Single-Crystalline Thin Films by a Rare Molecular Calcium Carboxyphosphonate Trimer Offer Prophylaxis From Metallic Corrosion

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ABSTRACT In this communication, we report the synthesis and crystallographic characterization of a rare molecular linear trimer composed of Ca^{2+} and a carboxyphosphonate (hydroxyphosphonoacetate, HPAA), namely $Ca_3(HPAA)_2(H_2O)_{14}$. The two $HPAA^{3-}$ ligands function as bridges between the three Ca^{2+} ions. The central Ca^{2+} center is found in an octahedral environment, whereas the peripheral Ca^{2+} centers are in an 8-coordinated environment. This $Ca_3(HPAA)_2(H_2O)_{14}$ trimer was found to be an effective corrosion inhibitor for carbon steel surfaces at pH 7.3. Furthermore, we have proven by a variety of techniques that the identity of the anticorrosion film is the same as the rationally synthesized $Ca_3(HPAA)_2(H_2O)_{14}$.

KEYWORDS: calcium • phosphonates • corrosion inhibitors • thin films

As a naturally abundant element, calcium has been at the epicenter of inorganic biochemistry for several decades (1). From a structural point of view, Ca^{2+} is intriguing. Its coordination number, geometry, or the nuclearity of materials produced is difficult to predict reliably (2). Coordination of Ca^{2+} by anionic ligands (carboxylates, phosphonates, sulfonates, and their "mixed" analogs) almost invariably results in coordination polymers (1D, 2D, or 3D) (3). Therefore, low-nuclearity, Ca-based molecular systems are extremely rare. However, these are intensively sought synthetically as models for calcium binding proteins (bearing biologically relevant ligands) (4) or as molecular MOCVD precursors for solid-state materials and thin films (5). A search for homonuclear Ca complexes with nuclearity >2 in the CCDC has returned 11 trimers, 17 Ca tetramers, 1 pentamer, 4 hexamers, 2 octamers, 1 nonamer, and 1 dodecamer (6). Organometallic complexes excluded, only a handful of Ca oligomers have been synthesized and structurally characterized.

In recent years, our interests have been focusing on metal phosphonate materials and their relevance to crystal engineering (7) and other applications, such as corrosion control (8). Corrosion of metal surfaces and its control present challenging problems, both from an academic (9) and industrial standpoint (10). Researchers have been striving
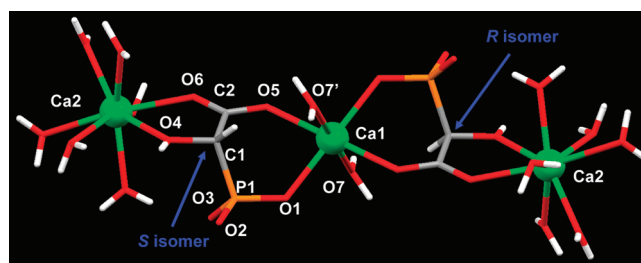

FIGURE 1. Molecular structure of the $Ca_3(HPAA)_2(H_2O)_{14}$ trimer.

to unveil the intricacies of corrosion mechanisms, with the aim of providing effective ways of control. Of the plethora of corrosion inhibitors, attention has been paid lately to phosphonate-based inhibitors (11) and, as recently reported, metal phosphonate hybrids that exhibit cation-phosphonate anticorrosion synergy (12). At the molecular level, it is exceedingly difficult to unequivocally establish the true molecular identity of the anticorrosion film, so commonly surface techniques are employed (EDS, XPS, and the like) (13). Herein, we report on the molecular identity of an anticorrosion film composed of a rare calcium carboxyphosphonate trimer, its rational synthesis, and its crystal structure.

When water-soluble Ca^{2+} salts are reacted with a racemic mixture of R- and S-hydroxyphosphonoacetic acid (HPAA) at circumneutral pH, a highly crystalline product is quantitatively obtained (6). Its molecular structure from single-crystal X-ray diffraction data revealed a linear trimer, whose Ca atoms are bridged by two tris-deprotonated HPAA ligands (Figure 1) (14).

There are some noteworthy structural features. The central Ca is 6-coordinated, whereas the two end Ca are 8-coordinated. The central Ca is surrounded by two chelating

Table 1. Corrosion Rates and % Inhibition[b] in the Absence (Control) or Presence of HPAA or Combinations of Ca²⁺ and HPAA[a]

		corrosion rates (CR, $\times 10^{-3}$ mm/year)			
inhibitor	inhibitor concentration (mM)	pH 2.0		pH 7.3	
control		283	0% inhibition	69	0% inhibition
HPAA	0.176			41	40.6% inhibition
HPAA	1.76	155	48.1% inhibition	73	metal dissolution
HPAA	17.56	492	metal dissolution	192	metal dissolution
HPAA	175.6			466	metal dissolution
Ca²⁺+HPAA	0.176			22	68.1% inhibition
Ca²⁺+HPAA	1.76			4	94.2% inhibition
Ca²⁺+HPAA	17.56	353	metal dissolution	13	81.2% inhibition
Ca²⁺+HPAA	175.6	c	c	c	c

[a] Corrosion rate is calculated from the equation $CR = [534.57(\text{mass loss})]/[(\text{area})(\text{time})(\text{metal density})]$. Units: CR in mm/year, mass loss in mg, area in cm², time in hours, metal density = 7.85 g/cm³. [b] "% Inhibition" is defined as $[(CR_{control} - CR_{inhibitor})/CR_{control}]100$. [c] CR's were not determined because of severe bulk precipitation of $Ca_3(HPAA)_2(H_2O)_{14}$.
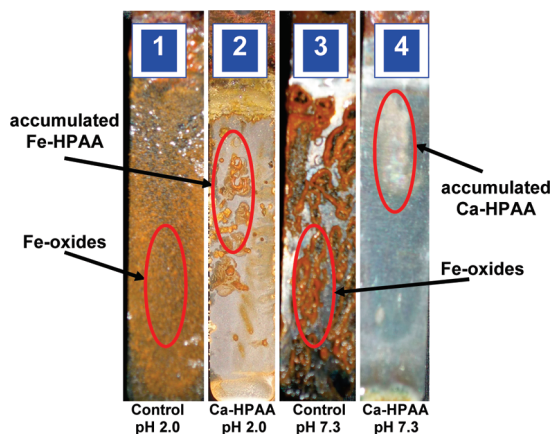

FIGURE 2. Anticorrosive effect of Ca-HPAA films on carbon steel. The effect of Ca-HPAA synergistic combinations is dramatically demonstrated in specimen 4.

HPAA³⁻ ligands. Each HPAA³⁻ ligand binds to the central Ca through a phosphonate and a carboxyl O. The slightly distorted octahedron is completed with two water molecules trans to each other. The end Ca's sit in a coordination environment that resembles that of a bicapped trigonal prism. They are coordinated by a carboxyl O and the −OH group and six water molecules. Both R and S isomers of HPAA are incorporated into the trinuclear complex. The phosphonate moiety is completely deprotonated ($-PO_3^{2-}$); however, it is found to act as a monodentate ligand for the central Ca.

This is particularly surprising, as possible substitution of at least one of the labile water molecules (at the end Ca's) would have occurred, resulting in a hypothetical 2D structure. Stabilization by strong hydrogen bonds could explain why the $-PO_3^{2-}$ moiety is found deprotonated, yet noncoordinating. Indeed, both noncoordinating phosphonate O's participate in a total of 7 H-bonds. Specifically, O(2) interacts with three Ca_end-bound waters from neighboring trimers (contacts 2.710−2.900 Å) and the −OH group of HPAA. O(3) is H-bonded to three Ca-bound water molecules (two inter- and one intramolecular interactions; contacts 2.740−2.774 Å). Several metal-HPAA materials have been reported in the literature but they all are invariably coordination polymers (15).

Assessment of corrosion inhibitory activity was based on mass loss measurements from carbon steel specimens, following a well-established protocol (16). The effectiveness
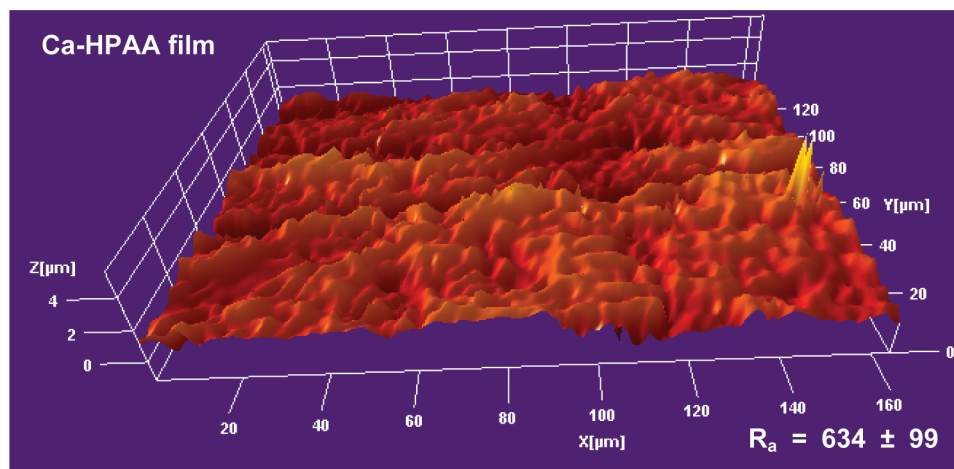

FIGURE 3. Anticorrosion film morphology viewed by VSI. Grid size is 9×10^4 μm^2. The height of z-axis is 4 μm. R_a is the average surface roughness, or average deviation, of all points from a plane fit to the test part of the surface.

of corrosion protection by synergistic combinations of Ca^{2+} and HPAA, in a 1:1 ratio is dramatically pH-dependent (Table 1 and Figure 2).

At pH 2.0, mass loss from the steel specimens is profound resulting in high corrosion rates. However, specimen **2** (Figure 2) appears relatively clean from corrosion products, presumably because HPAA (either free or metal-bound) at the surface acts as a Fe-oxide dissolving agent. We have observed a similar behavior in corrosion experiments with M^{2+} (Sr or Ba) and HPAA (8) in the Ca-phosphonobutane-1,2,4-tricarboxylic acid system (17). At pH 7.3, corrosion rates are appreciably suppressed (Table 1) in the presence of combinations of Ca^{2+} and HPAA (specimen **4**), reaching nearly quantitative inhibition.

The corrosion specimens (at pH 7.3) and film material were subjected to studies by vertical scanning interferometry (VSI, Figure 3), SEM, FT-IR, and EDS (see the Supporting Information) in order to fully characterize the protective coating. Data show that at pH 2.2 (ineffective protection) the only material identified on the steel specimens was iron oxide, whereas Ca^{2+} was completely absent or found in traces. Therefore, our interest focused on identifying the molecular identity of the inhibiting film at pH 7.3.

The inhibiting film (see Figures 2 and 3 and SEM images in the Supporting Information) is fairly uniform and contains Ca^{2+} and P (from externally added Ca^{2+} and HPAA), in an approximate 3:2 molar ratio (by EDS), suggesting a ratio of three Ca^{2+} and two $HPAA^{3-}$ ligands. FT-IR of the filming material showed multiple bands (in the $950-1200$ cm^{-1} region) associated with the phosphonate groups and two bands at 1590 and 1650 cm^{-1} (assigned to the $\nu_{C=O}$ stretches), that closely match those of $Ca_3(HPAA)_2(H_2O)_{14}$ (see the Supporting Information). An XRD powder pattern of the Ca-HPAA anticorrosion film deposited on a carbon steel substrate is identical to that of a crystalline sample of $Ca_3(HPAA)_2(H_2O)_{14}$ (see the Supporting Information). This is unequivocal proof that the protective film on the steel surface is $Ca_3(HPAA)_2(H_2O)_{14}$.

Herein we reported the synthesis and structural characterization of a rare Ca trinuclear compound, $Ca_3(HPAA)_2(H_2O)_{14}$. When generated in situ, it acts as an excellent corrosion inhibitor at circumneutral pH by creating an anticorrosive protective film on a steel surface. The molecular identity of the film is that of $Ca_3(HPAA)_2(H_2O)_{14}$. In closing, it should be noted that the Ca-HPAA film forms irreversibly on the steel surface and its anticorrosion prophylaxis persists for extended periods (months).

Supporting Information Available: Synthesis and characterization details (PDF); and crystallographic information for $Ca_3(HPAA)_2(H_2O)_{14}$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Data were collected on a Nonius Kappa CCD area detector diffractometer at 150(2) K with Mo Kα ($\lambda = 0.71073$ Å). $Ca_3(HPAA)_2(H_2O)_{14}$: Colorless prisms ($0.25 \times 0.35 \times 0.20$ mm^3), triclinic, space group $P\bar{1}$, with $a = 6.29940(10)$ Å, $b = 9.2525(2)$ Å, $c = 11.2079(2)$ Å, $\alpha = 66.7085(11)°$, $\beta = 86.1892(11)°$, $\gamma = 87.2087(10)°$, $V = 598.512(19)$ Å^3, and $Z = 1$, d_{calcd} (g/cm^3) $= 1.882$, total reflections 2730, refined reflections ($I_{net} > 2\sigma I_{net}$)) 2528, number of parameters 220, $R_1 = 0.0212$ (0.0234, all data), $wR_2 = 0.0572$ (0.0584, all data), GOF = 1.053. CCDC code: 766599.

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