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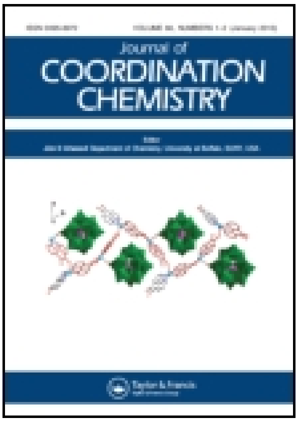

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Synthesis, characterization, and crystal structure of a 2-D metal diphosphonate: $Cu_3(H_2O)_2[HO_3PCH_2N(CH_3)CH_2PO_3]_2 \cdot 2H_2O$

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Synthesis, characterization, and crystal structure of a 2-D metal diphosphonate: $Cu_3(H_2O)_2[HO_3PCH_2N(CH_3)CH_2PO_3]_2 \cdot 2H_2O$

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Hydrothermal reaction of *N*-methyl-iminobis(methylenephosphonic acid), $CH_3N(CH_2PO_3H_2)_2$, (H_4L) with copper(II) acetate afforded a new layered Cu(II) amino diphosphonate, $Cu_3(H_2O)_2(HL)_2 \cdot 2H_2O$ (**1**). Compound **1** was studied by IR spectroscopy, TGA/DTA data, and X-ray diffraction (XRD) techniques. The XRD patterns are the same for the hydrated and the dehydrated complexes. A single-crystal X-ray crystallographic determination reveals copper in two different coordination environments. Cu1 has a distorted elongated tetragonal octahedral geometry, whereas Cu2 has a square-pyramidal distorted geometry. The HL trianion is a pentadentate ligand with a deprotonated nitrogen atom and two oxygen atoms of each phosphonate binding to copper. Hydrogen bonds between lattice water molecules in interlayer spaces and the non-coordinated phosphonate oxygen atoms as well as water ligands leads to a 3-D supramolecular network structure.

Keywords: Copper; Diphosphonate; Crystal structure; Hydrothermal synthesis

1. Introduction

Metal diphosphonates have structures ranging from 0-D cages, 1-D chains, 2-D layers to 3-D frameworks and potential applications as catalysts, molecular sieves, non-linear optical materials, and magnetic materials [1–5]. Efforts to prepare and structurally characterize crystalline metal complexes of iminomethylenediphosphonic acids, *R*$N(CH_2PO_3H_2)_2$, have resulted in several products representing versatile structure types, variable modes of phosphonate coordination, and different coordination networks that depend on reaction conditions and coordination preferences of the metal [6]. The majority of structural studies have focused on metal complexes of iminomethylenediphosphonic acids with $R = H$ [7–11] and CH_3 [12–14]. *N*-methyl-iminobis(methylenephosphonic acid) occurs in a zwitterionic form in the solid state (scheme 1a) [15] and studies on the coordination chemistry at room temperature and hydrothermal conditions have shown that the acid system can form metal phosphonates

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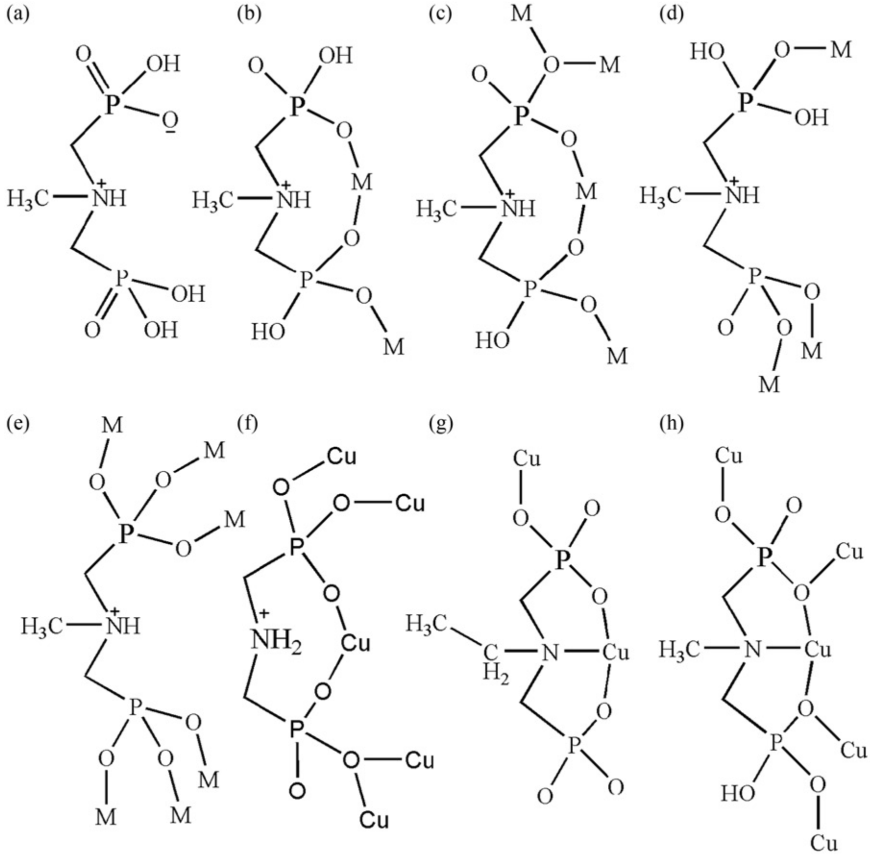

Scheme 1. H_4L and its coordination modes in complexes with divalent metal ions, as well as those of iminobis(methylenephosphonic acid) and *N*-ethyliminobis(methylenephosphonic acid) in copper(II) complexes.

with a variety of structures and different coordination modes such as layered complexes (M = Mn, Cd) (scheme 1b) [12, 13], bilayered complexes (M = Pb) (scheme 1c) [14], and a zinc(II) complex with a 1-D double chain structure (scheme 1d) [12]. A zinc(II) complex with a 3-D network structure has also been reported (scheme 1e) [13]. The amino group of the ligand in all the complexes was protonated and remained uncoordinated.

The structural and coordination properties of a complex formed upon the interaction of copper(II) ion and *N*-methyl-iminobis(methylenephosphonic acid) has not been reported. Copper complexes attract significant attention for potential uses as antimicrobial, antiviral, anti-inflammatory, antitumor agents, enzyme inhibitors, and/or chemical nucleases [16]. In the copper complex of $H_2O_3PCH_2NH_2^+CH_2PO_3H^-$ (scheme 1f), the amino group was protonated and remained uncoordinated [7]. However, in the copper complex of *N*-ethyl-iminobis(methylenephosphonic acid) under weak basic conditions (pH ~ 8) the nitrogen of the ligand was deprotonated and coordinated to copper (scheme 1g) [17]. Deprotonation of the amine depends on the affinity of the metal ions for nitrogen and the chelate rings [12]. For further investigation in this area [18, 19], we report here the synthesis, characterization, and crystal structure of a copper(II) derivative of *N*-methyl-iminobis(methylenephosphonic acid) (H_4L): $Cu_3(H_2O)_2(HL)_2 \cdot 2H_2O$ (**1**).

2. Experimental

2.1. *Materials and general methods*

All chemicals were of reagent grade quality and obtained from commercial sources without purification. Hydrothermal syntheses were carried out in 20 mL poly(tetrafluoroethylene) stainless steel container under autogeneous pressure. IR spectrum of **1** was recorded with a Shimadzu model IR-460 spectrometer using KBr pellets from 4000 to 400 cm^{-1}. Elemental analysis was performed with a Heraeus CHN-O-RAPID elemental analyzer. TG and DTA data were recorded with a Perkin-Elmer Pyris Diamond TG/DTA thermal analysis system under oxygen with a heating rate of 10 K min^{-1}. The molecular structure plot and simulated X-ray diffraction (XRD) powder pattern based on single-crystal data were prepared using Mercury software [20]. XRD powder measurements were performed using a Philips X'pert diffractometer with monochromated Cu-Kα radiation.

2.2. *Syntheses of $Cu_3(H_2O)_2(HL)_2 \cdot 2H_2O$ (1)*

N-methyliminobis(methylenephosphonic acid) (H_4L) was prepared by a Mannich type reaction according to the procedure described previously [21]. A mixture of H_4L (0.52 mmol, 0.104 g) and $Cu(OAc)_2 \cdot H_2O$ (0.52 mmol, 0.114 g) in deionized water (5.0 mL), adjusted to pH = 5, was sealed in a 20 mL Teflon-lined stainless steel autoclave and then heated at 140°C for 5 days. After the mixture was slowly cooled to room temperature, blue crystals were filtered off, washed with distilled water, and dried at room temperature (yield: *ca* 43% based on Cu). M.p. 239°C. Anal. Calcd for $C_6H_{24}Cu_3N_2O_{16}P_4$: C, 10.36; H, 3.45; N, 4.03. Found: C, 10.41; H, 3.49; N, 4.01. IR (KBr, cm^{-1}): $\nu = 3515$ (m), 3240 (m), 3130 (m), 2985 (m), 2375 (m), 1648 (w), 1450 (w), 1229 (m), 1244 (w), 1164 (s), 1057 (m), 1033 (s), 999 (s), 963 (s), 935 (s), 895 (w), 762 (w), 733 (m), 614 (m), 582 (m), 456 (m).

2.3. *Crystallography*

Data collection was performed with a Bruker Smart CCD-1000 diffractometer [22] at 120(2) K. Diffractometer was equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data sets were corrected for Lorentz and polarization factors as well as for absorption using SADABS or a multiscan method [23]. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXTL version 5.10 [24]. All non-hydrogen atoms were refined by anisotropic thermal parameters. All hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data and

Table 1. Crystal data collection and structure refinement parameters for **1**.

Formula	$C_6H_{24}Cu_3N_2O_{16}P_4$
Formula weight	694.77
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cells dimensions (Å, °)	
a	7.4434(11)
b	8.0534(12)
c	10.0367(15)
α	107.497(2)
β	103.631(3)
γ	106.713(2)
Volume (Å^3), Z	514.26(13), 1
Calculated density (Mg m^{-3})	2.243
Absorption coefficient (mm^{-1})	3.466
F(000)	349
Crystal size (mm^3)	$0.19 \times 0.16 \times 0.13$
θ range for data collection (°)	1.90–29.00
Index ranges	$13 \leq h \leq 13$; $-18 \leq k \leq 18$; $-23 \leq l \leq 23$
Reflections collected/unique (R_{int})	26,831/5931 (0.0287)
Completeness to θ (%)	99.8
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8446 and 0.7122
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5931/0/180
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	0.0411, $wR_2 = 0.0863$
R indices (all data)	$R_1 = 0.0522$, $wR_2 = 0.0923$
Largest difference peak and hole (e Å^{-3})	2.187 and −1.138

structural refinements for **1** are summarized in table 1. Selected bond lengths and angles are given in "Supplementary material".

3. Results and discussion

Reaction of *N*-methyliminobis(methylenephosphonic acid) (H_4L) with copper acetate, *via* a hydrothermal reaction under weak acidic conditions, affords 3 : 2 (M : L) complex, $Cu_3(H_2O)_2(HL)_2 \cdot 2H_2O$ (**1**). The IR spectrum exhibits intense absorptions at 400–500 cm^{-1}, assigned to Cu–N and a series of strong bands at 935–1242 cm^{-1}, which are attributed to the stretching vibrations of the phosphonate PO_3 groups [25]. The metal–ligand (Cu–O) stretching vibration is at 582 cm^{-1}. The water stretching vibration (ν_s(OH)) appears at 3515 cm^{-1} and one sharp band at 1647 cm^{-1} corresponds to the bending vibrations of lattice water.

The XRD powder pattern was collected to check the purity of the bulk sample of **1** as well as the stability of porous framework. The results are in agreement with the simulated XRD powder pattern based on single-crystal data. Figure S1 (Supplementary material) shows the X-ray diffraction patterns of **1** before (a) and after heating at 200°C for 4 h (b). Both powder patterns are similar (although the intensities are different),

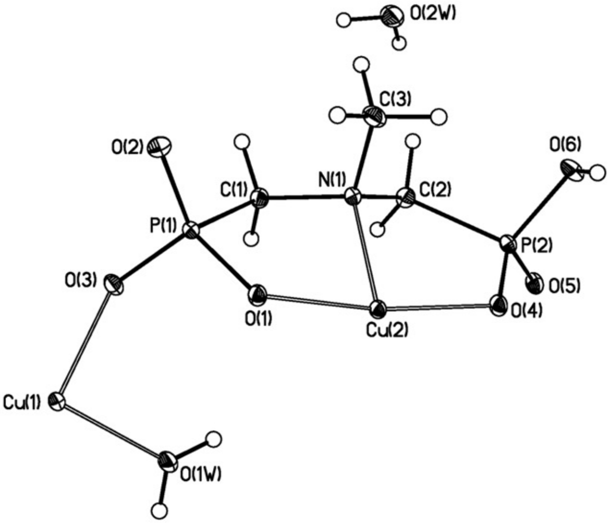

Figure 1. The asymmetric unit of **1** at 50% probability level with the atom-labeling scheme.

consistent with crystallinity being retained upon removal of lattice water. IR spectra of the hydrated and dehydrated complexes show striking similarities, as shown in figure S2. The OH stretching and bending modes are not present in the dehydrated compound.

The TGA diagram of **1** reveals stepwise mass losses (figure S3, Supplementary material). The first step is loss of three water molecules, which begins at 70°C and is completed at 130°C. The loss is accompanied by an endothermic DTA peak. The weight loss of 8.4% is in agreement with the calculated value (7.8%). The second weight loss (5.6%) is from 130°C to 240°C, as an endothermic peak corresponding to loss of one water ligand and a water molecule formed by condensation of hydrogen phosphonate. The weight loss at 240–460°C, with an exothermic DTA peak at 380°C, is assigned to decomposition and dissociation of the bisphosphonate groups and collapse of the lattice structure. Approximately 23% (by weight) of residue remains at 870°C.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$. Figure 1 shows the asymmetric cell of **1** with an atom-labeling scheme. The asymmetric unit contains three Cu(II) ions, two ligands, and two water molecules. The solids exhibit two different Cu coordination environments. Cu1 exhibits "4 + 2" Jahn–Teller distorted geometry through coordination to four phosphonate oxygen atoms (O(3), O(3)#1, O4#2, and O4#3; #1: $-x+1$, $-y-1$, $-z$, #2: $-x+1$, $-y$, $-z$, and #3 x, $y-1$, z) from four different ligands and two water molecules. Two O3 and water oxygen atoms are in the equatorial positions with Cu1–O3 and Cu1–O(1W) distances of 1.954(2) and 1.968(1) Å, respectively, that are normal for equatorial Cu–O bonds [7]. The axial Cu1–O4 distances are 2.623(1) Å. Three *trans* angles are exactly 180° and the *cis* angles are in the range 84.15(5)–95.85(5)°.

As shown in figure 1, Cu2 is five-coordinate by a tridentate chelating HL trianion (O(1), O(4), and N(1)), and two phosphonate oxygen atoms (O(1) and O(5)) from two other phosphonate ligands. The coordination geometry around copper(II) ion can be best described as a "Jahn–Teller" distorted square-pyramid with the elongated axial

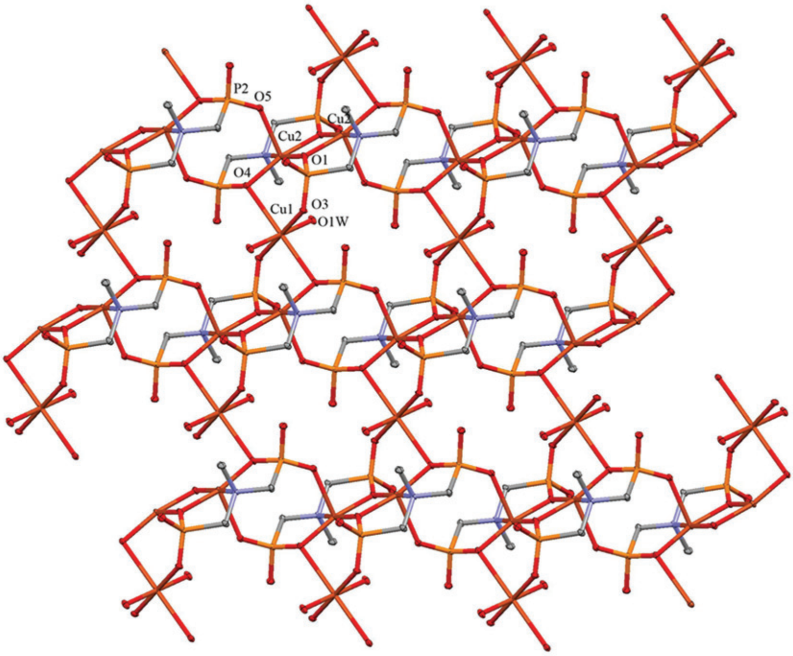

Figure 2. The layered structure of **1** viewed in the *ab*-plane. All hydrogen atoms and uncoordinated water molecules are omitted for clarity.

bond. The copper(II) is situated slightly out (0.135 Å) of the square plane formed by O(1), O(1)#2, O(4), N(1). The mean deviation of the equatorial plane is 0.0684 Å, with the largest deviation of 0.074 Å at O(1). The Cu–O (1.980(1), 1.947(1) and 1.944(1) Å, respectively) and Cu–N (2.000(2) Å) distances are significantly shorter than the axial Cu–O bond (2.272(1) Å). The *trans* bond angles around the Cu2 are 167.93(6) and 169.51(6)° while the *cis* angles range from 82.63(6) to 102.38(6)°. The coordination geometry is different from those reported in $Cu_3[NH_2(CH_2PO_3)_2]_2$ with a same M/L ratio (3 : 2), in which the copper(II) ions are octahedral or tetrahedral [7].

The ligand is pentadentate (O1, O3, O4, O5, N1), chelating tridentate with one copper(II) (Cu2) (O(1), O(4) and N(1)) and also bridging four other metal ions (2Cu2 + 2Cu1) (scheme 1h). O(1) and O(4) are bidentate metal linkers. The diphosphonate is −3 with one phosphonate oxygen still protonated as indicated by the longer bond length (P(2)–O(6) 1.570(2) Å) compared to the other five P–O bond lengths. The shorter P–O bond length, P(1)–O(2) 1.495(2), corresponds to the localized P=O. The P–O coordinated to copper has P–O bond lengths intermediate to P–OH and P=O. Coordination around phosphorus corresponds to a disordered tetrahedron. The amine group also exhibits tetrahedral geometry, as deduced from the C–N–C bond angles which average to 109.45°.

The coordination mode in **1** is significantly different from those observed in complexes of H_4L with other metal ions. We report the first example of coordination of ligand nitrogen to the metal (scheme 1). The deprotonation of the nitrogen even in acidic conditions and coordination to copper shows higher affinity of copper than other metals for nitrogen.

Table 2. Hydrogen-bond geometries for **1** (Å, °).

D–H–A	d(D–H)	d(H ··· A)	d(D ··· A)	∠DHA
O(1W)–H(2W) ··· O(2W) [x, $y-1$, $z-1$]	0.85	1.80	2.647(2)	174
O(1W)–H(1W) ··· O(5) [$-x$, $-y$, $-z$]	0.85	1.87	2.719(2)	173
O(2W)–H(4W) ··· O(2) [$x-1$, y, z]	0.85	2.12	2.853(2)	145
O(2W)–H(3W) ··· O(2) [$-x+1$, $-y$, $-z+1$]	0.85	1.89	2.744(2)	179
O(6)–H(1O) ··· O(3) [x, $y+1$, z]	0.85	1.73	3.581(2)	173

Each pair of Cu2 are bridged by two bidentate phosphonate oxygen atoms (O(1) and O(1A)) and two diphosphonate groups to form a four-membered ring Cu_2O_2 with Cu2–Cu2 separation of 2.95 Å and an eight-membered ring Cu2–(O4–P2–O5)2–Cu2 with Cu2–Cu2 separation of 4.99 Å, respectively, forming a 1-D chain along the *a*-axis. Two adjacent chains are connected through Cu1–O4 and Cu1–O3 bonds to form a 2-D metal phosphonate layer parallel to the *ab*-plane (figure 2). The interlayer distance is about 10.0 Å.

Lattice water molecules are located in the interlayer space (figure S4, Supplementary material), forming hydrogen bonds with non-coordinated phosphonate oxygen atoms as well as water ligands (table 2), resulting in a 3-D supramolecular network structure. In addition to the hydrogen bonds discussed above, the protonated phosphonate oxygen (O6) and coordinated water (O1W) are involved in strong hydrogen bonds with O3 and O5 phosphonate oxygen atoms, respectively (table 2).

Supplementary material

The crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-742031 ($C_6H_{24}P_4Cu_3N_2O_{16}$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: C441223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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