

Rapid Communication

2D and 3D alkaline earth metal carboxyphosphonate hybrids: Anti-corrosion coatings for metal surfaces

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Received 11 December 2007; accepted 30 December 2007

Available online 6 January 2008

Abstract

Reactions of Mg^{2+} (**1**), Ca^{2+} (**2**), Sr^{2+} (**3**), or Ba^{2+} (**4**) salts with hydroxyphosphonoacetic acid (HPAA) at a 1:1 ratio yield *M*-HPAA layered coordination polymers. The crystal structures of **3** (two phases) and **4** have been determined by single crystal X-ray crystallography. Both stereoisomers (*R* and *S*) of HPAA are incorporated in the metal-HPAA materials. Synergistic combinations of Sr^{2+} or Ba^{2+} and HPAA at pH 7.3 are effective corrosion inhibitors for carbon steel, but are ineffective at pH 2.0.

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Keywords: Phosphonates; Phosphonocarboxylates; Corrosion; Inhibition; Inorganic–organic hybrids; Alkaline earth metals

The use of (poly)phosphonic acids in supramolecular chemistry, crystal engineering and materials chemistry during the recent years has undoubtedly widened these fields [1]. Apart from the interest phosphonates have attracted in the context of fundamental research, they are also been used extensively in several other technological areas, such as chemical water treatment [2], oilfield drilling [3], minerals processing [4], corrosion control [5], metal complexation and sequestration [6], dental materials [7], enzyme inhibition [8], bone targeting [9], cancer treatment [10], etc. There are several metal phosphonate materials whose structures exhibit interesting features that depend on the nature of M^{n+} (coordination number and deprotonation degree in particular), number of phosphonate groups, presence of other functional moieties (carboxylate, sulfonate, amine, hydroxyl), and, naturally, on process variables (reactant ratio, temperature, pressure). Synthesis of metal phosphonates is usually performed in aqueous solutions, so it is not surprising that water is commonly found in their

lattice, participating in extensive hydrogen bonding, which is predominant in these architectures resulting in 1-D, 2-D, and 3-D supramolecular networks [11].

In this communication we describe syntheses of a series new alkaline earth metal hydroxyphosphonoacetates, *M*-HPAA (hydroxyphosphonoacetic acid = HPAA, *M* = Mg, Ca, Sr (two phases), Ba) and structural characterization of last three. These polymeric inorganic–organic hybrids have the general formulae, $M[(\text{HO}_2\text{CCH}(\text{OH})\text{PO}_3\text{H})(\text{H}_2\text{O})_x](\text{H}_2\text{O})_y$, with *x* and *y* determining the amount of metal-coordinated and lattice water, respectively. Crystalline materials containing metal-coordinated HPAA^{2-} are obtained as products from reactions of HPAA and $M\text{Cl}_2$ salts (*M* = Mg, **1**; Ca, **2**; Sr, **3a**, **3b**; Ba, **4**) in a 1:1 molar ratio under ambient conditions and low pH (2–3) [12]. These materials have been applied as inhibiting anti-corrosion films for the protection of steel metal surfaces.

Phosphonate additives, initially applied as replacements for carcinogenic chromate [5a] in metallic corrosion protection, have since then found extensive use [5b–d]. There is a consensus in literature reports on a *synergistic* action of dissolved M^{2+} and phosphonates that has been assigned to metal–phosphonate inhibiting films on the metallic surface [13]. Recently, we initiated a systematic effort to study

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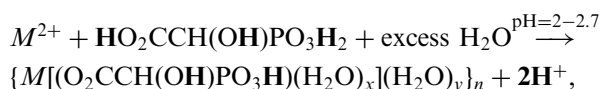
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metal–phosphonate films on metal surfaces, focusing on their accurate description at the molecular level [14].

A generalized reaction can be written as follows (proton content on the HPAA ligand is also shown) [12]:



$M = \text{Mg}$, $x = 2$, $y = 0$ (**1**); Ca , $x = 2$, $y = 0$ (**2**); Sr , $x = 3$, $y = 1$ (**3a**); Sr , $x = 2$, $y = 0$ (**3b**); Ba , $x = 2$, $y = 0$ (**4**).

The identity of **3a**, **3b** and **4** has been confirmed by single crystal X-ray crystallography [16]. At $\text{pH} \sim 2.7$ H_3PAA possesses a “2–” overall charge (HPAA^{2-}) [15]. In principle, its association with M^{2+} cations leads to neutral, polymeric materials. **3a** is 2D layered polymer consisting of “ $\text{Sr}(\text{HPAA})(\text{H}_2\text{O})_3$ ” units that are connected through a Sr–O(carboxylate) linker. The Sr-atoms are 8-coordinated. Sr–O bond distances range from 2.5030(17) to 2.6916(18) Å. Consequently, each HPAA ligand is coordinated to three symmetry related Sr^{2+} centers (Fig. 1).

The hydroxyl group remains protonated with its oxygen atom found at a 2.5786(17) Å from Sr. The coordination environment of Sr could best be described as a bicapped octahedron. There is one H_2O of crystallization *per* asymmetric unit. O–Sr–O angles range from 70.13(5)° to 98.96(7)°. Each HPAA acts as a double chelate bridge between two Sr ions (a carboxyl and the hydroxyl oxygens

chelate one Sr, while the other carboxyl and a phosphono-oxygen chelate another Sr). This type of bridging creates a zig-zag chain with alternating “Sr” and “HPAA” units with an Sr–Sr–Sr angle of 136.27°. These zig-zag chains are connected through Sr–O(carboxyl) linkages found on every other Sr, thus creating a corrugated layer that runs parallel to the *bc* plane. The closest Sr⋯Sr *intralayer* contact is 4.231 Å, whereas the closest Sr⋯Sr *interlayer* contact is 7.150 Å. Neighboring layers are connected through extensive hydrogen bonding interactions that involve the water molecule of crystallization (Fig. 1). Materials **3b** and **4** are isostructural. In the 3D structure of **4**, each HPAA links to five symmetry-equivalent, 9-coordinated Ba centers through its phosphonate group (bridging three Ba ions), the carboxylate group (bridging two Ba) and the protonated hydroxyl moiety (coordinating terminally one Ba center, Fig. 1).

There are no H_2O 's of crystallization, but two Ba-coordinated waters. In all structures both *R* and *S* HPAA isomers are incorporated in the layers. In **3a**, each “double” layer is *R*–*S*–*R*–*S*–... In **3b**(**4**), the *R* and *S* isomers are interwoven into a complicated 3D arrangement (see Supplementary Material).

There are a few metal-HPAA structures available for Zn, Cd, Sb, Co, Mn, Fe, but are different than those reported herein, mainly due to incorporation of amine templating agents used in synthesis [17].

A corrosion experiment is designed [18] to verify previous literature reports and undoubtedly confirm that

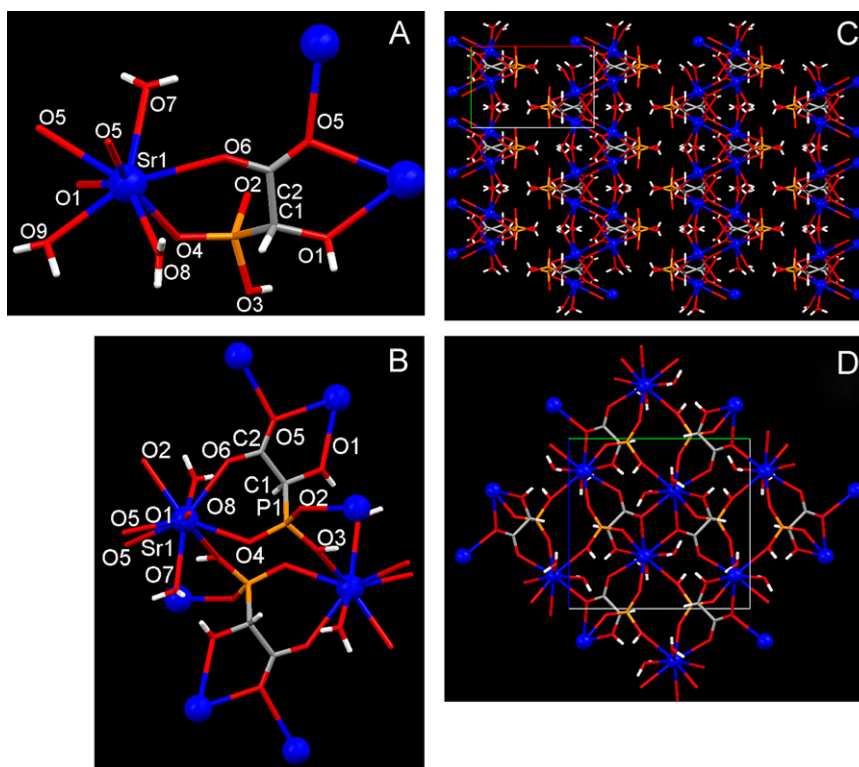


Fig. 1. Coordination environments of Sr in **3a** (A) and Ba in **4** (B) showing the multiple bridging of HPAA. (C) 2D, layered structure of Sr-HPAA (**3a**). Water molecules between the vertical layers have been omitted for clarity. (D) 3D structure of Ba-HPAA (**4**) showing the packing along the *c*-axis and the Ba-coordinated waters filling the pores. Color codes: *M* (Sr, Ba), blue; P, orange; C, gray; O, red; H, white.

the protective material acting as a corrosion barrier is an organic–inorganic hybrid composed of M^{2+} ($M = \text{Sr}, \text{Ba}$) and HPAAs. Although differentiation between the “control” and “metal-HPAA”-protected specimens is profound within the first hours, the corrosion experiments were left to proceed over a 6-day period, see Figure 2. Anti-corrosion inhibitory activity was based on mass loss measurements [18]. Synergistic combinations of M^{2+} and HPAAs, in a 1:1 ratio (under identical conditions used to

prepare crystalline M -HPAA), appear to keep the steel specimens free of corrosion products, but corrosion rates are higher than the “control” (0.299 mm/yr for the “control”, 0.465 mm/yr for Sr+HPAA and 0.397 mm/yr for Ba+HPAA). This may be attributed to the fact that metal+HPAA combinations actually act as Fe-oxide dissolvers at pH 2.0, rather than corrosion inhibitors. We have observed a similar behavior in similar experiments with M^{2+} ($M = \text{Ca}, \text{Zn}$) and 2-phosphonobutane-1,2,4-tricarboxylic acid [14c]. We have demonstrated that the thin layer that forms on the steel specimens and in bulk (after the corrosion experiments are left for prolonged time) is composed of Fe-HPAA. Thus, we abandoned corrosion experiments at this aggressive pH and resorted to circumneutral pH regions.

At higher pH (7.3) corrosion rates are dramatically suppressed (0.142 mm/yr for the “control”, 0.0005 mm/yr for Sr+HPAA and 0.0005 mm/yr for Ba+HPAA), reaching a virtually 100% corrosion inhibition efficiency. The corrosion specimens and film material were subjected to SEM, FT-IR, XRF and EDS studies (Figs. 2 and 3).

SEM images reveal a fairly uniform inhibiting film that contains M^{2+} (Sr or Ba from externally added salts) and P (from added HPAAs), in an approximate 1:1 molar ratio. Fe was also present, apparently originating from the

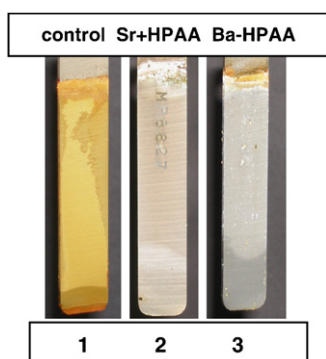


Fig. 2. The anti-corrosive effect of M -HPAA films on carbon steel at pH = 7.3. Corrosion inhibition by M^{2+} + HPAAs ($M = \text{Sr}$ or Ba) synergistic combinations is dramatically demonstrated (specimens 2, and 3).

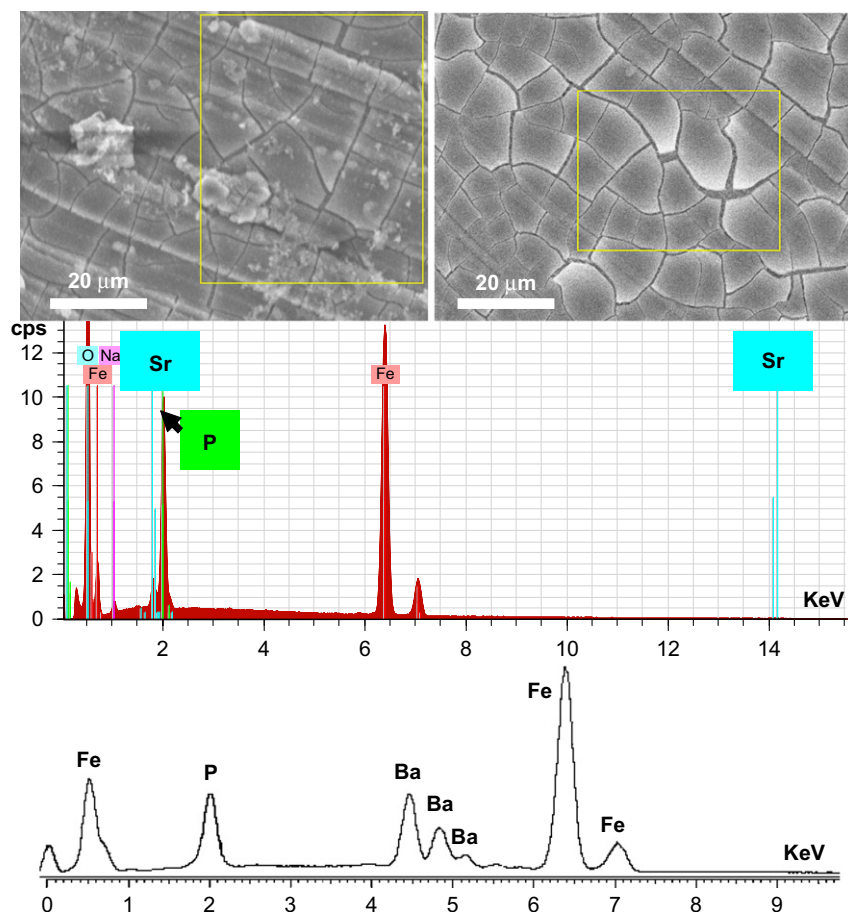


Fig. 3. Anti-corrosion film morphology: Ba-HPAA (upper left) and Sr-HPAA (upper right) at pH 7.3. Film cracking is due to drying. Identification of film components (Sr, Ba, and P) was possible by XRF (Sr, middle) and EDS (Ba, lower).

carbon steel specimen. Infra-red spectra of the filming material showed multiple bands associated with the phosphonate groups in the 950–1200 cm^{-1} region and bands in the 1550–1650 cm^{-1} due to the carboxylate group that match exactly those of authentically prepared metal-HPAA materials (see Supplementary Material).

In this communication a conveniently synthesized and structurally characterized series of divalent metal-HPAA organic–inorganic hybrid polymeric materials is described. When generated *in situ*, they act as corrosion inhibitors by creating anti-corrosive protective films on a carbon steel surface. Although the field of metal phosphonate chemistry is mature, there is still a plethora of opportunities in basic research [19] and other application areas [20]. The only limiting factor in further development of this field is phosphonate ligand availability through designed organic synthesis.

Acknowledgments

To the Department of Chemistry, University of Crete and the GSRT (Contract # 2006-207c) for financial support, and to Biolab Water Additives for a sample of HPAA.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.12.034.

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reflections ($I_{\text{net}} > 2\sigma I_{\text{net}}$) 1529, number of parameters 125, $R = 0.0229$ (0.0239, all data), $R_w = 0.0614$ (0.0618, all data), GoF = 1.081. **Ba-HPAA (4)**: rectangular plates ($0.26 \times 0.21 \times 0.08$ mm). Crystals are monoclinic, space group $P2_1/n$, with $a = 6.427(6) \text{ \AA}$, $b = 11.786(15) \text{ \AA}$, $c = 10.615(13) \text{ \AA}$, $\beta = 91.47(10)^\circ$, $V = 803.8(16) \text{ \AA}^3$, and $Z = 4$, d_{calcd} (g/cm^3) 2.705, total reflections 4735, refined reflections ($I_{\text{net}} > 2\sigma I_{\text{net}}$) 1715, number of parameters 125, $R = 0.0285$ (0.0290, all data), $R_w = 0.0747$ (0.0751, all data), GoF = 1.166. Copies of crystallographic data for the following structures may be obtained free of charge from CCDC: Sr-HPAA (**3a**) ref. no. 607004, Sr-HPAA (**3b**) ref. no. 615683, and Ba-HPAA (**4**) ref. no. 614291.

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