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Two new supramolecular metal diphosphonates: Synthesis, characterization, crystal structure and inhibiting effects on metallic corrosion

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Abstract

Two new divalent metal(II) aminodiphosphonates with layered structure, namely, $Cu(H_3L^1)_2.2H_2O$ (1), $[H4L^1 = methyl-N(CH_2PO_3H_2)_2]$ and $Cd_2(H_2L^2)_4(2)$, $[H_4L^2 = n-propyl-N(H_3L^2)_4(2), [H_4L^2 = n-propyl-N(H_4L^2)_4(2), [H_4L^2)_4(2), [H_4L^2$ N(CH₂PO₃H₂)₂] were synthesized and characterized. The Cu(II) ions in complex 1 are octahedrally coordinated by four oxygen atoms from two chelating ligands and two phosphonate oxygen atoms from two neighboring $Cu(H_3L^1)_2$ units. The $Cu(H_3L^1)_2$ units are interconnected by bridging phosphonate groups, forming a 2-D metal phosphonate layer. The structure of complex 2 contains two unique Cd(II) ions octahedrally-coordinated by six phosphonate oxygen atoms from four H_2L^2 diphosphonate anions. Corrosion inhibition performances of 1 and 2 were also compared with each other in order to study the effect of combinations of externally added Cd/H₄L² and Cu/H₄L¹ (1:1 ratio) on corrosion rates of carbon steel. It was found that at pH 3.0, Cd/H_4L^2 or Cu/H_4L^1 combinations do not have noticeable corrosion inhibition efficiency for carbon steel. In contrast, at pH 7.0, higher corrosion inhibition efficiency was achieved for Cd/H_4L^2 . Physical characterizations such as scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR) were applied to study the corrosion specimens and film material. Accel

Keywords: Metal phosphonates; Crystal structures; Corrosion; Inhibition ; Layered materials

1. Introduction

The chemistry of metal phosphonates is of a great deal of importance because of their potential applications in catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1]. The structures of metal phosphonates are mainly affected by factors such as the extent of deprotonation for the diphosphonate ligand, the nature of metal ion, the nature of substitution in the ligand [2-11]. Studies of metal complexes with aminodiphosphonic acids, RN(CH₂PO₃H₂)₂, have shown that the R substituent on the amine group plays an important role on the metal phosphonates structure [12-14]. So far, few works have been conducted on metal phosphonates based on alkylsubstituted aminodiphosphonates. For the purpose of understanding the effect of substituent R group on metal phosphonates structure with alkyl-substituted aminodiphosphonic acids, two alkyl derivatives of RN(CH₂PO₃H₂)₂ were synthesized, namely, methyl-N(CH₂PO₃H₂)₂ (H_4L^1) and n-propyl-N(CH₂PO₃H₂)₂ (H₄L²). Methyliminobis(methylenephosphonic acid) (H_4L^1) has complexes Mn $(H_3L^1)_2$.H₂O, Cd $(H_3L^1)_2$.H₂O, Pb (H_2L^1) , Cu₃ $(H_2O)_2(HL^1)_2$.2H₂O, $Zn_3(HL^1)_2$ and $Zn(H_2L^1)(H_2O)$ as reported in literature [15-18]. Among mentioned complexes, the first four complexes exhibit layered structures while $Zn_3(HL^1)_2$ form a 3-D network and $Zn(H_2L^1)(H_2O)$ adapt a double chain structure. The complexes of $Zn(H_2L^2)$, $Mn_2[(HL^2)(H_2O)F]$. H_2O and Cd_2L^2 have been synthesized under hydrothermal conditions for H_4L^2 ligand [19,20]. The structural and coordination properties of copper(II) and cadmium(II) complexes with H_4L^1 and H_4L^2 ligands, under mild reaction conditions, have not been reported yet. The above mentioned reactions leads to preparation of two new metal aminodiphosphonates with slightly condensed structure, namely, $Cu(H_3L^1)_2.2H_2O$ (1), and $Cd_2(H_2L^2)_4(2).$

Generally, phosphonate additives have been widely applied as inhibitors against corrosion [21, 22]. Phosphonates, blended with certain metal cations and polymers, reduce the optimal

inhibitor concentration needed for inhibition regarding their synergistic effects of dissolved M^{2+} and polyphosphonates [23]. Synergism plays an important role in the inhibition process serving as the basis to develop new corrosion inhibitor formulations. Despite the significant body of literature, the molecular identity of the thin protective metal phosphonate films has not been fully understood.

Herein, we study the synthesis, crystal structure, and physical characterization of 1 and 2 and their application as inhibitors for the carbon steel corrosion.

2. Experimental

2.1. Materials and Physical techniques

All chemicals were of reagent grade quality and obtained from commercial sources without further purification. IR spectra of these compounds were recorded with a Shimadzu model IR-460 spectrometer using KBr pellets in the range 4000-400 cm⁻¹. The elemental analyses were performed with a Heraeus CHN-O-RAPID elemental analyzer. ¹H, ¹³C, and ³¹P NMR spectra of the ligand were recorded in D₂O with a Bruker (Avance DRS) 500 spectrometer. For the ³¹P solution NMR spectra in D₂O 85 % H₃PO₄ was applied as standard reference. TGA data were recorded with a Perkin-Elmer Pyris Diamond TG/DTA thermal analysis system in an oxygen atmosphere with a heating rate of 10 K.min⁻¹. Melting points were obtained with an Electrothermal instrument. The samples were characterized by a scanning electron microscope (SEM) Philips XL30 and S-4160. Single crystal of 1 was mounted on a Bruker Smart CCD-1000 using Mo-K_a radiation (λ = 0.71069 Å) and a graphite monochromator at 120(2) K. All data sets were corrected for Lorentz and polarization factors as well as for absorption using the SADABS program or a multiscan method [24]. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F² by SHELXTL version 5.10 [25]. All non-hydrogen atoms were refined by anisotropic thermal

parameters. The hydrogen atoms were located at the geometrically calculated positions and refined with isotropical thermal parameters. Single crystal of 2 was mounted on a Xcalibur, Atlas, Gemini ultra using Cu-K α radiation (λ = 1.54180 Å) at 120(2) K. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on F2 by SHELXL-97 [26]. Some of the data collection and refinement parameters are summarized in table 1. Selected bond lengths and angles are given in the table 2 of Supplementary Material.

2.2. Syntheses

2.2.1. Synthesis of H_4L^1 and H_4L^2

The aminodiphosphonic acids, H_4L^1 and H_4L^2 , were prepared by a Mannich type reaction according to procedures previously described [27]. For preparation of the H_4L^2 , n-propyl amine (Merck, 83 mmol) was mixed with hydrochloric acid (Merck, 30 cm³), deionized water (30 cm³), and phosphorous acid (Fluka, 249 mmol). The mixture was allowed to reflux at 120 °C for 1 h, then paraformaldehyde (Aldrich, 332mmol) was added in small portions over a period of 1 h, and the mixture was then refluxed for an additional 1 h. Removal of solvents afforded 18.15 g of a white powder of n-propyliminobis(methylenephosphonic acid) (yield 93 %). Its purity was confirmed by NMR measurements and elemental analysis. ³¹P NMR shows only one single peak at 8.14 ppm. ¹H NMR: 0.78 ppm (CH3,t, 3H), 1.61 ppm (CH2, m, 2H), 3.28 ppm (CH2, m, 2H), 3.40 ppm (-CH₂-, d, 4H, JH-P = 12.5 Hz). Anal. Calcd. for C5H15NO6P2:C, 24.30; H, 6.12; N, 5.67. Found: C, 24.25; H, 6.06; N, 5.61.

2.2.2. Syntheses of $Cd-H_4L^2$ and $Cu-H_4L^1$ at pH 3.0

2.2.2.1 Synthesis of $Cu(H_3L^1)_2.2H_2O(1)$

A quantity of hydrated copper chloride (4.39mmol) is dissolved in deionized water (25mL) and H4L¹ (4.39mmol) is added to it dropwise under vigorous stirring. Solution pH is adjusted to 3.0 with 1.0 M NaOH. The clear, slightly yellow solutions are stored at ambient temperature. Large octahedral blocks crystallize after 7 days. (yield: ca. 62% based on Cu). m.p. 250 °C. Anal. Calcd. for $C_6H_{24}CuN_2O_{14}P_4(\%)$: C, 13.45; H, 4.52; N, 5.23. Found: C, 13.40; H, 4.48; N, 5.29. IR (KBr, cm⁻¹): v = 3417 (m), 3023 (m), 1658 (m), 1473 (m), 1211 (s), 1115 (s), 1004 (s), 721 (m), 585 (m).

2.2.2.2 Synthesis of $Cd_2(H_2L^2)_4(2)$

A quantity of hydrated Cadmium chloride (4.39mmol) is dissolved in deionized water (25mL) and H4L² (4.39mmol) is added to it dropwise under vigorous stirring. Solution pH is adjusted to 3.0 with 1.0M NaOH. The clear, slightly yellow solutions are stored at ambient temperature. Large octahedral blocks crystallize after 4 days. (yield: ca. 71 % based on Cd). m.p. 293 °C. Anal. Calcd. for $C_{20}H_{52}Cd_2N_4O_{24}P_8(\%)$: C, 19.91; H, 4.31; N, 4.64. Found: C, 19.95; H, 4.26; N, 4.67. IR (KBr, cm⁻¹): v = 3421 (m), 3053 (m), 2358 (w), 1598(s), 1423 (m), 1131 (s), 993 (s), 784 (m), 581 (m).

2.2.3. Syntheses of $Cd-H_4L^2$ and $Cu-H_4L^1$ at pH 7.0

The same procedures as given above were followed except that the solution pH was adjusted to 7.0 with 1.0 M NaOH and immediate precipitation of solids is observed. Yield is 70% for Cu-H₄L¹ IR (KBr, cm⁻¹): v = 3435 (s), 3092 (w), 1676 (m), 1641(m), 1433 (w), 1291 (m), 1125 (s), 1071 (s), 1000 (s), 945 (s), 811 (m), 624 (m), 550 (m), 478 (s) for Cd-H₄L² (yield: 80 %) IR (KBr, cm⁻¹): v = 3450 (w), 3053 (m), 2400 (m), 1641(m), 1459 (m), 1115 (s), 1024 (s), 928 (s), 764 (m), 576 (s), 454 (m).

These products are amorphous based on powder XRD measurements (Fig. S1). These are not the same compounds as those synthesized at pH 3.0 and have the different molecular structures.

2.3 Corrosion Inhibition Protocol

Corrosion gravimetric experiments were accomplished in order to study the nature of the anticorrosion film on steel surface. For mass loss measurement, corrosion test were carried out using rectangular coupons measuring $1.5 \times 6 \times 0.2$ cm of carbon steel C1010. All experimental procedures such as preparation and cleaning were carried out based on ASTM G31 nom [28].

Each specimen immersed in blank (no inhibitor) or test solution (450 mL).All experiments performed at pH 3 and 7 for H_4L^1 and H_4L^2 at 3 different concentrations (0.5, 1 and 5mM). Synergism effect of Cd+ H_4L^2 and Cu+ H_4L^1 with 1:1 molar ratio at 1mM concentration was investigated tpH 3 and 7.

Corrosion process was monitored by visual inspection for five days. Then, the specimens are bring out from solution and protective film which is formed at pH=7 and in presences of (metal+H₄L) materials were collected and subjected to FT-IR. Moreover, surface analysis was investigated through SEM and EDS.

3. Results and discussion

3.1 Crystal Structures of Metal Phosphonates

Reaction of methyliminobis(methylenephosphonic acid) (H_4L^1) with copper(II) chloride yields a layered metal phosphonate, Cu $(H_3L)_2.2H_2O$, 1, which has a M/L ratio of 1:2. The asymmetric unit of complex 1 contains one Cu(II) ion, two ligands, and two water molecules (Figure 1). Cu atom lies on center of symmetry and is octahedrally coordinated by four oxygen atoms from two chelating ligands and two phosphonate oxygen atoms from two

neighboring $Cu(H_3L)_2$ units. Cu1 exhibits "4+2" Jahn–Teller distorted geometry through coordination to six phosphonate oxygen atoms (2O(1), 2O(4), and 2O(6)) from four different ligands. The basal plane of the polyhedron is defined by the atoms 2O(1), and 2O(4). The Cu-O bond distances involving these oxygens are in the range of 1.951-1.952 Å. The axial Cu1– O6 distances are 2.566 Å. Three trans angles are exactly 180° and the cis angles are in the range of 87.18(9)–92.82(9)°. Each ligand acts as a tridentate ligand by chelating with one copper atom and bridging with another Cu(II) ion, thus forming an eight-membered chelate ring. This ring is composed of Cu1, O1, P1, C1, N1, C2, P2, O4 atoms (Figure 1). The nitrogen atom and both phosphonate groups of the ligand are 1H-protonated, thus each ligand carries a negative charge of one, and two ligands are needed to balance the two positive charges of a Cu(II) ion. The lattice water molecules (O1W) are not coordinated to the Cu(II) ions, but form strong hydrogen bonds with phosphonate oxygen atoms (O1W...O2 2.830 Å, O1W...O3 2.674 Å, and O1W...O5 2.528 Å) (Table 2). The $Cu(H_3L)_2$ units are interconnected by bridging phosphonate groups, forming a 2D metal phosphonate layer along the (200) plane (Figure 2(a)). The bridging phosphonate groups (P2, O4, O5, O6) form 16membered rings (4Cu1, 4P2, 4O4, 4O6) with copper atoms separation of 6.76 Å (Figure 2(b)). The unidentate-coordinating phosphonate groups (P1, O1, O2, O3) are attached above and below the plane. The methyl groups are oriented toward the cavity created by the 16membered rings as shown in figure 2(a). Hydrogen bonds are formed between phosphonate oxygen atoms within a layer (O2...O6 2.570 Å), as well as between nitrogen atoms and phosphonate oxygen atoms within the layer (N1-H1...O1 2.783 Å (166°), N1- H1...O4 3.067 Å (122°)) (Table 2).

These metal phosphonate layers are connected only by lattice water molecules via hydrogen bonds discussed above and form a 3-D supramolecular hydrogen-bonded network (Figure 3).

Upon reaction with copper(II) chloride under weak acidic conditions at room temperature, one more proton on another phosphonate group is deprotonated; thus a complex with 1:2 (M/L) is formed. The ligand adopts a tridentate chelate and a bridging coordinate mode to form a layer structure. The uncoordinated phosphonate oxygens are available for intra- and interlayer hydrogen bonding.

Compound 2 crystallizes in the Triclinic space group Pī. The asymmetric unit of 2 with z=1 contains two unique Cd(II) ions and four different partially deprotonated H₂L² anions (Fig. 4). As shown in fig. 4, each two Cd (II) ions are octahedrally-coordinated by six phosphonate oxygen atoms from four diphosphonate anions. The Cd–O distances range from 2.237(5) to 2.339(4) Å (Table 2) which are comparable to those reported for other Cd(II) aminodiphosphonates [19,20]. The trans angles are exactly 180° and the cis angles are in 83.20(2)–96.80(2)° range. The H₂L² anion chelates with a Cd (II) ion bidentately and also bridges with other Cd(II) ion, thus forming an eight-membered chelate ring (Cd–O–P–C–N–C–P–O). Three phosphonate oxygen atoms (O1, O2 and O4) are involved in metal coordination and atoms (O3, O5 and O6) remain non-coordinated.

The interconnection of the Cd(II) ions via bridging diphosphonate ligands leads to a 2D metal phosphonate layer along the (001) plane (Figure 5). Within the 2D metal phosphonate layer, there are 16-member atomic rings composed of four Cd(2Cd1, 2Cd2) and four phosphonate anions. The propyl groups of the ligands are orientated toward the cavity created by the 16-membered rings as shown in figure 5. Within these layers, hydrogen bonds are formed between phosphonate oxygen atoms (O9...O1 2.642Å, O6...O8 2.721Å, O12...O3 2.492Å), as well as between nitrogen and phosphonate oxygen atoms within the layer (N1-H1...O10 2.832Å, N2- H2...O4 2.721Å) (Table 2).

Between two adjacent layers, hydrogen bonds are formed via non-coordinated phosphonate oxygen atoms (O5...O11 2.512Å), and form a 3-D supramolecular hydrogen-bonded network (Figure 6). The propyl groups of the phosphonate ligands occupy the interlayer space.

3.2 IR spectra and Thermogravimetric analyses

IR spectra for the two compounds 1 and 2 were recorded between 4000 and 400 cm⁻¹ (Fig. S2). The IR spectrum of 1 shows an intense and broad band in the O-H stretching vibration region at 3500-3200 cm⁻¹, which is consistent with the presence of the lattice water and the hydrogen bonds. The bonds at 2956 cm⁻¹ for 1 and 2978 cm⁻¹ for 2 are due to the CH₂ stretching vibrations. The band at 2760 cm⁻¹ for 2 is likely due to v(P-OH), which is characteristic of hydrogen phosphonate [29]. The bending vibration of the tetrahedral O₃PC groups for 1 is found at 573 cm⁻¹. The compounds also show typical C-H stretching vibrations and bending vibrations of low intensities of CH₂ attached to the nitrogen atoms, near 2700 and 1440 cm⁻¹, respectively. This complexes show a series of strong bands in the 1200-900 cm⁻¹ region, which are attributed to the stretching vibrations of the tetrahedral C–PO₃ groups [30]. Additional medium and sharp bands at low energy (between 800 and 400 cm⁻¹) are found, probably due to bending vibrations of the tetrahedral O₃PC groups and M–O (M=Cu and Cd) stretching vibrations.

A TGA diagram of complex 1 (Fig. S3) shows three major weight losses. The first step is the loss of two lattice water molecules, started at 120 °C. The observed weight loss at 190 °C (7.27%) is in agreement with the calculated value of 6.72%. The second weight loss of 5.54% from 233 to 290 °C corresponds to the pyrolysis of the methyl group of the ligand (calculated: 6.60 %). The combustion of the remaining organic parts of the ligand starts at 300 °C. The final product is mainly Cu(PO₃)₂, a metal metaphosphate, and the calculated weight loss of 28.96% is in agreement with the observed one (29.59%). The TGA of 2 shows

that it is stable up to 300°C. Above this temperature, it gradually loses weight until 800°C. The total weight loss (65.8%) corresponds to burning of the organic ligands in good agreement with the calculated value (66.7%). The final product is assumed to be mixture of $Cd(PO_3)_2$ and CdO.

3.3 Corrosion Studies

Phosphonates are mostly known for their antiscaling and antifouling properties [31]. However, some literatures are introduced synergistic effect of phosphonates with metal ions as carbon steel corrosion inhibitor. at first, corrosion experiments were conducted to investigate corrosion inhibition effect of H_4L^2 and H_4L^1 on carbon steel specimens at pH 3 and 7. This experiment was carried out in order to determine the optimum concentration of both inhibitors at two pH conditions (Table 3).

Figure 7 demonstrates the concentration effect of H_4L^2 on corrosion inhibition of carbon steel at pH 7. Based on mass loss measurements, corrosion rate for Blank specimen (no inhibitor) was 0.564 mm/y, whereas for specimen containing 1mM H_4L^2 was 0.300 mm/y which means 46.8% corrosion inhibition efficiency for H_4L^2 at this concentration. Decreasing concentration of H_4L^2 to 0.5 mM decreases the performance (0.461mm/y, 18.3% inhibition efficiency). It should be noted that an increase in H_4L^2 to 5mM adversely affect inhibition efficiency and causes metal dissolution (0.620 mm/y). Table 3 shows corrosion rates for H_4L^2 and H_4L^1 at pH 3 and 7, it is obvious that pH has a profound role in carbon steel corrosion. A decrease of 4 pH units causes about three-fold increase in the corrosion rate (from 0.564 to 1.832 mm/y for Blank specimen). Based on these results, 1 Mm H₄L was chosen as the optimum concentration and synergistic effect of $Cd^{2+}-H_4L^2$ and $Cu^{2+}-H_4L^1$ in 1:1 molar ratio was investigated through mass loss measurement (Table 3 and Figure 8).

Initially, corrosion experiments were performed at pH 3.0 (under identical conditions used to prepare crystalline M-H₄L at pH 3). Based on mass loss measurement, the corrosion rate for the Blank sample (no inhibitor) was 1.832 mm/y, whereas it was the 1.982 and 2.187 mm/y for Cd-H₄L² and Cu-H₄L¹, respectively (Table 3). Corrosion rates in the presence of inhibitors are greater than those for blank sample (Figure 8, left). It can be explained by several statements. First, metal phosphonates (Cd-H₄L² and Cu-H₄L¹) are too soluble to deposit onto the metal surface; therefore they do not form a protective film layer on carbon steel surface. Second, H₄L² and H₄L¹ react preferentially with Fe-oxide layer which exists on carbon steel surface as it immerses in the solution, before they interact with soluble Cd²⁺ or Cu²⁺. Another presumption is that Cd-H₄L² and Cu-H₄L¹ compounds that may form in solution never reach the steel surface as they undergo bulk precipitation. Since no precipitate forms in the bulk in our corrosion experiment at pH 3.0, this assumption is not acceptable. Due to the lack of performance of Cd-H₄L² and Cu-H₄L¹ as corrosion inhibitors at pH 3.0, no further experiments were performed at this pH.

Synergistic combination of metal ions and H_4L materials at pH 7.0 were investigated through mass loss measurements (Figure 8, right). To further characterization of the corrosion, the specimens and film materials were studied by SEM, EDS and FT-IR techniques. Although diffraction between the Blank and metal- H_4L specimens was evident within the first hours, the corrosion experiment was left to proceed over a 5 days period.

A combination of Cd^{2+} and H_4L^2 in a 1:1 molar ratio offers excellent corrosion protection for carbon steel. Based on mass loss measurement, the corrosion rate for the blank specimen was 0.564 mm/y, whereas for the $Cd^{2+}-H_4L^2$, it was 0.005 mm/y which means 99.1% inhibition efficiency (Figure 8, specimen 4, 5). It can be observed from SEM micrograph that carbon steel surface was strongly damaged in the absence of the inhibitor (Figure 9-A). However, figure 9-B shows carbon steel surface and protective film are adsorbed on specimen surface

which is responsible for inhibition of corrosion with $Cd^{2+}-H_4L^2$. The corresponding EDS spectra shows that the inhibiting film is a material containing Cd (Cd from externally added salt) and P (from added H_4L^2) in an approximately 1:1 ratio. Fe was also present originating from the carbon steel surface. Further study of the protective film was carried out using FT-IR spectroscopy. Fig. S4 shows FT-IR spectra of the protective film (from a corrosion specimen with $Cd^{2+}-H_4L^2$ at pH 7) and $Cd^{2+}-H_4L^2$ that synthesized at pH 7, a similar FT-IR spectrum was obtained. There is an excellent agreement between two spectra.

Figure 8, specimen 6 shows synergism effect of $Cu-H_4L^1$ at pH 7. Based on mass loss measurement, the corrosion rate for this specimen was 0.631 mm/y, whereas for blank specimen was 0.564 mm/y. Therefore, $Cu-H_4L^1$ essentially enhances the dissolution of bare metal. None of assumptions that mentioned at pH 3 are acceptable here; Since, SEM image and corresponding EDS spectra prove that protective film was covered carbon steel surface at pH 7 (Figure 9-C). Another assumption would be that metal phosphonate film (Cu-H_4L¹) was nonuniform and porous in microscopic nature. This would lead to localize attack and metal pitting. Metal pits are obvious in SEM image (Figure 9-C) which are shown by black arrows in (Figure 8). Fig. S5 shows FT-IR spectra of the protective film (from a corrosion specimen with Cu-H_4L¹ at pH 7) and Cu-H_4L¹ that was synthesized at pH 7. The FT-IR spectra in Fig. S5 indicates that the molecular structure of the filming material is not the same as the synthesized compound at pH 7.

Comparison of the FT-IR spectra in Figures (S4, S5) and those (for 1 and 2) in Figure S2 indicates that the molecular structure of the filming material is not the same as the structurally characterized materials 1 and 2. Several attempts have devoted in order to synthesize Cd- H_4L^2 and Cu- H_4L^1 crystalline materials at pH 7, instead, powder products could be obtained. As shown by XRD analyze, these compounds are amorphous (Figure S1).

4. Conclusions

Two new Cu(II) and Cd(II) compounds were synthesized under mild reaction conditions at room temperature with two different layered structures. The results indicated that the mild reaction conditions result in a lower condensed structure. The Cu(II) ions in complex 1 are octahedrally coordinated by four oxygen atoms from two chelating ligands and two phosphonate oxygen atoms from two neighboring Cu(H₃L¹)₂ units, forming a 2-D metal phosphonate layer. The structure of complex 2 contains two unique Cd(II) ions which are octahedrally-coordinated by six phosphonate oxygen atoms from four H₂L² diphosphonate anions. The corrosion inhibition performances of the two synthesized complexes were compared with each other. It was found that at pH 3.0, the combinations of Cd/H₄L² or Cu/H₄L¹ (1:1 ratio) are ineffective corrosion inhibitors for carbon steel while a significant corrosion inhibition efficiency was achieved at pH 7.0 for Cd/H₄L².

Supporting information available

TGA diagrams of compounds 1 and 2, XRD powder patterns and FT-IR spectra (in KBr pellets) of corrosion films and compounds 1 and 2.

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Appendix A. Supplementary material

Crystallographic data for the structure of 1 and 2 reported in this paper have been deposited with the Cambridge Crystallographic Data center, CCDC Number 763103 for 1 and 1061932 for 2. Copies of this information may be obtained free of charge from The Director, CCDC,12 Union Road, Cambridge, CB21EZ, UK (Fax:+44-1223-336-033;e-mail: deposit@ccdc.cam.ac.uk).

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Table legends

Table 1. Crystal data and structure refinement for complex 1 and 2.

Table 2. Selected bond lengths (Å), angles (°) and hydrogen bonds for compound 1 and 2.

Table 3. Corrosion rates and inhibition efficiency of carbon steel in presence and absence of H_4L or $M^{2+}-H_4L$ combination obtained from weight loss measurements.

Figure captions

Fig. 1 ORTEP representation of the asymmetric unit of 1. Thermal ellipsoids are drawn at 50% probability.

Fig. 2 (a) Ball and stick representation of a copper(II) phosphonate layer along the [200] plane. (b) One 16-membered ring of $(-Cu-O-P-O_{4})_{4}$ of 1. The dotted lines indicate hydrogen bonds.

Fig. 3 View of 3-D crystal structure of complex 1 along the b axis. The dotted lines indicate hydrogen bonds.

Fig. 4 ORTEP representation of the asymmetric unit of 2. Thermal ellipsoids are drawn at 50% probability.

Fig. 5 The 2D metal phosphonate layer along the (001) plane of complex 2.

Fig. 6 View of 3-D crystal structure of complex 2 along the a axis. The dotted lines indicate hydrogen bonds.

Fig. 7 H_4L^2 concentration effect on corrosion inhibition of carbon steel at pH=7. The specimen corresponding to 5mM H_4L^2 has higher corrosion rate than the specimen which immersed in Blank solution (no inhibitor). This indicates metal dissolution at this concentration.

Fig. 8 Effect of metal-H₄L films on carbon steel corrosion behavior at pH 3 and 7. Specimen 5 show synergistic inhibition effect of Cd and H_4L^2 compared to Blank (no inhibitor)

specimens 4. Specimen 3 and 6 have higher corrosion rate than Blank specimens which indicate metal dissolution.

Fig. 9 SEM micrograph and corresponding EDS spectra of carbon steel surface after immersion in a solution with pH 7 for 5 days. A) Blank (no inhibitor), B) Cd-H₄L², C) Cu-H₄L¹.

Supporting information

Fig. S1 XRD powder patterns of a) $Cu(H_4L^1)$ As-synthesized at pH 7 and b) $Cd(H_4L^2)$ Assynthesized at pH 7.

Fig. S2 FT-IR (in KBr pellets) of compounds a) 1 and b) 2.

Fig. S3 TGA diagrams of compounds 1 and 2.

Fig. S4 a) FT-IR (in KBr pellets) of $Cd(H_4L^2)$ corrosion film at pH 7 b) FT-IR of $Cd(H_4L^2)$ As-synthesized at pH 7.

Fig. S5 a) FT-IR (in KBr pellets) of Cu(H₄L¹) corrosion film at pH 7 b) FT-IR of Cu(H₄L¹) As-synthesized at pH 7 .

Compound	1	2
Molecular formula	$C_6H_{24}N_2O_{14}P_4Cu$	$C_{20}H_{52}Cd_2N_4O_{24}P_8$
Formula weight	535.69	1205.24
Crystal color, habit	Light blue	Colorless
Dimensions, mm	$0.2 \times 0.20 \times 0.05$	0.242×0.13 ×0.034
Crystal system	Monoclinic	Triclinic
a, Å	10.150(1)	9.5742(4)
b, Å	8.745(6)	9.7009(4)
c, Å	10.313(8)	12.3625(6)
α, deg	90	69.400(4)
β, deg	102.661(3)	73.961(4)
γ, deg	90	89.811(4)
$V, Å^3$	893.2(8)	1027.31(8)
space group	P 21/c	Pī
Z, Calculated density (mg.m ⁻³)	2, 1.992	1, 1.942
F(000)	550	604.0
θ range, deg	3.09 - 29.00	3.98- 67.03
Absorption coefficient, mm ⁻¹	1.656	12.056
T, K	120(2)	120(2)
λ, Å	0.71073	1.54180
Reflections collected	9565	3644
Independent reflections	2371 [R(int) = 0.0451]	2999 [R(int) = 0.0624]
Final R indices	R1 = 0.0470, wR2 = 0.0900	R1 = 0.0467, wR2 = 0.1224
R indices (all data)	R1 = 0.0630, wR2 = 0.0955	R1 = 0.0589, wR2 = 0.1305
$GOF \text{ on } F^2$	1.009	1.065
peak, hole /eÅ ⁻³	1.404 , -0.586	2.085, -1.278

Table 1. Crystal data and structure refinement for complex 1 and 2.

Accepted many

	0			1	
complex 1					
Cu(1)-O(1)	1.952(2)	P(1)-O(2)	1.577(2)	O(4)-Cu(1)-O(4)#1	180.0
Cu(1)-O(1)#1	1.952(2)	P(1)-O(1)	1.527(2)	O(4)-Cu(1)-O(1)#1	87.18(9)
Cu(1)-O(4)	1.951(2)	P(1)-O(3)	1.474(2)	O(4)#1-Cu(1)-O(1)#1	92.82(9)
Cu(1)-O(4)#1	1.951(2)	P(2)-O(5)	1.503(2)	O(4)-Cu(1)-O(1)	92.82(9)
Cu(1)-O(6)	2.566(2)	P(2)-O(4)	1.563(2)	O(4)#1-Cu(1)-O(1)	87.18(9)
Cu(1)-O(6)#1	2.566(2)	P(2)-O(6)	1.514(2)	O(1)#1-Cu(1)-O(1)	180.0
Hydrogen Bond of 1					
O(2)-H(2O)O(6)#5	2.570(3)	172	N(1)-H(1N)O(1)#3	2.783(4)	166
O(5)-H(5O)O(1W)#1	2.528(3)	171	O(1W)-H(1W)O(3)#4	2.674(3)	165
N(1)-H(1N)O(4)#2	3.067(4)	122	O(1W)-H(2W)O(2)#6	2.830(3)	158
complex 2					
Cd(1)-O(1)	2.288(4)	P(1)-O(1)	1.521(4)	O(1)-Cd(1)-O(7)	88.9(1)
Cd(1)-O(7)	2.285(5)	P(1)-O(2)	1.492(5)	O(1)-Cd(1)-O(10)	83.2(2)
Cd(1)-O(10)	2.244(5)	P(1)-O(3)	1.547(5)	O(10)-Cd(1)-O(1)	96.8(2)
Cd(2)-O(2)	2.237(5)	P(2)-O(4)	1.511(4)	O(2)-Cd(2)-O(4)	91.7(2)
Cd(2)-O(4)	2.240(3)	P(2)-O(5)	1.483(5)	O(2)-Cd(2)-O(8)	96.2(2)
Cd(2)-O(8)	2.339(4)	P(2)-O(6)	1.568(5)	O(4)-Cd(2)-O(8)	88.5(2)
Hydrogen Bond of 2					
O(9)-H(9O)O(1)	2.642(5)	165(8)	O(3)-H(3O)O(12)	2.492(5)	164(9)
N(2)-H(2N)O(4)#3	2.721(9)	151(9)	O(11)-H(11O)O(5)#2	2.512(5)	167(7)
O(6)-H(6O)O(8)#1	2.721(5)	164(8)	N(1)-H(1N)O(10)	2.832(8)	171(7)

Table 2. Selected bond lengths (Å	Å), angles (°) and hydrogen bonds for compound 1	and 2.
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Symmetry transformations used to generate equivalent atoms For 1 : #1 -x+1,-y+1,-z+1; #2 -x+1,y-1/2,-z+3/2; #3 x,-y+1/2,z+1/2; #4 -x+2,-y+1,-z+1; #5 -x+1,y+1/2,-z+3/2 ; #6 x,y,z For 2 : #1 -x, -y + 2, -z; #2 -x + 1, -y + 2, -z - 1; #3 x, y + 1, z.

Table 3- Corrosion rates ^a and inhibition efficiency^b of carbon steel in presence and absence of H_4L or $M^{2+}-H_4L$ combination obtained from weight loss measurements

H4L or metal	concentration	Corrosion rat	te (mm/y)		
+ H4L material	(mM)	pH=3.0		pH=7.0	
Blank		1.832		0.564	
H4L ²	0.5	1.702	7.1% inhibition	0.461	18.3% inhibition
	1	1.522	16.9% inhibition	0.300	46.8% inhibition
	5	1.910	metal dissolution	0.620	Metaldissolution
Cd+ H4L ²	1 ^c	1.982	metal dissolution	0.005	99.1% inhibition
H4L ¹	0.5	1.676	8.5% inhibition	0.482	14.5% inhibition
	1	1.502	18% inhibition	0.353	37.4% inhibition
	5	2.037	metal dissolution	0.590	metal dissolution
Cu+ H4L ¹	1 ^c	2.187	metal dissolution	0.631	metal dissolution

^aThe corrosion rate is calculated from the equation CR= $[(8.76 \times 10^4)(\text{mass loss})]/[(area)(\text{time})(\text{metal density})]$. Units: CR in mm/y, mass loss in g, area in cm², time in h, metal density= 7.86 g/cm³.

^b Inhibition efficiency is defined as [(CR_{Blank}-CR_{inhibited})/CR_{Blank}]×100

^c Concentration refers to [M²⁺] and [H4L] that are added in 1:1 molar ratio



Figure 2.



Fig. 4











Fig. 9

Graphical abstract

Two new metal phosphonates have been synthesized and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. corrosion inhibition performances 1 and 2 are also compared.

