Dinuclear Five-Coordinate Copper(II) Complexes with Chelating Diphosphonic Acid Ligands: Hydrothermal Synthesis, Structure, and Thermal Properties

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Abstract. The synthesis of two new diphosphonic acid ligands, [ethane-1,2-diylbis(azanediyl)]bis[(4-chlorophenyl)methylene]diphosphonic acid (L₁P), [ethane-1,2-diylbis(azanediyl)]bis[(4-bromophenyl)methylene]diphosphonic acid (L₂P), and their corresponding copper complexes, $Cu_2(L_1P)_2$ (1) and $Cu_2(L_2P)_2$ (2) are described herein. Complex 2 was structurally characterized with X-ray single crystal diffraction. The structure of 2 consists of five-coordinate

Introduction

There has been a growing interest in the synthesis and characterization of metal phosphonates due to their potential applications as catalysts, single molecular magnets, sorbents, ion exchangers, protonic conductors, and scale inhibitors.^[1-5] In general, metal phosphonates are also reported to form discrete coordination complexes, one-dimensional (1D) chain structures, two-dimensional (2D) layered and three-dimensional (3D) structures.^[6-9] One remarkable feature of these compounds is that they are capable to form numerous hydrogen bonds, which often contribute to the understanding of the associated chemistry and mechanism of metal-assisted phosphate ester hydrolysis.^[9–11] Much effort has focused on the rational design and controlled synthesis of coordination complexes using phosphonate ligands and factors such as the performance of organic ligand, the metal ion, and the reaction conditions influence the molecular structure and modify properties of metal phosphonates, which are important in practical applications.

A variety of $(O_3P$ -tether-PO₃) ligands and numerous metal diphosphonate complexes of type $[M_n(O_3P$ -tether-PO₃)_m] were described in recent years.^[12–14] Although $[O_3PCH(R)NH(CH_2)_2$ -NHCH $(R)PO_3$] type ligands also seem to be good candidates for such studies, according to our search, only a few complexes were reported. *Fan* and co-workers have copper(II) ions with a distorted square pyramidal arrangement doubly bridged by OPO from phosphonate groups. The Cu–Cu distance is 4.7810(2) Å. The crystal packing is determined by interdinuclear hydrogen bonds, which lead to one-dimensional chains. The results of thermogravimetric investigations (TG-DTA), UV/Vis diffuse reflectance, infrared and (¹H and ¹³C) NMR spectroscopy, as well as elemental analyses of compounds **1** and **2** are also presented.

reported the structures of the complexes $[NH_3CH(CH_3)-CH_2NH_3]_2M_2[O_3PCH(Ph)NH(CH_2)_2NHCH(Ph)PO_3]_2\cdot H_2O$, $(M = Zn^{II} \text{ and } Cd^{II})$ and $Zn_2[O_3PCH(Ph)NH(CH_2)_2NHCH-(Ph)PO_3]_2(HNO_3)_2\cdot 4H_2O.^{[15,16]}$

In this work, we present the synthesis, spectral, and elemental analysis of two new diphosphonic acid ligands, [ethane-1,2divlbis(azanediyl)]bis[(4-chlorophenyl)methylene]diphosphonic acid (L₁P), [ethane-1,2-diylbis(azanediyl)]bis[(4-bromophenyl)methylene]diphosphonic acid (L2P) and their corresponding dinuclear copper(II) complexes, $Cu_2(L_1P)_2$ (1) and $Cu_2(L_2P)_2$ (2). These complexes were obtained by hydrothermal reactions between the phosphonate ligands (L_XP) with CuSO₄ in aqueous media by modifying reaction parameters such as the pH, temperature of the reaction mixture, and molar ratio of the starting materials ($L_X P/Cu^{2+}$). Complexes 1 and 2 were characterized by thermogravimetric (TG-DTA), CHN, Energy Dispersive X-ray (EDX) analyses, and UV/Vis diffuse reflectance, IR, and (¹H and ¹³C) NMR spectroscopy. The structure of 2 was determined by X-ray single crystal diffraction. The spectral properties of these compounds are also discussed.

Results and Discussion

The formation of diphosphonic acid ligands takes place in two steps (Scheme 1). The first step in this process involves the formation of a diimine ligand (L_x) by the reaction of ethylenediamine with benzaldehyde derivatives. In the second step, trimethyl phosphite reacts with diimine ligand to afford the diphosphonic acid ligand (L_xP) . The ligands were insoluble in water and common organic solvents such as MeOH, EtOH, MeCN, THF, DMSO, and DMF, but soluble in aqueous alkali solution.



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Scheme 1.

In this study, two new copper complexes 1 and 2 were obtained by hydrothermal reaction between the ligand (L_XP) and CuSO₄ in an aqueous solution. Factors, which have a profound impact in the product formation in hydrothermal syntheses are concentration, pH, temperature of the reaction mixture, and molar ratio of starting materials (L_XP/Cu^{2+}).^[17] Therefore, several individual hydrothermal reactions were performed under various conditions of CuSO₄ to L_XP molar ratio, temperature (T = 120 to 170 °C in steps of 20 °C, t = 3 d), and pH 5–8 for the synthesis of the complexes 1 and 2. A comparison between the EDX analyses, XRD pattern, IR spectra, and elemental analyses of products of the above individual experiments indicates that products are identical.

Cu₂(L₁P)₂ (1) is only formed at 150 °C. The compound is formed over a wide range of molar ratios of L₁P/Cu²⁺ = 1:1, 1:1.5, 1:2, 1:4 and 2:1, which approximately correlates with pH 6–8. Cu₂(L₂P)₂ (2) is mainly formed at temperatures from 150 to 170 °C in approximately the same field of formation (L₂P/ Cu²⁺ = 1:1, 1:1.5, 1:2, and 2:1) as compound 1 (pH 6–7).

Compounds 1 and 2 were obtained as microcrystalline products under above mentioned conditions. Thus, the reaction mixtures were diluted by addition of water for growth of microcrystalline products having larger crystallite size, which makes them suitable for single-crystal X-ray diffraction. This approach led to the formation of single crystal of complex 2. However, 1 was only isolated as a microcrystalline compound. Therefore, the composition of 1 was determined based on thermogravimetric (TG-DTA), CHN, Energy Dispersive X-ray (EDX), and X-ray diffraction analyses (Figure 1) as well as UV/Vis diffuse reflectance and IR spectroscopy.





The assignments for the ¹H NMR spectra of the ligands are presented in the Experimental Section. The signals are assigned based on the splitting of the resonance signals, spin coupling constants and literature data. The ¹H NMR spectra of L_1P and L_2P show a multiplet signals for the –NCH(Ph)– protons. Furthermore, the ¹³C NMR spectra of these ligands show two doublet signals for the –N¹³CH(Ph)– carbon atoms. In the presence of two chiral carbon atoms in the ligands, it seems that diastereomers are present in solution. This is in accordance with the molecular structure determined by the X-ray crystal structure analysis for complex **2** (dimeric molecule have two ligands with different chairalities for NCH(Ph)– carbon atoms of each ligand)

The synthesized compounds were studied by IR spectroscopy. The broad band at 3251 cm^{-1} for L_1P or 3260 cm^{-1} for L_2P can be attributed to the P–OH stretching vibration of the ligands. The corresponding deformation band appears at 1627 cm⁻¹ for L_1P and 1615 cm⁻¹ for L_2P .^[18–20] The bands at 3063 cm⁻¹ for L_1P and 3078 cm⁻¹ for L_2P can be assigned to the N–H stretching vibration. The corresponding N–H deformation vibrations of L_1P and L_2P appear at 1342 and 1369 cm⁻¹, respectively.^[16] Bands corresponding to aromatic and aliphatic C–H stretching vibrations of the L_1P and L_2P are observed between 3017 and 2921 cm⁻¹. The P=O stretching vibration of the phosphonate group in L_1P and L_2P appears as strong band around 1200 cm⁻¹, whereas the bands between 833–1188 cm⁻¹ are assigned to Stretching vibrations of the tetrahedral CPO₃ groups and to C–C vibrations.

The bands at 3235 cm⁻¹ for **1** and 3242 cm⁻¹ for **2**, respectively, can be assigned to the P–OH stretching vibrations of the complexes. The bands at 3063 cm⁻¹ for **1** and 3045 cm⁻¹ for **2**, respectively, are due to the N–H stretching vibration. The corresponding N–H deformation vibrations of compounds **1** and **2** appear at 1348 and 1352 cm⁻¹, respectively. The weak bands around 2926 to 3024 cm⁻¹ are probably due to the vibration of aromatic and aliphatic C–H bonds. Bands at 1165 and 1153 cm⁻¹ are due to P=O stretching vibrations of compounds **1** and **2**, respectively. Compounds **1** and **2** exhibit typical bands in the range 816–1090 cm⁻¹, which are due to the stretching vibrations of the –CPO₃ group and to C–C vibrations.^[17]

The diffuse reflectance UV/Vis spectra of **1** and **2** show a broad absorption band in the visible region at 648 and 659 nm, which is assigned to a d_{xy} , $d_{yz} \rightarrow d_{x^2-y^2}$ transition.^[21–23] This spectral feature clearly reveals the presence of five-coordinate arrangement around the central Cu²⁺ ion and is more consistent with square pyramidal or distorted square pyramidal (SP) arrangement.^[24,25] The absorption spectra of the complexes have absorption bands in the 200–300 nm range (see Experimental Section) attributed to ligand-centered $\pi \rightarrow \pi^*$ and/or charge transfer transitions.^[20,26]

The perspective view of the dimeric copper(II) complex, $Cu_2(L_1P)_2$ indicating atom-numbering scheme with thermal ellipsoids at 50% probability is illustrated in Figure 2. The crystallographic data for compound **2** is summarized in Table 1. Selected bond lengths, bond angles, and torsion angles are listed in Table 2.



Figure 2. Crystal structure of $Cu_2(L_2P)_2$ (2) (a) Conformer A (the atom-labeling scheme is shown for clarity), (b) Conformer B (hydrogen atoms are omitted for clarity).

The asymmetric unit of the complex consists of two independent molecules (A and B).

Though the coordination arrangement of copper(II) is very similar in both structures, there are small differences in bond lengths and bond angles.

It is interesting that the molecules are centrosymmetric and have a dimeric structure, where two copper ions are doubly bridged by OPO groups forming an eight-membered dinuclear ring. The arrangement of the chair like, eight membered ring (Figure 3) (Cu-O1-P1-O6-Cui-O1i-P1i-O6i) is very similar to that of the previously reported metal diphosphonate compounds.^[16,27-28] Each copper atom in the dinuclear complex displays a five-coordinate distorted square-pyramidal coordination, though there is appreciable distortion towards trigonal bipyramid with trigonality index, $\tau = 0.22$ for A and 0.21 for **B** [τ is the parameter describing the degree of trigonal distortion and is defined as $\tau = (\theta 1 - \theta 2)/60$, where $\theta 1$ and $\theta 2$ are two largest ligand–metal–ligand angles, $\tau = 0$ for ideal squarepyramid (SP) and $\tau = 1$ for ideal trigonal bipyramid (TBP)].^[29] The equatorial plane formed by oxygen and nitrogen atoms (for example O1, O5, N2, and N1), whereas one phosphonate oxygen atom (O6i) from the neighboring ligand (L₂P) is the apex occupying the fifth site. The distance from copper atom to the least square plane formed by O1, O2, N2, and N1 is 0.1420(4) Å in A and 0.1275(4) Å in B. The axial Cu–O6i



 Table 1. Crystal data and single-crystal X-ray diffraction refinement details for compound 2.

Formula	C32H ₃₆ Br ₄ Cu ₂ N ₄ O ₁₂ P ₄
Formula weight	1239.25
Temperature /K	200
Wavelength /Å	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	8.8467(13)
b /Å	12.9976(19)
c /Å	19.433(3)
a /°	73.074(3)
β /°	85.701(3)
y /°	83.489(3)
V /A ³	2121.9 (5)
Ζ	2
Density /g·cm ⁻³	1.940
μ / mm^{-1}	4.98
F(000)	1220
Crystal size	$0.36 \times 0.08 \times 0.08$
Theta range for data collection	2.97 to 30.0
Inday ranges	$-12 \le h \le 12, -18 \le k \le 18,$
Index Tanges	$-27 \le l \le 27$
Reflections collected	32745
Independent reflections	12327 [$R(int) = 0.0367$]
Completeness to $\theta = 30.0^{\circ}$	99.5%
Absorption correction	Empirical
Max. and min. transmission	0.8256 and 0.2671
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12327 / 0 / 523
Goodness-of-fit on F^2	1.139
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0402, wR_2 = 0.0781$
R indices (all data)	$R_1 = 0.0662, wR_2 = 0.0849$
Largest diff. peak and hole /e·Å ⁻³	1.263 and -0.946

bond length is 2.3620(19) Å in A and 2.3733(19) Å in B, which links the complex molecules to a dimeric structure, resulting in a Cu-Cu distance of 4.98010(9) Å in A and 5.0068(9) Å in **B**. This distance is near the range of reported values of ca. 5 Å observed for polyatomic bridges.^[16,30] The bond lengths of Cu-O1 and Cu-O5 are 1.9392(18) and 1.9715(19) Å in A and 1.9401(18) and 1.9718(19) Å in B, respectively, which are similar to the Cu-O bond length of other five coordinated copper(II) complexes.^[27] The average Cu-Namine bond length is 2.015 Å. The axial oxygen-metalligand angles differ from the ideal values for a square pyramid varying from 80.98(8)° (N2A-Cu1A-O6A) to 107.52(9)° (N1A-Cu1A-O6A) in A and 80.66(8)° (N2B-Cu1B-O6B) to 106.63(8)° (N1B-Cu1B-O6B) in B. Likewise, the basal ligand-metal-ligand angles vary between 85.37(9)° (N1A-Cu1A-N2A) and 97.66(8)° (O1A-Cu1A-O5A) in A and 85.65(9)° (N1B-Cu1B-N2B) and 97.72(8)° (O1B-Cu1B-O5B) in **B**. Such distortion could be due to the restriction induced by the fused chelate ring.

Each ligand (L₂P) acts as pentadentate ligand, chelating to the one Cu^{II} ion through its amine nitrogen atoms N1 and N2, oxygen O1 and O5 from the P–O group and bridges another Cu^{II} ion by phosphoryl oxygen O6 from the P=O group forming six five-membered rings and one eight-membered ring. The dihedral angle between the planes constituted by the chelate rings Cu101P1C1N1 and Cu105P2C10N2 is $4.04(8)^{\circ}$ in **A** and $4.32(7)^{\circ}$ in **B**, whereas the dihedral angle between the

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Table 2. Selected bond lengths /	Å and angles /° for two indep	pendent molecules of compound 2.
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Molecule A		Molecule B	
Bond lengths			
Cu1A–O1A	1.9392(18)	Cu1B–O1B	1.9401(18)
Cu1A–O5A	1.9715(19)	Cu1B–O5B	1.9718(19)
Cu1A–N1A	2.008(2)	Cu1B–N1B	2.013(2)
Cu1A–N2A	2.018(2)	Cu1B–N2B	2.021(2)
Cu1A–O6A	2.3620(19)	Cu1B–O6B	2.3733(19)
Bond angles			
O1A-Cu1A-O5A	97.66(8)	O1B-Cu1B-O5B	97.72(8)
O1A-Cu1A-N1A	88.58(8)	O1B-Cu1B-N1B	88.51(8)
O5A-Cu1A-N2A	90.21(8)	O5B-Cu1B-N2B	90.17(8)
N1A-Cu1A-N2A	85.37(9)	N1B-Cu1B-N2B	85.65(9)
O1A-Cu1A-O6A	95.07(7)	O1B-Cu1B-O6B	94.54(7)
O5A-Cu1A-O6A	93.04(7)	O5B-Cu1B-O6B	93.44(7)
N1A-Cu1A-O6A	107.52(9)	N1B-Cu1B-O6B	106.63(8)
N2A-Cu1A-O6A	80.98(8)	N2B-Cu1B-O6B	80.66(8)
O5A-Cu1A-N1A	157.95(9)	O5B-Cu1B-N1B	158.50(9)
O1A-Cu1A-N2A	171.40(9)	O1B-Cu1B-N2B	171.02(9)



Figure 3. Chair conformation of the eight-membered chelate ring.

chelate plane Cu101P1C1N1 and the adjacent chelate ring CuN1C8C9N2 is $7.60(6)^{\circ}$ in **A** and $5.97(7)^{\circ}$ in **B**. This shows that the tetradentate chelating ligand is puckered, while coordinating to copper(II). Two {CPO₃} moieties coordinate with copper atoms by two different modes, one of them acting as a monodentate mode and the other adopting a bidentate fashion. The coordination environment around phosphorus atoms of each L is approximately tetrahedral since the average of six angles involving phosphorus are 109.45° and 109.40° (**A** and **B**) for P(1) and P(2), respectively.

The structure of each independent molecule in the complex is stabilized by an extensive system of intermolecular hydrogen bonds and the one-dimensional chains are formed along a axis (Figure 4). The phosphoryl oxygen atom (O3) excluded from complexation acts as an acceptor for the formation of intermolecular hydrogen bond type interactions with the hydrogen atoms H(2A) and H(1X) of the neighboring complex. Furthermore, hydrogen atoms H(2A) and H(1X) take part in the same hydrogen bonding to the phosphoryl oxygen atoms of the neighboring complex molecules (Table 3). On the other hand, there are strong intramolecular hydrogen bonds in the molecule, in which hydroxyl groups of phosphonate unit act as hydrogen donors, whereas bridged oxygen atoms from adjacent phosphonate group act as acceptors. The short O-O distances (2.676 Å) indicate very strong mutual electrostatic interactions.



Figure 4. N–H···O and O–H···O hydrogen bonds are forming chains of $Cu_2(L_2P)_2$ (2) molecules along *a* axis.

The thermal properties of the copper(II) complexes were studied in the range 25–800 °C. It reveals that they do not contain adsorbed or coordinated water or solvent molecules, which is in agreement with the analytical and spectroscopic data. The complexes are stable in air at room temperature.

The mass loss of complex 1 starts at 265 °C. DTA shows a strong exotherm centered at 305 °C with an associated weight loss of 28% (Figure 5). A second broad exothermic effect is observed in the temperature range of 400–610 °C corresponding to a weight loss of 42%. These weight losses are in agreement with the loss of the organic components to yield Cu₂P₂O₇ (weight loss observed 70%, weight loss calcd. 72%). As shown in Figure 6, the weight loss of complex 2 starts at 260 °C. The thermal analysis of 2 shows also two steps in the decomposition. DTA shows a strong exotherm centered at 295 °C followed by a broad exotherm in the temperature range of 390–600 °C accompanied by two weight loss of 33 and 42%. The final product is Cu₂P₂O₇ (weight loss observed 75%, weight loss calcd. 76%). The similarities in the TG/DTA curves of 1 and 2, suggest closely related structures.



Table 3. Hydrogen bonds D-H···A for two independent molecules of compound 2.

Molecule	<i>D</i> –Н••• <i>А</i>	Α	<i>d</i> (<i>D</i> -H)	<i>d</i> (H••• <i>A</i>)	$d(D \cdot \cdot \cdot A)$	<(<i>D</i> H <i>A</i>)	
A	N1A-H1AX···O3A	[-x+1, -y, -z+1]	0.93	2.062	2.893	147.96	
	O2A-H2AA···O3A	[-x+2, -y, -z+1]	0.84	1.787	2.621	171.38	
	O4A-H4AA•••O6A	[x, y, z]	0.84	1.85	2.676	167.34	
В	N1B-H1BX···O3B	[-x+2, -y+1, -z]	0.93	2.079	2.903	146.85	
	O2B-H2BA···O3B	[-x+3, -y+1, -z]	0.84	1.781	2.615	171.43	
	O4B-H4BA···O6B	[x, y, z]	0.84	1.848	2.677	168.55	



Figure 5. TGA-DTA curves for $Cu_2(L_1P)_2$ (1).



Figure 6. TGA-DTA curves for $Cu_2(L_2P)_2$ (2).

Conclusions

Two new diphosphonic acid ligands, [ethane-1,2-diylbis(azanediyl)]bis[(4-chlorophenyl)methylene]diphosphonic acid (L_1P), [ethane-1,2-diylbis(azanediyl)]bis[(4-bromophenyl) methylene]diphosphonic acid (L_2P) and their corresponding two copper complexes $Cu_2(L_1P)_2$ (1) and $Cu_2(L_2P)_2$ (2) were synthesized and characterized by elemental analysis, UV/Vis diffuse reflectance, infrared, and (¹H and ¹³C) NMR spectroscopy. Additionally, the solid-state structure of 2 consists of five-coordinate in distorted square pyramidal arrangement copper(II) ions doubly bridged by OPO from phosphonate. The structure of each independent molecule in the complex is stabilized by an extensive system of intermolecular hydrogen bonds and the one-dimensional chains are formed along the *a* axis. The diffuse reflectance UV/Vis spectra of **1** and **2** show a broad absorption band in the visible region at 648 and 659 nm, which is in agreement with a distorted square pyramidal arrangement. The complexes are stable up to a temperature of about 260 °C

Experimental Section

General: All reagents were analytical grade commercial products and were used without further purification. Elemental analyses were performed with a Heraeus CHN-ORAPID elemental analyzer. Infrared spectra were recorded with a Bruker Tensor 27 spectrophotometer. NMR spectra were obtained with a Bruker Avance DRX 250 (250 MHz) spectrometer. Proton chemical shifts are reported in part per million (ppm) relative to an internal standard of Me₄Si. UV/Vis spectra were obtained with a Shimadzu UV-260 spectrophotometer. The compositional analyses were done by energy dispersive X-ray (EDX, Kevex, Delta ClassI). Thermogravimetric analysis was carried out with a Perkin–Elmer Pyris thermal analysis system with a heating rate of 10 K·min⁻¹.

Syntheses

N,*N*'-**Bis(4-chlorobenzylidene)ethane-1,2-diamine** (**L**₁): To a solution of 4-chlorobenzaldehyde (4 g, 28 mmol) in diethyl ether (30 mL) was added a solution of ethylenediamine (0.84 g, 14 mmol) in diethyl ether (20 mL) and the resulting mixture was stirred for 45 min at room temperature. Afterwards, the solution was filtered, volatiles removed and the remaining white solid was washed with diethyl ether and dried in vacuo. Yield 90%; m.p.: 14°C. Anal. for C₁₆H₁₄Cl₂N₂(305.21): calcd. C 62.97; H 4.62; N 9.18%; found: C 62.01; H 4.65; N 9.17%. **IR** (KBr): $\tilde{v} = 1643$ (C=N), 1484 (C=C), 817 (= CH) cm⁻¹.

N,N'-**Bis(4-bromobenzylidene)ethane-1,2-diamine (L₂):** This compound was prepared by a procedure similar to that for the synthesis of *N,N'*-bis(4-chlorobenzylidene)ethane-1,2-diamine (L₁) using 4-bromobenzaldehyde (4 g, 22 mmol) to form *N,N'*-Bis(4-bromobenzylidene)ethane-1,2-diamine as a white solid. Yield 90%; m.p.: 14&C. Anal. for C₁₆H₁₄Br₂N₂ (394.11): calcd. C 48.76; H 3.58; N 7.11%; found: C 48.74; H 3.59; N 7.11%. **IR** (KBr): $\tilde{v} = 1641$ (C=N), 1479 (C=C), 816 (= CH) cm⁻¹.

[Ethane-1,2-diylbis(azanediyl)]bis[(4-chlorophenyl)

methylene]diphosphonic Acid (L₁P): The ligand [ethane-1,2-diylbis-(azanediyl)]bis[(4-chlorophenyl)methylene]diphosphonic acid was prepared according to reported procedures.^[16] A mixture of trimethyl phosphite (1.66 g, 10 mmol) and L₁ (1.52 g, 5 mmol) was dissolved in

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glacial acetic acid (20 mL). This mixture was stirred at 80-85 °C for 3 h. Afterwards the solvent was removed by evaporation using rotary evaporator to give viscous yellow oil. HCl (12 m, 15 mL) was added to the above oil and the mixture was heated to reflux for about 3 h. Excess HCl was removed at reduced pressure and distilled water (5.4 mL) was added. The resulting solution was heated to reflux for 1 h to give a white solid. The compound was purified using distilled water and acetone solution to yield 65% white powder solid, m.p. 242 °C. C₁₆H₂₀Cl₂N₂O₆P₂ (469.20): calcd. C 40.96; H 4.30; N 5.97 %; found C 40.99; H 4.33; N 5.95%. IR (KBr): v = 3251 m, 3063 m, 2929 w, 2975 w, 3017 w, 1627 s, 1495 s, 1415 w, 1342 m, 1210 s, 1162 s, 1083 s, 1012 s, 930 s, 853 s, 770 w, 711 m, 677 m, 630 m, 556 m, 508 m, 446 m cm⁻¹. ¹**H NMR** (NaOD+D₂O): δ = 2.34 (s, 4 H, NCH₂CH₂N), 3.42 [m, 2 H, 2(-NCHPh-)], 7.04-7.14 (m, 8 H, 2ArH). ¹³C NMR (NaOD+D₂O): $\delta = 46.1(-N^{13}CH_2^{13}CH_2N-)$, 61.9 (d, ${}^{1}J_{p-c} = 6.5$ Hz), 63.6 d, ${}^{1}J_{p-c} = 5.5$ Hz), 127.9, 128.19, 130.0, 131.6, 137.9, 137.9. ³¹**P** NMR (NaOD+D₂O): δ = 15.35, 15.44.

[Ethane-1,2-diylbis(azanediyl)]bis[(4-bromophenyl)

methylene]diphosphonic Acid (L₂P): This compound was prepared by a procedure similar to that for the synthesis of L₁P using *N*,*N*'bis(4-bromobenzylidene)ethane-1,2-diamine (L₁, 1.97 g, 5 mmol). Yield: 70% solid, m.p.: 264 °C. C₁₆H₂₀Br₂O₆N₂P₂ (558.10): calcd. C 34.43; H 3.61; N 5.02%; found C 34.42; H 3.61; N 5.03%. **IR** (KBr): $\tilde{v} = 3260$ m, 3078 m, 2921 w, 2962 w, 3011 w, 1615 s, 1488 s, 1414 m, 1369 m, 1215 s, 1188 s, 1072 s, 1010 s, 936 s, 833 m, 759 m, 707 m, 653 w, 626 w, 554 s, 473 w cm⁻¹. ¹H NMR (NaOD+D₂O): $\delta =$ 2.48 (s, 4 H, NCH₂CH₂N), 3.52 [m, 2 H, 2(–NCHPh–)], 7.08–7.39 (m, 8 H, 2ArH). ¹³C NMR (NaOD+D₂O): $\delta = 46.0(-N^{13}CH_2^{13}CH_2N-)$, 61.7 (d, ¹*J*_{p-c} = 6.2 Hz), 63.8 d, ¹*J*_{p-c} = 5.7 Hz), 119.9, 130.3, 130.4, 131.0, 131.4, 138.2. ³¹P NMR (NaOD+D₂O): $\delta = 14.83$, 14.88.

Cu₂(L₁P)₂ (1): A mixture of CuSO₄ (0.129 g, 0.516 mmol) and L₁P (0.39 g, 0.705 mmol) in distilled water (8 mL) and adjusted to pH 6 with Me₄NOH was kept in a Teflon-lined autoclave at 165 °C for 3 d. After slow cooling to room temperature, a microcrystalline product was obtained. Yield 45%. C₁₆H₁₈Cl₂CuN₂O₆P₂ (530.73): calcd. C 36.21; H 3.42; N 5.28%; found C 36.80; H 3.49; N 5.36%. **IR** (KBr): $\tilde{v} = 3235$ m, 3063 m, 3021 w, 2926 w, 1598 s, 1482 m, 1434 m, 1348 m, 1248 m, 1165 s, 1090 s, 1036 s, 1008 s, 940 s, 916 s, 841 s, 816 s, 768 m, 708 m, 593 s, 587 m, 502 m, 440 m cm⁻¹. DRUV/Vis (nm): 230, 289, 646. EDX measurement: atomic ratio P/Cl/Cu = 2:2:1.

Cu₂(L₂P)₂ (2): A mixture of CuSO₄ (0.129 g, 0.516 mmol) and L₂P (0.33 g, 0.591 mmol) in distilled water (12 mL) was strongly stirred and the pH value of the resultant solution was adjusted to 7 by slow addition of Me₄NOH. The resultant blue solution was kept in a Teflon-lined autoclave at 150 °C for 3 d. After slow cooling to room temperature, blue blocky crystals were obtained. Yield 40%. C₁₆H₁₈Br₂Cu-N₂O₆P₂ (619.63): calcd. C 31.01; H 2.93; N 4.52%; found C 31.14; H 2.97; N 4.55%. **IR** (KBr): $\tilde{v} = 3242$ m, 3045 m, 3024 w, 2938 w, 1590 s, 1497 m, 1450 m, 1352 m, 1248 m, 1153 s, 1073 m, 1026 s, 1007 s, 957 s, 933 s, 855 s, 810 s, 760 s, 711 s, 609 s, 487 m, 468 m, 440 s cm⁻¹. DRUV/Vis (nm): 221, 291, 646. EDX measurement: atomic ratio P/Br/Cu = 2:2:1.

X-ray Crystallography: Crystals of **2**, which were suitable for X-ray crystallography, were obtained as described above. A summary of the key crystallographic information is given in Table 1. Diffraction measurements for the crystals in oil were recorded with a Bruker Apex CCD diffractometer fitted with Mo- K_{α} radiation. The raw frame data were processed using SAINT^[31] and SADABS^[32] to yield the reflection data file. The structures were solved with direct methods and re-

fined with full-matrix least-squares procedures (SHELXTL-97)^[33] with anisotropic thermal parameters for all non-hydrogen atoms.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-853051 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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