LETTER

Novel Calcium Carboxyphosphonate/polycarboxylate Inorganic–Organic Hybrid Materials from Demineralization of Calcitic Biomineral Surfaces

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ABSTRACT Dissolution of biologically important sparingly soluble salts, such as calcium carbonate and calcium oxalate, is possible by use of carboxyl- and carboxyl/phosphonate-bearing, anionic additives, citrate, malate, carboxyphosphonate, and butane tetracarboxylate. Calcium-containing dissolution products have been identified, characterized, and independently synthesized. These are polymeric materials composed of calcium and the additive as the ligand. Their full characterization was carried out by single-crystal X-ray crystallography and other techniques.

KEYWORDS: calcite dissolution • inorganic–organic hybrids • phosphonates • carboxylates • calcium carbonate

$CaCO_3$ is principally found in three morphologies—calcite (rhombohedral), aragonite (needles), and vaterite (polycrystalline spheres)—and is one of the most widespread minerals in nature (1) and industry (2). It is abundant in geological scales (3) but also in biominerals (4), mainly as the exoskeleton in shells or cell walls or as the mechanical support in spicules and spines. The mechanical properties of these structures continue to amaze scientists when compared to synthetically engineered calcium carbonate (5). These superb mechanical properties stem from the composite character of $CaCO_3$ biominerals, particularly the complicated organization of its components, organic and inorganic (6). The essential, albeit complicated, role of biopolymers (containing acidic residues, such as carboxylate or phosphate) in the formation of $CaCO_3$ biominerals is well-established (7). Some of these biopolymers end up embedded within the $CaCO_3$ matrix, resulting in bioengineered organic–inorganic composites (8). Demineralization, which could be envisioned as the converse of biomineralization, is also evident in nature (9) and industry (10). Demineralization is often used as a laboratory approach in order to liberate the organic matrix from the mineral under study. A troublesome issue is the aggressive chemical reagents used, leading to the harsh destruction of both mineral and organic phases and to corresponding artifacts. Thus, valuable information about the true nature of the biomineral's organic matrix or skeletal formation is often lost. The dissolution of $CaCO_3$ has also been studied extensively in the context of a plethora of other processes, including neutralization of acidic lakes (11), sedimentation of carbonates in marine environments (12), weathering processes (13), and acidization of petroleum wells (14) (for productivity enhancement). It is therefore apparent that studying $CaCO_3$ dissolution brings about benefits for several technological and biological disciplines.

In this paper, we report $CaCO_3$ (calcite) dissolution studies by polycarboxylates (1,2,3,4-butanetetracarboxylic acid, BTCA), hydroxycarboxylates (D,L-malic acid, MAL; citric acid, CIT), and carboxyphosphonates (carboxyethylphosphonic acid, CEPA) and structural characterization of the calcium-containing products. These products are calcium-additive coordination polymers that were also independently synthesized and structurally characterized.

The same calcite dissolution protocol was followed for the "control" (no additives) and in the presence of BTCA, MAL, CIT, and CEPA (15). Calcite dissolution at pH 5.4 occurs at a slow rate and at <40% efficiency (Figure 1). The addition of the aforementioned additives is accompanied by vigorous effervescence (release of CO_2). The presence of the additives enhances both the dissolution rate and the overall dissolution efficiency (Figure 1). Points that are at the upper left part of the graph increase the dissolution efficiency, and those that are at the lower right enhance the dissolution rate. However, points located at the upper right enhance both the dissolution efficiency *and* rate. In other words, these additives are both fast and efficient dissolvers of $CaCO_3$.

Apparently, CIT and BTCA are the most efficient $CaCO_3$ dissolvers, followed by MAL, and last by CEPA. The undissolved calcite crystals were found to contain no additives (by Fourier transform infrared spectroscopy FTIR) (16). All filtrates, after prolonged periods, precipitate solid microcrystalline products. These products were studied by FTIR,

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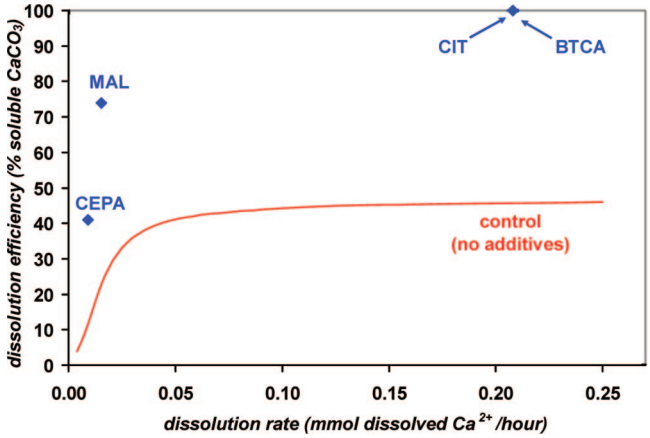

FIGURE 1. $CaCO_3$ dissolution in the absence (control) and presence (CEPA, MAL, CIT, and BTCA) of additives.

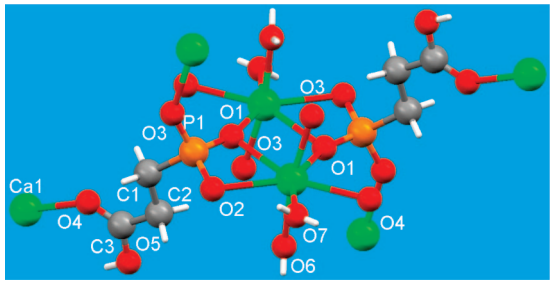

FIGURE 2. Structure of the phosphonate-bridged calcium "dimer" in Ca-CEPA. The coordination of CEPA is also shown.

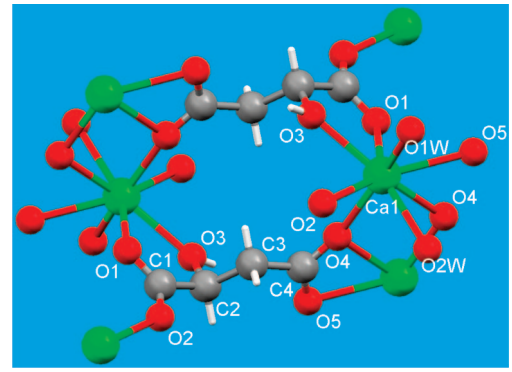

FIGURE 3. Structure of the carboxylate-bridged calcium "dimer" in the structure of Ca-MAL. This "dimer" can be envisioned as the building block for the construction of layers that interact via hydrogen bonds and run along the *a* axis.

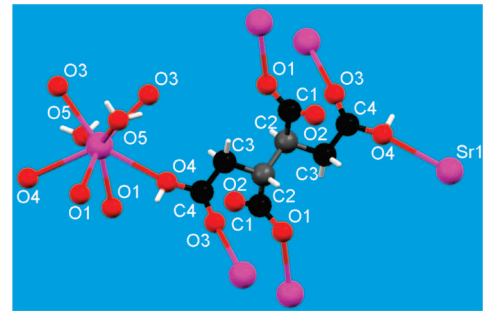

FIGURE 4. Coordination of BTCA. Each BTCA coordinates to six Sr^{2+} centers, creating a three-dimensional architecture.

powder X-ray diffraction, and elemental analyses (C, H, and N) (16). They all contain calcium-coordinated additives, based on shifted characteristic vibrations of the carboxylate and/or phosphonate groups. Synthetic efforts (17) to synthesize these materials starting from soluble calcium sources led to the isolation of crystalline solids that were characterized by a variety of methods (16). Three materials were structurally characterized (18): Ca-CEPA, Ca-MAL, and Sr-BTCA. We pursued structural characterization of the latter because all efforts to prepare suitable single crystals of Ca-BTCA had failed in our hands. The calcium center in Ca-CEPA is seven-coordinated (monocapped octahedron; Figure 2). Thus, there are two water molecules, four phosphonate oxygen atoms, and one carboxylic oxygen atom in the calcium coordination sphere. These are phosphonate O3 and O1 atoms, water O6 and O7 atoms, phosphonate O2 and O1 atoms, and O4 of the carboxylic group.

The octahedron can be visualized having the four oxygen atoms (O3, O3, $O6_{water}$, and $O7_{water}$) as the equatorial ligands and $O4_{carboxylate}$ occupying one of the two axial positions, while O2 and O3 (both from the phosphonate group) occupy the second axial position, forming a four-membered chelate with Ca^{2+}. The $Ca-O_{water}$ bond distances are 2.3850(14) and 2.4229(16) Å. The $Ca-O_{phosphonate}$ bond distances range from 2.3212(13) to 2.5240(13) Å. The structure of Ca-CEPA could be described as "ladder-type" architecture. The ladder is composed of CaO_7 polyhedra linked by the carboxylate moiety. It should be noted that the phosphonate group is doubly deprotonated, while the carboxylate group remains protonated (O5) and coordinates to Ca^{2+} through its carbonyl O4. Although metal-CEPA materials are known (19), this is the first calcium-containing CEPA coordination polymer.

The calcium center in Ca-MAL is eight-coordinated (bicapped octahedron), surrounded by two waters, one hydroxyl oxygen atom, and five carboxyl oxygen atoms (Figure 3).

The $Ca-O_{water}$ bond distances are 2.372(10) and 2.475(8) Å. The $Ca-O_{carboxylate}$ bond distances range from 2.338(9) to 2.585(10) Å. The malate ligand is doubly deprotonated and chelates four Ca^{2+} cations. The carboxylate neighboring the hydroxyl group forms a five-membered chelate with calcium, whereas the second carboxylate at the opposite end forms a four-membered chelate with a neighboring Ca^{2+}, while it bridges (through O4) an adjacent Ca^{2+}. There is one lattice water in the structure. The structure of Ca-MAL is best described as a layered motif. Each layer is composed of edge-sharing Ca^{2+} dimers (in essence, each layer is composed of two sublayers). These dimers are linked together via the carboxylate ends. The layers interact via hydrogen bonds involving the lattice water. Malate salts (organic or metal-containing) have been reported (20). The structures of two calcium malate compounds have been reported (20a, 20b), but our Ca-MAL is distinctly different from these.

In the Sr-BTCA structure, Sr^{2+} is eight-coordinated (bicapped octahedron), surrounded by two waters and six carboxylate oxygen atoms (Figure 4). The $Sr-O_{water}$ bond distances are 2.5179(16) and 2.8414(16) Å. The $Sr-O_{carboxylate}$ bond distances range from 2.5641(15) to 2.5855(15) Å. The BTCA ligand is doubly deprotonated and chelating six Sr^{2+} cations. It should be noted that the two

"central" −COO groups are each singly deprotonated (carboxylate groups), while the "end" −COO groups are fully protonated (carboxylic acid groups). Notably, there are no chelate rings in the structure.

The carboxylate moieties are coordinated to Sr^{2+} in a monodentate fashion, whereas the carboxylic acid groups bridge two adjacent Sr^{2+} cations in a η^2,μ_2 mode. There are no lattice waters. The structure of Sr-BTCA can be described as three-dimensional. Structurally characterized M-BTCA compounds (M = Na, Mn, Co, Ni, Zn, Cu) are rather rare in the literature (21).

It is apparent that calcite dissolution rates depend on a plethora of variables (based on literature reports and our research). These include (a) the nature and number of groups on the additive, (b) the pH of dissolution, (c) the additive concentration, (d) the temperature, etc. On the basis of these reported results, it appears that the calcite dissolution efficiency is directly proportional to the number of anionic coordinating moieties: BTCA (four carboxylates) ≈ CIT (three carboxylates and one hydroxyl) > MAL (two carboxylates and one hydroxyl) > CEPA (one carboxylate and one phosphonate). It is also interesting to note that the number of calcium ions *per* coordinating ligand parallels the dissolution efficiency of the ligand. CEPA binds three calcium ions, MAL binds four, whereas CIT coordinates to five calcium ions and BTCA to six calcium (strontium) centers. It is therefore reasonable to state that a high number of coordinating moieties on the dissolver molecule enhances the surface complexation (a necessary first step in calcite dissolution) onto Ca^{2+} sites, with subsequent ligand-induced detachment of the Ca^{2+} ion from the calcite crystal surface. A systematic large-scale structure/function relationship study to relate the number of calcium-coordinating groups on the additive backbone and dissolution efficiency is currently lacking. Further studies along this direction are currently underway in our laboratories as a follow-up to our recent efforts (22).

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Supporting Information Available: Detailed crystallographic data (CIF), additional structural views, FTIR, and SEM. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for these structures (CCDC nos.: **Ca-MAL**, 297415; **Ca-CEPA**, 607002; **Sr-BTCA**, 607003) have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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(15) The dissolution protocol is based on the reaction of each ligand with $CaCO_3$ (calcite) in aqueous mixtures at specific pH values. In general, the procedure is as follows (details for each experiment are given in tabular form in the Supporting Information): A quantity of calcite (Mississippi Lime Co., Alton, IL; Brunauer−Emmett−Teller surface area 10.0 m^2/g) is suspended in deionized water. Then a quantity of the ligand is added as a solid, and the pH is adjusted with HCl or NaOH stock solutions to 5.4. The suspension is left under mild stirring for a specified time period (anywhere from 24 h to 10 days, depending on the experiment) and then filtered to isolate $CaCO_3$, which did not dissolve. The

latter is washed with deionized water, oven-dried, and weighed. On the basis of the initial and final $CaCO_3$ mass, the dissolution efficiency of each ligand is calculated. Control experiments (no ligands added) are also carried out.

(16) See the Supporting Information.

(17) Similar synthetic protocols were used for the syntheses of Ca-CEPA, Ca-MAL, and Sr-BTCA compounds. A quantity of the ligand (0.5 mmol) is dissolved in 50 mL of in-house deionized water. After the ligand dissolves, a quantity of metal hydroxide (0.5 mmol) is slowly added as a solid. The pH is adjusted to ~5.4 with a 0.1 M NaOH solution and left to stand. After a prolonged period of time (1 day for Ca-CEPA, 30 days for Ca-MAL, and 25 days for Sr-BTCA), single crystals appeared, were isolated by filtration, and were washed with deionized water. Elemental analysis and spectroscopic characterization information are given in the Supporting Information. Ca-CIT was synthesized according to Sheldrick, B. *Acta Crystallogr.* **1974**, *B30*, 2056−2057.

(18) X-ray data: X-ray diffraction data were collected on a SMART 1K CCD diffractometer at 293(2) K with Mo Kα (λ = 0.710 73 Å). Crystallographic details for Ca-CEPA: colorless plates (0.21 × 0.10 × 0.08 mm), monoclinic, space group $P2_1/c$, with a = 5.5362(6) Å, b = 18.135(4) Å, c = 7.915(2) Å, β = 95.013(17)°, V = 791.6(3) Å^3, and Z = 4, d_{calcd} = 1.914 g/cm^3, total reflections 4817, refined reflections [$I_{net} > 2\sigma(I_{net})$] 1551, no. of parameters 126, R1 = 0.0249 (0.0278, all data), wR2 = 0.0689 (0.0702, all data), GOF = 1.072. Crystallographic details for Ca-MAL: colorless plates (0.40 × 0.35 × 0.04 mm), triclinic, space group $P\bar{1}$, with a = 6.32(3) Å, b = 7.50(2) Å, c = 9.06(3) Å, α = 97.4(3)°, β = 97.2(3)°, γ = 93.24(18)°, V = 421(3) Å^3, and Z = 2, d_{calcd} = 1.784 g/cm^3, total reflections 2011, refined reflections [$I_{net} > 2\sigma(I_{net})$] 1112, no. of parameters 122, R1 = 0.0685 (0.0710, all data), wR2 = 0.1818 (0.868, all data), GOF = 1.094. Crystallographic details for Sr-BTCA: colorless plates (0.17 × 0.14 × 0.08 mm), orthorhombic, space group *Pbcn*, with a = 11.286(3) Å, b = 9.1194(17) Å, c = 11.107(3) Å, V =1143.2(5) Å^3, and Z = 4, d_{calcd} = 2.067 g/cm^3, total reflections 6654, refined reflections [$I_{net} > 2\sigma(I_{net})$] 1084, no. of parameters 99, R1 = 0.0254 (0.0314, all data), wR2 = 0.0660 (0.0684, all data), GOF = 1.073.

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