Metal Tetraphosphonate “Wires” and Their Corrosion Inhibiting Passive Films

Konstantinos D. Demadis, Eleni Barouda, Raphael G. Raptis, and Hong Zhao


Downloaded from http://pubs.acs.org on January 27, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
Metal Tetraphosphonate “Wires” and Their Corrosion Inhibiting Passive Films
Konstantinos D. Demadis,* Eleni Barouda, Raphael G. Raptis,† and Hong Zhao‡

Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete, Voutes Campus, Heraklion, Crete GR-71003, Greece

Received October 23, 2008

Herein, we describe the preparation and characterization of five new divalent metal tetrathosphonates, M-HDTMP [M = Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Cu$^{2+}$; HDTMP = hexamethylenediaminetetraakis(methylene phosphonate) di-anion]. Materials {Sr-[(HDTMP)(H$_2$O)$_6$]·2H$_2$O}, (1), {Ba[(HDTMP)(H$_2$O)$_6$]·2H$_2$O}, (2), and {Cu[(HDTMP)(H$_2$O)$_6$]·6H$_2$O}, (3), as well as (en)(HDTMP)·2H$_2$O (en = ethylene diammonium) cation) have been structurally characterized. Structures depend on the coordination requirements of the M$^{2+}$ center and waters of crystallization content. The formation and characterization of effective anticorrosion passive films of M-HDTMP (M = Sr$^{2+}$ and Ba$^{2+}$) are also reported.

The research area of coordination polymers is by now an established field of chemical science. The combination of metal centers or clusters with a phalanx of polyfunctional ligands can create limitless possibilities for inorganic–organic hybrid solids. Factors that affect the fate of end product(s) are multiple: nature of M$^{n+}$, coordination number, nature and number of functional groups and ligand charge, different coordinating moieties, and, naturally, process variables (temperature, solvent, pressure, etc.). Phosphonates find widespread utility in crystal engineering mainly because of their increased availability through organic synthesis (e.g., Arbuzov or Mannich reactions). Metal phosphonate materials are commonly coordination polymers, occasionally exhibiting microporous properties. Features that are sought in such functional materials are intercalation, catalysis, sorption and storage, and ion exchange. Hydrogen bonds are predominant and usually responsible for the stabilization of such architectures resulting in one-, two-, and three-dimensional supramolecular networks.

Phosphonate additives have been extensively tested as inhibitors for scale inhibition and metallic corrosion protection. There is a consensus in literature reports on a synergistic action of dissolved M$^{2+}$ (M = usually an alkaline-earth metal or Zn) and polyphosphonates that is explained on the basis of inhibiting metal phosphonate film formation on the metallic surface. However, little is known about the molecular structure of these inhibiting films. Recently, we initiated a

systematic effort in delineating the mechanisms of metal phosphonate films on metal surfaces, focusing on their accurate description at the molecular level.[13] Herein, we describe the syntheses[14] of five novel divalent metal tetraphosphonates, M-HDTMP [M = Mg2+, Ca2+, Sr2+, Ba2+, and Cu2+; HDTMP = hexamethyleneaminitetrakis-(methylene phosphonate) diamid]. Compounds [Sr(HDTMP)·(H2O)3·2H2O] (1), [Ba(HDTMP)(H2O)2·2H2O] (2), and [Cu(HDTMP)(H2O)3·6H2O] (3), as well as (en)HDTMP·2H2O (en = ethylenediamonium cation) were structurally characterized.[15] Crystal structures depend on the coordination requirements of the M2+ center and waters of crystallization content. The formation and characterization of anticorrosion passive films of M-HDTMP (M = Sr2+ and Ba2+) are also described.

Reactions of water-soluble M2+ (M = Mg, Ca, Sr, Ba, and Cu) inorganic salts with HDTMP yield single-phase products [based on powder X-ray diffraction (XRD) patterns, except the Cu-HDTMP system, which yields multiple phases], with varying amounts of coordinated and lattice waters (see the Supporting Information). The structure of (en)HDTMP·2H2O (Figure 1) is composed of discrete en2+ and HDTMP2− ions and dominated by hydrogen bonds between −NH3+ (from en2+) and phosphonate groups (from HDTMP2−), and the two lattice waters. All M-HDTMP compounds have a one-dimensional chain structure. The isostructural M-HDTMP [M = Sr (1), Ba (2); Figure 1] compounds form a zigzag, corrugated arrangement with an “opening” angle of (PO−M−O(P) of 115.9(2)° (for Sr) and 117.66(8)° (for Ba). The coordination environment of the eight-coordinated Sr2+ (Ba2+) center in 1 (2) can be described as a bicapped octahedron. The M−M−M angles are very similar, 150.3(2)° for 1 and 149.7(2)° for 2. The Cu-HDTMP (3) compound is one-dimensional, and in contrast to compounds 1 and 2, the Cu···Cu···Cu “chain” is linear. The Cu2+ center is six-coordinated.

The Jahn–Teller effect is profoundly demonstrated in the Cu−O(H2O) bond distances; two are 1.9672(19) Å and the other two 2.434(3) Å. All three structures share a common structural feature that two phosphonate arms (one from each N) are not metal-coordinated but are “dangling” and participate in hydrogen bonds with neighboring −POH moieties and H2O molecules. Only three other M-HDTMP structures (very different from 1–3) are available in the literature with Zn13a Co16a and Cu.16b Thermogravimetric analysis studies showed that there is a major loss at ∼116 °C (∼16.2% for 1 and ∼12.9% for 2; see the Supporting Information). This loss corresponds to ∼6.5 molecules of H2O for 1 or 2. Above 400 °C, both compounds undergo loss that corresponds to all eight molecules of water for 1 and 2.

Corrosion experiments were performed[17] in order to study the nature of the protective anticorrosion coating. Corrosion inhibitory activity was based on mass loss measurements.[17] The effectiveness of corrosion protection by synergistic combinations of M2+ and HDTMP, in a 1:1 ratio is dramatically pH-dependent (Table 1 and Figure 2). At “harsh” pH regions (~2.2), mass loss from the steel specimens is profound, resulting in high corrosion rates. However, specimens 2 and 3 (Figure 2) appear free of corrosion products, presumably because HDTMP (either free or metal-bound) at the surface acts as an iron oxide dissolving agent. We have observed a similar behavior in

References:
[15] All starting materials are commercial. HDTMP was from Solutia Inc.
[17] Corrosion protocol: NACE Standard TM0169-95 (item no. 21200). Herein some protocol details pertinent to this study are provided. Specimens (carbon steel C1010 from Metal Samples Corrosion Monitoring Systems, Munford, AL) were immersed in a “control” (no inhibitor) or in a “test” solution (100 mL, containing Sr2+ or Ba2+ and HDTMP in a 1:1 molar ratio, at various levels (Table 1). The pH (2.2 or 7.0) was adjusted by the addition of an HCl or NH4OH solution. Corrosion rates are determined after 5 days from mass loss measurements; see the protocol above. 

Table 1. Corrosion Rates and Percent Inhibition obtained in the Absence (Control) and Presence of HDTMP or M\(^{2+}\)-HDTMP Combinations

<table>
<thead>
<tr>
<th>M-HDTMP compound</th>
<th>additive concentration (mM)</th>
<th>pH 2.2</th>
<th>pH 7.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>no additives</td>
<td>2.435</td>
<td>0.682</td>
</tr>
<tr>
<td>HDTMP</td>
<td>0.5</td>
<td>1.865</td>
<td>23.5% inhibition</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>2.387</td>
<td>2.666  metal dissolution</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3.129</td>
<td>metal dissolution</td>
</tr>
<tr>
<td>Sr-HDTMP</td>
<td>0.5</td>
<td>3.060</td>
<td>0.2344 65.7% inhibition</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>1.168</td>
<td>metal dissolution</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.181</td>
<td>10.3% inhibition</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.152</td>
<td>1.152  metal dissolution</td>
</tr>
<tr>
<td>Ba-HDTMP</td>
<td>0.5</td>
<td>3.055</td>
<td>0.093 86.4% inhibition</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.062</td>
<td>90.1% inhibition</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.888</td>
<td>metal dissolution</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.097</td>
<td>85.8% inhibition</td>
</tr>
</tbody>
</table>

Percent inhibition is defined as \(\left(1 - \frac{CR_{\text{control}}}{CR_{\text{inhibited}}}\right) \times 100\). The corrosion rate is calculated from the equation \(CR = \frac{[(\text{mass loss})/(\text{area})(\text{time})(\text{metal density})]}{\text{time}}\). Units: CR in mm/year, mass loss in mg, area in cm\(^2\), time in h, metal density = 7.85 g/cm\(^3\). The concentration refers to \([M^{2+}]\) and \([\text{HDTMP}]\) that are added in a 1:1 molar ratio. The ineffectiveness of a Sr-HDTMP film at higher \([Sr^{2+}]\) and \([\text{HDTMP}]\) may be due to bulk precipitation of the Sr-HDTMP (1) compound before reaching the steel surface.

Table 1 obtained in the Supporting Information. Their elemental analyses were consistent with the formulas \(\{M_2[(\text{HDTMP})(\text{H}_2\text{O})_{12}]\}_{\text{a}}\) (M = Sr and Ba). In turn, these formulas are consistent with a second metal site being coordinated by two “dangling” phosphonate oxygen atoms (from two neighboring “chains”) along with six \(\text{H}_2\text{O}\) molecules. Such a hypothetical structure would lead to a ladder-type architecture. The formation of Cu-HDTMP on carbon steel is not possible because of immediate \(\text{Cu}^{2+}\) reduction to \(\text{Cu}^0\) metal with concomitant plating of the steel specimen.

Herein we reported syntheses and structural characterization of divalent M-HDTMP (\(M^{2+} = \text{Sr}, \text{Ba}, \text{and Cu}\)) coordination polymers. When generated in situ, they act as corrosion inhibitors at circumneutral pH by creating anticorrosive protective films on a steel surface. Although the field of metal phosphonate chemistry is rather mature, there is still a plethora of opportunities in basic research and industrially significant application areas.

Acknowledgment. We thank the GSRT and University of Crete Special Research Account (ELKE) for funding (Project KA 2573) and Dr. V. Ramos for technical assistance.

Supporting Information Available: Full details of the synthesis and characterization and also CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC802032Y

Figure 2. Anticorrosive effect of M-HDTMP films on carbon steel. The effect of M-HDTMP synergistic combinations is dramatically demonstrated (specimens 2, 3, 5, and 6).

Figure 3. Anticorrosion film morphology viewed by VSI. The grid size is \(9 \times 10^4 \mu\text{m}^2\). The height of the \(z\) axis is 3 µm. \(R_a\) is the average surface roughness, or average deviation, of all points from a plane fit to the test part of the surface.

Anticorrosive effect of M-HDTMP films on carbon steel. The effect of M-HDTMP synergistic combinations is dramatically demonstrated (specimens 2, 3, 5, and 6).

corrosion experiments with \(M^{2+}\) (Ca or Zn) and phosphonobutane-1,2,4-tricarboxylic acid. At pH 7.0, corrosion rates are appreciably suppressed (Table 1) in the presence of combinations of \(\text{Sr}^{2+}\) or \(\text{Ba}^{2+}\) and HDTMP (specimens 5 and 6). Corrosion rates are concentration-dependent for Sr-HDTMP, whereas they are insensitive to Ba-HDTMP levels.

However, when HDTMP (without \(M^{2+}\) ions) is used at pH 7.0, corrosion rates increase, apparently because of the increased iron oxide dissolution ability of the further deprotonated HDTMP (Table 1). The corrosion specimens (at pH 7.0) and film material were subjected to studies by vertical scanning interferometry (VSI; Figure 3), scanning electron microscopy (SEM), FT-IR, X-ray fluorescence, energy-dispersive spectrometry, and X-ray photoelectron spectroscopy in order to characterize the protective coating. Most data are found in the Supporting Information. Data show that at pH 2.2 (ineffective protection) the only free of charge via the Internet at http://pubs.acs.org.

IC802032Y

(18) Variation in the corrosion rates could be linked to different HDTMP complex formation constants for \(\text{Sr}^{2+}\) and \(\text{Ba}^{2+}\). Such data are unavailable. Similar formation constants (7.40–7.56) have been reported for a “shorter” tetraphosphonate, EDTMP. See Sawada, K.; Miyagawa, T.; Sakaguchi, T.; Doi, K. J. Chem. Soc., Dalton Trans. 1993, 3777. Thus, differences observed in the corrosion rates may be due to the physical stability of the M-HDTMP anticorrosion film.

(19) When a Cu specimen comes in contact with a solution of free HDTMP (~1.0 mM), higher corrosion rates (0.469 mm/year) than those for the control (0.131 mm/year) are observed. Apparently, Cu metal oxidation/dissolution occurs with concomitant formation of Cu-HDTMP, shown by FT-IR (see the Supporting Information).