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Syntheses, Structures, and Photoluminescence Properties of Metal(II) Halide Complexes with Pyridine-Containing Flexible Tripodal Ligands

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Seven coordination compounds, $[Zn(L_3)Cl_2]\cdot MeOH\cdot H_2O$ (**1**), $[Mn(L_3)_2Cl_2]\cdot 0.5EtOH\cdot 0.5H_2O$ (**2**), $[Cu_3(L_2)_2Cl_6]\cdot 2DMF$ (**3**), $[Cu_3(L_2)_2Br_6]\cdot 4MeOH$ (**4**), $[Hg_2(L_4)Cl_4]$ (**5**), $[Hg_2(L_4)Br_4]$ (**6**), and $[Hg_3(L_4)_2I_6]\cdot H_2O$ (**7**), were synthesized by the reactions of ligands 1,3,5-tris(3-pyridylmethoxyl)benzene (L_3), 1,3,5-tris(2-pyridylmethoxyl)benzene (L_2), and 1,3,5-tris(4-pyridylmethoxyl)benzene (L_4) with the corresponding metal halides. All the structures were established by single-crystal X-ray diffraction analysis. In complexes **1** and **2**, L_3 acts as a bidentate ligand using two of three pyridyl arms to link two metal atoms to result in two different 1D chain structures. In complexes **3** and **4**, each L_2 serves as tridentate ligand and connects three Cu(II) atoms to form a 2D network structure. Complexes **5** and **6** have the same framework structure, and L_4 acts as a three-connecting ligand to connect Hg(II) atoms to generate a 3D 4-fold interpenetrated framework, while the structure of complex **7** is an infinite 1D chain. The results indicate that the flexible ligands can adopt different conformations and thus can form complexes with varied structures. In addition, the coordination geometry of the metal atom and the species of the halide were found to have great impact on the structure of the complexes. The photoluminescence properties of the complexes were investigated, and the Zn(II), Mn(II) and Hg(II) complexes showed blue emissions in solid state at room temperature.

Introduction

Coordination polymers containing transition metal ions and organic bridging ligands have been rapidly developed in recent years because of their fascinating structures and potential applications as functional materials in electronic, magnetic, optical, and catalytic fields.[1−6] Coordination interactions between labile metal centers and multidentate organic ligands form the primary structure which can be further organized to supramolecular structures through weak noncovalent interactions, such as hydrogen bonding and $\pi-\pi$ interactions.[7] Therefore, the key steps in building coordination polymers are to rationally design the ligand and to choose metal ions with suitable coordination geometry. Over

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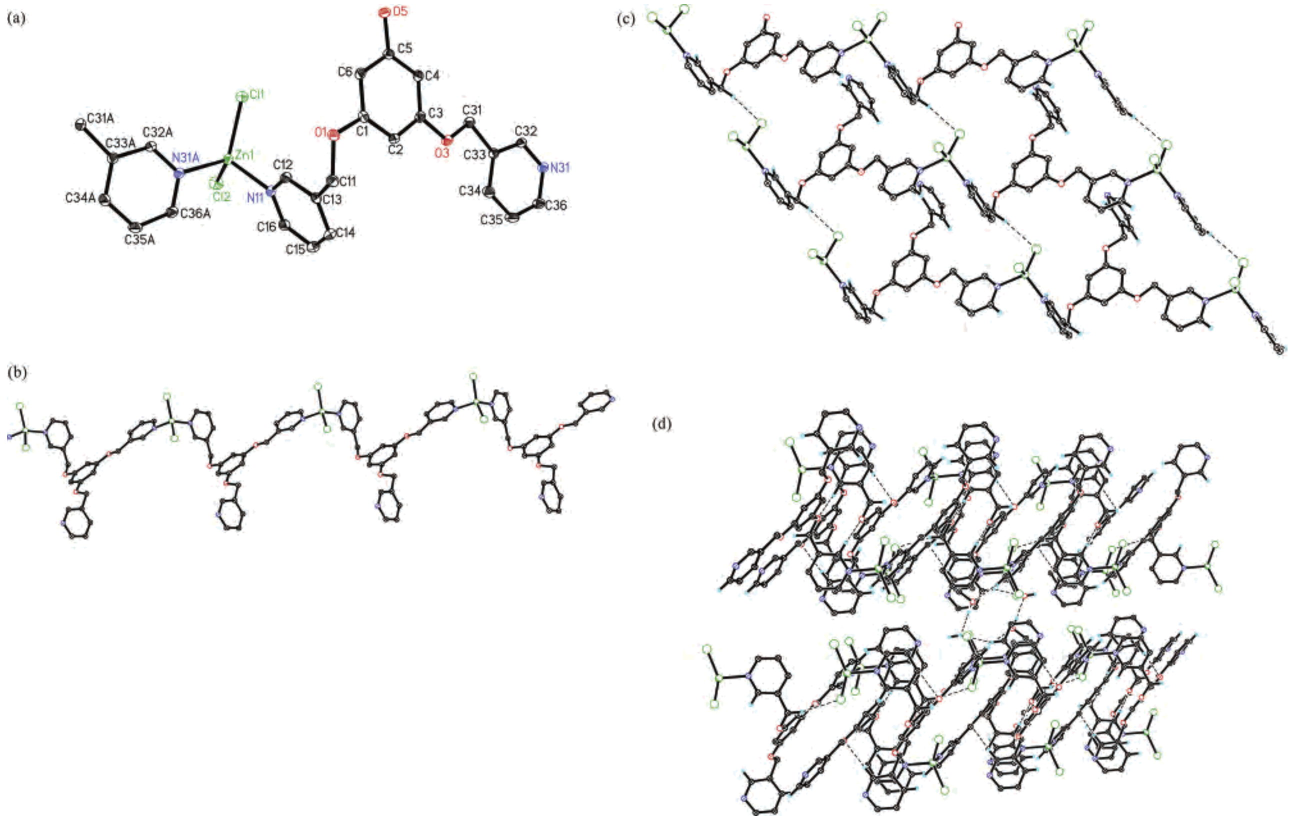

Figure 1. (a) Coordination environment around the Zn(II) atom in **1** with thermal ellipsoids at 50% probability displacement; the methanol, water molecules, and hydrogen atoms were omitted for clarity. (b) Infinite 1D chain structure of **1**. (c) 2D network in **1** formed through hydrogen bonds indicated by dashed lines. (d) Crystal packing diagram for **1**, in which the hydrogen bonds are indicated by dashed lines.

the past decades, there have been various examples of metal−organic coordination frameworks obtained by using pyridyl-based bridging ligands, including simple 2-connecting (4,4′-bipyridine),[8] 3-connecting (2,4,6-tripyridyl-1,3,5-triazine), and even, 4-connecting (tetrapyridylporphyrin) and 6-connecting ligands.[9,10] However, most of these reported pyridyl-based bridging ligands used in construction of the coordination frameworks are rigid. Coordination polymers with flexible pyridyl-based ligands are not well-known up to now, possibly because of the difficulties in predicting resulted structures. In contrast to the rigid ligands, the conformation of flexible ones is variable. Thus, they can meet the coordination geometrical requirement of metal ions through changing their conformation and can control and adjust the structure of the resulting coordination frameworks.

In recent years, we focused our attention on the synthesis, structure, and property of coordination frameworks with flexible organic ligands, for example, 1,3,5-benzenetriacetic acid and 1,3,5-tris(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene.[11] As an extension of our studies, we designed and synthesized three pyridine-containing tripodal ligands, 1,3,5-tris(2-pyridylmethoxyl)benzene (L_2), 1,3,5-tris(3-pyridylmethoxyl)benzene (L_3), and 1,3,5-tris(4-pyridylmethoxyl)benzene (L_4), and reactions of these ligands with various metal halides were carried out. Here, we report the crystal structure and photoluminescence properties of seven complexes $[Zn(L_3)Cl_2]\cdot MeOH\cdot H_2O$ (**1**), $[Mn(L_3)_2Cl_2]\cdot 0.5EtOH\cdot 0.5H_2O$ (**2**), $[Cu_3(L_2)_2Cl_6]\cdot 2DMF$ (**3**), $[Cu_3(L_2)_2Br_6]\cdot 4MeOH$ (**4**), $[Hg_2(L_4)Cl_4]$ (**5**), $[Hg_2(L_4)Br_4]$ (**6**), and $[Hg_3(L_4)_2I_6]\cdot H_2O$ (**7**).

Experimental Section

General Methods. All chemicals are of reagent grade obtained from commercial sources and used without further purification. Solvents of methanol (MeOH), ethanol (EtOH), *N*,*N*-dimethylformamide (DMF), acetonitrile (MeCN), etc. were purified according to the standard methods. Ligands L_2, L_3, and L_4 were prepared by a method similar to that reported for preparation of α,α′-bis-(3,5-bis(phenylthiamethyl)phenyloxy)-α″-phthalimidomesitylene.[12] C, H, and N analyses were made on a Perkin-Elmer 240C Elemental Analyzer at the Analysis Center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker Vector22 FT-IR spectro-

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Table 1. Crystallographic Data for Complexes **1**−**7**

	1	**2**	**3**
chemical formula	$C_{25}H_{27}Cl_2N_3O_5Zn$	$C_{49}H_{46}Cl_2N_6O_7Mn$	$C_{54}H_{56}Cl_6Cu_3N_8O_8$
fw	585.77	956.76	1348.39
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2/c$	$C2/m$
cryst size (mm)	0.20 × 0.15 × 0.05	0.20 × 0.15 × 0.01	0.25 × 0.25 × 0.10
a (Å)	8.902(5)	35.122(13)	23.799(12)
b (Å)	10.740(7)	7.767(3)	17.669(12)
c (Å)	14.633(7)	16.511(7)	7.973(4)
α (deg)	79.979(18)	90.00	90.00
β (deg)	78.027(15)	98.55(3)	108.314(15)
γ (deg)	83.597(19)	90.00	90.00
V, (Å^3)	1343.6(13)	4454(3)	3183(3)
Z	2	4	2
λ (Å)	0.71075	0.71075	0.71075
D_{calcd} (g cm^{-3})	1.448	1.427	1.407
μ(Mo Kα) (cm^{-1})	11.52	4.77	13.00
T (K)	200	200	200
unique reflns	6097	10 175	3751
R_{int}	0.0359	0.1208	0.0886
obsd reflns	4221	3342	2336
R1^a/wR2^b	0.0289/0.0530	0.0431/0.0430	0.0901/0.2399

	4	**5**	**6**	**7**
chemical formula	$C_{52}H_{58}Br_6Cu_3N_6O_{10}$	$C_{24}H_{21}Cl_4Hg_2N_3O_3$	$C_{24}H_{21}Br_4Hg_2N_3O_3$	$C_{48}H_{44}I_6Hg_3N_6O_7$
fw	1597.12	942.42	1120.26	2180.06
cryst system	monoclinic	orthorhombic	orthorhombic	triclinic
space group	$C2/m$	$Pbca$	$Pbca$	$P\bar{1}$
cryst size (mm)	0.20 × 0.20 × 0.04	0.17 × 0.15 × 0.12	0.15 × 0.15 × 0.15	0.10 × 0.10 × 0.10
a (Å)	24.299(11)	7.596(3)	7.7648(18)	15.427(3)
b (Å)	17.688(11)	24.397(6)	25.174(6)	16.466(4)
c (Å)	8.110(4)	28.642(6)	28.672(5)	24.960(5)
α (deg)	90.00	90.00	90.00	78.940(7)
β (deg)	106.954(15)	90.00	90.00	80.930(7)
γ (deg)	90.00	90.00	90.00	76.733(8)
V (Å^3)	3334(3)	5308(2)	5604(2)	6013(2)
Z	2	8	8	4
λ (Å)	0.71075	0.71075	0.71075	0.71075
D_{calcd} (g cm^{-3})	1.591	2.359	2.655	2.408
μ(Mo Kα) (cm^{-1})	45.96	119.91	166.79	107.69
T (K)	200	200	200	200
unique reflns	3918	6054	6402	27 222
obsd reflns	1753	4460	4478	12 435
R_{int}	0.1394	0.0704	0.0914	0.1221
R1^a/wR2^b	0.1094/0.2706	0.0513/0.1157	0.0570/0.1247	0.0948/0.2037

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = |\sum w(|F_o|^2 - |F_c|^2)|/\sum|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

photometer by using KBr pellets. The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with a xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the pass width is 5.0 nm.

Preparation of the Complexes. $[Zn(L_3)Cl_2]\cdot MeOH\cdot H_2O$ (1). A buffer layer of 5 mL of a methanol/water (4/1, v/v) mixed solvent was carefully layered over 0.8 mL of an aqueous solution of $ZnCl_2$ (16.4 mg, 0.12 mmol); then 6 mL of a methanol solution of L_3 (72 mg, 0.18 mmol) was layered over the buffer layer. Yellow platelet single crystals were obtained after four weeks in a 55% yield. Anal. Calcd for $C_{25}H_{27}Cl_2N_3O_5Zn$: C, 51.26; H, 4.64; N, 7.17. Found: C, 51.30; H, 4.40; N, 7.24. IR data (KBr pellet, cm^{-1}): 1610s, 1596s, 1439m, 1484m, 1166s, 1150s, 1057m, 816m, 703m.

$[Mn(L_3)_2Cl_2]\cdot 0.5EtOH\cdot 0.5H_2O$ (2). A solution of $MnCl_2\cdot 6H_2O$ (14.0 mg, 0.06 mmol) in EtOH (6 mL) was dropped slowly into a EtOH solution (6 mL) of L_3 (47.2 mg, 0.12 mmol) to give a clear pale yellow solution. The mixture was left to stand at ambient temperature for four weeks. Platelet colorless crystals were obtained in a 45% yield. Anal. Calcd for $C_{49}H_{46}Cl_2N_6MnO_7$: C, 51.26; H, 4.64; N, 7.17. Found: C, 51.30; H, 4.40; N, 7.24. IR data (KBr pellet, cm^{-1}): 1604s, 1483s, 1434m, 1162s, 1051m, 811m, 698m.

$[Cu_3(L_2)_2Cl_6]\cdot 2DMF$ (3). Complex **3** was prepared by mixing a 1:1.5 molar ratio of $CuCl_2\cdot 2H_2O$ (6.8 mg, 0.04 mmol) and ligand L_2 (24.0 mg, 0.06 mmol) in MeOH/MeCN/DMF (1/1/1, v/v) mixed solvent (12 mL). The reaction mixture was stirred for about 20 min. Dark blue single crystals suitable for X-ray diffraction were obtained in a 41% yield by slow diffusion of diethyl ether into the filtrate for several days. Anal. Calcd for $C_{54}H_{56}Cl_6Cu_3N_8O_8$: C, 48.10; H, 4.19; N, 8.31. Found: C, 47.99; H, 4.28; N, 8.38. IR data (KBr pellet, cm^{-1}): 1658m, 1609s, 1438m, 1387m, 1152s, 1059m, 824m, 766m.

$[Cu_3(L_2)_2Br_6]\cdot 4MeOH$ (4). The title complex was synthesized by similar procedures to those of complex **3** using $CuBr_2$ (8.9 mg, 0.04 mmol) instead of $CuCl_2\cdot 2H_2O$. Yield: 36%. Anal. Calcd for $C_{52}H_{58}Br_6Cu_3N_6O_{10}$: C, 39.11; H, 3.66; N, 5.26. Found: C, 39.03; H, 3.54; N, 5.37. IR data (KBr pellet, cm^{-1}): 1613s, 1448m, 1385m, 1168s, 1150s, 1059m, 809m.

$[Hg_2(L_4)Cl_4]$ (5). A solution of ligand L_4 (24.0 mg, 0.06 mmol) in acetonitrile (20 mL) was added dropwise into a solution (20 mL) of $HgCl_2$ (16.3 mg, 0.06 mmol) in methanol with stirring. Then the resulting mixture was filtered and allowed to stand at room temperature. Several days later, yellow crystals suitable for single-crystal X-ray diffraction analysis were obtained from the filtrate with an 80% yield. Anal. Calcd for $C_{24}H_{21}N_3O_3Cl_4Hg_2$: C, 30.59; H, 2.25; N, 4.46. Found: C, 30.85; H, 2.34; N, 4.55. IR data (KBr pellet, cm^{-1}): 1616s, 1593s, 1438m, 1385m, 1168s, 1072s, 1011m, 803m.

$[Hg_2(L_4)Br_4]$ (6). The complex was synthesized by method similar to that of complex **5** except that $HgCl_2$ was replaced by $HgBr_2$ (21.6 mg, 0.06 mmol) with an 82% yield. Anal. Calcd for $C_{24}H_{21}N_3O_3Br_4Hg_2$: C, 25.73; H, 2.03; N, 3.86. Found: C, 25.87; H, 2.12; N, 3.95. IR (KBr, cm^{-1}): 1612s, 1593s, 1435m, 1380m, 1172s, 1070s, 1011m, 806m.

$[Hg_3(L_4)_2I_6]\cdot H_2O$ (7). An acetonitrile solution (20 mL) of ligand L_4 (24.0 mg, 0.06 mmol) was slowly dropped into a methanol solution (20 mL) of HgI_2 (27.2 mg, 0.06 mmol) with stirring. The resulting mixture was filtered and allowed to stand at room temperature. Several days later, yellow crystals suitable for single-crystal X-ray diffraction analysis were obtained in a 78% yield. Anal. Calcd for $C_{48}H_{44}I_6Hg_3N_6O_7$: C, 26.45; H, 2.03; N, 3.86. Found: C, 26.71; H, 2.11; N, 3.97. IR data (KBr pellet, cm^{-1}): 1612s, 1598s, 1484m, 1445m, 1378m, 1170s, 1052m, 821m.

Crystallography. Thecrystallographic data for complexes **1**−**7** were collected using a Rigaku RAXIS−RAPID imaging plate diffractometer at 200 K, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71075$ Å). The structures were solved by direct methods with SIR92[13] and expanded using Fourier techniques.[14] All non-hydrogen atoms were refined anisotropically using the full-matrix least-squares method. The hydrogen atoms, except for those of the water molecules, were generated geometrically. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.[15] The C401, O401, and O402 atoms in complex **2**, the C11, C12, C13, C14, and N11 atoms in complex **3**, and the C11, C12, C13, C14, C15, C16, and N11 in complex **4** are disordered into two positions with a site occupation factor of 0.5.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**−**7**[a]

1							
Zn1−N11	2.0361(18)	Zn1−N31#1	2.0510(18)	Zn1−Cl1	2.2295(10)	Zn1−Cl2	2.2304(11)
N11−Zn1−N31#1	101.52(6)	N11−Zn1−Cl1	108.60(5)	N31−Zn1−Cl2#1	104.97(5)	Cl1−Zn1−Cl2	120.33(4)
N31−Zn1−Cl1#1	109.85(5)	N11−Zn1−Cl2	109.92(4)				
2							
Mn1−N131#3	2.297(3)	Mn1−N11	2.314(3)	Mn1−Cl1	2.5272(13)	Mn1−Cl2	2.5299(13)
Mn1−N111	2.344(3)	Mn1−N31#2	2.348(3)				
N131−Mn1−N11#3	178.65(11)	N131−Mn1−N111#3	83.75(9)	N111−Mn1−Cl1	89.76(7)	N31−Mn1−Cl1#3	90.70(7)
N11−Mn1−N111	94.91(9)	#3N131−Mn1−N31#3	96.45(9)	N131−Mn1−Cl2#3	88.28(8)	N11−Mn1−Cl2	91.59(7)
N11−Mn1−N31#3	84.89(9)	N111−Mn1−N31#3	179.50(11)	N111−Mn1−Cl2	90.84(7)	N31−Mn1−Cl2#3	88.71(7)
N131−Mn1−Cl1#3	90.89(7)	N11−Mn1−Cl1	89.26(8)	Cl1−Mn1−Cl2	178.91(4)		
3							
Cu1−N11	1.996(10)	Cu2−N31	1.997(5)	Cu1−O1	2.586	Cu2−O3	2.501
Cu1−Cl1	2.257(3)	Cu2−Cl2	2.279(2)				
N11−Cu1−N11#4	139.9(6)	N11−Cu1−N11#5	180.0	N31−Cu2−N31#6	180.0	Cl1−Cu1−Cl1#4	180.0
N11−Cu1−N11#4	180.0	N11−Cu1−N11#5	139.9(6)	N31−Cu2−Cl2	89.85(17)	N31−Cu2−Cl2#6	90.16(17)
N11−Cu1−Cl1	82.9(3)	N11−Cu1−Cl1	97.1(3)	N31−Cu2−Cl2#6	90.15(17)	Cl2−Cu2−Cl2#6	180.0
4							
Br1−Cu1	2.46(5)	Cu1−N11	1.963(12)	Cu1−O1	2.628	Cu2−O3	2.529
Br2−Cu2	2.4289(19)	Cu2−N31	1.998(9)				
N11−Cu1−N11#4	180.0	N11−Cu1−N11#4	135.3(9)	Br1−Cu1−Br1#4	180.0	N31−Cu2−N31	180.0
N31−Cu2−Br2	89.6(3)	N11−Cu1−Br1	77.3(8)	N31−Cu2−Br2	90.4(3)	N11−Cu1−N11#7	135.3(9)
N11−Cu1−Br1	102.7(8)	Br2−Cu2−Br2	180.0				
5							
Hg1−N11	2.325(7)	Hg1−Cl1	2.372(2)	Hg2−Cl3	2.410(3)	Hg2−Cl4#10	2.906(3)
Hg1−Cl2	2.378(2)	Hg1−N31#8	2.451(7)	Hg2−Cl3#9	2.968(3)	Cl3−Hg2#10	2.969(3)
Hg2−N51	2.250(7)	Hg2−Cl4	2.406(3)	Cl4−Hg2#9	2.906(3)	Cl3−Hg2−Cl3#9	93.04(8)
N11−Hg1−Cl1	104.26(19)	N11−Hg1−Cl2	107.03(19)	Cl4−Hg2−Cl3	128.28(11)	N51−Hg2−Cl4#10	87.6(2)
Cl1−Hg1−Cl2	139.52(9)	N11−Hg1−N31#8	101.8(2)	Cl4−Hg2−Cl4#10	94.96(9)	Cl3−Hg2−Cl4#10	85.69(9)
Cl1−Hg1−N31#8	97.85(19)	Cl2−Hg1−N31#8	100.18(19)	N51−Hg2−Cl3#9	94.7(2)	Cl4−Hg2−Cl3#9	177.74(9)
N51−Hg2−Cl4	108.8(2)	N51−Hg2−Cl3	122.9(2)				
6							
Hg1−N11	2.322(8)	Hg1−N31	2.406(9)	Hg2−Br3	2.5384(13)	Hg2−Br4#9	3.0264(16)
Hg1−Br2	2.5081(13)	Hg1−Br1	2.5169(13)	Hg2−Br3#10	3.0903(14)		
Hg2−N51	2.255(8)	Hg2−Br4	2.5284(15)				
N11−Hg1−Br2	109.1(2)	N11−Hg1−N31	103.8(3)	N51−Hg2−Br4#9	87.5(2)	Br4−Hg2−Br3	125.71(5)
N11−Hg1−Br1	103.9(2)	N31−Hg1−Br2	103.2(2)	Br3−Hg2−Br4#9	87.93(4)	Br4−Hg2−Br4#9	92.89(5)
Br2−Hg1−Br1	132.90(5)	N31−Hg1−Br1	100.4(2)	Br4−Hg2−Br3#10	86.72(4)	N51−Hg2−Br3#10	93.9(2)
N51−Hg2−Br3	125.0(2)	N51−Hg2−Br4	109.2(2)	#9Br4−Hg2−Br3#10	178.60(4)	Br3−Hg2−Br3#10	91.22(4)
7							
Hg1−N11	2.405(16)	Hg1−N111	2.418(14)	Hg4−N311	2.395(14)	Hg4−N211	2.407(18)
Hg1−I1	2.6278(18)	Hg1−I2	2.6530(18)	Hg4−I7	2.639(2)	Hg4−I8	2.6479(17)
Hg2−N131	2.400(17)	Hg2−N31	2.438(15)	Hg5−N331	2.387(18)	Hg5−N231	2.438(17)
Hg2−I3	2.638(2)	Hg2−I4	2.6621(18)	Hg5−I9	2.6327(18)	Hg5−I10	2.6525(15)
Hg3−N151#11	2.412(17)	Hg3−N51	2.442(16)	Hg6−N251	2.40(2)	Hg6−N351#11	2.425(16)
Hg3−I6	2.634(2)	Hg3−I5	2.667(2)	Hg6−I11	2.630(2)	Hg6−I12	2.666(2)
N11−Hg1−N111	89.3(5)	N11−Hg1−I1	107.2(4)	N311−Hg4−N211	91.2(6)	N311−Hg4−I7	100.8(4)
N111−Hg1−I1	103.5(4)	N11−Hg1−I2	104.5(4)	N211−Hg4−I7	104.0(5)	N311−Hg4−I8	106.7(4)
N111−Hg1−I2	103.1(4)	I1−Hg1−I2	138.39(6)	N211−Hg4−I8	105.0(5)	I7−Hg4−I8	139.15(6)
N131−Hg2−N31	90.5(5)	N131−Hg2−I3	105.2(5)	N331−Hg5−N231	89.4(6)	N331−Hg5−I9	107.2(4)
N31−Hg2−I3	102.3(4)	N131−Hg2−I4	105.1(4)	N231−Hg5−I9	102.6(4)	N331−Hg5−I10	103.4(4)
N31−Hg2−I4	105.1(4)	I3−Hg2−I4	138.53(7)	N231−Hg5−I10	104.3(5)	I9−Hg5−I10	139.12(6)
N151−Hg3−N51#11	91.6(6)	N151−Hg3−I6#11	104.6(4)	N251−Hg6−N351#11	91.0(6)	N251−Hg6−I11	107.3(5)
N51−Hg3−I6	106.5(4)	N151−Hg3−I5#11	101.4(4)	N351−Hg6−I11#11	107.8(4)	N251−Hg6−I12	101.8(5)
N51−Hg3−I5	100.5(4)	I6−Hg3−I5	141.61(11)	N351−Hg6−I12#11	101.0(4)	I11−Hg6−I12	138.16(10)

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

Results and Discussion

Structure Description of 1. The crystal structure of complex **1** is shown in Figure 1a. Each Zn(II) atom is coordinated by two Cl atoms and two N atoms of pyridine groups from two different L_3 ligands. The bond lengths of Zn−N and Zn−Cl range from 2.0361(18) to 2.2304(11) Å, and the bond angles of N−Zn−N, Cl−Zn−Cl, and N−Zn−Cl vary from 101.52(6) to 120.33(4)° (Table 2). Therefore, the coordination geometry of the Zn(II) atom is distorted tetrahedral. On the other hand, each L_3 ligand links two Zn(II) atoms to form an infinite one-dimensional (1D) chain structure (Figure 1b). It is noteworthy that only two of three pyridyl groups in each L_3 ligand take part in the coordination with metal atoms, while the additional one is free of coordination.

The 1D chains are further linked by hydrogen bonds to give rise to a three-dimensional (3D) structure. First, the adjacent 1D chains are linked by C−H···Cl hydrogen-bonding interactions to form a two-dimensional (2D) network as illustrated in Figure 1c. The C···Cl distance of 3.741(3)

Table 3. Hydrogen Bonding Data for Complexes **1**, **2**, **5**, and **6**[a]

D−H···A	D···A (Å)	D−H−A	D−H−A (deg)
1			
O11−H25···O12	2.776(3)	O11−H25−O12	178
O12−H26···Cl2#1	3.223(3)	O12−H26−Cl2	172
O12−H27···N51#2	2.802(3)	O12−H27−N51	177
C11−H5···Cl1#3	3.741(3)	C11−H5−Cl1	166
C12−H6···O1#4	3.292(3)	C12−H6−O1	144
C36−H15···O11#3	3.220(3)	C36−H15−O11	142
C52−H18···O3#5	3.463(3)	C52−H18−O3	164
C54−H19···O12#6	3.405(3)	C54−H19−O12	161
2			
C11−H11B···Cl2#7	3.735(4)	C11−H11B−Cl2	171
C111−H11D···Cl2#7	3.763(3)	C111−H11D−Cl2	168
C12−H12···Cl1	3.424(4)	C12−H12−Cl1	123
C131−H13B···Cl1#8	3.655(3)	C131−H13B−Cl1	157
C151−H15A···O402#9	3.512(8)	C151−H15A−O402	160
C16−H16···Cl2	3.392(4)	C16−H16−Cl2	129
C31−H31B···Cl1#8	3.758(3)	C31−H31B−Cl1	168
C32−H32···Cl2#10	3.375(4)	C32−H32−Cl2	126
C36−H36···Cl1#10	3.374(4)	C36−H36−Cl1	131
C401−H40B···N51#11	3.10(3)	C401−H40B−N51	152
C51−H51A···O401#12	3.460(8)	C51−H51A−O401	175
C54−H54···O3#13	3.338(4)	C54−H54−O3	143
C112−H112···Cl1	3.406(4)	C112−H112−Cl1	126
C116−H116···Cl2	3.378(4)	C116−H116−Cl2	132
C136−H136···O103#14	3.279(4)	C136−H136−O103	139
C136−H136···Cl1#10	3.404(3)	C136−H136−Cl1	121
C154−H154···O101#15	3.340(4)	C154−H154−O101	147
5			
C15−H8···Cl4#1	3.519(10)	C15−H8−Cl4	154
C31−H10···O5#16	3.479(11)	C31−H10−O5	165
C51−H17···Cl1#17	3.695(9)	C51−H17−Cl1	161
C52−H18···Cl4#18	3.346(9)	C52−H18−Cl4	126
6			
C15−H8···Br4#1	3.605(10)	C15−H8−Br4	156
C31−H11···O5#19	3.512(13)	C31−H11−O5	166
C51−H16···Br1#20	3.750(11)	C51−H16−Br1	157
C52−H18···Br4#21	3.415(12)	C52−H18−Br4	127

[a] Symmetry transformation used to generate equivalent atoms: #1 1 − *x*, 1 − *y*, 1 − *z*; #2 −1 + *x*, *y*, 1 + *z*; #3 −1 + *x*, *y*, *z*; #4 1 − *x*, −*y*, −*z*; #5 1 − *x*, 1 − *y*, −*z*; #6 *x*, *y*, −1 + *z*; #7 *x*, −1 + *y*, *z*; #8 *x*, −*y*, −1/2 + *z*; #9 1 − *x*, −1 + *y*, 3/2 − *z*; #10 *x*, 1 − *y*, −1/2 + *z*; #11 −*x*, 1 + *y*, 3/2 − *z*; #12 −*x*, −*y*, 1 − *z*; #13 −*x*, *y*, 1/2 − *z*; #14 *x*, 1 + *y*, *z*; #15 1 − *x*, *y*, 3/2 − *z*; #16 2 − *x*, 1 − *y*, 1 − *z*; #17 −1/2 + *x*, *y*, 1/2 − *z*; #18 1/2 + *x*, *y*, 3/2 − *z*; #19 −*x*, 1 − *y*, 1 − *z*; #20 1/2 + *x*, *y*, 1/2 − *z*; #21 −1/2 + *x*, *y*, 3/2 − *z*.

Å and the C−H−Cl angle of 166° indicate the formation of a C−H···Cl hydrogen bond in complex **1**. Similar C−H···Cl hydrogen bonds with C···Cl distances varying from 3.335 to 3.821 Å have been reported in an anion-templated rotaxane-like complex.[16a] Mukherjee et al. reported a series of coordination compounds with C−H···Cl hydrogen-bonding interactions.[16b,16c] Hydrogen-bonding data are summarized in Table 3. In addition, the uncoordinated N atom of pyridyl group in complex **1** acts as an acceptor to form an O−H···N hydrogen bond with water molecule, together with C−H···O and O−H···Cl hydrogen bonds to further link the 2D networks to generate the 3D framework structure (Figure 1d).

Structure Description of 2. To investigate the influence of metal center with different coordination geometry on the structure of resulting complex, the reaction of ligand L_3 with $MnCl_2·6H_2O$ was carried out, and complex **2** was isolated. The crystal structure of **2** is shown in Figure 2a. The Mn(II) atom is coordinated by four N atoms and two chloride anions with an octahedral coordination environment. The four N atoms from four different L_3 ligands are located in the equatorial plane with N−Mn−N angles varying from 83.75(9) to 179.50(11)°, and the Mn−N bond lengths range from 2.297(3) to 2.348(3) Å (Table 2). The two apical positions of each Mn(II) atom are occupied by two chloride anions with Mn1−Cl1 and Mn1−Cl2 bond lengths of 2.5272(13) and 2.5299(13) Å, respectively, which are longer than those of Mn−N bonds in the equatorial plane.

Similar to L_3 in complex **1**, there is one pyridyl group in each L_3 not coordinating with metal atom in complex **2**, and thus, each L_3 ligand acts as a bidentate ligand to bridge two Mn(II) atoms. Such a coordination mode makes complex **2** an infinite 1D chain structure (Figure 2b), which is obviously different from the 1D chain structure of complex **1** (Figure 1b). There are 28-membered $Mn_2(L_3)_2$ macrocycles within the 1D chain of **2** formed by two L_3 ligands and two Mn(II) atoms with a Mn(II)···Mn(II) distance of 8.26 Å. There are face-to-face $\pi-\pi$ interactions between the pyridine rings within the $Mn_2(L_3)_2$ cycle since the two pyridine ring planes with dihedral angle of 2.5° have a centroid-to-centroid distance of 3.60 Å as shown in Figure 3b, in which the $\pi-\pi$ interactions are indicated by dashed lines. Furthermore, the C−H···O hydrogen bonds connect the 1D chains to form a 2D network structure (Figure 2c). Then, C−H···N hydrogen bonds formed between the N atom of uncoordinated pyridine group of ligand L_3 and the solvent ethanol molecule with a C···N distance of 3.10(3) Å and a C−H−N angle of 152° (Table 3), together with C−H···Cl hydrogen bonds link the 2D networks to give a 3D structure (Figure 2d).

Structure Description of 3 and 4. Ligand L_2 was reacted with $CuCl_2·2H_2O$ and $CuBr_2$, respectively, to see the effect of the halide on the structure of the complexes. The structures of complexes **3** and **4** were determined by X-ray crystallographic analysis, and the results indicate that they have the same framework structure, although the uncoordinated solvent molecules are different. Thus, as an example, only the structure of complex **3** is described here in detail.

The structure analysis revealed that there are two crystallographically independent Cu(II) atoms in complex **3**, that the coordination environments of Cu1 and Cu2 are similar (Figure 3a), and that the bond lengths of Cu−Cl and Cu−N and bond angles of N−Cu−Cl around the Cu1 and Cu2 are also similar, as listed in Table 2. Each Cu(II) atom is coordinated by two chlorides and two N atoms from two different L_2 ligands. In addition, it is worth noting that the O atoms of ligand L_2 also participate coordination with the metal atom since the distances of Cu1−O1 and Cu2−O3 are 2.586 and 2.501 Å, respectively. A longer Cu−O distance of 2.790 Å has been reported in complex $Ca[Cu(OAc)_4]·6H_2O$ (OAc = acetate).[17] Therefore, each Cu(II) atom in complex **3** is six-coordinated with octahedral coordination geometry. In contrast to the fact that only two of three pyridyl groups of ligand L_3 are coordinated with metal atoms in

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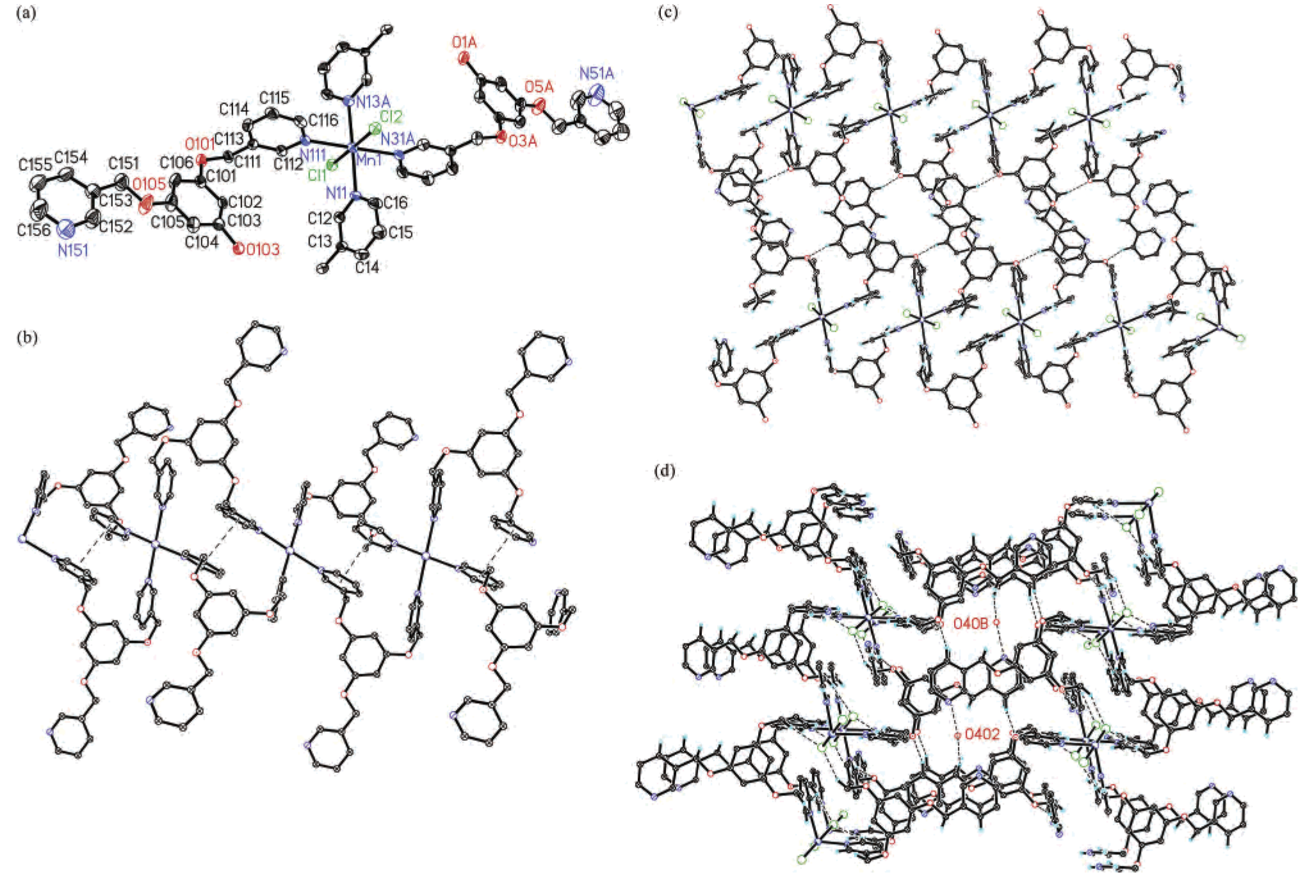

Figure 2. (a) Coordination environment around the Mn(II) atom in **2** with thermal ellipsoids at 50% probability; the ethanol, water molecules, and hydrogen atoms were omitted for clarity. (b) Infinite 1D chain structure of **2**, $\pi\cdots\pi$ interactions indicated by dashed lines. (c) 2D network of **2** formed by hydrogen bonds, which are indicated by dashed lines. (d) Crystal packing diagram for **2** in which the hydrogen bonds indicated by dashed lines.

complexes **1** and **2**, from Figure 3a, it can be clearly seen that the ligand L_2 acts as a three-connector using its three pyridyl groups to coordinate with three Cu(II) atoms. On the other hand, each Cu(II) atom links two L_2 ligands to generate a 2D network structure containing M_6L_6 macrocycles (Figure 3b).

From the crystal packing diagram of complex **3** as shown in Figure 3c, the 2D layers repeat in an ···AAA··· stacking sequence with open channels occupied by DMF molecules (by methanol molecules in complex **4**). There are face-to-face $\pi-\pi$ interactions between the two adjacent layers because the centroid-to-centroid distance between the two parallel pyridine ring planes is 3.97 Å (Figure S1).

Structure Description of 5 and 6. In addition to ligands L_3 and L_2 with 3- and 2-pyridyl groups, respectively, we also prepared a ligand with 4-pyridyl groups, namely, L_4. Reactions of ligand L_4 with $HgCl_2$, $HgBr_2$, and HgI_2 were carried out, and complexes **5**, **6**, and **7** were obtained. It is interesting that complexes **5** and **6** have the same structure, but the structure of complex **7** is different from that of **5** and **6**, as shown by the X-ray structure analysis (Table 1 and vide post). The results indicate that there is no great influence of Cl^- and Br^- on the structure of the complexes **5** and **6**, as well as **3** and **4** as mentioned above. However, the I^- has a remarkable impact on the structure of complex **7**.

Because complexes **5** and **6** have the same framework structure, only the structure of complex **5** is described here in detail. X-ray single-crystal diffraction analysis revealed that complex **5** crystallizes in orthorhombic space group *Pbca*. As exhibited in Figure 4a, complex **5** contains two kinds of Hg(II) atoms with different coordination environments. Furthermore, the chloride anions play two different roles in complex **5** (i.e., Cl1 and Cl2 coordinate with Hg1 as terminal ligands, while Cl3 and Cl4 serve as bridging ligands to link two Hg2 atoms to form an infinite Hg2(μ-Cl3, Cl4) 1D chain (Figure 4b)). However, all the chloride anions act as terminal ligands in complexes **1**, **2**, and **3**. Each Hg1 atom is coordinated by two N atoms from two different L_4 ligands and two terminal chlorides with N_2Cl_2 donor set. The terminal Hg−Cl distances are 2.378(2) and 2.372(2) Å (Table 2), respectively, which are similar to the previously reported terminal Hg−Cl distances (from 2.34(1) to 2.43(1) Å) in complex [(3,5-dimethylpyrazol-1-yl)methane]$HgCl_2$.[18] The Cl−Hg1−N angles are in the range from 97.85(19) to 107.03(19)°, and the angles of N11−Hg1−N31 and Cl1−Hg1−Cl2 are 101.8(2) and 139.52(9)°, respectively. Thus, the coordination geometry of Hg1 can be described as a distorted tetrahedron. The coordination environment of the Hg2 atom is different from that of Hg1. Each Hg2 is five-coordinated by one N atom from a L_4 ligand with a Hg2−N51 bond length of 2.250(7) Å, and the four remaining sites of Hg2 are occupied by four chloride anions, which act as

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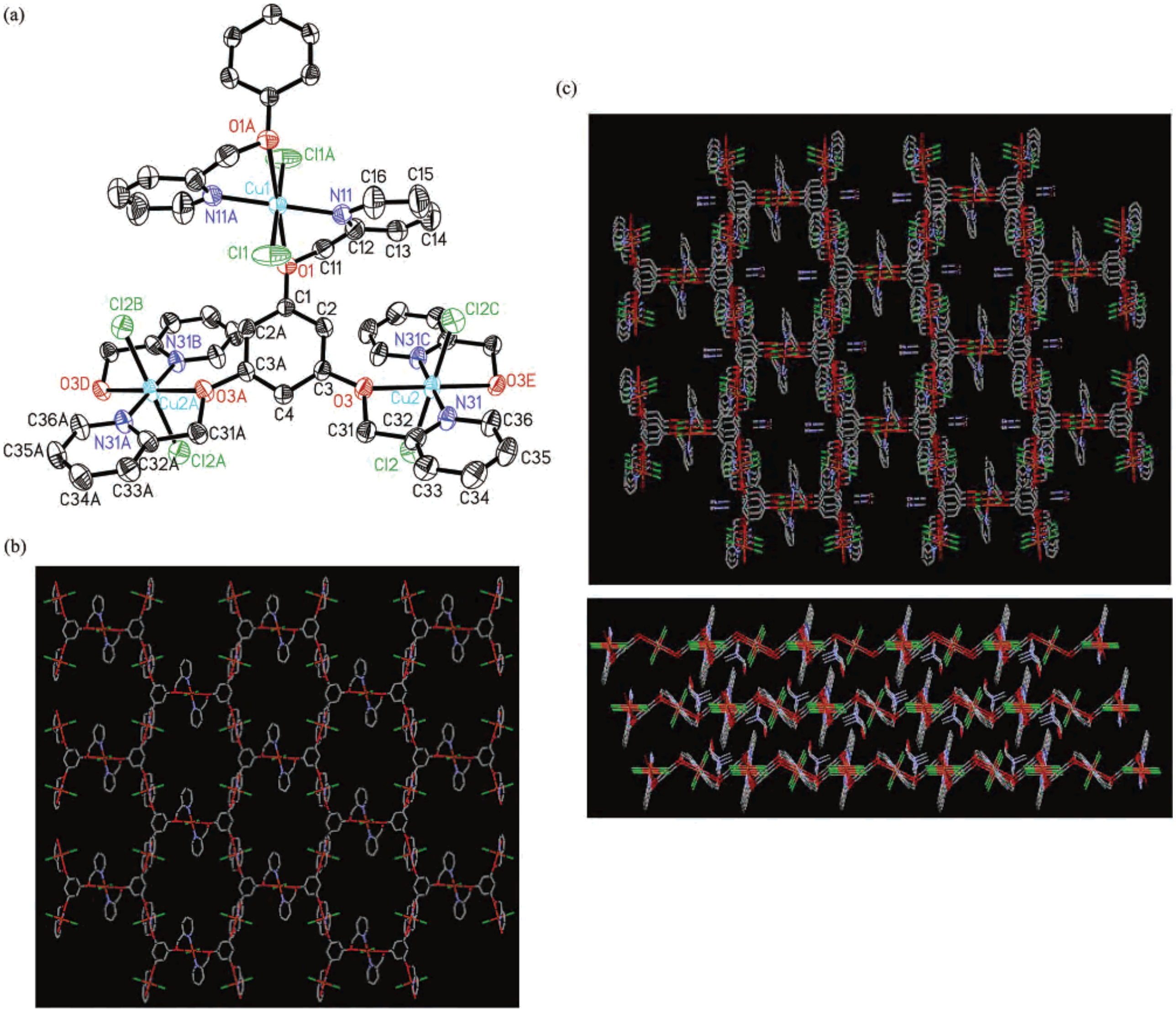

Figure 3. (a) Coordination environments of the Cu(II) atoms in complex **3** with thermal ellipsoids at 50% probability; the hydrogen atoms were omitted for clarity. (b) The 2D network structure of **3**, hydrogen atoms were omitted for clarity. (c) Top and side views of the crystal packing diagram of **3**.

bridges to link two Hg2 atoms (Figure 4a and b). The bridging Hg−Cl bond lengths are from 2.406(3) to 2.969(3) Å (Table 2), which is close to the reported bridging Hg−Cl bond lengths (from 2.368(3) to 2.909(2) Å) in the pentacoordinated Hg(II) complex, L^1HgCl_2 (L^1 = 2-[(E)-2-(4-methylphenyl)-1-diazenyl]pyridine),[19] but they are very different from those (from 2.317(8) to 3.240(8) Å) in the reported four-coordinated Hg(II) complex $[Hg(C{\wedge}N\text{-dpp})Cl]_2$ (dpp = 2,9-diphenyl-1,10-phenanthroline).[20] The bond angles of N−Hg2−Cl are in the range from 87.6(2) to 122.9(2)° and the Cl3A−Hg2−Cl4A bond angle is 177.74(9)° (Table 2); thus, the coordination geometry of Hg2 can be regarded to be a distorted trigonal bipyramid. On the other hand, each L_4 ligand acts as a three-connecting linker in complex **5** to link two Hg1 and one Hg2 atoms, while the Hg1 center servers as two-connecting node. Therefore, a 2D network structure is achieved as illustrated in Figure 4c, if the Hg2(μ-Cl3,Cl4) 1D chain linkage is neglected. Six L_4 ligands (each uses two of three arms) are linked together by eight Hg(II) atoms (four Hg1 and four Hg2) to form a M_8L_6 macrocycle, in which the separations (centroid of benzene ring-to-centroid of benzene ring) of X1A−X1B, X1B−X1C, X1C−X1D, X1D−X1E, X1E−X1F, and X1F−X1A are 19.78, 15.71, 15.71, 19.78, 15.71, and 15.71 Å, respectively (Figure 4c). The 2D networks are further held together by the Hg2(μ-Cl3,Cl4) 1D chain linkage to give a 3D coordination framework as shown in Figure 4d.

There are large 1D channels in each individual 3D framework of complex **5** (Figure 4d). The size of the channel is defined by the M_8L_6 macrocycle as mentioned above, which is large enough to include three additional such 3D frameworks, as exhibited in Figure 4e with formation of C−H···Cl and C−H···O hydrogen bonds (Table 3). In other words, the entire structure of complex **5** is a 3D framework with 4-fold interpenetration as schematically shown in Figure 4f.

Structure Description of 7. By variation of the halide, complex **7** was obtained. X-ray crystallographic analysis revealed that compound **7** crystallizes in the triclinic $P\bar{1}$ space

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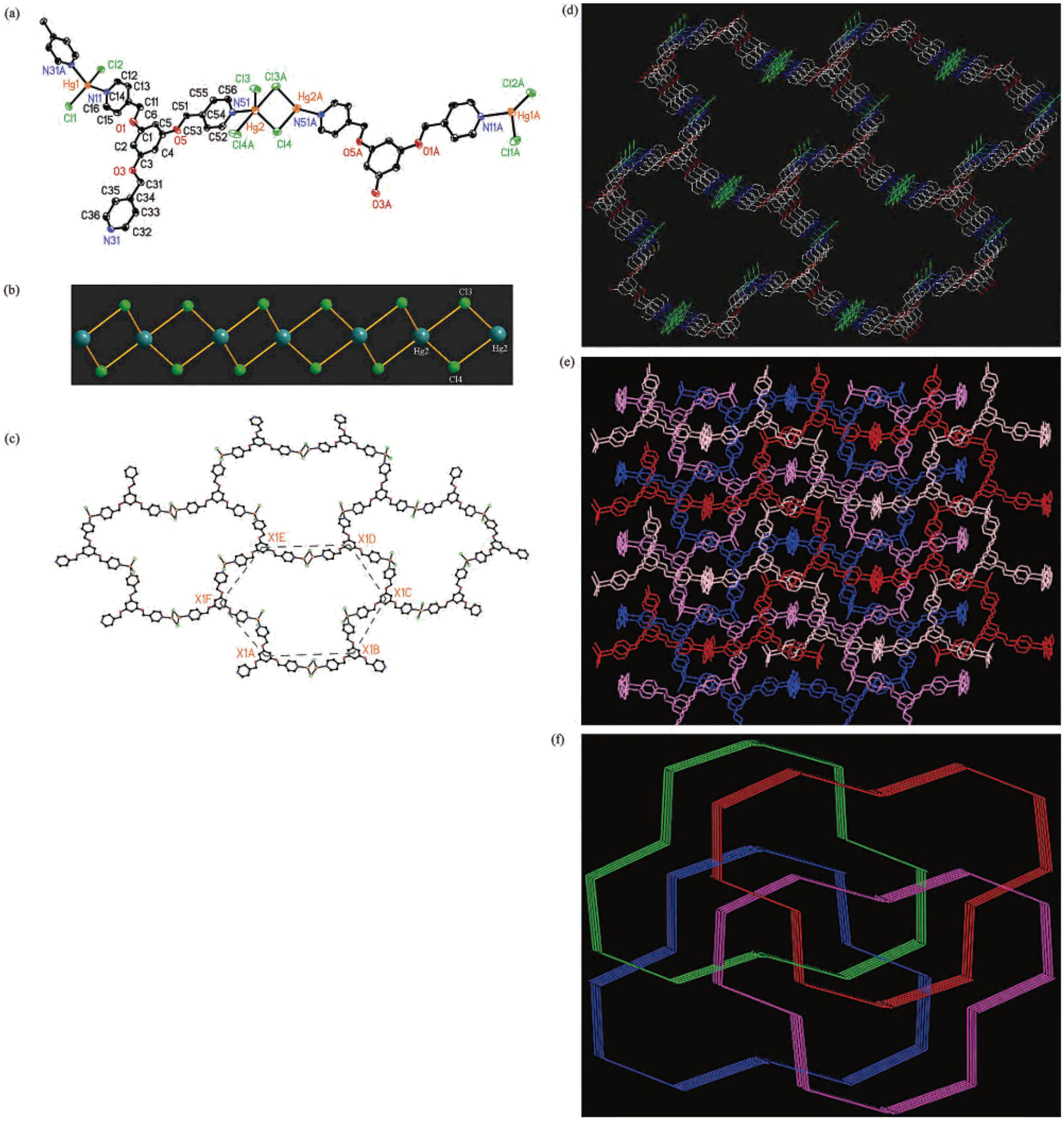

Figure 4. (a) Coordination environments of the Hg(II) atoms in **5** with thermal ellipsoids at 50% probability displacement; the hydrogen atoms were omitted for clarity. (b) 1D Hg2(μ-Cl3, Cl4) inorganic chain in **5**. (c) 2D network structure in **5**. (d) Single independent 3D framework structure of **5**. (e) View of 4-fold interpenetrated 3D structure of **5**. (f) Schematic drawing of 4-fold interpenetrated 3D structure of **5**.

group. The coordination environment around the Hg(II) center in the complex **7** is shown in Figure 5a with the atom numbering scheme. Each Hg(II) atom is coordinated by two N atoms from two different L_4 ligands and two iodide anions. The bond lengths of Hg−N range from 2.387(18) to 2.442(16) Å, and those of Hg−I vary from 2.6278(18) to 2.667(2) Å. The bond angles of N−Hg−I are in the range of 100.5(4)−107.8(4)°, and the ones of I−Hg−I are vary from 138.16(10) to 141.61(11)° (Table 2). So the coordination geometry around each Hg(II) center in complex **7** can be described as a distorted tetrahedron (Figure 5a). The deviation from tetrahedron is probably caused by the strong preference of metal for soft donors such as the I atoms with large atom size and weak preference for N atoms.[21,22]

On the other hand, each L_4 ligand acts as a three connector to link three Hg(II) atoms. It is interesting that each L_4 uses two of its three arms to join two Hg(II) atoms resulting in a 32-membered macrocycle with a Hg1⋯Hg2 distance of 15.98 Å; then the rings are further connected by coordination of Hg3 with the N atom of the third arm to give rise to an infinite 1D pearl-like chain structure as shown in Figure 5b. The 1D chains are repeated alternately in an ⋯ABAB⋯

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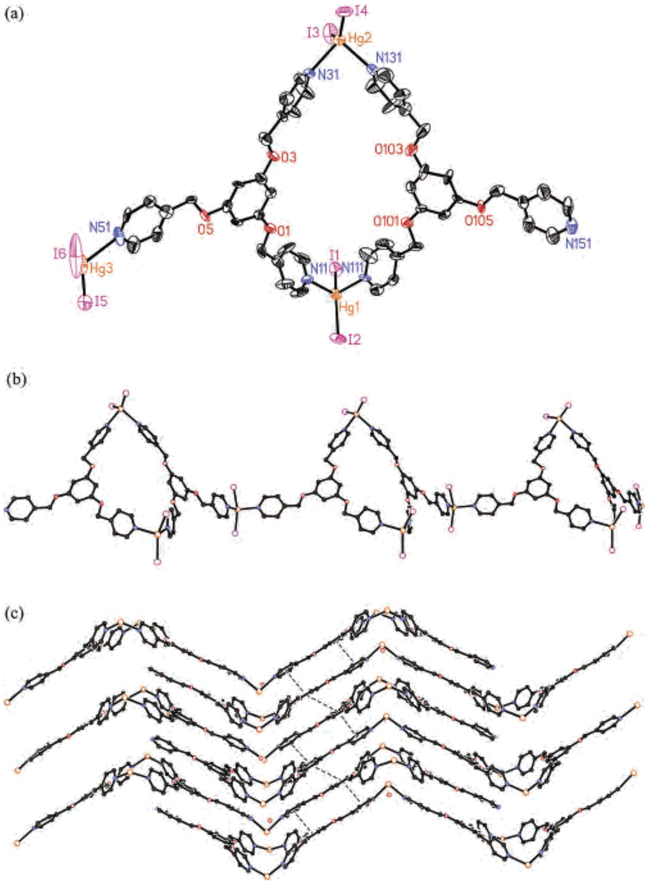


Figure 5. (a) Coordination environments of the Hg(II) atoms in **7** with thermal ellipsoids at 50% probability displacement; the hydrogen atoms were omitted for clarity. (b) Infinite 1D chain structure of **7**. (c) 2D layer structure of **7** with $\pi-\pi$ interactions indicated by dashed lines.

fashion and connected by $\pi-\pi$ interactions between the benzene and pyridine rings with a centroid-to-centroid distance of 3.56 Å and a dihedral angle of 6.3°, as well as between the two benzene rings with a centroid−centroid distance of 3.93 Å and a dihedral angle of 9.3° to give a 2D structure, as shown in Figure 5c, in which the $\pi-\pi$ interactions are indicated by dashed lines.

Comparison of the Structures. The X-ray crystallographic analysis revealed that complexes **1**−**7** have 1D chain (**1**, **2**, and **7**), 2D network (**3** and **4**), and 3D 4-fold interpenetrated framework (**5** and **6**) structures. Complexes **1** and **2** have the same ligand, L_3, and the same halide, chloride, but they have different 1D structures (Figures 1b and 2b) because of the different coordination geometries of Zn(II) and Mn(II),while the different structures of complexes **2** and **3** (Figures 2b and 3b) with the same halide, chloride, and the same coordination geometry of Mn(II) and Cu(II) are caused by the different ligands of L_3 and L_2. Complexes **5** (**6**) and **7** have the same ligand, L_4, and same metal centers, and thus, their different structures (Figures 4d and 5b) are contributed by the different halides of chloride and iodide. Furthermore, the halides coordinated with the metal atoms as terminal ligands in all complexes, except for those in complexes **5** and **6** with both terminal and bridging halides.

In addition, it is interesting that the ligands showed different conformations in complexes **1**−**7** as illustrated in Scheme 2. To elucidate the conformation of each ligand, the dihedral angles between the pyridyl ring and central benzene ring planes ($\varphi 1$) and the torsion angles of C1−O−C2−C3 ($\varphi 2$), as labeled in Scheme 1, were calculated, and the results are summarized in Table 4. When the value of $\varphi 1$ is close to 0 or 180°, it means that the pyridyl ring is close to being coplanar with the central benzene ring plane; otherwise, when the value of $\varphi 1$ is close to 90°, the pyridyl ring is nearly perpendicular to the central benzene ring. On the other hand, a value of $\varphi 2$ close to 0 implies that the flexible arm is extended to the central benzene ring plane, and a value of $\varphi 2$ near 90° indicates the flexible arm locates above or below the central benzene ring plane. According to the $\varphi 1$ and $\varphi 2$ values listed in Table 4, it is clear that flexible ligands L_2, L_3, and L_4 adopt different conformations in complexes **1**−**7** (Scheme 2). For example, ligand L_3 in **1** and **2** with different 1D chain structures showed different conformations: only one pyridyl group in **1** locates above the benzene ring plane, while in the case of **2**, both pyridyl groups coordinated with metal atoms locate above the benzene ring plane. In particular, all the small values of $\varphi 1$ and $\varphi 2$ of ligand L_4 in complex **5** indicate that ligand L_4 in **5** has an extended conformation, which is responsible for the large channel in the 3D structure and leads to 4-fold interpenetration of 3D frameworks as described above.

Scheme 1. Schematic Structure of Ligands L_2, L_3, and L_4

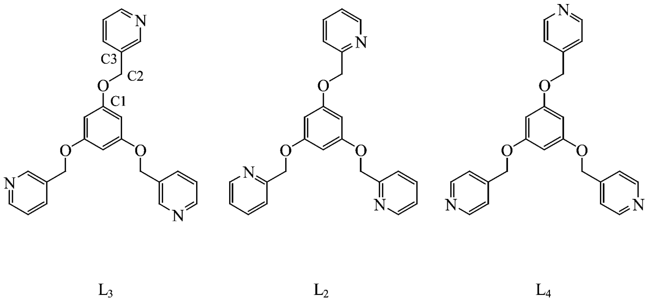


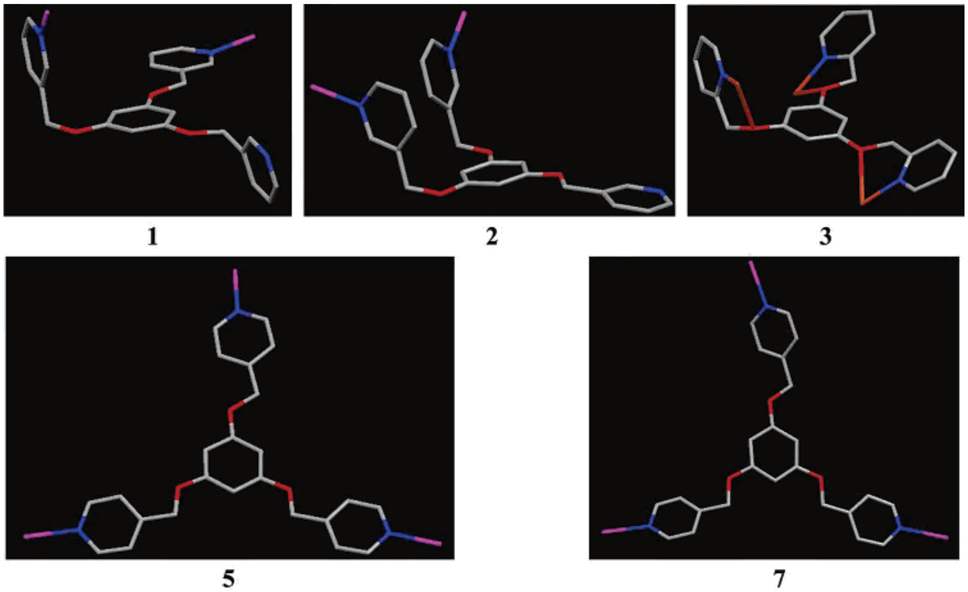
Table 4. Conformational Parameters for Complexes **1**−**7**

	$\varphi 1$ (deg)[a]	$\varphi 1$ (deg)	$\varphi 1$ (deg)	$\varphi 2$ (deg)[b]	$\varphi 2$ (deg)	$\varphi 2$ (deg)
1	89.7	3.6	81.7	107.6	1.0	16.9
2	103.2	97.6	13.4	90.8	112.6	12.2
3	92.3	143.5	143.5	91.5	12.4	12.4
4	83.1	143.2	143.2	93.7	12.3	12.3
5	15.4	4.6	4.1	3.4	2.6	4.0
6	13.7	4.2	5.3	3.4	2.1	4.9
7	47.9	147.7	6.3	3.4	2.2	7.4

[a] $\varphi 1$ refers to the dihedral angle between the pyridyl ring and central benzene ring planes. [b] $\varphi 2$ refers to the torsion angle defined by C1−O−C2−C3; C1, C2, and C3 are labeled in Scheme 1.

Luminescence Properties of Complexes. Coordination polymers have been reported to have ability to adjust the emission wavelength of organic materials through incorporation of metal centers.[23] Therefore, it is important to investigate the luminescence properties of coordination polymers in view of potential applications as light-emitting diodes (LEDs).[23] The luminescent behaviors of the ligands and complexes **1**−**7** were studied at room temperature in the solid state. No clear luminescence was detected for Cu(II)

Scheme 2. Different Conformations of Ligands in Complexes **1**, **2**, **3**, **5**, and **7**



complexes **3** and **4** under the experimental conditions. It has been reported that metal ions such as Cu(II) can quench the luminescence.[24] In contrast to **3** and **4**, intense photoluminescence was observed for complexes **1**, **2**, **5**, **6**, and **7**, and the emission spectra are shown in Figure 6. Complexes **1** and **2** with ligand L_3 exhibit photoluminescence with emissions at 402 and 425 nm, respectively, upon excitation at 352 nm, which is similar to that of ligand L_3 with an emission maximum at 420 nm under the same excitation wavelength. For complexes **5**, **6**, and **7**, blue emissions with maxima at 450, 452, and 457 nm were observed upon excitation at 396 nm, while free ligand L_4 displays an emission maximum at 420 nm under the same conditions. The observed emissions of complexes **1**, **2**, **5**, **6**, and **7** are probably contributed by the $\pi-\pi^*$ intraligand fluorescence since similar emissions were also observed for the ligands themselves.[25] The observed red or blue shift of the emission maximum between the complexes and the corresponding ligand was considered to mainly originate from the influence of the coordination of metal atom to the ligand.

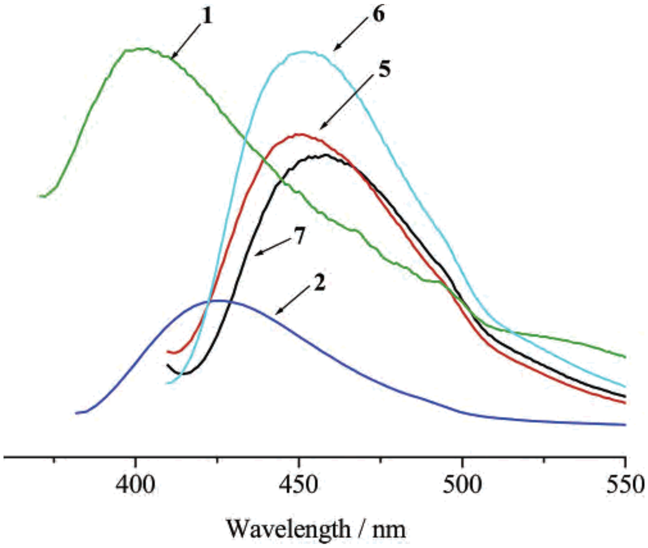


Figure 6. Emission spectra of complexes **1**, **2**, **5**, **6**, and **7** in the solid state at room temperature.

Conclusion

Three flexible tripodal ligands, L_2, L_3, and L_4, with 2-, 3-, and 4-pyridyl groups were prepared and used to react with metal halides of Zn(II), Mn(II), Cu(II), and Hg(II). Seven coordination complexes with 1D, 2D, and 3D framework structures were obtained, and their crystal structures and photoluminescence properties were investigated. The results showed that the flexible tripodal ligands can adopt varied conformations when they interact with metal atoms having different coordination requirement and thus form complexes with different structures. On the other hand, the halides of Cl^- and Br^- have no remarkable influence; however, the I^- has great impact on the structure of the complexes. The Zn(II)$-L_3$, Mn(II)$-L_3$, and Hg(II)$-L_4$ complexes showed blue fluorescence, while in the Cu(II)$-L_2$ complexes, no clear emissions were observed.

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Supporting Information Available: X-ray crystallographic data in CIF format and crystal packing diagram for **3** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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