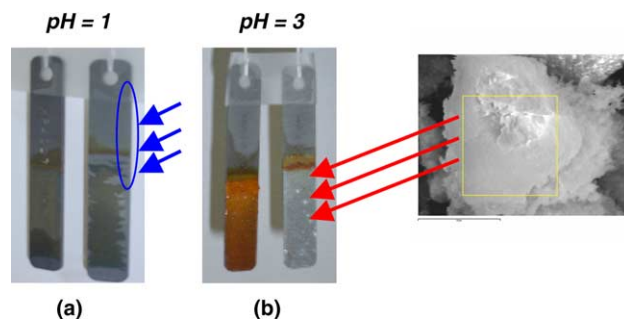


Fig. 3. Corrosion inhibition by Zn-AMP. In both images, the left specimen is the control, no inhibitor present; right specimen is with Zn²⁺/AMP combination present, both in 1 mM. Zn-AMP (image (a)) partially inhibits corrosion at pH 1, as evidenced by areas that are not corroded (indicated by blue arrows). Corrosion inhibition is dramatically obvious at pH 3 (image (a)). Formation of Zn-AMP can be clearly seen on the steel specimen as a thin white layer, with additional material accumulated at certain locations (white spots, indicated by red arrows). The inset is a magnification of a Zn-AMP particle of ~10 μm in size.

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Appendix A. Supplementary data

Details on crystal data, bond lengths and bond angles, SEM images, FT-IR, XRF and EDS spectra of the Zn–AMP single crystals as well as the filming Zn–AMP material (five pages), and the cif file are deposited. Crystallographic data for the structure reported herein have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 257224. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2004.12.019.

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ucts are cleaned by a standard method to determine corrosion rates from mass loss. It should be noted that these conditions are purposely exaggerated compared to those found in actual field applications.

[22] See [Supplementary Material](#).

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