Inorganic–Organic Hybrid Molecular Ribbons Based on Chelating/Bridging, “Pincer” Tetraphosphonates, and Alkaline-Earth Metals

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ABSTRACT: Syntheses and structures of alkaline earth metal ions and EDTMP, ethylenediamine-tetrakis(methyleneephosphonate), are reported. The isostructural Ca2+ and Sr2+ analogs have 1D topologies, with EDTMP acting as both chelating and bridging ligand. The M-EDTMP compounds act as Fe-oxide removers from corroded surfaces.

The renaissance of metal phosphonate chemistry is witnessed by numerous significant publications that originate from several research groups around the world. Apart from “curiosity-driven”, basic research, metal phosphonates have found important applications in medicine (e.g., palliation of metastatic bone cancer, antiresorption agents, osteoarthritits drugs, etc.), water treatment (extraction of metals, mineral scale inhibition, corrosion control), gas storage and capture, dentistry (adhesives in dental composites), and dispersion technology (rheology modification). On the other hand, alkaline-earth metal ions, in particular Ca2+ and Sr2+, play an important role in bone mineral formation and Ca2+ metabolism. Therefore, the study of interactions between alkaline-earth metals and phosphonates presents a fruitful area of research that has repercussions in several front-line disciplines.

In this communication, we report syntheses, structural characterization and some functional properties of alkaline-earth metal tetraphosphonate materials of the general formulas \( [M(EDTMP)(H_2O)]_n \) \( M = Ca^{2+} (1), Sr^{2+} (2) \) possessing 1D topologies and an unprecedented EDTMP chelating/bridging coordination mode. Iron oxide dissolution mediated by these M-EDTMP materials \( M = Ca^{2+} \) and \( Sr^{2+} \) is also reported. To the best of our knowledge, this is the first use of phosphonates for iron oxide dissolution.

EDTMP is a tetraphosphonic acid that can potentially dissociate its 8 protons (two \( H^+ \) from four \( PO_2H_2 \)) depending on solution pH (see the Supporting Information for speciation curves). The basic \( N \) groups remain protonated up to pH of ~10. Therefore, EDTMP can be described as a “zwitter-ionic” ligand. At pH 4, each phosphonate group is monodeprotonated, thus EDTMP possesses an overall \( -2^+ \) charge. It is therefore ideal for the construction of divalent metal phosphonate frameworks based on simple charge neutralization principles. Thus, reactions of watersoluble \( M^{2+} \) \( (M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) \) inorganic salts with EDTMP in acidic pH’s yield extended coordination polymers (see reaction scheme below and the Supporting Information). All syntheses produce single-phase products based on powder XRD. In the reaction scheme, proton content is highlighted in blue.

The structures of \((NH_4)_2(EDTMP)\), 1, and 2 have been determined by single-crystal X-ray crystallography. In the structure of \((NH_4)_2(EDTMP)\), EDTMP exists as a discrete dianion, neutralized by two \( NH_4^+ \) ions (Figure 1, upper). The whole 2D layered structure is stabilized by hydrogen bonds between the \(-P=O\) and \(-P-O^+\) groups and the \( NH_4^+ \) cations or the protonated \( N \) atom (see the Supporting Information). Other structural features in \((NH_4)_2(EDTMP)\) compare well with those of EDTMP acting as both chelating and bridging ligand.
The action of EDTMP (no metals added) and M-EDTMP (M = Ca\(^{2+}\), Sr\(^{2+}\)) were studied and compared to the “control” (no additives). Quantification of corrosion rates (CR) by an established method\(^{13}\) (see caption of Figure 3) is indicative of the ability of a certain additive to protect a corroding surface. When CR is lower than that for the control, corrosion is inhibited. When CR is higher than the control, base metal corrosion/loss (carbon steel in this case) occurs. These results must be combined with visual examination of specimen morphology. High CR’s in combination with corrosion product-free surfaces is an indication that the additive removes corrosion products. When carbon steel corrosion occurs at pH 3 (control), CR is 17.31 \(\mu\)m/year and the morphology of the steel surface resembles specimens 2 or 3. When the same experiments are repeated at pH 7, CR for the control is 7.62 \(\mu\)m/year (surface 4),\(^{14}\) whereas it is 27.67 \(\mu\)m/year for Ca\(^{2+}\) (surface 5) and 30.85 \(\mu\)m/year for Sr\(^{2+}\) (surface 6). As mentioned above, increased CR’s indicate that metal loss occurs; however, examination of the steel specimens demonstrates a dramatic chemical cleaning effect. Figure 3 shows that specimens 5 and 6 are free of corrosion products at pH 7. A similar Fe-oxide removal action has been observed when PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid) is used in combination with Ca\(^{2+}\) or Zn\(^{2+}\) ions.\(^{15}\) Undoubtedly, high Fe-oxide removal performance is due to the presence of phosphonate moieties with high affinity for Fe\(^{3+}\).\(^{16}\)

To determine the fate of the dissolved Fe\(^{3+}\) from the steel specimens, we isolated and studied the byproducts of the Fe-oxide dissolution process. It was demonstrated by FT-IR spectroscopy and elemental analyses that the dissolution product at pH 3 is a Fe-EDTMP complex, if either EDTMP or Ca-EDTMP (1) are used. We synthesized and characterized a Fe-EDTMP compound at pH 3 with a formula Fe(EDTMP)\(\cdot\)H\(_2\)O, whose FT-IR spectrum matches exactly that of the dissolution product (see the Supporting Information). The dissolution product does not contain any Ca or Sr, but
amorphous (by XRD) products were isolated and studied by SEM/Ca\[(EDTMP)(H2O)2\]
Experiments were also carried out that involved reaction of interaction of Ca-EDTMP with the Fe-oxide surface. Precipitates and O is confirmed by EDS. This is proof that there is an initial at pH 7 in the presence of Ca-EDTMP, the presence of Ca, P, Fe, only Fe, P and O are identified by EDS. If dissolution takes place use of Ca(Sr)-EDTMP additives for Fe-oxide removal is recom-

such Fe3+/M2+ cation exchange has been observed in similar corrosion protection systems with alkaline earth metal hydroxyphosphonoacetate complexes.14b When the dissolution experiment is performed at pH 7 in the presence of EDTMP alone, only Fe, P and O are identified by EDS. If dissolution takes place at pH 7 in the presence of Ca-EDTMP, the presence of Ca, P, Fe, and O is confirmed by EDS. This is proof that there is an initial interaction of Ca-EDTMP with the Fe-oxide surface. Precipitates were isolated and studied by SEM. Images are shown in Figure 4. Experiments were also carried out that involved reaction of Ca\[(EDTMP)(H2O)2\]\ H2O (1) with soluble iron (from (Fe(NH4)2(SO4)2⋅6H2O) at pH 3 and 7. Nonstoichiometric and amorphous (by XRD) products were isolated and studied by SEM/EDS and revealed presence of Ca, P, O, and Fe. It is very likely that the noncoordinated P--O moieties complex Fe3+ and incorporate it into Ca-EDTMP.

Herein, we described the syntheses and structural characterization of two novel isosstructural Ca(Sr)-EDTMP 1D coordination polymers. They contain zwiter-ionic EDTMP2− in an unprecedented chelating/bridging coordination mode. On the basis of our results, use of Ca(Sr)-EDTMP additives for Fe-oxide removal is recom-

Figure 4. Fe3O4 particles isolated after reaction with Ca\[(EDTMP)(H2O)2\]\ H2O (1), upper (pH 3) and middle (pH 7). Ca and P were identified by EDS on the surface of the particles. Comparative FT-IR of Fe3O4, Ca\[(EDTMP)(H2O)2\]\ H2O (1), and of the product of their interaction.

REFERENCES


(8) (NH4)2(EDTMP): EDTMP acid (from Solutia Inc., 1.5 mmol, 0.71 gr) was suspended in ~40 mL of DI water. Using a 1 M NH4OH stock solution, the pH was adjusted to ~4 and the solid dissolved. This clear colorless solution was left for 1 week. Single
crystals of (NH₄)₂(EDTMP) appeared and were isolated by filtration. Yield: 65%. M-EDTMP (M = Ca, Sr, 2) EDTMP acid (1.5 mmol, 0.71 gr) was suspended in ~40 mL of DI water. Using a 1 M NH₄OH stock solution the pH was adjusted to ~4 and the solid dissolved. To that clear and colorless solution was gradually added a quantity of the hydrated metal chloride (1.5 mmol, 0.4 gr, molar ratio 1:1) as a solid under constant stirring. The pH dropped, but was readjusted with a 1 M stock solution of NH₄OH to ~4. The homogeneous solution was left at quiescent conditions. After several days single crystals of (NH₄)₂(EDTMP) appeared and were isolated by filtration. Dried in air. Yields: 50% for Ca-EDTMP, 60% for Sr-EDTMP. Further information on full characterization of these products is provided in the Supporting Information.

(9) X-ray diffraction data were collected on a SMART 1K CCD diffractometer at 298(2) K with Mo Kα (λ = 0.71073 Å). Crystallographic details. (NH₄)₂(EDTMP): rectangular plates (0.25 x 0.18 x 0.08 mm), monoclinic, space group P2₁/c, with a = 8.0117(17) Å, b = 6.8313(9) Å, c = 16.5259(17) Å, β = 98.758(11)°, V = 893.9(2) Å³, and Z = 2, d_{calcd} (g/cm³) = 1.747, total reflections 5969, refined reflections (I_{net}) 1766, number of parameters 138, R₁ = 0.0341 (0.0385, all data), wR₂ = 0.0935 (0.0961, all data), GOF = 1.146. Ca-EDTMP (1): rectangular plates (0.11 x 0.08 x 0.05 mm), monoclinic, space group C2/c, with a = 13.206(3) Å, b = 10.368(2) Å, c = 13.763(3) Å, β = 97.367(18)°, V = 1868.9(7) Å³, and Z = 4, d_{calcd} (g/cm³) = 1.877, total reflections 5926, refined reflections (I_{net}>2σ(I_{obs})) 1794, number of parameters 138, R₁ = 0.0341 (0.0385, all data), wR₂ = 0.0935 (0.0961, all data), GOF = 1.146. Sr-EDTMP (2): blocks (0.25 x 0.18 x 0.13 mm). Crystals are monoclinic, space group C2/c, with a = 13.449(4) Å, b = 10.3649(18) Å, c = 13.912(5) Å, β = 98.40(8)°, V = 1918.5(9) Å³, and Z = 4, d_{calcd} (g/cm³) = 2.000, total reflections 5969, refined reflections (I_{net}>2σ(I_{obs})) 1898, number of parameters 141, R₁ = 0.0256 (0.0291, all data), wR₂ = 0.0701 (0.0717, all data), GOF = 1.040. Copies of crystallographic data for the following structures may be obtained free of charge from the CCDC: (NH₄)₂(EDTMP), ref. no. 625197; Ca-EDTMP (1), ref. no. 605561; Sr-EDTMP (1), ref. no. 603911.


(13) Carbon steel surface cleaning protocol. A modified protocol was based on NACE Standard TM0169—95 (item 21200), National Association of Corrosion Engineers, Houston TX. Corrosion specimens (carbon steel C1010) are prepared according to the above protocol. Each specimen (carbon steel C1010 from Metal Samples Corrosion Monitoring Systems, Munford, AL) is immersed in a control solution (no inhibitor) or in a test solution (10.0 mM M₂EDTMP at pH 3 or 7) and corrosion progress is monitored by visual inspection for ~6 days. Then the specimens are removed from solution, surface samples are taken for spectroscopic studies and corrosion products are cleaned by the standard method above to determine corrosion rates from mass loss based on the above NACE Standard. In general, corrosion rates are lower as pH increases, see: (a) Sastri, V. S. Corrosion Inhibitors: Principles and Applications; John Wiley & Sons: Chichester, U.K., 1998; p 737. (b) Demadis, K. D.; Papadaki, M.; Raptis, R. G.; Zhao, H. Chem. Mater. 2008, 20, 4835. (c) Demadis, K. D.; Papadaki, M.; Raptis, R. G.; Zhao, H. J. Solid State Chem. 2008, 181, 679.
