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Two d^{10}-Metal Coordination Polymers Constructed from Flexible Ligands: Syntheses, Crystal Structures, and Luminescent Properties[1]

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Abstract—Two new complexes, Zn(Glut)(Bix) · $2H_2O$ (**I**) and Cd(Pda)(Bimb) (**II**) (H_2Glut = glutaric acid, H_2Pda = 1,3-phenylenediacetic acid, Bix = 1,4-bis(imidazol-1-ylmethyl)benzene and Bimb = 1,4-di(1*H*-imidazol-1-yl)butane) were obtained under hydrothermal conditions by employing mixed ligands with metal salts and characterized by elemental analysis, IR, TGA, and Single crystal X-ray diffraction. Complex **I** presents a two-dimensional 2-fold interpenetrating layer structure. Whereas complex **II** is a two-dimensional layer network and exhibits a typical (4,4) topological net. The infrared spectra, thermogravimetric and luminescent properties were also investigated in detail for two complexes.

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INTRODUCTION

The rational design and construction of coordination polymers have received a great deal of attention because of their various architectures and topologies as well as their potential application in the fields of magnetism, electric conductivity, molecular adsorption, molecular recognition, and catalysis [1–4]. Many works have been devoted to the selection or design of suitable ligands containing certain features. Among the reported studies, organic ligands with carboxylate groups are of especial interest because they can adopt a variety of coordination modes and result in diverse multidimensional frameworks [5–7]. Most studies have been focused on the rigid carboxylate ligands, such as isophthalate (H_2Ip), 5-tertbutyl-isophthalate (H_2Tbip), 1,4-benzenedicarboxylate (H_2Bdc) and so on [8–11], however, coordination polymers containing flexible multicarboxylate ligands have been less reported to date [12–15]. The flexible multicarboxylate ligands can adopt various conformations according to geometric requirements when they react with different metal salts and may afford unpredictable and intriguing frameworks, which can help further understanding of the assembly process of supramolecular networks. Therefore, their assembly with metal ions holds much appeal to chemists.

On the other hand, flexible bis(imidazole) ligands bearing alkyl spacers, for example, 1,4-bis(1*H*-imidazol-1-yl)-butane (Bimb) [16], 1,4-bis(imidazol-1-ylmethyl)-benzene (Bix) [17] and 1,3-bis(imidazol-1-ylmethyl)-benzene (MBix) [18] can freely rotate to meet the requirement of coordination geometries of metal ions in the assembly process. These versatile coordination ligands are able to react with transition metal ions to produce unique structural motifs with beautiful aesthetics and useful functional properties. Very recently, a series of coordination polymers containing carboxylate ligands and Bix or MBix have been reported [19, 20]. From another point of view, coordination polymers containing metal ions with a d^{10} configuration, such as Zn(II), Cd(II) and Hg(II), are potential materials for optical applications, such as fluorescence probes and nonlinear optical materials [21]. Herein, we report the syntheses, crystal structures and luminescent properties of two complexes, namely, Zn(Glut)(Bix) · $2H_2O$ (**I**) and Cd(Pda)(Bimb) (**II**) (H_2Glut = glutaric acid, H_2Pda = 1,3-phenylenediacetic acid, Bix = 1,4-bis(imidazol-1-ylmethyl)benzene, and Bimb = 1,4-di(1*H*-imidazol-1-yl)butane).

EXPERIMENTAL

All the reagents and solvents for syntheses and analyses were commercially available and employed as received without further purification. The Bix and Bimb ligands were prepared according to the reported method [22]. Elemental analyses (C, H, and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. The luminescent spectra for the powdered solid samples were measured at room temperature on a Hitachi F-4500 fluorescence spectrophotometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were

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carried out under the same experimental conditions. Thermal gravimetric analyses (TGA) were performed on a Netzsch STA-409PC instrument in flowing N_2 with a heating rate of 10°C min^{-1}.

Synthesis of I. A mixture containing $Zn(NO_3)_2 \cdot 6H_2O$ (29.6 mg, 0.1 mmol), H_2Glut (13.2 mg, 0.1 mmol), Bix (23.8 mg, 0.1 mmol), and NaOH (8.0 mg, 0.2 mmol) in 15 mL deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 150°C for 3 days. Colorless needle crystals of **I** were collected by filtration and washed with water and ethanol several times with a yield of 52%.

IR (KBr; ν, cm^{-1}): 3475 br, 3068 m, 2929 m, 1609 m, 1563 s, 1522 m, 1489 m, 1388 s, 1357 m, 1301 w, 1271 w, 1173 m, 1052 m, 1042 m, 1016 w, 953 w, 908 w, 853 m, 821 m, 635 w, 486 w.

For $C_{19}H_{24}N_4O_6Zn$

anal. calcd., %:	C, 48.57;	H, 5.15;	N, 11.93.
Found, %:	C, 48.52;	H, 5.19;	N, 12.02.

Synthesis of II. A mixture containing $Cd(NO_3)_2 \cdot 4H_2O$ (61.6 mg, 0.2 mmol), H_2Glut (13.2 mg, 0.1 mmol), Bimb (19.0 mg, 0.1 mmol) and $LiOH \cdot H_2O$ (8.2 mg, 0.2 mmol) in 15 mL deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 160°C for 3 days. Colorless block crystals of **II** were collected by filtration and washed with water and ethanol several times with a yield of 38%.

IR (KBr; ν, cm^{-1}): 3424 br, 3055 m, 2926 m, 2881 w, 1611 s, 1574 s, 1520 m, 1428 w, 1387 s, 1315 w, 1276 w, 1225 m, 1112 w, 1078 s, 1015 m, 941 w, 810 w, 728 w, 574 w, 522 w.

For $C_{20}H_{22}N_4O_4Cd$

anal. calcd., %:	C, 48.55;	H, 4.48;	N, 11.32.
Found, %:	C, 48.49;	H, 4.47;	N, 11.35.

X-ray diffraction analysis. Single-crystal data for complexes **I** and **II** were obtained on a Bruker Smart Apex II CCD with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 293(2) K using the ω scan technique. The data were integrated by using the SAINT program [23], which was also used for the intensity corrections for the Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [24]. The structures were solved by direct methods using the SHELXS-97 program [25], and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [26]. The hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELTXL crystallographic software package [26]. The details of the crystal parameters, data collection, and refinements for **I** are summarized in Table 1. Selected bond lengths and bond angles with their estimated standard deviations are listed in Table 2. Atomic coordinates and other structural parameters have been deposited with the Cambridge Crystallographic Data Centre (nos. 785375 (**I**) and 785376 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The asymmetric unit of **I** consists of one Zn(II) center, one $Glut^{2-}$, one Bix ligand and two lattice water molecules. Each Zn^{2+} ion is surrounded by two nitrogen donors of two bridging Bix ligands and two carboxylate oxygen donors of two μ_2-Glut ligands, affording a distorted tetrahedral geometry (Fig. 1a). The Zn–O and Zn–N bond distances (1.9429(18)–1.9843(17) and 2.0086(19)–2.0635(19) Å) and the bond angles (98.26(8)°–126.21(8)°) in **I** are similar to those in other complexes [27].

In **I**, the Glut ligand adopts bis(monodentate) coordination. Along the crystallographic *y* axis, the Bix ligands bridge the Zn(II) centers to form parallel zigzag chains, which are interconnected to each other through the Glut ligands to result in the infinite (4,4) layer (Fig. 1b). In the layer, two Bix ligands, two Glut ligands, and four Zn atoms form a repeating rhombic grid with a side length of 9.072 × 14.919 Å and a diagonal measurement of 16.708 × 18.182 Å based on the metal–metal distances. Two independent (4,4) layers interpenetrate each other in an antiparallel fashion (Fig. 1c). The corrugated nature of the layer may be attributed to the backbone flexibility of Bix.

It must be remarked that the lattice water molecules are inserted into the interlayer space, and they are linked to one another to form 1D water chains through hydrogen bonding, as shown in Fig. 1d. Although the hydrogen atoms on water were located in the electron-density difference maps and refined according to the riding model, the reasonable positions to be assigned to all H-atoms of water molecules did not be finished successfully. However, the structural discussion is still valid with the geometry of hydrogen bonds (involving molecules of water) determined with confidence based on the O···O distances. In **I**, it should be noted that the water chains involves two hydrogen bonds with water–water interactions and water–carboxylate oxygen. Thus, the water chains can be considered as 'glue' between the 2D units that form a 3D supramolecular structure through above hydrogen bonding interactions.

As shown in Fig. 2a, the asymmetric unit of **II** comprises half of Cd^{2+} ion, half of Pda ligand, and half of Bimb ligand. The six-coordinated center shows a hexa vertax holyhedron with two oxygen atoms (O(2), O(2*A*)) from the carboxylic groups of two different Pda ligands and two nitrogen atoms (N(1), N(1*A*)) of separate Bimb ligands in the equatorial plane, as well as

Table 1. Crystallographic parameters and a summary of data collection and refinement for **I** and **II**

Parameter	Value	
	I	**II**
M	469.79	494.82
Size, mm	0.26 × 0.10 × 0.06	0.26 × 0.24 × 0.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a, Å	9.3372(4)	11.6332(6)
b, Å	27.6573(12)	12.8814(7)
c, Å	9.0717(4)	13.4106(7)
β, deg	116.218(1)	96.639(1)
V, Å^3	2101.67(16)	1996.13(18)
Z	4	4
ρ_{calcd}, mg m^{-3}	1.485	1.647
F(000)	976	1000
θ Range, deg	1.47–25.50	2.37–25.50
Reflections collected	16354	8054
Independent reflections (R_{int})	3907 (0.0333)	1871 (0.0198)
Parameters	287	133
Goodness-of-fit on F^2	1.032	1.055
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0339$, $wR_2 = 0.0870$	$R_1 = 0.0238$, $wR_2 = 0.0597$
R indices, all data	$R_1 = 0.0419$, $wR_2 = 0.0912$	$R_1 = 0.0251$, $wR_2 = 0.0607$
Large diff. peak and hole, e Å^{-3}	0.440/–0.353	0.519/–0.394

Note: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

two oxygen atoms (O(1), O(1*A*)) from two different Pda ligands occupied the apical positions. The Cd–O and Cd–N bonds are in the range of 2.378(2)–2.413(3) and 2.251(2) Å, respectively. In **II**, the Cd(II) centers are connected to each other by Bimb to afford a 1D zigzag chain along the crystallographic *z* direction (Fig. 2b), in which the distance between two adjacent Cd^{2+} ions is 14.090 Å and the Cd···Cd···Cd angle is 129.40°. Furthermore, the 1D zigzag chains are interlinked by the Pda anions, constituting step-shaped 2D (4,4) networks that stack in a parallel fashion.

To characterize the thermal stabilities of the two complexes, we carried out TGA analyses (Fig. 3). The experiments were performed on samples consisting of numerous single crystals of **I** and **II** under a nitrogen atmosphere with a heating rate of 10°C/min. The TGA curve of **I** shows that the first weight loss of 7.08% between 60 and 120°C corresponds to the loss of two lattice water molecules per formula unit (calcd. 7.66%), then it stable up to 260°C. The framework collapsed in the temperature range 260–550°C before the final formation of a metal oxide. For **II**, the weight loss begins with decomposition starting at 310°C and ending above 550°C. The remaining weight of 23.98% corresponds to the percentage (25.95%) of CdO.

Another striking feature of **I** and **II** is that they exhibit intense blue photoluminescence upon the radiation of UV light in the solid state at room temperature. The intense broad emission bands at 446 nm ($\lambda_{ex} = 367$ nm) for **I** and 469 nm ($\lambda_{ex} = 402$ nm) for **II** are observed. For excitation wavelengths between 280 and 480 nm, there is no obvious emission observed for

Table 2. Selected bond lengths and angles in **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–O(1)	1.9429(18)	Zn(1)–N(3)$^{\#2}$	2.0086(19)
Zn(1)–O(3)$^{\#1}$	1.9843(17)	Zn(1)–N(1)	2.0635(19)
		II	
Cd(1)–N(1)	2.251(2)	Cd(1)–O(1)	2.413(3)
Cd(1)–O(2)	2.378(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(1)Zn(1)O(3)$^{\#1}$	118.15(8)	O(1)Zn(1)N(1)	98.26(8)
O(1)Zn(1)N(3)$^{\#2}$	126.21(8)	O(3)$^{\#1}$Zn(1)N(1)	98.35(7)
O(3)$^{\#1}$Zn(1)N(3)$^{\#2}$	107.08(9)	N(3)$^{\#2}$Zn(1)N(1)	102.60(8)
		II	
N(1)$^{\#3}$Cd(1)N(1)	123.52(14)	O(2)Cd(1)O(1)	54.01(9)
N(1)Cd(1)O(2)$^{\#3}$	128.22(9)	N(1)Cd(1)O(1)$^{\#3}$	83.94(9)
N(1)Cd(1)O(2)	91.62(9)	O(2)Cd(1)O(1)$^{\#3}$	129.29(11)
O(2)$^{\#3}$Cd(1)O(2)	93.76(13)	O(1)Cd(1)O(1)$^{\#3}$	176.18(15)
N(1)Cd(1)O(1)	94.25(10)		

* Symmetry codes: $^{\#1}x, y, z + 1$; $^{\#2}-x + 2, y + 1/2, -z + 3/2$; $^{\#3}-x, y, -z + 1/2$.

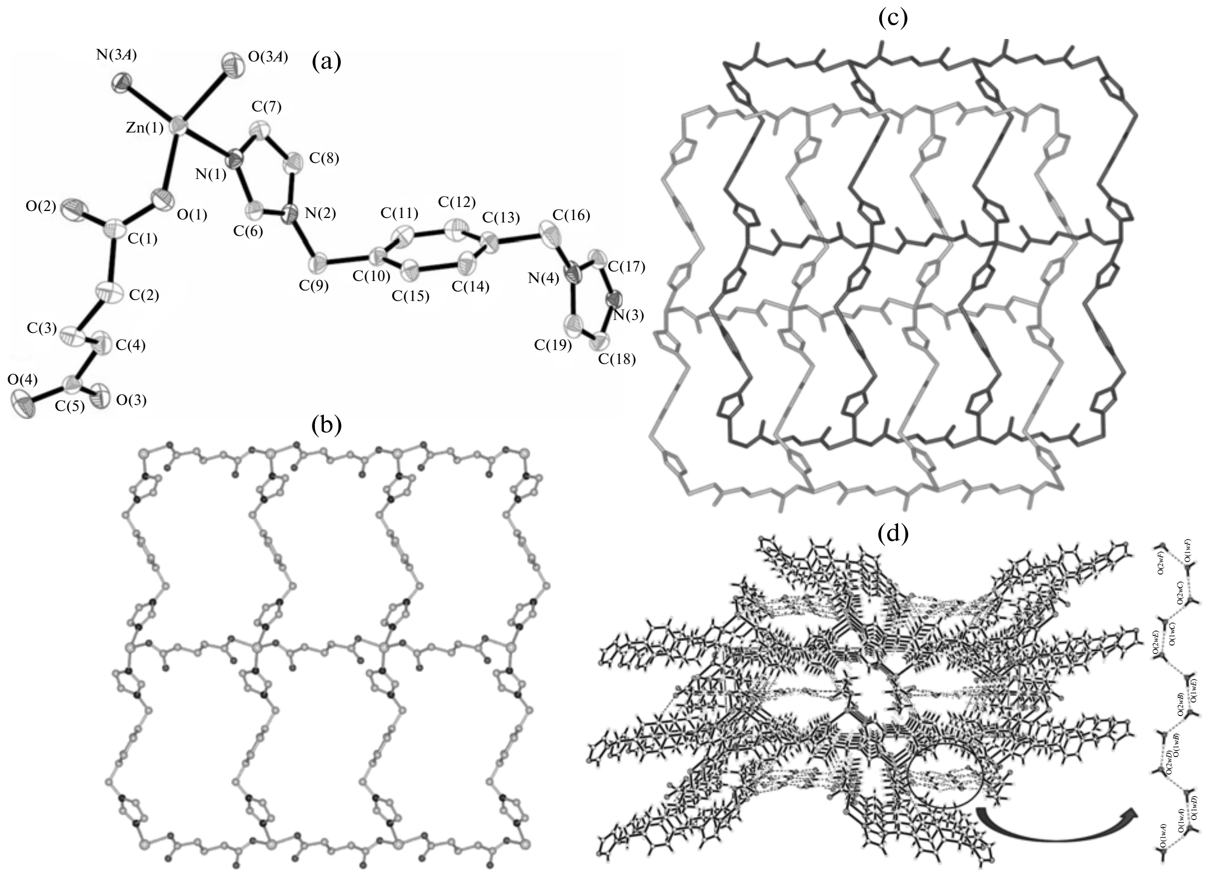

Fig. 1. Perspective view of the coordination environments of the Zn(II) atom in **I** with thermal ellipsoids at 30% probability (the lattice water molecules are omitted for clarity) (a); the two-dimensional network structure of **I** (b); perspective view of the two-fold interpenetrating 2D network of **I** (c); coordination environment of 1D water chains along the *z* axis (hydrogen bonds are donated as dashed line) (d).

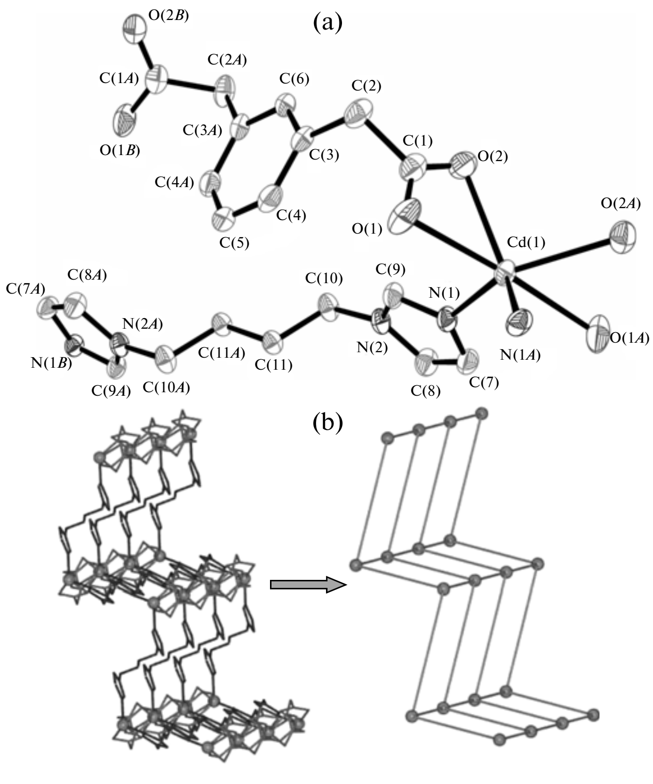

Fig. 2. Coordination environment of the Cd(II) atom in **II** with the ellipsoids drawn at the 30% probability level (hydrogen atoms were omitted for clarity) (a); the step-shaped 2D network of **II** (b).

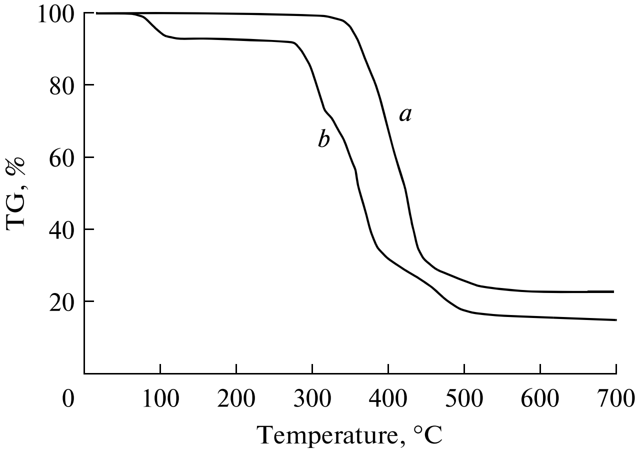

Fig. 3. TGA curves of complexes **I** (*a*) and **II** (*b*).

free H_2Pda and H_2Glut ligand under the same experimental conditions, while free Bix and Bimb ligand presents a photoluminescence emission at 393 nm (λ_{ex} = 342 nm) and 436 nm (λ_{ex} = 380 nm), respectively [28, 29]. In comparison with the Bix and Bimb ligands, the emission maximums of complexes **I** and **II** have changed. This may be attributable to a joint contribution of the intraligand $\pi^* \rightarrow \pi$ transitions, which effectively increase the rigidity of the ligand and reduce the loss of energy by nonradioactive decay, and charge transfer transitions between the coordinated ligands and the metal center [30–33]. These observations indicate that these condensed polymeric materials may be excellent candidates for potential photoactive materials, since they are thermally stable and insoluble in common polar and nonpolar solvents.

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