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Synthesis, Characterization, and Crystal Structures of Two New Divalent Metal Complexes of *N,N'*-Bis(phosphonomethyl)-1,10-diaza-18-crown-6: A Hydrogen-Bonded 1D Array and a 3D Network with a Large Channel

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Reaction of *N,N'*-bis(phosphonomethyl)-1,10-diaza-18-crown-6 (H_4L) with copper(II) acetate in 1:1 ethanol/water mixed solvents afforded a new crystal-engineered supramolecular metal phosphonate, $Cu(H_2L)$ (complex **1**). By reaction of the same ligand with cadmium(II) nitrate in a 2:1 (M/L) ratio in methanol, a cadmium(II) complex with a 3D network structure was isolated, $Cd_{2.75}(L)(H_2O)_7\cdot1.5NO_3\cdot7H_2O\cdot MeOH$ (complex **2**). The copper(II) complex crystallized in the monoclinic space group $P2_1/c$, with $a = 10.125(4)$, $b = 14.103(6)$, and $c = 14.537(6)$ Å, $\beta = 91.049(8)^\circ$, $V = 2075.4(16)$ Å^3, and $Z = 2$. The Cu(II) ions in complex **1** are 6-coordinated by two phosphonate oxygen atoms, two nitrogen, and two oxygen atoms from the crown ether ring. Their coordination geometry can be described as Jahn–Teller-distorted octahedral, with elongated Cu–O(crown) distances (2.634(4) and 2.671(4) Å for Cu(1) and Cu(2), respectively). The other two crown oxygen atoms remain uncoordinated. Neighboring two $Cu(H_2L)$ units are further interlinked via a pair of strong hydrogen bonds between uncoordinated phosphonate oxygen atoms, resulting in a one-dimensional supramolecular array along the *a* axis. The cadmium(II) complex is tetragonal, $P4_2/n$ (No. 86) with $a = 20.8150(9)$ and $c = 18.5846(12)$ Å, $V = 8052.0(7)$ Å^3, and $Z = 8$. Among four cadmium(II) atoms in an asymmetric unit, one is 8-coordinated by four chelating phosphonate groups, the second one is 8-coordinated by 6 coordination atoms from a crown ring and two oxygen atoms from two phosphonate groups, the third Cd(II) atom is octahedrally coordinated by three aqua ligands and three phosphonate oxygen atoms from three phosphonate groups, and the fourth one is 6-coordinated by four aqua ligands and two oxygen atoms from two phosphonate groups in a distorted octahedral geometry. These cadmium atoms are interconnected by bridging phosphonate tetrahedra in such a way as to form large channels along the *c* direction, in which the lattice water molecules, methanol solvent, and nitrate anions reside. The effect of extent of deprotonation of phosphonic acids on the type of complex formed is also discussed.

Introduction

Attachment of macrocyclic ligands into a polymeric matrix leads to a relatively new class of compounds with a variety of applications, such as efficient and economical industrial separations, ion transportation, isotope extraction, anion activation, sensoring and switching, liquid crystalline properties, and catalysis.[1−5] Recently we and others have successfully attached macrocyclic ligands to rigid layered frameworks of zirconium phosphates through exocylic phosphorylation of crown ethers.[5−7] However, the poor solubility and low crystallinity of these materials make their structural characterization a rather difficult task.[5−7] The divalent metal phosphonates, on the other hand, have relatively high

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(1) For an excellent overview on various aspects of crown ether chemistry by several distinguished scientists of this field, see volumes 1 and 10 of the multiple volume series: *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon Press: Oxford, U.K., 1996.

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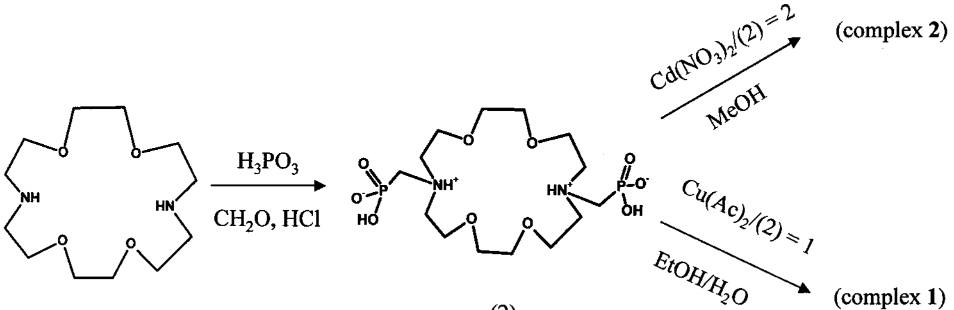
Scheme 1. Synthetic Routes for the Ligand and Its Cu(II) and Cd(II) Complexes



(1)

(2)

solubility in various solvents and are much more likely to yield single crystals or crystalline powders. Our results have shown that the crystal structures of metal(II) phosphonates containing monoaza crown ethers (such as aza-15-crown-5 and aza-18-crown-6) feature a one-dimensional chain, the so-called “macrocylic leaflet”, in which the metal ions are bridged by phosphonate groups. The crown ether moiety usually encapsulates a lattice water molecule, and its amine group remains protonated.[6,8] These ligands themselves also form macrocylic leaflets through pairs of strong hydrogen bonds between phosphonate groups.[6,8] Molecular species are obtained when all of the oxygen atoms in the crown ring are replaced by nitrogen atoms; so far these studies are only limited to triazacycles, tetraazacycles, and hexaazacycles.[9] In these complexes, the nitrogen atoms are coordinated to metal(II) ion (usually Cu(II) and Co(II)) due to the “macrocyclic effect” and the affinity of the nitrogen atom for copper(II) or cobalt(II) ion. These chelate ML units are further interlinked into a one-dimensional chain by hydrogen bonds between uncoordinated phosphonate oxygen atoms.[10] Two phosphonate groups can be attached to 1,10-diaza-18-crown-6 (**1**), forming a diphosphonic acid, *N,N′*-bis(phosphonomethyl)-1,10-diaza-18-crown-6 (H_4L, **2**) (See Scheme 1). X-ray structural analysis indicates that the two phosphonate groups are in the *trans* conformation.[11] Its zirconium(IV) complexes prepared in the presence of H_3PO_4 were proposed to have a pillared layered structure, on the basis of NMR data. The phosphonic acid groups bridge two layers and are spaced along the layer by the monohydrogen phosphate groups.[11] These compounds may exhibit interesting complexation properties. It was therefore of interest to determine whether reaction of the diazacrownphosphonic acid with divalent metal ions would yield similar layered compounds that were sufficiently crystalline to effect crystal structure solutions. Our recent such efforts resulted in a hydrogen-bonded one-dimensional supramolecular array, Cu(H_2L) (complex **1**) and a 3D network with a large tunnel, $Cd_{2.75}(L)(H_2O)_7 \cdot 1.5NO_3 \cdot 7H_2O \cdot MeOH$ (complex **2**). In both complexes, the crown ether moieties are coordinated with the metal ions. Herein, we report their synthesis, characterization, and crystal structures.

Experimental Section

Materials and Methods. Deionized water, used in all experiments, was purified to a resistivity of 17.6 MΩ cm with a Barnstead Nanopure II System. All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Solution NMR was recorded on a Varian Unity Plus 300 spectrometer. H_3PO_4 (EM Science, 85%) was used as ^{31}P standard reference. Elemental analysis data were obtained from Desert Analytics, Tucson, AZ. Thermogravimetric analysis was carried out with a TA 4000 unit, at a heating rate of 10 °C/min under an oxygen atmosphere. The magnetic measurements were performed on polycrystalline samples of the Cu(II) complex sealed in a plastic bag in an inert atmosphere with a SQUID susceptometer (Quantum Design, MPMS-XL-5) in the temperature range of 2−300 K at an applied magnetic field of 0.5 T. The diamagnetic contributions of the samples were corrected using Pascal’s constants.

Synthesis of *N,N′*-Bis(phosphonomethyl)-1,10-diaza-18-crown-6 (H_4L). 1,10-diaza-18-crown-6 (Aldrich) was phosphonomethylated by reacting it with phosphorous acid (Aldrich) and formaldehyde (Aldrich) in the presence of concentrated HCl (EM Science) according to the procedures previously described.[11] Its purity was confirmed by NMR measurements and elemental analysis. ^{31}P NMR shows only a single peak at 7.324 ppm. ^{1}H NMR: 3.438 ppm (N−CH_2−P, doublet, 4H, $J_{H-P} = 12.9$ Hz); 3.696 ppm (N−CH_2−C, 8H, triplet, $J_{H-H} = 4.2$ Hz); 3.774 ppm (N−C−CH_2−O, single, 8H), 3.924 ppm (O−CH_2−CH_2−O, triplet, 8H, $J_{H-H} = 4.5$ Hz). Anal. Found for $C_{14}H_{32}N_2O_{10}P_2$: C, 37.05; H, 7.02; N, 6.50; P, 13.89. Calcd: C, 37.33; H, 7.16; N, 6.22; P, 13.75.

Preparation of Cu(H_2L) (1). Under stirring, copper acetate (Matheson Coleman & Bell Manufacturing Chemists) (0.25 mmol) dissolved in 5 mL of 1:1 (volume ratio) deionized water−ethyl alcohol mixed solvent was mixed with a solution of *N,N′*-bis(phosphomethyl)-1,10-diaza-18-crown-6 (0.25 mmol) dissolved in 5.0 mL of the same EtOH−H_2O solvent. The resultant blue solution

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was filtered off and allowed to evaporate slowly at room temperature. After 2 weeks, blue crystals (30 mg) were obtained. However, recrystallization from the same solvent was needed to improve its crystallinity and get crystals suitable for structural analysis. Anal. Found for Cu(H_2L) (**1**)**:** C, 32.49; H, 5.74; N, 5.26; P, 12.34. Calcd: C, 32.85; H, 5.91; N, 5.47; P, 12.10.

Synthesis of $Cd_{2.75}(L)(H_2O)_7\cdot1.5NO_3\cdot7H_2O\cdot MeOH$ (2). The methods used for synthesizing complex **2** are similar to those for complex **1**. **C**admium(II) nitrate (Aldrich) (0.25 mmol) dissolved in 5 mL of methanol was mixed with a solution of *N*,*N*′-bis(phosphomethyl)-1,10-diaza-18-crown-6 (0.125 mmol) dissolved in 5.0 mL of the same solvent. The resultant solution was filtered off and allowed to evaporate slowly at room temperature. A 10 mg amount of colorless crystals was recovered after about 10 days. Anal. Found for complex **2:** C, 15.61; H, 5.54; N, 4.46; P, 5.34. Calcd: C, 15.89; H, 5.30; N, 4.33; P, 5.47.

Crystal Structure Determination. Single crystals of complexes **1** and **2** were mounted on a Bruker Smart CCD and diffraction data obtained using Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator at 110(2) K. The cell constants were indexed from reflections obtained from 60 frames collected with a 10 s exposure/frame. A hemisphere of data (1271 frames at 5 cm detector distances) was collected by the narrow-frame method with scan widths of 0.30° in ω and exposure time of 40 s/frame. The first 50 frames were recollected at the end of data collection to assess the stability of the crystal, and it was found that the decay in intensity was less than 1%. The data were corrected for the Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. An empirical absorption correction based on the ψ scan method was also applied to both data sets.

Both structures were solved using direct methods (SHELXTL) and refined by least-squares methods with atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms.[12] All hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters, and included in the structure factor calculations. Refinements for complex **1** were satisfactory, and all atoms were ordered. However, the Cd4 atom and two aqua ligands in complex **2** were found to be disordered. The occupancy factor for Cd4 atom was refined to be 0.484(2), and it was fixed to be 0.5 for ease of charge balance considerations. Water molecules O5w (O5w′) and O6w (O6w′) are disordered over two positions, respectively. The occupancy factor for the nitrate group (N4, O41, O42, O43) was also reduced to 0.5 for the sake of charge balance. The water molecules (except O1w, O2w, O3w), nitrate anions, and methanol solvent were refined with isotropic thermal parameters. Attempts to resolve the disorder problem in complex **2** by using a space group with a lower symmetry were not successful. The final difference Fourier maps showed featureless residual peaks of 1.275 e·Å^{-3} (0.98 Å from Cu1) and 2.572 e·Å^{-3} (0.03 Å from Cd1) for complexes **1** and **2,** respectively. Some of the data collection and refinement parameters are summarized in Table 1. Important bond lengths and angles for the two complexes are listed in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in the Supporting Information.

Table 1. Crystal Data and Structure Refinement for Complexes **1** and **2**

	1	**2**
empirical formula	$C_{14}H_{30}CuN_2O_{10}P_2$	$C_{15}H_{60}Cd_{2.75}N_{3.5}O_{29.5}P_2$
fw	511.88	1132.71
space group	$P2_1/c$ (No. 14)	$P4_2/n$ (No. 86)
a, Å	10.125(4)	20.8150(9)
b, Å	14.103(6)	20.8150(9)
c, Å	14.537(6)	18.5846(12)
β, deg	91.049(8)	90.0
V, Å^3	2075.4(16)	8052.0(7)
Z	4	
D_{calcd}, g cm^{-3}	1.638	1.869
temp, K	110(2)	110(2)
μ, mm^{-1}	1.261	1.620
GOF	0.945	1.077
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0492, 0.1169	0.0716, 0.1943
R1, wR2 (all data)	0.0922, 0.1317	0.0934, 0.2243

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

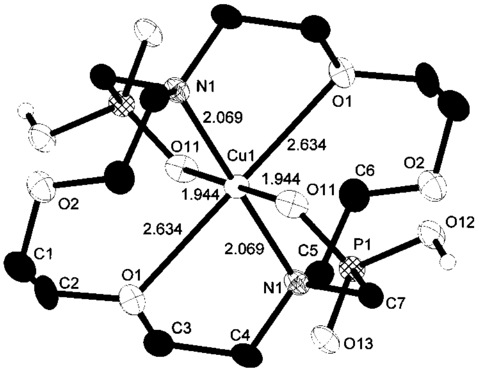

Figure 1. ORTEP representation of the asymmetric unit of Cu(1)(H_2L). Thermal ellipsoids are drawn at 50% probability.

Results and Discussion

Crystal Structure of Cu(H_2L) (1). There are two Cu(II) atoms in an asymmetry unit; both are located at the $\bar{1}$ site and have a similar coordination environment. The Cu(1)-(H_2L) unit is shown in Figure 1. Each Cu(II) atom is encapsulated by a ligand, being 6-coordinated by two nitrogen atoms and two oxygen atoms from the crown ether ring and two oxygen atoms from two phosphonate groups. The other two crown oxygen atoms remain uncoordinated. The Cu(1)−O(crown), Cu(1)−N(crown), and Cu(1)−O(phosphonate) distances are 2.634(4), 2.068(4), and 1.944(4) Å, respectively. The corresponding bond distances of Cu(2) are 2.671(4), 2.096(4), and 1.925(4) Å, respectively (Table 2). It is noticed that the Cu−O(crown) distances are much longer than those of Cu−O(phosphonate) and Cu−N(crown). The coordination geometry around the Cu(II) ions can be best described as a Jahn−Teller-distorted octahedron. This type of coordination geometry has been reported in a number of copper(II) complexes with 1,10-diaza-18-crown-6 and its acetate derivatives; in such cases, the two coordination sites occupied by two phosphonate oxygen atoms are replaced by anions (such as Cl$^-$, Br$^-$, SCN$^-$, etc.) or acetate oxygen atoms.[13,14] Jahn−Teller distortion is not so evident in copper(II) complexes with phosphorylated tetraazacycles, and all Cu−N(crown) distances are close to each other, probably

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Table 2. Bond Lengths (Å) and Angles (deg) for Complexes **1** and **2**[a]

Complex **1**

Cu(1)−O(11)	1.944(4)	Cu(1)−O(11)$^{\#1}$	1.944(4)	Cu(2)−(4)$^{\#2}$	2.671(4)	Cu(2)−O(4)	2.671(4)
Cu(1)−N(1)	2.068(4)	Cu(1)−N(1)$^{\#1}$	2.068(4)	P(1)−O(11)	1.499(4)	P(1)−O(13)	1.513(4)
Cu(1)−O(1)	2.634(4)	Cu(1)−O(1)$^{\#1}$	2.634(4)	P(1)−O(12)	1.548(4)	P(1)−C(7)	1.824(5)
Cu(2)−O(21)$^{\#2}$	1.925(4)	Cu(2)−O(21)	1.925(4)	P(2)−O(22)	1.505(4)	P(2)−O(21)	1.530(4)
Cu(2)−N(2)	2.096(4)	Cu(2)−N(2)$^{\#2}$	2.096(4)	P(2)−O(23)	1.560(4)	P(2)−C(17)	1.802(5)

Hydrogen Bonds and Angles

O(12)···O(13)$^{\#3}$	2.514(4)	O(22)···O(23)$^{\#4}$	2.501(4)	O(13)···O(12)$^{\#3}$	2.514(4)	O(23)···O(22)$^{\#4}$	2.501(4)
O(12)−H(12A)···O(13)$^{\#3}$	164.1(4)	O(22)···H(23A)$^{\#4}$−O(23)$^{\#4}$	167.0(4)	O(21)−Cu(2)−N(2)$^{\#2}$	91.57(19)	N(2)−Cu(2)−N(2)$^{\#2}$	180.000(1)
O(13)···H(12A)$^{\#3}$−O(12)$^{\#3}$	164.1(4)	O(23)−H(23A)···O(22)$^{\#4}$	167.0(4)	O(11)−P(1)−O(13)	114.5(2)	O(11)−P(1)−O(12)	109.6(2)
O(11)−Cu(1)−O(11)$^{\#1}$	180.0(2)	O(11)−Cu(1)−N(1)	88.15(18)	O(13)−P(1)−O(12)	111.9(2)	O(11)−P(1)−C(7)	103.6(3)
O(11)$^{\#1}$−Cu(1)−N(1)	91.85(18)	O(11)−Cu(1)−N(1)$^{\#1}$	91.85(18)	O(13)−P(1)−C(7)	111.4(2)	O(12)−P(1)−C(7)	105.1(2)
O(11)$^{\#1}$−Cu(1)−N(1)$^{\#1}$	88.15(18)	N(1)−Cu(1)−N(1)$^{\#1}$	180.0(4)	O(22)−P(2)−O(21)	114.4(2)	O(22)−P(2)−O(23)	111.1(2)
O(21)$^{\#2}$−Cu(2)−O(21)	180.0	O(21)$^{\#2}$−Cu(2)−N(2)	91.57(19)	O(21)−P(2)−O(23)	110.2(2)	O(22)−P(2)−C(17)	108.2(2)
O(21)−Cu(2)−N(2)	88.43(19)	O(21)$^{\#2}$−Cu(2)−N(2)$^{\#2}$	88.43(19)	O(21)−P(2)−C(17)	103.6(3)	O(23)−P(2)−C(17)	109.0(2)

Complex **2**

Cd(1)−O(21)$^{\#1}$	2.206(5)	Cd(1)−O(12)$^{\#1}$	2.277(5)	Cd(3)−O(1)	2.470(6)	Cd(3)−N(1)	2.480(7)
Cd(1)−O(3W)	2.290(6)	Cd(1)−O(2W)	2.295(6)	Cd(3)−O(3)	2.484(6)	Cd(3)−O(4)	2.536(6)
Cd(1)−O(13)	2.310(5)	Cd(1)−O(1W)	2.326(6)	Cd(4)−O(4W)	2.099(14)	Cd(4)−O(6W	2.193(19)
Cd(2)−O(12)$^{\#1}$	2.276(5)	Cd(2)−O(12)	2.276(5)	Cd(4)−O(23)$^{\#4}$	2.229(6)	Cd(4)−O(5W)	2.279(17)
Cd(2)−O(12)$^{\#2}$	2.276(5)	Cd(2)−O(12)$^{\#3}$	2.276(5)	Cd(4)−O(23)	2.342(5	Cd(4)−O(6W′)	2.38(2)
Cd(2)−O(13)$^{\#1}$	2.678(5)	Cd(2)−O(13)	2.678(5)	Cd(4)−O(7W)	2.59(2)	Cd(4)−Cd(4)$^{\#4}$	3.287(3)
Cd(2)−O(13)$^{\#2}$	2.678(5)	Cd(2)−O(13)$^{\#3}$	2.678(5)	P(1)−O(11)	1.512(5)	P(1)−O(13)	1.534(5)
Cd(3)−O(11)	2.307(5)	Cd(3)−O(22)	2.312(5)	P(1)−O(12)	1.539(5)	P(2)−O(22)	1.517(5)
Cd(3)−O(2)	2.416(7)	Cd(3)−N(2)	2.435(7)	P(2)−O(21)	1.518(6)	P(2)−O(23)	1.526(5)

Hydrogen Bonds

O(1W)···O(33)$^{\#5}$	2.718	O(1W)···O(43)$^{\#3}$	2.617	O(6W′)···O(33)$^{\#10}$	2.692	O(7W)···O(13W)	2.793
O(2W)···O(5W′)$^{\#6}$	2.666	O(2W)···O(6W′)$^{\#6}$	2.929	O(8W)···O(9W)	2.82	O(8W)···O(11W)	2.822
O(3W)···O(42)$^{\#1}$	2.945	O(4W)···O(10W)	2.810	O(8W)···O(14W)$^{\#11}$	2.564	O(9W)···O(9W)$^{\#10}$	2.846
O(4W)···O(33)$^{\#7}$	2.955	O(5W)···O(8W)$^{\#8}$	2.805	O(9W)···O(13W)$^{\#6}$	2.536	O(10W)···O(12W)	2.665
O(5W)···O(14W)$^{\#9}$	2.779	O(5W′)···O(6W)	2.789	O(11W)···O(32)	2.546	O(12W)···O(14W)	2.596
O(5W′)···O(8W)$^{\#8}$	2.787	O(6W)···O(7W)	2.702	O(12W)···O(31)$^{\#7}$	2.881	O(12W)···O(41)$^{\#2}$	2.615
O(6W)···O(13W)	2.620	O(6W)···O(32)$^{\#10}$	2.952	O(12W)···O(43)$^{\#2}$	2.933		
O(21)$^{\#1}$−Cd(1)−O(12)$^{\#1}$	102.90(18)	O(21)$^{\#1}$-Cd(1)−O(3W)	91.4(2)	O(2)−Cd(3)−O(3)	75.2(2)	N(2)−Cd(3)−O(3)	67.1(2)
O(12)$^{\#1}$−Cd(1)−O(3W)	87.70(19)	O(21)$^{\#1}$−Cd(1)−O(2W)	87.5(2)	O(1)−Cd(3)−O(3)	126.5(2)	N(1)−Cd(3)−O(3)	122.5(2)
O(12)$^{\#1}$−Cd(1)−O(2W)	102.2(2)	O(3W)−Cd(1)−O(2W)	170.1(2)	O(11)−Cd(3)−O(4)	95.10(18)	O(22)−Cd(3)−O(4)	150.8(2)
O(21)$^{\#1}$−Cd(1)−O(13)	176.84(19)	O(12)$^{\#1}$−Cd(1)−O(13)	78.36(17)	O(2)−Cd(3)−O(4)	88.2(2)	N(2)−Cd(3)−O(4)	131.2(2)
O(3W)−Cd(1)−O(13)	91.5(2)	O(2W)−Cd(1)−O(13)	89.35(19)	O(1)−Cd(3)−O(4)	77.8(2)	N(1)−Cd(3)−O(4)	67.9(2)
O(21)$^{\#1}$−Cd(1)−O(1W)	92.0(2)	O(12)$^{\#1}$−Cd(1)−O(1W)	162.7(2)	O(3)−Cd(3)−O(4)	64.7(2)	O(4W)−Cd(4)−O(6W)	146.2(7)
O(3W)−Cd(1)−O(1W)	83.1(2)	O(2W)−Cd(1)−O(1W)	87.0(3)	O(4W)−Cd(4)−O(23)$^{\#4}$	87.4(4)	O(6W)−Cd(4)−O(23)$^{\#4}$	124.4(5)
O(13)−Cd(1)−O(1W)	87.3(2)	O(12)$^{\#1}$−Cd(2)−O(12)	93.02(5)	O(4W)−Cd(4)−O(5W)	90.2(6)	O(6W)−Cd(4)−O(5W)	99.4(7)
O(12)$^{\#1}$−Cd(2)−O(12)$^{\#2}$	93.02(5)	O(12)−Cd(2)−O(12)$^{\#2}$	153.5(2)	O(23)$^{\#4}$−Cd(4)−O(5W)	91.2(5)	O(4W)−Cd(4)−O(23)	95.2(4)
O(12)$^{\#1}$−Cd(2)−O(12)$^{\#3}$	153.5(2)	O(12)−Cd(2)-O(12)$^{\#3}$	93.02(5)	O(6W)−Cd(4)−O(23)	76.5(5)	O(23)$^{\#4}$−Cd(4)−O(23)	88.1(2)
O(12)$^{\#2}$−Cd(2)−O(12)$^{\#3}$	93.02(5)	O(11)−Cd(3)−O(22)	92.13(19)	O(5W)−Cd(4)−O(23)	174.5(5)	O(4W)−Cd(4)−O(6W′)	172.6(6)
O(11)−Cd(3)−O(2)	149.0(2)	O(22)−Cd(3)−O(2)	99.9(2)	O(23)$^{\#4}$−Cd(4)−O(6W′)	99.4(5)	O(5W)−Cd(4)−O(6W′)	86.7(7)
O(11)−Cd(3)−N(2)	82.3(2)	O(22)−Cd(3)−N(2)	77.8(2)	O(23)−Cd(4)−O(6W′)	88.0(5)	O(4W)−Cd(4)−O(7W)	81.3(7)
O(2)−Cd(3)−N(2)	72.7(2)	O(11)−Cd(3)−O(1)	144.2(2)	O(6W)−Cd(4)−O(7W)	68.1(7)	O(23)$^{\#4}$−Cd(4)−O(7W)	166.9(6)
O(22)−Cd(3)−O(1)	79.8(2)	O(2)−Cd(3)−O(1)	66.5(3)	O(5W)−Cd(4)−O(7W)	82.2(7)	O(23)−Cd(4)−O(7W)	99.5(6)
N(2)−Cd(3)−O(1)	128.6(2)	O(11)−Cd(3)−N(1)	75.30(19)	O(6W′)−Cd(4)−O(7W)	91.6(7)	O(4W)−Cd(4)−Cd(4)$^{\#4}$	92.0(4)
O(22)−Cd(3)−N(1)	86.8(2)	O(2)−Cd(3)−N(1)	133.4(2)	O(6W)−Cd(4)−Cd(4)$^{\#4}$	102.6(5)	O(23)$^{\#4}$−Cd(4)−Cd(4)$^{\#4}$	45.42(14)
N(2)−Cd(3)−N(1)	152.2(2)	O(1)−Cd(3)−N(1)	69.5(2)	O(5W)−Cd(4)−Cd(4)$^{\#4}$	136.4(4)	O(23)−Cd(4)−Cd(4)$^{\#4}$	42.66(14)
O(11)−Cd(3)−O(3)	78.4(2)	O(22)−Cd(3)−O(3)	144.5(2)	O(6W′)−Cd(4)−Cd(4)$^{\#4}$	94.9(5)	O(7W)−Cd(4)−Cd(4)$^{\#4}$	141.1(5)

[a] Symmetry transformations used to generate equivalent atoms are the following. Complex **1**: #1, $-x$, $-y$, $-z$; #2, $-x + 1$, $-y$, $-z + 1$; #3, $-1 - x$, $-y$, $-z$; #4, $-x$, $-y$, $1 - z$. Complex **2**: #1, y, $-x + 1/2$, $-z + 1/2$; #2, $-x + 1/2$, $-y + 1/2$, z; #3, $-y + 1/2$, x, $-z + 1/2$; #4, $-x + 1$, $-y + 1$, $-z + 1$; #5, $1/2 + y$, $1 - x$, $-1/2 + z$; #6, $1 - y$, $-1/2 + x$, $-1/2 + z$; #7, $-1/2 + x$, $y + 1/2$, $1 - z$; #8, $y + 1/2$, $1 - x$, $z + 1/2$; #9, y, $-x + 1/2$, $-z + 3/2$; #10, $-x + 3/2$, $-y + 1/2$, z; #11, $x + 1/2$, $y - 1/2$, $1 - z$.

because of its smaller cavity than that of 1,10-diaza-18-crown-6 fits the copper(II) ion much better.[10] The two phosphonate groups are in the *trans* conformation, being on opposite sides of the crown ring. Each phosphonate group of the ligand in the copper(II) complex is 1H-protonated as in the case in the free ligand where the aza-nitrogen atoms are also protonated as illustrated in Scheme 1.[11] The P−O distances in the copper(II) complex are two short (O(11), O(13), O(21), O(22)) and one long (O(12) and O(23)) (Table 2); thus, O(12) and O(23) are most likely protonated. The phosphonate groups in copper(II) complexes with phosphorylated tetraazacycles are also 1H-protonated.[10] In the copper(II) complex, all phosphonate groups are unidentately coordinated to the copper(II) ions.

Similar to the structure of copper(II) complexes with phosphorylated tetraazacycles,[10] the Cu(H_2L) units are not isolated but are hydrogen-bonded into a 1D array along the *a* axis (Figure 2). It is interesting to note that in copper(II) complexes with phosphorylated tetraazacycles,[10] two neighboring units are interlinked by a single hydrogen bond, whereas, in complex **1**, two neighboring Cu(H_2L) units are interconnected by a pair of hydrogen bonds. This latter type

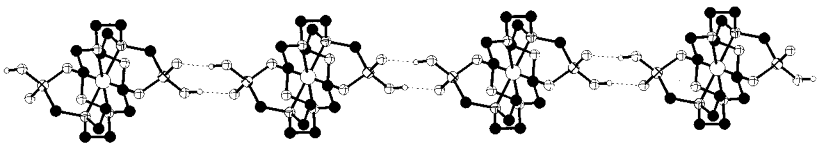


Figure 2. One-dimensional hydrogen-bonded Cu(1)(H_2L) chain along the *a* axis. The Cu, O, N, P, and C atoms are drawn as open (large), crossed, octanded, hatched, and black circles, respectively. Hydrogen atoms of the carbon atoms are omitted for clarity. Hydrogen bonds are represented by dotted lines.

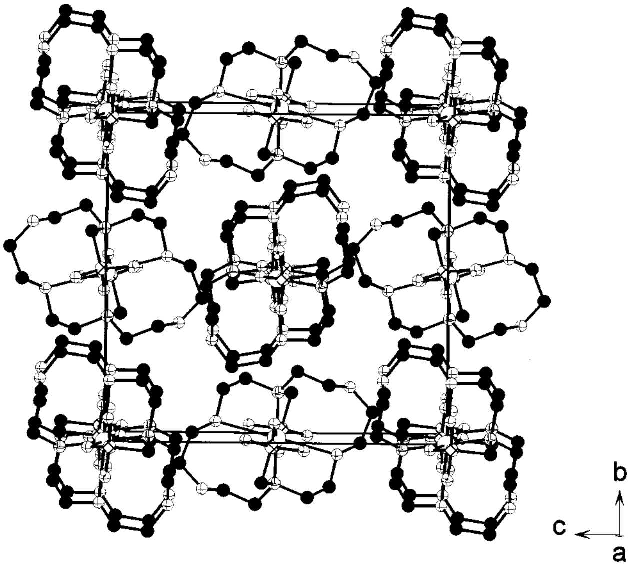


Figure 3. View of the structure of Cu(1)(H_2L) down the *a* axis. The Cu, O, N, P, and C atoms are drawn as open (large), crossed, octanded, hatched, and black circles, respectively. Hydrogen atoms of the carbon atoms are omitted for clarity.

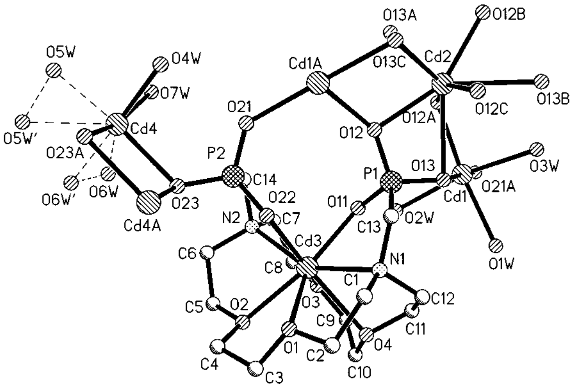


Figure 4. Asymmetric unit of complex **2**. The lattice water molecules, methanol molecule, and nitrate groups are omitted for clarity.

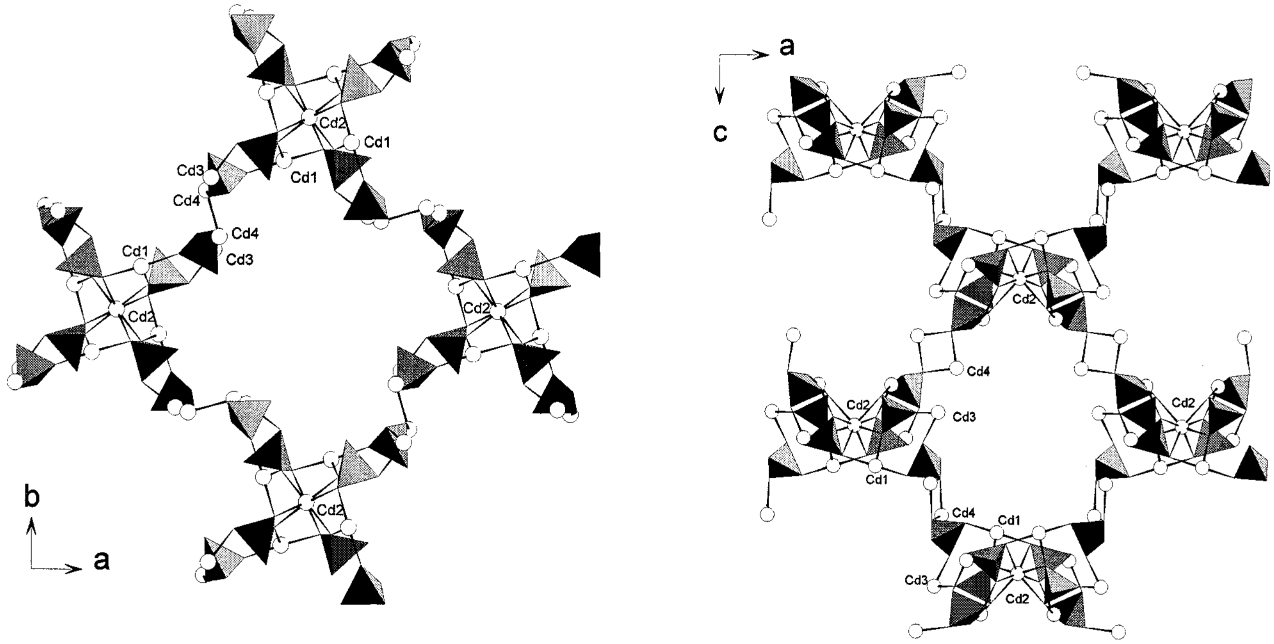
of hydrogen bonding has been reported in the macrocyclic leaflets of phosphorylated aza-15-crown-5 and aza-18-crown-6.[8] The hydrogen bonds in Cu(1)(H_2L) chain have an O···O distance of 2.514(4) Å. The bond angles for these hydrogen bonds are 164.1(4)°. The hydrogen bond distances and angles in the Cu(2)(H_2L) array are 2.501(4) Å and 167.0(4)°, respectively.

These Cu(H_2L) chains are held together by van der Waals forces (Figure 3).

Crystal Structure of $Cd_{2.75}(L)(H_2O)_7 \cdot 1.5NO_3 \cdot 7H_2O \cdot MeOH$ (2). The coordination around the cadmium atoms is shown in Figure 4. Among the four cadmium atoms in the asymmetry unit, two are 8-coordinated (Cd2 and Cd3) and two are 6-coordinated (Cd1 and Cd4). The Cd1 atom is octahedrally coordinated by three aqua ligands and three oxygen atoms of three phosphonate groups from three different ligands. The Cd−O distances range from 2.206(5) to 2.326(6) Å. The Cd2 atom lies on a position of $\bar{4}$ symmetry; it is 8-coordinated by four chelating phosphonate groups utilizing the O12 and O13 oxygen atoms. The Cd−O distances are 4 short (2.276(5) Å) and 4 long (2.678(5) Å). The Cd3 atom is encapsulated by the crown moiety, being 8-coordinated by 6 heteroatoms of a single crown ring and two oxygen atoms from two phosphonate groups attached to the crown ring (O22 and O11). The mean Cd−O(crown), Cd−N(crown), and Cd−O(phosphonate) distances are 2.477(6), 2.458(7), and 2.310(5) Å, respectively. The refined occupancy factor for Cd4 atom is close to 0.484(2); for convenience of charge balance, it was fixed at 50%. Cd4 is 6-coordinated by 4 aqua ligands and two phosphonate oxygen atoms. Its coordination geometry can be described as a severely distorted octahedron. Two aqua ligands (O5w and O6w) are disordered, and each has two orientations. The Cd4−O distances range from 2.099(14) to 2.81(2) Å.

Unlike those in the *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 free ligand and its copper(II) complex, two phosphonate groups of the ligand in the cadmium complex are in the *cis* conformation; i.e., they are on the same side of the crown ring. Both phosphonate groups of the ligand in complex **2** have been completely deprotonated, and the P−O distances are very close, ranging from 1.512(5) to 1.539(5) Å. For comparison, those of the free ligand are 1.482(2), 1.507(2), and 1.572(1) Å, respectively; the longer bond corresponds to the P−O bond for the protonated oxygen.[11] The coordination modes for the two phosphonate groups are different. One phosphonate group (P1, O11, O12, O13) adopts the μ^5- chelate and bridging mode; it chelates (O12 and O13) to a Cd2 atom and bridges (O12 and O13) with two Cd1 atoms and one Cd3 atom (O11). The Cd1−Cd2 separation is 3.702(1) Å. The second phosphonate group bridges with four cadmium atoms (2 Cd4, 1 Cd1, and 1 Cd3); this kind of coordination mode has been found in the cadmium(II) complex with *N*-(phosphonomethyl)-aza-18-crown-6.[8] Two Cd4 atoms are bridged through the O23 atom, resulting in a short metal−metal distance (3.287(3) Å).

The bridging of cadmium atoms through phosphonate groups results in a large channel (Figure 5). This large channel is formed by interconnection of 4 Cd2, 8 Cd1, 8 Cd3, and 8 Cd4 atoms through 16 bridging phosphonate tetrahedra and runs parallel to the *c* axis. The solvent molecules (water and methanol) as well as nitrate groups occupy the cavity of the large tunnel (Figure 6). A number of hydrogen bonds are formed between water molecules and nitrate groups (Table 2).



(a) (b)

Figure 5. View of a big tunnel created by the interconnection of cadmium atoms and phosphonate groups of the ligand along the (a) *c* axis and (b) *b* axis. The cadmium atoms and the phosphonate groups are represented by open circles and tetrahedra, respectively.

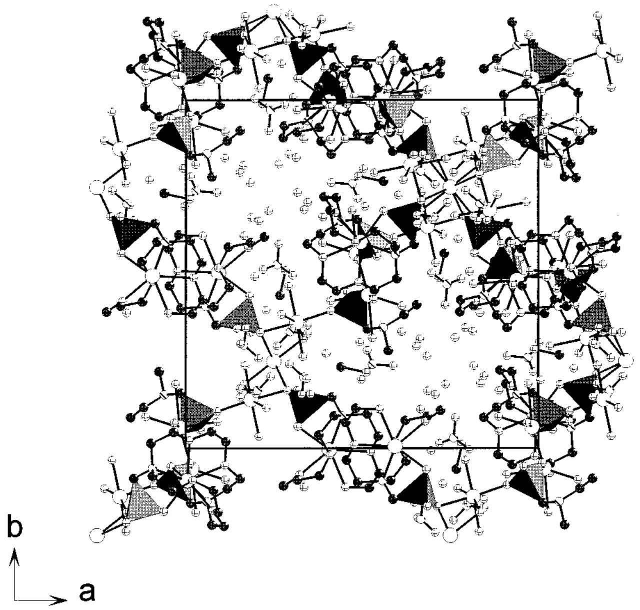


Figure 6. View of the structure of $Cd_{2.75}$(*N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6)$(H_2O)_7$·$1.5NO_3$·$7H_2O$· MeOH down the *c* axis. The phosphonate groups are represented by tetrahedra. The Cd, O, N, and C atoms are drawn as open, crossed, hatched, and black circles, respectively.

The structures of the above divalent metal phosphonates with *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 differ greatly from the two Zr(IV) complexes with the same ligand.[11] Both $Zr_2(H_2L)_{0.75}(PO_4)(HPO_4)_{0.5}$·2.5F·$4H_2O$ (complex **3**) and $Zr(H_2L)_{0.33}$ $(HPO_4)_{1.34}$·0.66F·$1.8H_2O$ (complex **4**), which are prepared in the presence of phosphoric acid and HF, have pillared layered structures. The zirconium atoms are bridged by orthophosphate groups within the layers and O_3P groups with either pendant OH group or cross-linking azacrown phosphonate groups. The crown rings in complex **4** are spaced farther apart than those in complex **3** since complex **4** contains a larger amount of spacers (HPO_4 groups). The crown ring is rigid and is not coordinated to the metal ion. The amount of spacers present in the structure controls the size of the pores formed.[11] The structures of complexes **1** and **2** also differ from those macrocylic leaflets that are common for phosphorylated mono-aza-crown ethers and their metal complexes.[8] We think that the degree of deprotonation of the ligand together with the nature of the metal ions has a strong effect on the structures of metal phosphonates isolated, as our previous studies indicated.[15−17] This conclusion has been well illustrated by ours as well as other previous studies on the metal phosphoantes with *N*-phosphonomethyl)iminodiacetic acid(H_4PMIDA).[15,16] Reaction of H_4PMIDA with various metal ions under different pH values yielded metal complexes with different types of structures isolated. The coordination modes adopted in these metal complexes depend on the degree of deprotonation of the H_4PMIDA and the nature of the metal ions.[15,16] Another good example showing the important role of deprotonation of ligand on the structural type of metal phosphonates is *N*-methyl-iminobis(methylenephosphonic acid) (CH_3NH-$(CH_2PO_3H_2)(CH_2PO_3H)$, H_4L'). Three types of divalent metal diphosphonates have been isolated: layered $M(H_3L')_2$·$2H_2O$ (M = Mn, Cd), $Zn(H_2L')(H_2O)$ featuring a double chain,

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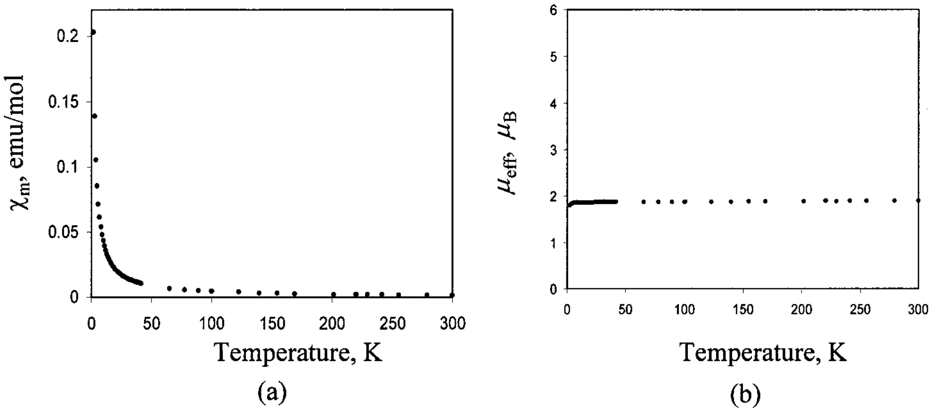

Figure 7. Magnetic property measurements for Cu(H_2L): (a) plot of the molar susceptibility (χ_m) as a function of temperature (T); (b) plot of the effective magnetic moments (μ_{eff}) as a function of the temperature (T).

and $Zn_3(HL')_2$ with a 3D network structure, in which one, two, and three protons/ligand have been removed, respectively.[17]

N,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 (H_4L), like phosphonomethyl-aza-15-crown-5 and phosphonomethyl-aza-18-crown-ether, exists as a zwitterion, a proton of each phosphonate group being transferred to an amine group (see Scheme 1).[8] These zwitterions are interconnected into a one-dimensional chain via pairs of hydrogen bonds between protonated phosphonate oxygen atoms and unprotonated phosphonate oxygen atoms, forming so-called "macrocyclic leaflets" in which the crown ether molecules are positioned as leaves on a twig.[8] It is much more difficult to remove the second proton of the phosphonate group and the proton of the amine group. By using a layering technique (very mild reaction conditions), phosphorylated aza-15-crown-5 and aza-18-crown-6 complexes with divalent and trivalent metal ions were obtained.[8] In the structures of this type of "macrocyclic leaflet", the stem of the leaflet is formed by metal ions bridged by phosphonate groups instead of hydrogen bonds as in the free ligands. The second proton on the phosphonate group is removed in the process, but the amine group remains protonated, which decreases the coordination ability of the crown ring to a metal ion. Thus, the crown ether molecule remains uncoordinated and only encapsulates a water molecule inside its cavity.[8]

Unlike aza-15-crown-5 and aza-18-crown-6, 1, 10-diaza-18-crown-6 has two amine groups. This additional amine group makes 1,10-diaza-18-crown-6 and its derivations better complexing agents for divalent metal ions such as copper(II) and cadmium(II) ions, as indicated by a large number of these complexes reported.[9] Upon complexation with copper(II) ions, the two amine groups of *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 are deprotonated. As the coordination ability of a phosphonate oxygen atom is stronger than that of a crown oxygen atom, and usually a copper(II) ion has a normal coordination number of 6, two crown oxygen atoms remain uncoordinated. The unidentately coordinated phosphonate group is still 1H-protonated; hence, these Cu(H_2L) units can be interlinked by hydrogen bonds into a 1D array. Each phosphonate group acts both as donor and acceptor of the hydrogen bonds. When the cadmium(II) ion with a larger ionic radius is used instead of a copper(II) ion and a ratio of metal/ligand of 2, complex **2** was formed. The phosphonate groups adopt a *cis* conformation instead of the *trans* one adopted in the copper(II) complex and the free ligand. The crown ring acts like a cap with two phosphonate groups as two ears hanging on the cap, which fits a 8-coordinated cadmium(II) ion very well. Both phosphonate groups are completely deprotonated; each of them connects with four cadmium(II) ions, resulting in a 3D network with large channels.

The coordination fashion of *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 in the copper(II) complex has a remarkable similarity with that of *N*,*N*′-bis(acetato)-1,10-diaza-18-crown-6 (H_4L). Such similarity was also found in metal complexes with phosphorylated and acetate derivatives of tetraazacycles.[10] However, the hydrogen bonding in metal complexes with the acetate derivatives is less important and also much weaker. The tetrahedral geometry of the 1H-protonated phosphonate group is a perfect donor and acceptor of hydrogen bonds.

Thermogravimetric Analysis. A TGA diagram of complex **1** shows two major weight losses. These two processes overlap. The first step is the release of a water molecule formed by the condensation of hydrogen phosphonate groups that starts at 272.9 °C, and the second step, the pyrolysis of the organic group, which is completed at about 806 °C. The final product is $Cu(PO_3)_2$, a metal metaphosphate. The total weight loss is 55.65%, which is in good agreement with the calculated weight loss of 56.53%. TGA analysis for complex **2** is not available due to the very small amount of sample available.

Magnetic Property Study. The results for Cu(H_2L) (complex **1**) are shown in Figure 7. The molar susceptibility increases with the decrease in temperature (Figure 7a). The dependence of the effective magnetic moment (μ_{eff}) for Cu(H_2L) complex is shown in Figure 7b. At room temperature the measured μ_{eff} of 1.90 μ_B corresponds to a copper(II) ion (1.73 μ_B). At 2 K, the μ_{eff} value is 1.80 μ_B; thus, there is no magnetic exchange interaction between copper(II) ions. From the crystal structural analysis, the Cu···Cu distances between two neighboring Cu(H_2L) units within a chain are 10.125(1) and 10.127(1) Å, respectively; the nearest Cu···Cu separation between two $Cu(H_2L)$ units from neighboring chains is 8.681(1) Å. These distances indicate that each copper(II) ion should be expected to behavior as an isolated copper(II) d^9 ion.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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