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# Syntheses, Structures and Photoluminescence Properties of Ag(I), Cu(II), Zn(II) and Mn(II) Complexes with *N*,*N*′-Bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine

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Four novel coordination complexes, [Ag(bpb)]$NO_3 \cdot 2H_2O$ (**1**), [$Cu_2(CH_3COO)_4$(bpb)] (**2**), [$ZnCl_2(bpb)_2$] (**3**) and [$MnCl_2(bpb)_2$] (**4**) [bpb = *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine], with one-dimensional chain structures were synthesized and their structures were determined by X-ray crystallography. A structure analysis revealed that the bpb acts as a bridging ligand using two pyridyl N atoms to link two metal atoms, while the two imine N atoms do not participate in the coordination with the metal atoms. The photoluminescence properties of the title complexes were also studied. Although Cu(II) (**2**) and Zn(II) (**3**) complexes show intense violet-blue photoluminescence, no clear photoluminescence was observed for the Ag(I) (**1**) and Mn(II) (**4**) complexes.

Supramolecular chemistry is at the forefront of modern chemistry and recent years have witnessed a growing number of supramolecular systems which incorporate metal atoms as assembling and organizing centers.[1] Control of the molecular structure and topology is one of the major goals in supramolecular chemistry.[2,3] The self-assembly of these molecules is greatly influenced by such factors as the solvent,[4] template,[5] solution pH,[6] geometric requirements of metal ions and counter ions.[7] Thus employing transition metal ions and appropriate bridging organic ligands has become a dominant theme in the construction of supramolecular arrays.[8,9] Recently, coordination polymers of one- (1D), two- (2D) and three-dimensional (3D) infinite frameworks have been extensively studied. Infinite metal-organic frameworks are often assembled through the metal coordination of pyridone- or pyridine-based bridging ligands.[10–12] For example, the treatment of 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene (L) with $Cd(NO_3)_2$ generates a 1D chain with a backbone composed of a cyclic linkage with the stoichiometry of $ML_2$.[12]

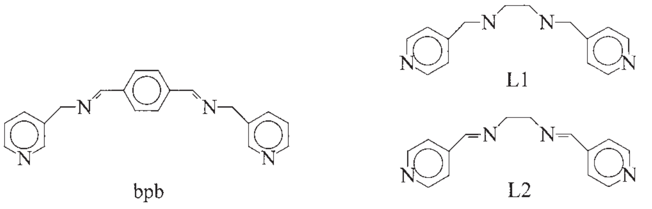

bpb L1 L2

Chart 1.

We have recently been exploring the assembly reaction of didentate and the bridging ligands 1,2-bis(4-pyridylmethylamino)ethane (L1) and 1,2-bis(4-pyridylmethyleneamino)ethane (L2) with transition-metal ions (Chart 1).[7,13] The results demonstrated that the flexible didentate and bridging ligand L1 gave 1D or 2D frameworks, depending on the metal ions and the counter anions, and the rigidity of organic ligand has a great effect on the construction of supramolecular frameworks. In order to further probe the influence of organic ligands on the formation of assemblies, we designed and synthesized a new flexible ligand, *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine (bpb), using the 1,4-benzenedimethylene group instead of the ethylene unit in L1 and L2. Here, we report on the syntheses, structural characterizations and properties of four novel compounds, namely [Ag(bpb)]$NO_3 \cdot 2H_2O$ (**1**), [$Cu_2(CH_3COO)_4$(bpb)] (**2**), [$ZnCl_2(bpb)_2$] (**3**) and [$MnCl_2(bpb)_2$] (**4**).

## Experimental

**General Procedures and Measurements.** All commercially available chemicals were of reagent-grade and used as received without further purification. Solvents were purified by the standard methods before use. Elemental analyses of C, H and N were taken on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. 500 MHz $^1$H NMR spectroscopic measurements were performed on a Bruker DRX-500 NMR spectrometer. Magnetic measurements on a poly-crystalline sample of complexes **2** and **4** were carried out using a CHAN-2000 Faraday magnetometer in the 75–300 K temperature range. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Diamagnetic corrections were made using Pascal's constants. Luminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer at room temperature (25 °C).

**Preparation of *N*,*N*′-Bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine (bpb).** This compound was synthesized by modified procedures reported for the preparation of $\alpha,\alpha'$-bis[di(2-pyridine)methylimino]-*m*-xylene.[14] Terephthalaldehyde (1.34 g, 0.01 mol) was dissolved in methanol (45 mL), and the solution was stirred for 0.5 h at room temperature; 3-(aminomethyl)pyridine (2.04

mL, 0.02 mol) was then added dropwise. The reaction mixture was refluxed for 8 h. After cooling to room temperature, the solution was concentrated, and then excess diethyl ether was added to the residue. After standing overnight at −18 °C, a white crystalloid solid was obtained by filtration, washed with diethyl ether and dried in a vacuum desiccator. Yield: 89%. Found: C, 76.36; H, 5.79; N, 17.62%. Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N 17.82%. $^1$H NMR ($CDCl_3$, 298 K) $\delta$ 4.87 (s, 4H), 7.31 (dd, $J = 7.8, 4.8$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 7.86 (s, 4H), 8.48 (s, 2H), 8.56 (d, $J = 4.8$ Hz, 2H), 8.65 (s, 2H).

**Preparation of [Ag(bpb)]$NO_3\cdot 2H_2O$ (1).** All procedures, for example the synthesis and measurement, were carried out in the dark. A mixture of $AgNO_3$ (34.0 mg, 0.2 mmol) in water (3 mL) and bpb (62.8 mg, 0.2 mmol) in acetonitrile (40 mL) was stirred for 10 minutes, and then filtered. Colorless crystals were obtained from the filtrate after standing for several days at room temperature. Yield: 70%. Found: C, 46.05; H, 4.49; N, 13.25. Calcd for $C_{20}H_{22}AgN_5O_5$: C, 46.17; H, 4.26; N, 13.46%. $^1$H NMR ($CD_3CN$, 298 K) $\delta$ 4.84 (s, 4H), 7.36 (dd, $J = 7.5, 4.5$ Hz, 2H), 7.76 (d, $J = 7.5$ Hz, 2H), 7.88 (s, 4H), 8.50 (s, 2H), 8.56 (d, $J = 4.5$ Hz, 2H), 8.61 (s, 2H).

**Preparation of [$Cu_2(CH_3COO)_4$(bpb)] (2).** A solution of $Cu(CH_3COO)_2\cdot H_2O$ (39.9 mg, 0.2 mmol) in methanol (6 mL) was carefully layered over a solution of bpb (62.8 mg, 0.2 mmol) in methanol (6 mL). After a few days, single crystals suitable for X-ray diffraction studies were obtained. Yield: 86% (based on copper acetate). Found: C, 49.70; H, 4.51; N, 8.10%. Calcd for $C_{28}H_{30}Cu_2N_4O_8$: C, 49.63; H, 4.46; N, 8.27%.

**Preparation of [$ZnCl_2(bpb)_2$] (3).** It was also prepared by a layering method using $ZnCl_2$ (13.6 mg, 0.1 mmol) in methanol (10 mL) and bpb (62.8 mg, 0.2 mmol) in methanol (10 mL). After a few days, crystals were obtained. Yield: 76%. Found: C, 62.57; H, 4.76; N, 14.57%. Calcd for $C_{40}H_{36}Cl_2N_8Zn$: C, 62.80; H, 4.74; N, 14.65%. $^1$H NMR (DMSO-$d_6$, 298 K) $\delta$ 4.83 (s, 4H), 7.39 (dd, $J = 7.5, 4.5$ Hz, 2H), 7.76 (d, $J = 7.5$ Hz, 2H), 7.87 (s, 4H), 8.48 (d, $J = 4.5$ Hz, 2H), 8.59 (s, 2H), 8.60 (s, 2H).

**Preparation of [$MnCl_2(bpb)_2$] (4).** This compound was obtained with a yield of 54% by the same method used for the preparation of **3** using $MnCl_2\cdot 4H_2O$ (19.8 mg, 0.1 mmol) instead of $ZnCl_2$. Found: C, 63.70; H, 4.88; N, 14.88%. Calcd for $C_{40}H_{36}Cl_2MnN_8$: C, 63.67; H, 4.81; N, 14.85%.

**Crystal Structure Determination.** The intensity data for the titled complexes were collected at 200 K on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.7107$ Å). The structures were solved by a direct method with SIR92,[15] expanded using Fourier techniques[16] and refined by a full-matrix least-square method anisotropically for non-hydrogen atoms. The hydrogen atoms, except for those of water molecules, were generated geometrically. All of the calculations were carried out on a SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.[17]

Details of the crystal parameters, data collection and refinements for complexes **1**, **2**, **3** and **4** are summarized in Table 1, and selected bond distances and angles are listed in Table 2.

## Result and Discussion

**Description of Crystal Structures.** The crystallographic study provides direct evidence for the structure of the complexes. As listed in Table 1, complexes **1**, **2**, **3** and **4** crystallize in the same crystal system with the same space group of $P\bar{1}$. However, the shapes of these complexes are different. Complexes **1** and **2** have zigzag and almost linear chain structures, respectively, while the structures of complexes **3** and **4** are hinged chains.

Figure 1 shows the crystal structure of complex **1** together with the atom numbering scheme. Each silver(I) atom is coordinated with two N atoms of the pyridyl unit from two different bpb ligands with nearly linear coordination geometry [N11–Ag–N21B = 174.0(2)°, Table 2]; in turn, each bpb ligand connects

Table 1. Crystallographic and Refinement Data for Complexes **1**, **2**, **3** and **4**

| Complex | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Chemical formula | $C_{20}H_{22}AgN_5O_5$ | $C_{28}H_{30}Cu_2N_4O_8$ | $C_{40}H_{36}Cl_2N_8Zn$ | $C_{40}H_{36}Cl_2MnN_8$ |
| Formula weight | 520.30 | 677.64 | 765.04 | 754.61 |
| Crystal system | triclinic | triclinic | triclinic | triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 9.2704(7) | 7.5582(7) | 7.6480(2) | 7.7188(5) |
| $b$/Å | 10.5258(6) | 8.3154(5) | 9.2949(5) | 9.3401(6) |
| $c$/Å | 11.7711(14) | 12.5861(11) | 12.7940(3) | 12.8647(6) |
| $\alpha$/° | 87.812(12) | 71.888(2) | 100.916(3) | 100.6707(12) |
| $\beta$/° | 73.059(10) | 77.723(4) | 102.547(3) | 102.597(5) |
| $\gamma$/° | 74.465(4) | 82.196(5) | 95.331(3) | 95.098(2) |
| Volume/Å$^3$ | 1057.63(16) | 732.57(10) | 863.14(6) | 881.38(9) |
| $Z$ | 2 | 1 | 1 | 1 |
| $D_{\mathrm{calcd}}$/g cm$^{-3}$ | 1.634 | 1.536 | 1.472 | 1.422 |
| $\mu$(Mo K$\alpha$)/mm$^{-1}$ | 0.995 | 1.507 | 0.910 | 0.569 |
| $F$(000) | 528 | 348 | 396 | 391 |
| Total data | 7566 | 6813 | 7240 | 8136 |
| Unique data | 4412 | 3303 | 3790 | 3979 |
| Observed data | 2658 | 2810 | 2454 | 3097 |
| No. of parameters | 280 | 190 | 232 | 232 |
| GOF on $F^2$ | 0.981 | 1.048 | 1.049 | 1.039 |
| $R$ indices [$(I) > 2\sigma(I)$] | 0.0763 | 0.0304 | 0.0643 | 0.0339 |
| $wR$ [$(I) > 2\sigma(I)$] | 0.1943 | 0.0732 | 0.1819 | 0.0807 |
| $R$ indices (all data) | 0.1243 | 0.0410 | 0.1109 | 0.0514 |
| $wR$ (all data) | 0.2175 | 0.0770 | 0.2033 | 0.0853 |

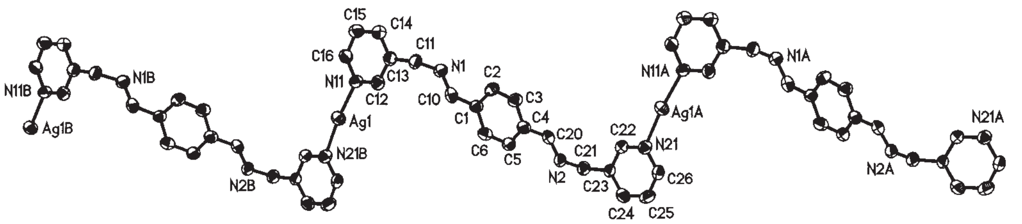


Fig. 1. Infinite 1D zigzag chain structure (cation part) of **1**. The anions, solvents and hydrogen atoms are omitted for clarity, and the thermal ellipsoids are drawn at 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **2**, **3** and **4**[a)]

| | | | |
|---|---|---|---|
| | | **1** | |
| Ag1–N21$^{\mathrm{i}}$ | 2.150(6) | Ag1–N11 | 2.160(6) |
| N21$^{\mathrm{i}}$–Ag1–N11 | 174.0(2) | | |
| | | **2** | |
| Cu1–O1 | 1.9661(15) | Cu1–O4$^{\mathrm{ii}}$ | 1.9732(15) |
| Cu1–O3 | 1.9675(16) | Cu1–N11 | 2.1797(17) |
| Cu1–O2$^{\mathrm{ii}}$ | 1.9683(15) | Cu1–Cu1$^{\mathrm{ii}}$ | 2.6288(5) |
| O1–Cu1–O3 | 89.56(7) | O2$^{\mathrm{ii}}$–Cu1–N11 | 93.95(6) |
| O1–Cu1–O2$^{\mathrm{ii}}$ | 168.10(6) | O4$^{\mathrm{ii}}$–Cu1–N11 | 94.24(7) |
| O3–Cu1–O2$^{\mathrm{ii}}$ | 89.05(7) | O1–Cu1–Cu1$^{\mathrm{ii}}$ | 85.41(5) |
| O1–Cu1–O4$^{\mathrm{ii}}$ | 88.07(7) | O3–Cu1–Cu1$^{\mathrm{ii}}$ | 85.61(5) |
| O3–Cu1–O4$^{\mathrm{ii}}$ | 168.15(6) | O2$^{\mathrm{ii}}$–Cu1–Cu1$^{\mathrm{ii}}$ | 82.71(4) |
| O2$^{\mathrm{ii}}$–Cu1–O4$^{\mathrm{ii}}$ | 90.89(7) | O4$^{\mathrm{ii}}$–Cu1–Cu1$^{\mathrm{ii}}$ | 82.63(5) |
| O1–Cu1–N11 | 97.95(6) | N11–Cu1–Cu1$^{\mathrm{ii}}$ | 175.36(5) |
| O3–Cu1–N11 | 97.59(7) | | |
| | | **3** | |
| Zn1–N11 | 2.269(4) | Zn1–N21$^{\mathrm{iii}}$ | 2.366(4) |
| Zn1–Cl1 | 2.4869(11) | | |
| N11–Zn1–N21$^{\mathrm{iv}}$ | 90.56(14) | N11$^{\mathrm{v}}$–Zn1–Cl1 | 89.49(11) |
| N11–Zn1–N21$^{\mathrm{iii}}$ | 89.44(14) | N21$^{\mathrm{iii}}$–Zn1–Cl1 | 89.60(10) |
| N11–Zn1–Cl1 | 90.51(11) | N21$^{\mathrm{iv}}$–Zn1–Cl1 | 90.40(10) |
| Cl1–Zn1–Cl1$^{\mathrm{v}}$ | 180.0 | N11–Zn1–N11$^{\mathrm{v}}$ | 180.0 |
| N21$^{\mathrm{iii}}$–Zn1–N21$^{\mathrm{iv}}$ | 180.0 | | |
| | | **4** | |
| Mn1–N11 | 2.2840(14) | Mn1–N21$^{\mathrm{iv}}$ | 2.3895(13) |
| Mn1–Cl1 | 2.5097(4) | | |
| N11–Mn1–N21$^{\mathrm{vi}}$ | 89.12(5) | N11–Mn1–Cl1 | 90.68(4) |
| N11–Mn1–N21$^{\mathrm{iv}}$ | 90.88(5) | N21$^{\mathrm{vi}}$–Mn1–Cl1 | 89.39(4) |
| N11–Mn1–Cl1$^{\mathrm{vii}}$ | 89.32(4) | N21$^{\mathrm{iv}}$–Mn1–Cl1 | 90.61(4) |
| Cl1–Mn1–Cl1$^{\mathrm{vii}}$ | 180.0 | N11–Mn1–N11$^{\mathrm{vii}}$ | 180.0 |
| N21$^{\mathrm{iv}}$–Mn1–N21$^{\mathrm{v}}$ | 180.0 | | |

a) Symmetry code: (i) $x, 1+y, -1+z$; (ii) $1-x, -y, 2-z$; (iii) $2-x, 1-y, 1-z$; (iv) $-2+x, -1+y, -1+z$; (v) $-x, -y, -z$; (vi) $2-x, 1-y, 2-z$; (vii) $-x, -y, 1-z$.

two silver(I) atoms to give a zigzag chain structure. The average Ag–N bond length of 2.155(6) Å of **1** is shorter than that of the silver(I) complex with the L1 ligand [2.360(3) Å].[13] It is noticeable that the imine N atoms of bpb did not participate in the coordination with the silver(I) atoms in **1**. However, in the case of the copper(I) complex of L2, two imine N and one pyridyl N atoms of the L2 coordinate to the metal atom.[7] From the crystal packing diagram of **1** shown in Fig. 2, it can be seen that the cationic chains and nitrate anions are connected by C–H···O hydrogen bonds. The existence and structural importance of such weak C–H···O hydrogen bonding interactions have been reported and discussed recently.[18] For example, the C–H···O hydrogen bonds have been observed in the complex $(C_{14}H_{12}N_2)[Cu(opba)]\cdot 3H_2O$ [opba = *o*-phenylenebis(oxamate)] with C–O distances ranging from 3.231(3) to 3.448(17) Å.[18a] The data of the hydrogen bonds for the complexes **1**–**4** are summarized in Table 3.

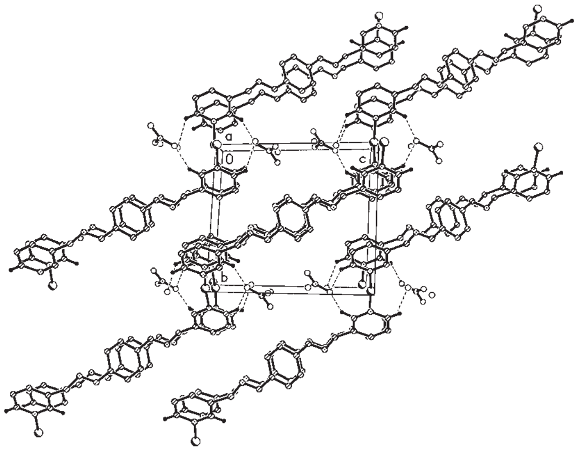


Fig. 2. Crystal packing diagram of complex **1** on *bc* plane with hydrogen bonds indicated by dashed lines.

A single-crystal X-ray structure analysis revealed that compound **2** is composed of dicopper tetracarboxylate units (Fig. 3) with a short Cu–Cu internuclear separation of 2.6288(5) Å, which is longer than that observed in $[Cu_2(CH_3COO)_4(H_2O)_2]$ [Cu···Cu: 2.616(1) Å].[14] The average bond length of the Cu–O bonds [1.9688(15) Å] is almost the same as that observed in $[Cu_2(CH_3COO)_4(H_2O)_2]$. Each copper(II) atom is in a square-pyramidal coordination geometry, neglecting the Cu–Cu interaction, with one pyridyl N atom from bpb ligand and four O atoms of four bridging acetate anions. The copper(II) atom is displaced by about 0.203 Å from the mean plane of four O atoms towards the pyridyl N atom, at the apical position of the pyramid with a Cu–N distance of 2.1797(17) Å (Table 2). Each bpb ligand links two dicopper tetracarboxylate units to generate a 1D linear sawtooth chain (Fig. 3). The 1D chains in complex **2** were further connected by inter-chain C–H···O hydrogen bonds (Table 3) to form a 2D network structure, as illustrated in Fig. 4. The bulk of the dicopper tetracarboxylate unit makes the ligand bpb adopt a near linear conformation.

In complexes **1** and **2**, each metal atom was coordinated with two pyridyl N atoms from two bpb ligands, as mentioned above. However, in the case of complexes **3** and **4**, both zinc(II) and manganese(II) atoms are six-coordinated with a $N_4Cl_2$ binding set

Table 3. Distances (Å) and Angles (deg) of Hydrogen Bonding for Complexes **1**, **2**, **3** and **4**$^{a)}$

| | | **1** | |
|---|---|---|---|
| D–H···A$^{b)}$ | Distance (D···A) | D–H–A | Angle (D–H–A) |
| C12–H8···O3$^{i}$ | 3.212(5) | C12–H8–O3$^{i}$ | 142.5 |
| C16–H11···O4 | 3.286(5) | C16–H11–O4 | 136.4 |
| C21–H13···O3$^{ii}$ | 3.412(5) | C21–H13–O3$^{ii}$ | 141.6 |
| C22–H15···O4 | 3.339(5) | C22–H15–O4 | 135.6 |
| C26–H18···O3$^{i}$ | 3.310(5) | C26–H18–O3$^{i}$ | 140.9 |
| | | **2** | |
| C3–H2···O2$^{iii}$ | 3.422(5) | C3–H2–O2$^{iii}$ | 160.1 |
| C32–H10···O1$^{iv}$ | 3.457(5) | C32–H10–O1$^{iv}$ | 150.5 |
| | | **3** | |
| C21–H14···Cl1$^{v}$ | 3.724(5) | C21–H14–Cl1$^{v}$ | 161.8 |
| C22–H15···Cl1$^{vi}$ | 3.350(5) | C22–H15–Cl1$^{vi}$ | 131.2 |
| C26–H18···Cl1$^{vii}$ | 3.390(5) | C26–H18–Cl1$^{vii}$ | 129.7 |
| | | **4** | |
| C21–H14···Cl1$^{v}$ | 3.7566(18) | C21–H14–Cl1$^{v}$ | 161.5 |
| C22–H15···Cl1$^{viii}$ | 3.3681(18) | C22–H15–Cl1$^{viii}$ | 131.8 |
| C26–H18···Cl1$^{vii}$ | 3.4174(17) | C26–H18–Cl1$^{vii}$ | 130.0 |

a) Symmetry code: (i) $1-x, -y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, -z$; (iv) $1-x, 1-y, -z$; (v) $1+x, 1+y, 1+z$; (vi) $2-x, 1-y, 1-z$; (vii) $2+x, 1+y, 1+z$; (viii) $2-x, 1-y, 2-z$. b) D: donor; A: acceptor.

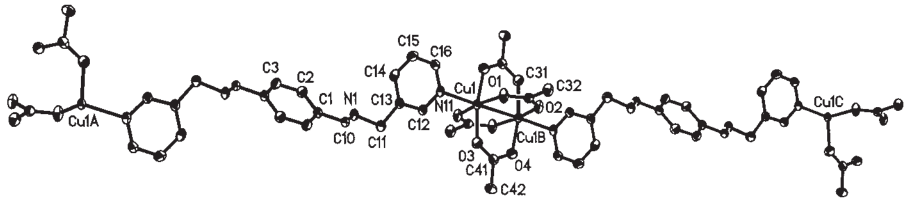


Fig. 3. Crystal structure of complex **2** with the thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

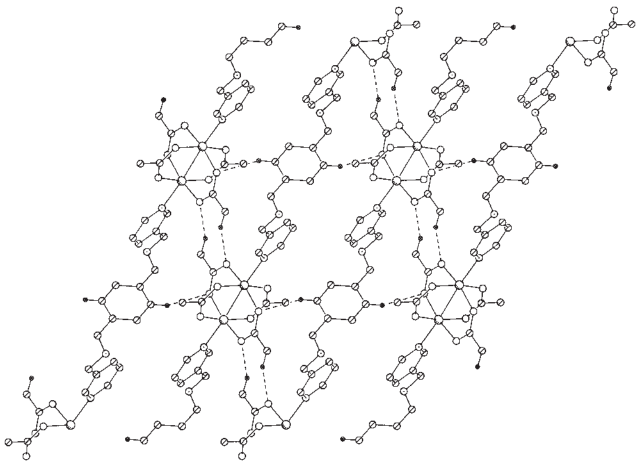


Fig. 4. 2D network structure of complex **2** with hydrogen bonds indicated by the dashed lines.

and a distorted octahedral geometry. From the crystal data listed in Table 1, it is clear that complexes **3** and **4** are isomorphous and isostructural. Figure 5 shows the structure of complex **3** with the atom-labeling scheme. The zinc(II) atom is coordinated by four pyridyl N atoms from four different bpb ligands, and the two additional positions are occupied by two chloride atoms with the *trans* configuration. Each bpb ligand in turn binds to two metal atoms to generate an infinite 1D hinged chain structure (Fig. 5). A similar hinged chain structure was observed in the silver(I) complex with the L1 ligand.[13a] The 1D chains were further connected by inter-chain C–H···Cl hydrogen bonds to form a 3D structure (Fig. 6). The distances of C···Cl are in the range of 3.350(5)–3.724(5) Å and the C–H–Cl angles are in the range from 129.7 to 161.8° (Table 3), which indicate the formation of C–H···Cl hydrogen bonds. Similar C–H···Cl interactions with C–Cl distances ranging from 3.335 to 3.821 Å have been reported in a anion-templated rotaxane-like complex and discussed in detail recently.[19]

It is noteworthy that the conformations of the bpb ligand are different in complexes **1**, **2** and **3** (as well as **4**). The bpb ligand has "Z" and "L" shapes in complexes **1** and **3** (**4**), respectively, while the conformation of the bpb ligand in **2** is almost linear. Such difference in the conformation of the bpb ligand causes different intra-chain metal-metal distances in complexes **1**, **2**, **3** and **4**. The longest intermetallic distance of 20.81 Å (e.g. Cu1···Cu1A and Cu1B···Cu1C in Fig. 3) was observed in complex **2** with a near linear conformation of the bpb ligand; the shortest one (15.49 Å) appeared in complex **1** with a "Z" shape of the bpb ligand. The

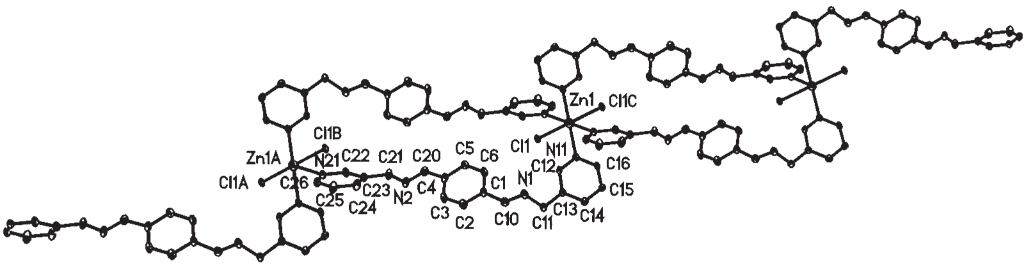


Fig. 5. Atomic displacement ellipsoid drawing (50% probability level) and atomic labeling system for the complex **3**. Hydrogen atoms are omitted for clarity.

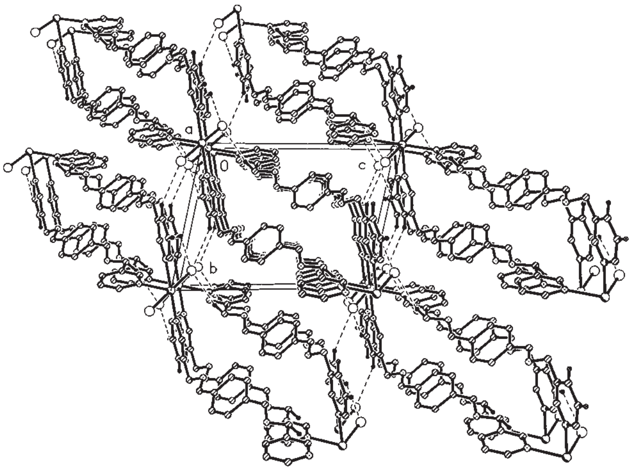


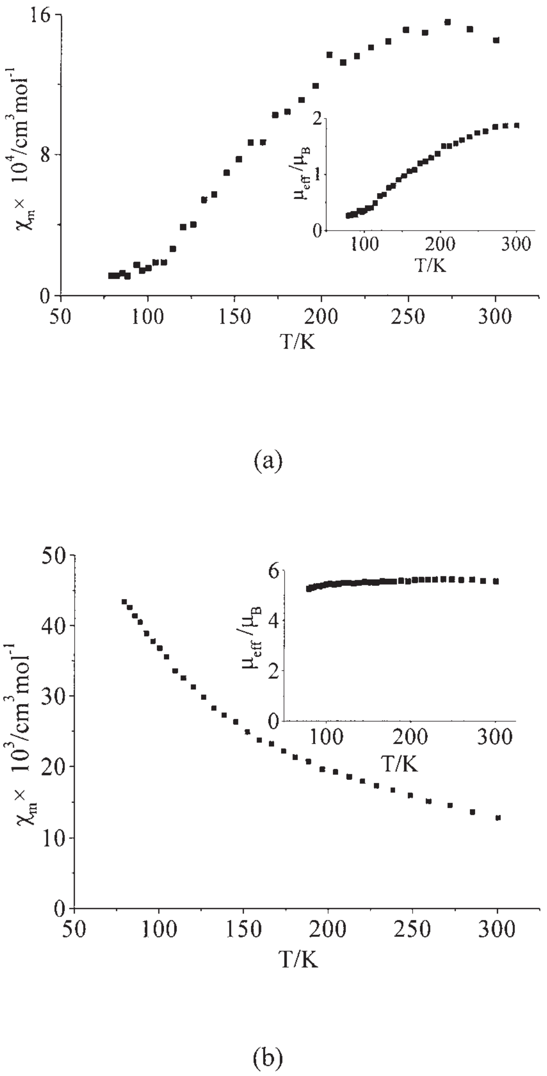
Fig. 6. 3D structure of **3** linked by C–H···Cl hydrogen bonds indicated by the dashed lines.

Zn···Zn and Mn···Mn separations are 18.10 and 18.28 Å in complexes **3** and **4** with an "L" shape of bpb, respectively.

From the crystal structures of complexes **1–4** described above and related metal complexes with the L1 and L2 ligands reported previously,[7,13] it can be clearly seen that the structure of the organic ligand has great influence on the structures of the assembly products. The amine N atoms of L1 and the imine N atoms of L2 together with their pyridyl N atoms coordinated to the metal atoms to form metal complexes with 1D or 2D structures,[7,13] while the imine N atoms of the bpb ligand did not coordinate to the metal atoms in complexes **1–4**. The L1 ligand formed a 1D hinged chain and 2D grid network complexes with $AgNO_3$ and $Cu(CH_3COO)_2 \cdot H_2O$, respectively, in which the Ag(I) and Cu(II) atoms are four-coordinated with a distorted tetrahedral and square planar geometry; all four N atoms of each L1 ligand coordinate to the metal atoms,[7,13a] while in the cases of complexes **1** and **2**, the Ag(I) atom and dicopper tetracarboxylate unit connect two bpb ligands to form 1D chains and only two of four N atoms of each bpb ligand bind to the metal atoms (vide supra). The non-coordination of the imine N atoms of the bpb ligand may probably be caused by a much more rigid spacer group of 1,4-benzenedimethylene in the bpb ligand compared with the flexible ethylene group in the L1 and L2 ligands, and by the lower electron density around the imine N atoms. The –C=N– groups in ligand bpb conjugate with the central benzene ring group and the electron density around the imine N atoms is decreased, so that the electron donation of the imine group is reduced. The non-coordination of imine N atoms makes the bpb as a derivative of the bipyridyl-based bridging ligand. The specific orientations of N-donors (3-pyridyl rather than well-studied 4-pyridyl) and the spacer moiety between the two pyridyl groups may result in novel network structures not achievable by other reported bridging ligands, such as 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethylene and 1,3-bis(4-pyridyl)propane.[20] Further studies on the reactions of the bpb ligand with other metal salts are now in progress.

**Magnetic Properties.** The variable-temperature magnetic susceptibilities of complexes **2** and **4** were measured over a temperature range of 70–300 K (Fig. 7). For complex **2**, the observed magnetic moments are 1.87 $\mu_B$ ($\mu_B \approx 9.27 \times 10^{-24}$ $J \cdot T^{-1}$) at 300 K and 0.20 $\mu_B$ at 75 K per dicopper tetracarboxylate unit. The magnetic moment decreases upon cooling, which indicates a typical behavior of the binuclear unit of copper(II) with the presence of antiferromagnetic interactions. The variation of the magnetic susceptibility with the temperature of **2** is similar to that observed in $[Cu_2(CH_3COO)_4(H_2O)_2]$ with the same dicopper tetracarboxylate unit, which implies that there is no practical magnetic interactions between the neighboring dicopper tetracarboxylate units due to their large separations of 20.81 Å (intra-chain) (vide supra) and 7.56 Å (inter-chains). The effective magnetic moment of **4** is 5.68 $\mu_B$ at 300 K, which is close to the value of 5.92 $\mu_B$ expected for the isolated high-spin Mn(II) ($S = 5/2$). The effective moment decreases slightly to a value of 5.36 $\mu_B$ at 75 K, indicating that there is only very weak magnetic interactions between the neighboring Mn(II) ions through the bridging bpb ligand, due to the long intermetallic distances of 18.28 Å (intra-chain) (vide supra) and 7.72 Å (inter-chains), as revealed by the X-ray crystal structure.

**Photoluminescence Properties.** The photoluminescence properties of complexes **1**, **2**, **3** and **4** were studied in the solid state. No clear photoluminescence was observed for the bpb and its silver(I) (**1**) and manganese(II) (**4**) complexes at room temperature. It is known that silver(I) and manganese(II) complexes may emit weak photoluminescence at low temperature, and that their luminescence at room temperature is unobservable.[21] In contrast to complexes **1** and **4**, the copper(II) (**2**) and zinc(II) (**3**) complexes show intense violet-blue photoluminescence under the same conditions. Complex **2** exhibits photoluminescence with emissions at 418 and 438 nm upon excitation at 360 nm and complex **3** displays photoluminescence with an emission maximum at 460 nm upon excitation at 398 nm and with an emission maximum at 444 nm upon excitation at 364 nm, as illustrated in Fig. 8. The photoluminescence behavior of copper(II) and zinc(II) complexes with various organic ligands has been extensively studied in recent years.[22] No emissions originating from metal-centered and metal-to-ligand (MLCT) or



(a)

(b)

Fig. 7. Temperature dependence of the magnetic susceptibilities of complexes **2** (a) and **4** (b). The inserts are the temperature dependence of the magnetic moments.

ligand-to-metal charge transfer (LMCT) excited states are expected for the zinc(II) complexes, since the Zn(II) ion is difficult to oxidize or to reduce due to its $d^{10}$ configuration.[22] Thus, the emissions observed in complex **3** are tentatively assigned to the $^1(\pi\text{–}\pi^*)$ intraligand fluorescence.[22a] The occurrence of emission of complex **2** is also considered to be dominated by intraligand emission due to the close resemblance of the emission bands between complexes **2** and **3**. The Cu(II) complex of L1 has been reported to show photoluminescence with the emission maximum at 430 nm upon excitation at 310 nm in the powdered solid state.[7] It is interesting that the zinc(II) complex **3** exhibits photoluminescence, while the manganese(II) complex **4** does not, although they are isostructural. It has been reported that the metal ions can enhance or quench the fluorescence of pyridine-containing compounds.[22] In the absence of a metal ion, the fluorescence of ligand bpb is probably quenched by the occurrence of a photoinduced electron transfer (PET) process due to the presence of a lone pair of nitrogen atoms.[22] Such a PET process is prevented by the complexation of bpb with metal ions; thus, the fluorescence intensity of bpb may be greatly enhanced by the coordination of Zn(II). In contrast to the zinc(II) complex **3**, the luminescence of complex **4** may probably be quenched by the Mn(II) ion.[22b] The results indicate that the photoluminescence properties of the metal-organic complexes depend on the nature of the organic ligand as well as the metal ions.

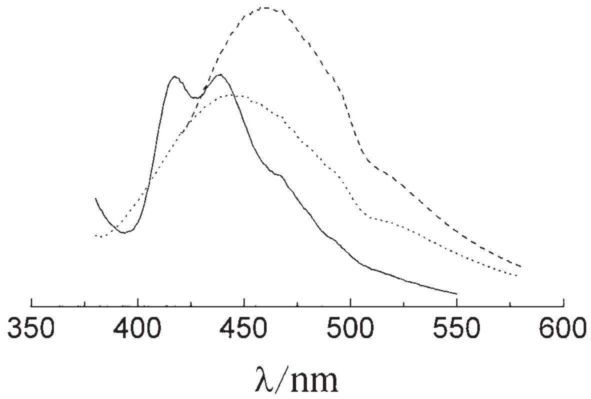


Fig. 8. Photo-induced emission spectrum of **2** with $\lambda_{ex} = 360$ nm (—) and photo-induced emission spectrum of **3** with $\lambda_{ex} = 364$ nm (···) and $\lambda_{ex} = 398$ nm (- - -) in the solid state at room temperature.

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