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Metal–Organotetraphosphonate Inorganic–Organic Hybrids: Crystal Structure and Anticorrosion Effects of Zinc Hexamethylenediaminetetrakis(methylenephosphonate) on Carbon Steels

Konstantinos D. Demadis,*,† Christos Mantzaridis,† Raphael G. Raptis,‡ and Gellert Mezei‡

Department of Chemistry, University of Crete, 300 Leoforos Knossos, Heraklion GR-71409, Crete, Greece, and Department of Chemistry, University of Puerto Rico at Rio Piedras, San Juan, Puerto Rico 00931-3346

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The synthesis and structural characterization of the first polymeric M–HDTMP organic–inorganic hybrids are described [M = Zn^{2+}, Ca^{2+}; HDTMP = hexamethylenediaminetetrakis(methylenephosphonate)]. The 3D crystal structure of the Zn^{2+} analogue [Zn(HDTMP)·H_2O] is described. The Zn center is found in a distorted octahedral environment of phosphonate oxygens. There is a long Zn···O interaction (2.622 Å) originating from a protonated –P–OH group. Synergistic combinations of Zn^{2+} and the tetraphosphonate are found to form films that protect against the corrosion of carbon steels.

Organic phosphonates are used extensively in a wide array of technological areas and applications.[1] These range from industrially important processes, such as chemical water treatment,[2] to biological and medicinal uses, such as regulation of calcium metabolism or treatment of calcium-related disorders.[3] In water chemical technology, organic phosphonates are used as mineral scale inhibitors.[4] In medical and pharmaceutical applications, they are used extensively as regulators of calcium phosphate metabolism,[5] particularly in relation to hydroxyapatite, the major inorganic constituent of bone.[6] Their utility in supramolecular chemistry and crystal engineering has also been noted in the literature.[7]

Zn^{2+} is used extensively as an anodic inhibitor for metallic corrosion protection.[8] Literature reports point to a synergistic action of Zn^{2+} and polyphosphonates that is explained in terms of metal phosphonate inhibiting films on the metallic surface.[9] An accurate description of these protective materials at the molecular level is lacking. In this Communication, we describe the preparation and crystal and molecular structure of a Zn−HDTMP polymeric inorganic−organic hybrid, $\{Zn[(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2]\cdot H_2O\}_n$ (HDTMP=hexamethylenediamine-tetrakis(methylenephosphonate), and its application as an inhibitor for the corrosion of steel.

Reaction of zwitterionic HDTMP and $ZnCl_2$ at pH ~2.2 in a 1:1 molar ratio under ambient conditions gives $\{Zn[(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2]\cdot H_2O\}_n$ (Zn−HDTMP; proton content on HDTMP also shown)[10]

$$ZnCl_2 + (H_2O_3PCH_2)(HO_3PCH_2)N(H)(CH_2)_6N(H) - (CH_2PO_3H)(CH_2PO_3H_2) \xrightarrow{H_2O} \{Zn[(HO_3PCH_2)_2N(H) - (CH_2)_6N(H)(CH_2PO_3H)_2]\cdot H_2O\}_n + 2HCl$$

The crystal structure of Zn−HDTMP[11] shows that it is a 3D coordination polymer. The Zn−O distances are unexceptional and consistent with those of other structurally characterized zinc phosphonates.[12] Zn^{2+} is found in a distorted octahedral environment (Figure 1, top) formed

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* To whom correspondence should be addressed. E-mail: demadis@chemistry.uoc.gr.

† University of Crete.

‡ University of Puerto Rico at Rio Piedras.

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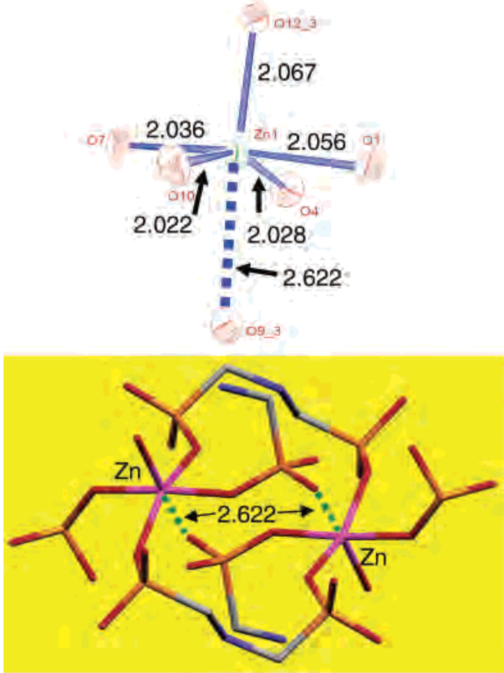

Figure 1. (Top) Coordination environment of the Zn^{2+} center displaying important bond distances (in angstroms). The nonlinear O(10)−Zn−O(4) angle is 156.03°. (Bottom) Coordination modes of the tepraphosphonate ligand. The C_6 carbon chain is omitted for clarity. The aminomethylene portions of the ligand and the Zn^{2+} centers create a "box" of ∼160 $Å^3$ capacity.

exclusively by phosphonate oxygens. An interesting feature is that the sixth oxygen ligand for Zn^{2+} originates from a protonated phosphonate oxygen, O(9), and forms a long interaction [2.622(3) Å] with Zn^{2+}. Apparently, this interaction offers local stabilization because of a strong hydrogen bond, O(9)−H(9)···O(3), 1.879 Å. The O(10)−Zn-O(4) angle deviates greatly from linearity (156.03°), compared to the O(7)−Zn−O(1) angle that is almost linear (175.83°). Two Zn^{2+} centers and the aminobismethylenephosphonate portions of HDTMP form an 18-membered ring (Figure 1, bottom), and there is a concentric 8-membered ring formed by the same Zn^{2+} centers and the protonated methylenephosphonate arm involved in the long Zn···O(9) interaction. The lattice water interacts weakly with O(5) (2.700 Å) and O(2) (2.964 Å). The absence of chelate rings is noteworthy, in contrast to several metal animomethylenephosphonate structures.[13] HDTMP's four phosphonate groups are coordinated to six different Zn^{2+} centers. O1 [from P(1)] and O4 [from P(2)] act as unidentate ligands to Zn^{2+}. O(10) and O(12) [both from P(4)] bridge two Zn^{2+} centers that are 4.395 Å apart. O(7) and O(9) [both from P(3)] also bridge two Zn^{2+} centers, but because of the long O(9)···Zn interaction (2.622 Å), their distance is much greater, 5.092 Å.

The Zn^{2+} centers reside very close to the unit cell edges, and the cell's interior is filled with the organic portion of the tetraphosphonate. The C_6 carbon chain runs almost parallel to the *bc* diagonal. Also, the molecule does not exhibit the expected zigzag configuration, but the portion C(2)−C(3)−C(5)−C(6) is in a syn rather in an anti configuration.

Structurally characterized metal tetraphosphonate materials are rare. To our knowledge, there is only one published metal HDTMP structure, that of polymeric Co−HDTMP, in which HDTMP is monodentate and bridging two $Co(H_2O)_4^{2+}$ centers.[14] Some structural details of zinc tetramethylenediaminetetraphosphonate have been reported.[15] The structure of Zn−HDTMP can be compared to that of $Ca[(HO_3PCH_2)_2N(H)CH_2C_6H_4CH_2N(H)(CH_2PO_3H)_2]\cdot 2H_2O$ containing a flexible cyclohexane ring linker.[16] Major structural differences between the two include the bidentate chelation of the tetraphosphonate to the metal center. These are absent in Zn−HDTMP. Similar to the Ca^{2+} structure noted above is the EDTMP-containing material $Mn[(HO_3PCH_2)_2N(H)(CH_2)_4(H)N(CH_2PO_3H)_2]$.[17]

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(10) Synthesis of $Zn[(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2]_n$, Zn−HDTMP. A 1:1 mixture of $ZnCl_2$ (EM Science, 0.32 g, 2.32 mmol) and HDTMP (4 mL of a 23% solution, 2.32 mmol) was prepared in deionized water. The pH was adjusted to 2.2 with dilute HCl, and the solution was set aside. After slow evaporation for 25 days, a white thin film formed, and small transparent crystals grew on it. The product was isolated by filtration and air-dried (yield 60%). Only one phase was identified based on XRD powder patterns. A 2:1 ratio of Zn to HDTMP affords the same material according XRD, FT-IR, and elemental analyses. Anal. Calcd for Zn−HDTMP: C, 20.92; H, 4.88; N, 4.88; Zn, 11.40. Found: C, 20.58; H, 5.01; N, 4.75; Zn, 11.12. An FT-IR spectrum of Zn−HDTMP (see Supporting Information) displays two major bands in the region 100−1200 cm^{-1}, assigned to the P═O stretch. The characteristic P−OH band appears at 2260 cm^{-1}. A weak band at ∼2600 cm^{-1} is the $N-H^+$ stretch. The C−N stretching vibration expected at ∼1100 cm^{-1} probably overlaps the P═O stretch. The C−N deformation appears at 1323 cm^{-1}. A weak band at 730 cm^{-1} is tentatively assigned to the P−C stretch. The $-CH_2-$ symmetric and antisymmetric stretches give rise to a group of bands in the 3050−2800 cm^{-1} region. Deformation of $-CH_2-$ appears at 1450 cm^{-1}.

(11) X-ray diffraction data were collected on a Siemens SMART 1K CCD diffractometer at 298(2) K with Mo Kα radiation ($\lambda = 0.71073$ Å) on an irregularly shaped Zn−HDTMP crystal (0.08 × 0.02 × 0.01 mm). Crystals are monoclinic, space group $P2_1/c$, with $a = 8.170(1)$ Å, $b = 13.656(2)$ Å, $c = 18.262(3)$ Å, $\beta = 93.413(3)°$, $V = 2034.0(5)$ $Å^3$, $Z = 4$, $d_{calcd} = 1.873$ g/cm^3. Data collection and refinement: total reflections, 11279; refined reflections ($I_{net} > 2.5\sigma I_{net}$), 2362; number of parameters, 281; R (R, all reflections), 0.0440 (0.0830); R_w (R_w, all reflections), 0.0939 (0.1051); GOF, 0.951.

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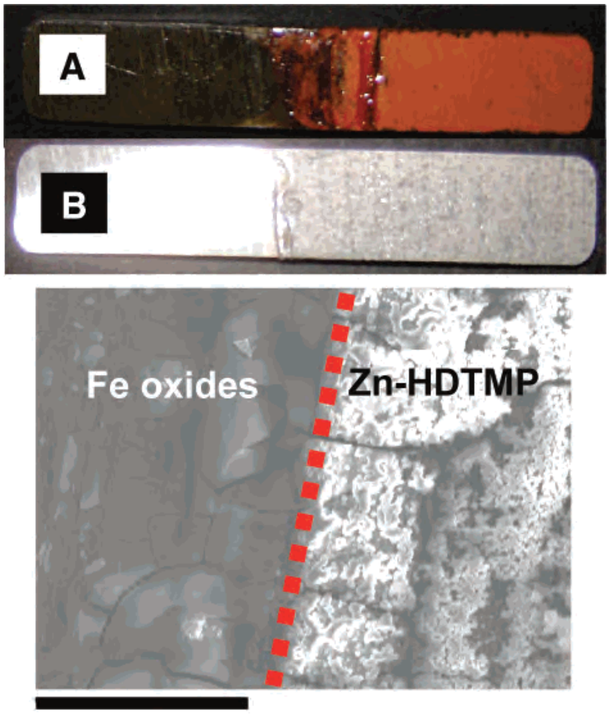

Figure 2. Anticorrosive effect of Zn−HDTMP films on carbon steel: (A) control, no inhibitor present; (B)1 mM Zn^{2+}/HDTMP synergistic combination, demonstrating dramatical corrosion inhibition. SEM image (bottom) of the interface (indicated by a dotted line) between the unprotected area (left) where growth of iron oxides is evident and the protected area (right) where a film of Zn−HDTMP has grown (bar = 100 μm).

Synergistic combinations of Zn^{2+} and organophosphonates are reported to exhibit inhibition performance superior to that of either Zn^{2+} or phosphonate alone. However, no mention is made regarding the identity of the inhibitor species involved in corrosion inhibition at the molecular level.

A corrosion experiment was designed[18] to verify the literature reports and demonstrate that the protective material acting as a corrosion barrier is an organic−inorganic hybrid composed of Zn^{2+} and HDTMP. A synergistic combination of Zn^{2+} and HDTMP in a 1:1 ratio (under conditions identical to those used to prepare crystalline Zn−HDTMP) offers excellent corrosion protection for carbon steel (Figure 2). Although differentiation between the control and Zn−HDTMP-protected specimens was profound within the first hours, the corrosion experiment was left to proceed over a 3-day period. According to mass loss measurements, the corrosion rate for the control sample is 7.28 mm/year, whereas that for the Zn−HDTMP-protected sample is 2.11 mm/year, a $\sim$170% reduction in corrosion rate.[19] The filming material was collected and subjected to FT-IR, XRF, and EDS studies.

These show that the corrosion-inhibiting film is a material containing Zn^{2+} (from externally added Zn^{2+}) and P (from added HDTMP) in an approximate 1:4 ratio. Fe was also present, apparently originating from the carbon steel specimen. FT-IR spectroscopy of the film material showed multiple bands associated with phosphonate groups in the 950−1200 cm^{-1} region that closely resemble those of the authentically prepared Zn−HDTMP material. For comparison, EDS and XRF spectra of protected and unprotected regions show the presence of Zn and P in the former, but their complete absence in the latter. Last, comparison between SEM images of the protected vs unprotected specimen areas also demonstrate the profound anticorrosive effect of Zn−HDTMP films (Figure 2).

In this Communication, a conveniently synthesized and structurally characterized Zn−HDTMP organic−inorganic hybrid polymeric material is described. When generated *in situ*, it acts as corrosion inhibitor by creating anticorrosive protective films on the carbon steel surface.

Organic polyphosphonates present a plethora of opportunities in basic research[19] and chemical technology.[20,21] They are versatile polydentate ligands for the construction of metal−organic hybrid architectures because of their accessibility through organic synthesis, structural variations, and multiple deprotonation processes and their ability to coordinate to virtually any metal site.

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Supporting Information Available: Various views of the structure, far- and mid-FT-IR spectra, XRD powder pattern of the Zn−HDTMP, crystallographic details (bond distances and angles), and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The structure has also been deposited with The Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge from the CCDC via the Web site www.ccdc.cam.ac.uk/data_request/cif (ref. no. CCDC-258076).

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(18) **Corrosion Inhibition Protocol.** Corrosion specimens (carbon steel C1010) were prepared according to established protocols.[9d] Each specimen was immersed in a control solution (no inhibitor) or in a test solution (1.0 mM Zn^{2+} and 1.0 mM HDTMP) at pH 2.2, and the progress of corrosion was monitored by visual inspection for 3 days. Then, the specimens were removed from solution, surface samples were taken for spectroscopic studies, and corrosion products were 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.

(19) Compare this with a $\sim$140% drop in corrosion rate with zinc aminotris(methylenephosphonate) inhibiting films.[13c]

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