

Phosphonopolycarboxylates as Chemical Additives for Calcite Scale Dissolution and Metallic Corrosion Inhibition Based on a Calcium-Phosphonotricarboxylate Organic–Inorganic HybridKonstantinos D. Demadis,^{*,†} Panagiotis Lykoudis,[†] 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, San Juan, Puerto Rico 00931-3346**Received November 22, 2005; Revised Manuscript Received March 8, 2006*

ABSTRACT: Misapplication of chemical water treatment inhibition technologies results in the formation of water-formed scale deposits (notably, CaCO_3 and BaSO_4) that interfere with proper system operation. These are removed by chemical additives through dissolution. Herein, we report the efficient dissolution of CaCO_3 at pH 4 by 2-phosphonobutane-1,2,4-tricarboxylic acid (H_3PBTC). We also report the identity of the Ca-containing dissolution product, characterized by single-crystal X-ray crystallography and a variety of spectroscopic techniques, as $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$. It is the first metal–PBTC complex reported to date. In the structure of polymeric $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$, Ca^{2+} is seven-coordinated, bound by two phosphonate oxygens, three carboxylate oxygens, and two water molecules. $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ was also prepared by designed synthesis by reacting various Ca^{2+} sources and H_3PBTC . Studies of anticorrosion properties of $\text{Ca}^{2+}/\text{H}_3\text{PBTC}^{2-}$ combinations are also reported.

Organic phosphonates are used extensively in a plethora of technological applications.¹ In medical and pharmaceutical applications, organic phosphonates are used extensively as regulators of calcium phosphate metabolism² and for treatment of calcium deposition diseases.³ Industrial applications include chemical water treatment,⁴ dispersion technology,⁵ and metallic corrosion control.⁶ In industrial water systems, phosphonates and mixed phosphonates/carboxylates are used as mineral scale inhibitors.⁷ Too often, sparingly soluble salts need to be removed by externally added agents. Chemical dissolution of inorganic salts is important in medicine,^{8a} dentistry,^{8b} archaeology,^{8c} industrial equipment cleaning, and other technology areas.^{8d} Although the dissolution process has been studied for a number of sparingly soluble salts by a variety of additives (EDTA and citrate most notably), information on the nature of dissolution products at the molecular level still lags behind. Reports only refer to the ability of added chelates to accelerate the dissolution process of inorganic scales. In another application area, metal ions such as Ca^{2+} and Zn^{2+} have been used extensively as anodic inhibitors for metallic corrosion protection.⁹ Literature reports indicate a synergistic inhibitory action of these metal ions and polyphosphonates. The observed synergy has been explained on the basis of metal–phosphonate inhibiting films on the metallic surface.¹⁰ Accurate description of these protective materials at the molecular level is rather scarce.^{6a,10a} Among the various scale inhibitors, 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) has attracted considerable attention because of its well-documented excellent properties, which have led to its extensive use in the field of chemical water treatment.

In this paper, we report the synthesis and crystal and molecular structures of the first metal salt of 2-phosphonobutane-1,2,4-tricarboxylic acid, $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$, the only structurally characterized complex of PBTC and its identification as the calcium-containing dissolution product of CaCO_3 (calcite) mineral salt. We also report the effect of H_3PBTC on corrosion of carbon steels in the presence of divalent cations, such as Ca^{2+} and Zn^{2+} .^{4b}

Crystalline $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ is obtained by reacting $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and PBTC in a 1:1 molar ratio.¹¹ It can also be prepared in high yields from CaO or $\text{Ca}(\text{OH})_2$ and PBTC in an aqueous suspension. Although CaO and $\text{Ca}(\text{OH})_2$ have limited solubility in water, they dissolve readily as they react with PBTC. The crystal

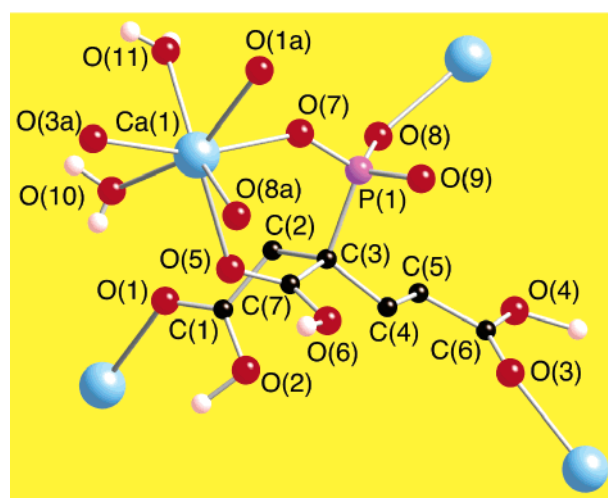


Figure 1. Fragment of the $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer, showing the coordination environment of the seven-coordinated Ca^{2+} and the tetradentate chelation mode of $\text{H}_3\text{PBTC}^{2-}$ to four Ca^{2+} centers.

structure of $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ ¹² reveals a polymeric material with $\text{H}_3\text{PBTC}^{2-}$ acting as a tetradentate chelate, Figure 1. The Ca^{2+} center is seven-coordinated in a capped octahedral environment, bound by two phosphonate oxygens, three carboxylate oxygens, and two water molecules. The phosphonate oxygens act as bridges between two neighboring Ca^{2+} centers located 6.781 Å apart. The protonation state of the phosphonate and carboxylate groups in $\text{H}_3\text{PBTC}^{2-}$ warrants some discussion. X-ray crystallography cannot give accurate H atom positions, so our arguments are based on P–O, C–O, and Ca–O bond distances. All P–O bond lengths are essentially equivalent (1.521, 1.517, and 1.521 Å). In contrast, C–O bond lengths are well separated into “short” (1.208–1.230 Å) and “long” (1.305–1.310 Å). The “long” C–O bonds correspond to the oxygen atoms that are protonated, and thus, noncoordinated. On the other hand, the “short” C–O bonds correspond to the oxygen atoms that are part of the carbonyl group and are coordinated to the Ca^{2+} center. There are several literature examples of metal phosphonate structures that have monodeprotonated, metal-coordinated, phosphonate groups.^{2a,4a,6a,10a,14,16,17,27,28} Careful examination of these structures reveals a *consistent* observation: the P–O bonds, P=O, or P–O(M), of the phosphoryl group are of approximately equal length and shorter than the P–O(H) bond of the protonated oxygen atom. The above is also true for noncoordinated phosphonates. On the basis of these

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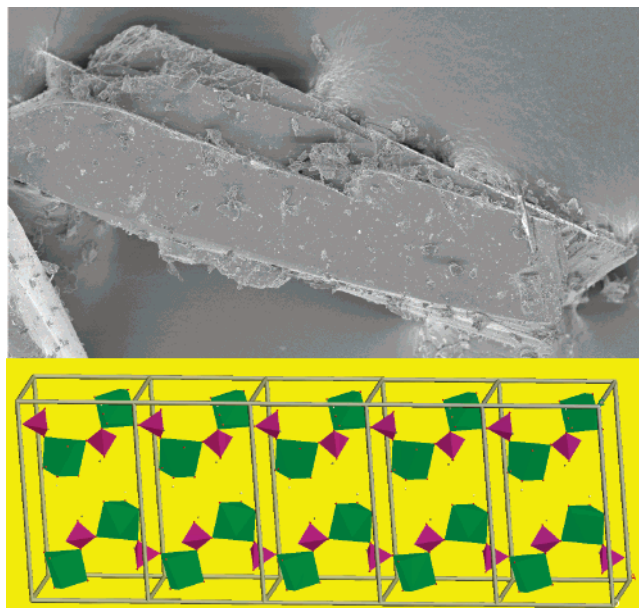


Figure 2. Single-crystal morphology of $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (upper). The crystal size is 40×110 microns. View of two zigzag chains over five unit cells formed by CaO_7 polyhedra (green) and PO_3C tetrahedra (magenta) that run parallel to the b -axis (lower).

arguments, we propose that the structure of $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ is best described as having a doubly deprotonated phosphonate with all three carboxylate groups protonated. The latter are coordinated to the Ca^{2+} center through their carbonyl moieties. It should be pointed out that all three phosphonate O-atoms are involved in $-\text{P}-\text{O} \cdots \text{HO}-\text{C}(=\text{O})$ hydrogen bonding to three carboxylate moieties.

This is consistent with the long $\text{Ca}-\text{O}(=\text{C})$ distances of $\text{Ca}(1)-\text{O}(1)$ 2.470(2) and $\text{Ca}(1)-\text{O}(5)$ 2.448(2) Å. Such $\text{Ca}-\text{O}=\text{C}(\text{OH})$ coordination mode is rare.^{2a,13} Fully deprotonated, metal-coordinated phosphonate groups in the presence of protonated carboxylate groups have been recently observed in the structure of $\text{Sm}[(\text{O}_3\text{PCH}_2)_2\text{NH}-\text{CH}_2\text{C}_6\text{H}_4-\text{COOH}] \cdot \text{H}_2\text{O}$.¹⁴ The phosphonate group and the carboxylate group oxygen atoms at the 2 position form a six-membered chelate with the Ca^{2+} center.

As mentioned above, the phosphonate group is doubly deprotonated. The $-\text{O}-\text{P}-\text{O}-$ moiety bridges two Ca^{2+} centers. On the basis of the similar $\text{Ca}-\text{O}(\text{phosphonate})$ bond distances of 2.378(2) and 2.385(2) Å the negative charge is delocalized over the entire $\text{O}-\text{P}-\text{O}$ moiety. $\text{Ca}-\text{O}_{\text{water}}$ distances, $\text{Ca}(1)-\text{O}(11)$ 2.352(3) and $\text{Ca}(1)-\text{O}(10)$ 2.445(3) Å, are consistent with those reported in the literature.^{2a,4a} There are numerous hydrogen bonding interactions in the structure of $\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$. Twelve out of 13 oxygens in the structure (except O(3)) participate in an intricate network of hydrogen bonds.¹⁵ The shortest $\text{O} \cdots \text{O}$ interactions are $\text{O}_{\text{carboxylate}}(2) \cdots \text{O}(8)_{\text{phosphonate}} = 2.518$ Å and $\text{O}_{\text{carboxylate}}(4) \cdots \text{O}(9)_{\text{phosphonate}} = 2.510$ Å and $\text{O}_{\text{carboxylate}}(6) \cdots \text{O}(7)_{\text{phosphonate}} = 2.652$ Å.

Interstitial water molecules are clustered close to the ab -plane. They are hydrogen-bonded to Ca-coordinated water molecules and carboxylate O-atoms, phosphate O-atoms, as well as to each other with $\text{O} \cdots \text{O}$ distances from 2.711 to 2.852 Å. The bridging $-\text{PO}_3$ tetrahedra and the CaO_7 polyhedra are arranged in a zigzag chain configuration that runs parallel to the b -axis. This is depicted in Figure 2 (lower) together with the morphology of the $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ single crystals Figure 2 (upper). The molecular structure of free H_3PBTC (crystallized as the monohydrate, $\text{H}_5\text{PBTC} \cdot \text{H}_2\text{O}$) shows both optical isomers R and S according to the Cahn–Ingold–Prelog sequence. Both R and S stereoisomers are also included in the structure of $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ in a regular pattern. Each chain shown in Figure 2 (lower) contains only one PBTC stereoisomer.

Uncomplexed H_3PBTC shows three intense bands in the IR spectrum due to the $\nu(\text{C}=\text{O})$ asymmetric stretch (1750, 1717, and 1636 cm^{-1}) and the $\nu(\text{P}=\text{O})$ asymmetric stretch at 1075 cm^{-1} . $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ shows an intense $\nu(\text{C}=\text{O})$ asymmetric stretch (1570 cm^{-1}) and a $\nu(\text{P}=\text{O})$ asymmetric stretch (1080 cm^{-1}). It is noteworthy that the $\nu(\text{C}=\text{O})$ stretch is profoundly shifted to lower frequency due to the weakening of the $\text{C}=\text{O}$ bond due to hydrogen bonding. A group of bands in $510\text{--}610 \text{ cm}^{-1}$ region are assigned to $\text{Ca}-\text{O}$ stretching vibrations.¹⁵

Several mixed metal–phosphonate/carboxylate complexes have been reported in the literature. Some contain one or more aminomethylene-phosphonate groups.¹⁶ These contain a N atom that can also coordinate to the metal center, thus forming stable five-membered rings via their aminomethylene-phosphonate moieties. Others contain one phosphonate and one carboxylate groups, such as $^-\text{OOC}(\text{CH}_2)_n\text{PO}_3^{2-}$.¹⁷ To our knowledge there are no structures reported of metal complexes that contain tricarboxylate/phosphonate ligands.

A dissolution experiment was set up¹⁸ to study the effect of PBTC on the dissolution rates of CaCO_3 (calcite). Dissolution of CaCO_3 in the absence of additives proceeds only to 4.2% after 5 days. It was found that PBTC greatly accelerates dissolution rates of CaCO_3 achieving quantitative dissolution within 9.5 min. 1,2,3,4-Butanetetracarboxylic acid (BTC) is structurally similar to PBTC in that it possesses four $-\text{COOH}$ groups instead of three $-\text{COOH}$ and one $-\text{PO}_3\text{H}_2$ groups for PBTC. This structural variation has a profound impact on its dissolution performance. BTC requires 30 min for CaCO_3 dissolution, a $\sim 300\%$ increase in dissolution time. EDTA requires approximately the same time as PBTC to dissolve CaCO_3 . Citric acid achieved CaCO_3 dissolution in 8.0 min. At the end of the CaCO_3 dissolution experiment by PBTC the working solution is set aside for partial solvent evaporation, followed by crystal formation of $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]$. This product was identified by FT-IR spectroscopy. Differences observed in CaCO_3 dissolution rates cannot be explained solely on the basis of variations in $\text{p}K_a$'s between the different acids.¹⁹ Both PBTC and EDTA show comparable CaCO_3 dissolution efficiencies and are doubly deprotonated at the pH regions of the dissolution experiment. BTC and citric acid, on the other hand, are monodeprotonated but exhibit dramatically different dissolution rates, with citric acid being 3.75 times faster than BTC.

Dissolution of inorganic scale deposits has been reported before.^{8,20} Those studies focus on dissolution rates and crystal surface modification effects, but no effort was made for the characterization of the metal-containing dissolution products. The initial step in M^{2+} ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) salt dissolution is surface complexation of the negatively charged polydentate ligand through its carboxylate or phosphonate moieties onto the positively charged M^{2+} lattice ions. In fact, it is not unreasonable to assume that PBTC approaches a CaCO_3 crystal surface through its $-\text{PO}_3\text{H}^-$ moiety. This is based on the structural similarities between the lattice CO_3^{2-} and the $-\text{PO}_3^{2-}$ anions. The same concept is invoked to justify and explain the effect of PBTC and other phosphonates as crystal growth inhibitors of sparingly soluble salts such as CaCO_3 and BaSO_4 .²¹ Last, it should also be noted that orthophosphate (o-PO_4^{3-}) has a strong inhibiting effect on CaCO_3 crystal growth.²² The apparent differences in dissolution efficiencies between ineffective BTC and efficient citric acid, EDTA and PBTC can also be linked to the stability of the Ca-containing dissolution products, which may be a driving force for the dissolution process. There are no known Ca complexes of BTC, but formation of seven-membered rings between Ca and two neighboring carboxylate groups can be envisioned. In the known structures of Ca-citrate ($\text{Ca}(\text{citrate}) \cdot 3\text{H}_2\text{O}$)²³ and Ca-EDTA [$\text{Ca}(\text{CaEDTA}) \cdot 7\text{H}_2\text{O}$],²⁴ there are several five- and six-membered rings that exhibit higher stability than seven-membered rings.

A corrosion experiment was set up^{25,26} to investigate the nature of the protective material acting as a corrosion barrier. On the basis of visual observations, a combination of Ca^{2+} and H_3PBTC in a



Figure 3. Phenomenology of the anticorrosive effect of Ca-PBTC films on carbon steel. The upper specimen is the “control” (A), no inhibitor present. Surface “cleanliness” in the lower specimen (B) by a 1 mM Ca^{2+} /PBTC equimolar combination is demonstrated, but overall metal loss is enhanced (see text).

1:1 molar ratio (under identical conditions used to prepare crystalline $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$) appears to offer excellent corrosion protection for carbon steel (Figure 3). However, based on mass loss measurements^{25,26} the corrosion rate for the “control” sample is 0.16 mm/year, whereas for the “Ca-PBTC” protected sample 1.17 mm/year, a ~ 10 -fold increase in corrosion rate. Therefore, PBTC essentially enhances the dissolution of “bare” metal, presumably forming soluble Fe-PBTC complexes. In contrast to aminomethylene-tris-phosphonate (AMP),^{10a} PBTC does not form stable metal–phosphonate protective films. This is consistent with the low complex formation constant for Ca-PBTC, 4.4.²⁷

Herein we report the synthesis and crystal structure of the coordination polymer $[\text{Ca}(\text{H}_3\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$, the Ca-containing dissolution product of CaCO_3 by PBTC. Although citric acid was a slightly better CaCO_3 dissolver, it shows no applicable inhibition properties toward calcium-containing scale deposits.²⁸ PBTC, on the other hand and depending on the targeted application, exhibits multifunctional properties because it is both an effective CaCO_3 dissolver and CaCO_3 inhibitor.^{4b,4c,29} An attempt to study the anticorrosion properties of PBTC in the presence of Ca^{2+} ³⁰ showed that the Ca^{2+} /PBTC combination is ineffective in corrosion protection; although it maintains metal surfaces free of Fe-oxides, it leads to substantial metal loss.

Phosphonocarboxylates are attractive compounds for a number of areas including fundamental research and industrial applications. They can be used as ligands for the construction of metal–organic hybrids³¹ because of their versatility, multiple deprotonation processes, and ability to coordinate to metal cations and clusters.³²

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Supporting Information Available: Various views of the structure, far and mid FT-IR spectra, an XRD powder pattern, SEM images of single crystals, crystallographic details (bond distances and angles), and the cif file of the title compound. Copies of crystallographic data may be obtained free of charge from CCDC, ref. no. 258096.

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- A quantity of PBTC (5.0 mL of a 50% w/v PBTC acid solution in water, corresponding to 12.52 mmol of PBTC) was added to 25 mL of deionized water under constant stirring. Solution pH was constantly monitored and was found to be 0.7 after PBTC addition. Then, 12.52 mmol of $\text{Ca}(\text{OH})_2$ (0.702 g) or CaO (0.927 g) or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (1.84 g) was added gradually in small quantities. Final solution pH depends on the Ca^{2+} source used. For example, in the case of $\text{Ca}(\text{OH})_2$ or CaO after their addition was complete the final pH was 4.1. When $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was used, the pH was lower, but it was adjusted to 4.2 by the addition of dilute NaOH solution. Upon standing of the sample for ~ 3 days, single crystals of $[\text{Ca}(\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]$ appeared. They were isolated by filtration and air dried. Yield: 2.71 g (57%). Elemental analysis: Calcd for $\text{CaC}_7\text{H}_{17}\text{O}_{13}\text{P}$ ($[\text{Ca}(\text{PBTC})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]$) MW 380.08, Ca 10.52, C 22.10, H 4.47, N 0.0. Found Ca 11.10, C 21.85, H 4.22, N 0.0. Details on spectroscopic characterization are given in Supporting Information.
- X-ray diffraction data were collected on a SMART 1K CCD diffractometer at 298(2) K with Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) on a Ca-PBTC crystal (rectangular plate, $0.12 \times 0.06 \times 0.01 \text{ mm}$). Crystals are monoclinic, space group $P2_1/n$, with $a = 7.260(1) \text{ \AA}$, $b = 10.352(2) \text{ \AA}$, $c = 18.692(3) \text{ \AA}$, $\beta = 94.087(3)^\circ$, $V = 1401.3(1) \text{ \AA}^3$, and $Z = 4$, d_{calcd} (g/cm^3) 1.802, total reflections 7683, refined reflections ($I_{\text{net}} > 2\sigma(I_{\text{net}})$) 1522, number of parameters 210, $R = 0.0434$ (0.0926, all data), $R_w = 0.0729$ (0.0832, all data), GOF = 0.902.
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- CaCO_3 dissolution protocol. Calcite was a commercial sample (Mississippi Lime Co., Alton, IL, BET surface area $10.0 \text{ m}^2/\text{g}$). PBTC (5.0 mL of a 50% w/v solution in water, corresponding to 12.52

mmol) was added to deionized water up to a volume of 50 mL, under constant stirring. To that solution, 0.626 g (6.26 mmol) of CaCO₃ was added. The solution pH was adjusted to 3.1 by the addition of NaOH. Instantly, release of CO₂ gas was noted, and the solid CaCO₃ dissolved completely within 9.5 min, yielding a clear colorless solution of pH 4.2. The reaction container was left open standing for 10 days while partial water evaporation occurred. At that time, a crystalline precipitate appeared, which was isolated by filtration. FT-IR analysis shows that this was identical to [Ca(PBTC)(H₂O)₂·2H₂O] prepared as above. The same experiment was repeated, except that no PBTC was added to the dissolution mixture. Dissolution of CaCO₃ was observed only at 4.2% over the course of 5 days. Dissolution experiments were also run with EDTA (12.52 mmol) that dissolved the same amount of CaCO₃ (0.626, 6.26 mmol) in 10.0 min. Citric acid (12.52 mmol) dissolved CaCO₃ (0.626, 6.26 mmol) in 8.0 min. When BTC (1,2,3,4-butanetetracarboxylic acid) was used as a CaCO₃ dissolver dissolution was complete after 30 min, at which time precipitation of a noncrystalline Ca-BTC complex occurred. We have not fully characterized this material.

- (19) pK_a values: PBTC, 1.7 (−PO₃H[−]), 3.43 (first −COOH), 4.45 (second −COOH), 5.97 (third −COOH), 8.13 (−PO₃^{2−}); citric acid (−COOH groups only), 3.13, 4.76, 6.40; BTC: 3.43, 4.58, 5.85, 7.16; EDTA, 1.99, 2.67, 6.16, 10.26. pK_a values are taken from Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999; 8.36 (for citric acid), 8.33 (for BTC), 8.46 (for EDTA). The pK_a's for PBTC are taken from Salvado, V.; Escoda, M. L.; de la Torre, F. *Polyhedron* **1999**, *18*, 3275.
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- (25) Corrosion inhibition protocol. Corrosion specimens (carbon steel C1010) were prepared according to established protocols.²⁶ Each specimen was immersed in a control solution (no inhibitor) or in a test solution with the same composition as described in ref 11, at pH = 4.0 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 method²⁶ to determine corrosion rates from mass loss. It should be noted that these conditions were purposely exaggerated compared to those found in actual field applications.
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- (29) PBTC has been used as an effective alumina dispersant in the direct coagulation casting process.^{3d}
- (30) Corrosion protection experiments carried out with Zn²⁺/PBTC synergistic combinations show corrosion protection that is worse than the control (0.46 mm/year) but better than Ca²⁺/PBTC combinations. Compare the higher complex formation constant for Zn-PBTC (8.3) to that of Ca-PBTC (4.4).²⁷
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