



# 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,  $\text{Cu}(\text{H}_3\text{L}^1) \cdot 2\text{H}_2\text{O}$  (**1**), [ $\text{H}_4\text{L}^1 = \text{methyl-N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ] and  $\text{Cd}_2(\text{H}_2\text{L}^2)_4$  (**2**), [ $\text{H}_4\text{L}^2 = \text{n-propyl-N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ] 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  $\text{Cu}(\text{H}_3\text{L}^1)_2$  units. The Cu ( $\text{H}_3\text{L}^1$ )<sub>2</sub> 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  $\text{H}_2\text{L}^2$  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  $\text{Cd}/\text{H}_4\text{L}^2$  and  $\text{Cu}/\text{H}_4\text{L}^1$  (1:1 ratio) on corrosion rates of carbon steel. It was found that at pH 3.0,  $\text{Cd}/\text{H}_4\text{L}^2$  or  $\text{Cu}/\text{H}_4\text{L}^1$  combinations do not have noticeable corrosion inhibition efficiency for carbon steel. In contrast, at pH 7.0, higher corrosion inhibition efficiency was achieved for  $\text{Cd}/\text{H}_4\text{L}^2$ . 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.

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## 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,  $\text{RN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , 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 alkyl-substituted 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  $\text{RN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  were synthesized, namely, methyl-N( $\text{CH}_2\text{PO}_3\text{H}_2$ )<sub>2</sub> ( $\text{H}_4\text{L}^1$ ) and n-propyl-N( $\text{CH}_2\text{PO}_3\text{H}_2$ )<sub>2</sub> ( $\text{H}_4\text{L}^2$ ).

Methyliminobis(methylenephosphonic acid) ( $\text{H}_4\text{L}^1$ ) has complexes  $\text{Mn}(\text{H}_3\text{L}^1)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cd}(\text{H}_3\text{L}^1)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Pb}(\text{H}_2\text{L}^1)$ ,  $\text{Cu}_3(\text{H}_2\text{O})_2(\text{HL}^1)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}_3(\text{HL}^1)_2$  and  $\text{Zn}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})$  as reported in literature [15–18]. Among mentioned complexes, the first four complexes exhibit layered structures while  $\text{Zn}_3(\text{HL}^1)_2$  form a 3-D network and  $\text{Zn}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})$  adapt a double chain structure. The complexes of Zn ( $\text{H}_2\text{L}^2$ ),  $\text{Mn}_2[(\text{HL}^2)(\text{H}_2\text{O})\text{F}] \cdot \text{H}_2\text{O}$  and  $\text{Cd}_2\text{L}^2$  have been synthesized under hydrothermal conditions for  $\text{H}_4\text{L}^2$  ligand [19,20]. The structural and coordination properties of copper(II) and cadmium(II) complexes with  $\text{H}_4\text{L}^1$  and  $\text{H}_4\text{L}^2$  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,  $\text{Cu}(\text{H}_3\text{L}^1)_2 \cdot 2\text{H}_2\text{O}$  (**1**), and  $\text{Cd}_2(\text{H}_2\text{L}^2)_4$  (**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  $\text{M}^{2+}$  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

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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  $\text{cm}^{-1}$ . The elemental analyses were performed with a Heraeus CHN-O-RAPID elemental analyzer.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of the ligand were recorded in  $\text{D}_2\text{O}$  with a Bruker (Avance DRS) 500 spectrometer. For the  $^{31}\text{P}$  solution NMR spectra in  $\text{D}_2\text{O}$  85%  $\text{H}_3\text{PO}_4$  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  $\text{K min}^{-1}$ . 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  $\text{Mo-K}\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ) 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  $F^2$  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 isotropic thermal parameters. Single crystal of **2** was mounted on a Xcalibur, Atlas, Gemini ultra using  $\text{Cu-K}\alpha$  radiation ( $\lambda=1.54180 \text{ \AA}$ ) at 120(2) K. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on  $F^2$  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 Table 2 of Supplementary material.

### 2.2. Syntheses

#### 2.2.1. Synthesis of $\text{H}_4\text{L}^1$ and $\text{H}_4\text{L}^2$

The aminodiphosphonic acids,  $\text{H}_4\text{L}^1$  and  $\text{H}_4\text{L}^2$ , were prepared by a Mannich type reaction according to procedures previously described [27]. For preparation of the  $\text{H}_4\text{L}^2$ , *n*-propyl amine (Merck, 83 mmol) was mixed with hydrochloric acid (Merck, 30  $\text{cm}^3$ ), deionized water (30  $\text{cm}^3$ ), and phosphorous acid (Fluka, 249 mmol). The mixture was allowed to reflux at 120 °C for 1 h, then paraformaldehyde (Aldrich, 332 mmol) 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.  $^{31}\text{P}$  NMR shows only one single peak at 8.14 ppm.  $^1\text{H}$  NMR: 0.78 ppm (CH<sub>3</sub>, t, 3 H), 1.61 ppm (CH<sub>2</sub>, m, 2 H), 3.28 ppm (CH<sub>2</sub>, m, 2 H), 3.40 ppm (–CH<sub>2</sub>–, d, 4 H,  $J_{\text{H-P}} = 12.5 \text{ Hz}$ ). Anal. Calcd. for  $\text{C}_5\text{H}_{15}\text{NO}_6\text{P}_2$ : C, 24.30; H, 6.12; N, 5.67. Found: C, 24.25; H, 6.06; N, 5.61.

#### 2.2.2. Syntheses of $\text{Cd-H}_4\text{L}^2$ and $\text{Cu-H}_4\text{L}^1$ at pH 3.0

**2.2.2.1. Synthesis of  $\text{Cu}(\text{H}_3\text{L}^1)_2 \cdot 2\text{H}_2\text{O}$  (1).** A quantity of hydrated copper chloride (4.39 mmol) is dissolved in deionized water (25 mL) and  $\text{H}_4\text{L}^1$  (4.39 mmol) is added to it dropwise under vigorous stirring. Solution pH is adjusted to 3.0 with 1.0 M NaOH.

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

Compound	1	2
Molecular formula	$\text{C}_6\text{H}_{24}\text{N}_2\text{O}_{14}\text{P}_4\text{Cu}$	$\text{C}_{20}\text{H}_{52}\text{Cd}_2\text{N}_4\text{O}_{24}\text{P}_8$
Formula weight	535.69	1205.24
Crystal color, habit	Light blue	Colorless
Dimensions, mm	$0.2 \times 0.20 \times 0.05$	$0.242 \times 0.13 \times 0.034$
Crystal system	Monoclinic	Triclinic
<i>a</i> , Å	10.150(1)	9.5742(4)
<i>b</i> , Å	8.745(6)	9.7009(4)
<i>c</i> , Å	10.313(8)	12.3625(6)
$\alpha$ , deg	90	69.400(4)
$\beta$ , deg	102.661(3)	73.961(4)
$\gamma$ , deg	90	89.811(4)
<i>V</i> , Å <sup>3</sup>	893.2(8)	1027.31(8)
space group	<i>P</i> 21/ <i>c</i>	<i>P</i> <i>r</i>
<i>Z</i> , Calculated density (mg m <sup>−3</sup> )	2, 1.992	1, 1.942
<i>F</i> (000)	550	604.0
$\theta$ range, deg	3.09 – 29.00	3.98–67.03
Absorption coefficient, mm <sup>−1</sup>	1.656	12.056
<i>T</i> , K	120(2)	120(2)
$\lambda$ , 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 on $F^2$	1.009	1.065
Peak, hole /eÅ <sup>−3</sup>	1.404, −0.586	2.085, −1.278

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  $\text{C}_6\text{H}_{24}\text{CuN}_2\text{O}_{14}\text{P}_4$ (%): C, 13.45; H, 4.52; N, 5.23. Found: C, 13.40; H, 4.48; N, 5.29. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu=3417$  (m), 3023 (m), 1658 (m), 1473 (m), 1211 (s), 1115 (s), 1004 (s), 721 (m), 585 (m).

**2.2.2.2. Synthesis of  $\text{Cd}_2(\text{H}_2\text{L}^2)_4(2)$ .** A quantity of hydrated Cadmium chloride (4.39 mmol) is dissolved in deionized water (25 mL) and  $\text{H}_4\text{L}^2$  (4.39 mmol) 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 4 days. (yield: ca. 71% based on Cd). m.p. 293 °C. Anal. Calcd. for  $\text{C}_{20}\text{H}_{52}\text{Cd}_2\text{N}_4\text{O}_{24}\text{P}_8$ (%): C, 19.91; H, 4.31; N, 4.64. Found: C, 19.95; H, 4.26; N, 4.67. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu=3421$  (m), 3053 (m), 2358 (w), 1598(s), 1423 (m), 1131 (s), 993 (s), 784 (m), 581 (m).

#### 2.2.3. Syntheses of $\text{Cd-H}_4\text{L}^2$ and $\text{Cu-H}_4\text{L}^1$ 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  $\text{Cu-H}_4\text{L}^1$  IR (KBr,  $\text{cm}^{-1}$ ):  $\nu=3435$  (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  $\text{Cd-H}_4\text{L}^2$  (yield: 80%) IR (KBr,  $\text{cm}^{-1}$ ):  $\nu=3450$  (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

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