

Syntheses, Crystal Structures, and Spectral Properties of Two Coordination Compounds Based on 1,2-Bis(benzimidazolyl)benzene

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Two new benzimidazolyl-containing complexes have been synthesized by reactions of Cu^{II} salts and 1,2-bis(benzimidazolyl)benzene (H₂bbbz) with two different dicarboxylate ligands. When phthalate acid (H₂pt) was employed as secondary ligand, a 0D molecular complex Cu(H₂bbbz)(pt)·(H₂pt) (**1**) was furnished and when the secondary ligand was instead by a linear bridging ligand of terephthalic acid (H₂tp) a 1D zipper-like coordination polymer [Cu(H₂bbbz)(tp)·2(C₂H₅OH)·H₂O]_n (**2**) was obtained, suggesting the structure-direction effect of the secondary dicarboxylate ligand. The preliminary investigation on the spectral properties of the complexes was also presented.

Key Words : Copper (II), 1,2-Bis(benzimidazolyl)benzene, Dicarboxylate, Crystal structures, Spectral properties

Introduction

The rational design and synthesis of novel metal-organic coordination complexes have attracted great interests for decades, owing to their structural diversities¹ and potential applications in molecular magnetism,² ion exchange,³ gas storage and sequestration,⁴ catalysis,⁵ non-linear optics,⁶ luminescence⁷ and porosity or zeolitic behaviors.⁸ So far, a number of investigations focused on the theoretical analysis and practical manipulation about the controllable self-assembly of coordination complexes have been studied.⁹ The control of dimensionality of the complexes, however, is still an arduous challenge to chemists, because the final structures are always influenced by various factors.¹⁰ It is well known that the coordination mode of ligand is to a certain extent the key factor that can determine the final structural dimensionalities of the compounds. Change of the organic ligand, such as the length, flexibility and conformational preference can result in a remarkable class of complexes bearing diverse architectures and functions.¹¹

Imidazole and benzimidazole ligands, widely used in research of novel coordination compounds especially the zeolitic imidazolate frameworks (ZIFs), have been proved to be good candidates for multifunctional ligands.¹² For example, 2,2'-bibenzimidazole (H₂bbim)¹³ and its analogues,¹⁴ can serve as neutral bidentate, tridentate or tetradentate ligands to assemble multidimensional coordination complexes from 0D molecules to 3D polymers. The asymmetric ligands, 2-(3-pyridyl)benzimidazole (3-PyBim) and 2-(4-pyridyl)benzimidazole (4-PyBim), can coordinate with different metal to provide low dimensional building units which are able to propagate into 1D, 2D, or 3D structures *via* hydrogen bonds and other intermolecular weak interactions.¹⁵

On the other hand, design and construction of coordination complexes based on polycarboxylate anions and metal ions have aroused enormous attentions.¹⁶ Many researches have been intensively focused on construction of coordination complexes by exploiting saturated aliphatic dicarboxylate ligands, which are of special interests due to their conformational versatilities,

including discrete zero-dimensional (0D) complexes,^{1(d)} 1D polymeric chains,¹⁷ 2D layers¹⁸ and 3D frameworks.¹⁹ For the aromatic carboxylate ligands, such as 1,4-benzenedicarboxylic (H₂bdc) acid and 1,2,4,5-benzenetetracarboxylic acid (H₄btec) are extensively exploited in the construction of architectures through their self-assembly, forming coordination polymer chains, layers or networks.²⁰

Taking this into consideration, we selected two dicarboxylic acids as secondary ligands to tune the dimensionality of the complexes based on benzimidazole-like ligands. Although many metal-polycarboxylate complexes based on benzimidazole-like ligands have been obtained and reported, the metal-organic compounds derived from 1,2-bis(benzimidazolyl)benzene (H₂bbbz),²¹ however, have not been investigated before.

In this work, two metal-organic coordination complexes based on H₂bbbz have been prepared by reaction of Cu(II) salts, H₂bbbz with phthalate acid (H₂pt) and terephthalic acid (H₂tp). Compound **1** Cu(H₂bbbz)(pt)·(H₂pt) is a mononuclear compound and compound **2** [Cu(H₂bbbz)(tp)·2(C₂H₅OH)·H₂O]_n features a zipper chain in the structure.

Experimental

General. All chemicals and solvents used were analytically pure and without further purification. Elemental analysis for C, H, and N was carried out on a Perkin-Elmer 2400 II elemental analyzer. The UV absorption spectra was recorded on a model UV-2501 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on a Model RF-5301 spectrofluorimeter (Shimadzu, Japan).

Synthesis.

Synthesis Cu(H₂bbbz)(pt)·(H₂pt) (1**):** To an aqueous solution (5 mL) of Cu(NO₃)₂·1.5H₂O (45.67 mg, 0.2 mmol) was added an ethanol solution (10 mL) of H₂bbbz (38.24 mg, 0.1 mmol), and then added H₂pt (16.60 mg, 0.1 mmol) to the mixture. After stirring for 20 min, the mixture was left for evaporating at room temperature for several days to obtain purple block crystal (yield *ca.* 20% based on Cu^{II}). Anal. Calcd for C₅₆H₃₈CuN₈O₈ (%):

Table 1. Crystallographic data for complex **1** and **2**

	1	2
Formula	C56 H38 Cu N8 O8	C62 H58 Cu2 N8 O13
M_r	1014.47	1250.24
Cryst. size, mm ³	0.45 × 0.38 × 0.34	0.47 × 0.43 × 0.15
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/c
<i>a</i> , Å	11.493(5)	24.358(2)
<i>b</i> , Å	15.851(7)	18.3295(1)
<i>c</i> , Å	27.637(15)	16.8531(2)
α , deg	103.667(9)	90
β , deg	91.845(9)	129.82
γ , deg	107.709(6)	90
<i>V</i> , Å ³	4631(4)	5778.7(6)
<i>Z</i>	4	4
D_{calc} , g cm ⁻³	1.452	1.437
μ (Mo K α), mm ⁻¹	0.541	0.809
<i>F</i> (000), e	2084	2592
<i>hkl</i> range	-13 ≤ <i>h</i> ≤ 13, -17 ≤ <i>k</i> ≤ 18, -32 ≤ <i>l</i> ≤ 19	-29 ≤ <i>h</i> ≤ 28, -21 ≤ <i>k</i> ≤ 21, -20 ≤ <i>l</i> ≤ 20
Refl. measured	24803	16597
Refl. unique	16136	5134
<i>R</i> _{int}	0.0391	0.0486
Param. refined	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) ^a (all reflexions)	0.1213/0.2126	0.0674/0.1140
GoF (<i>F</i> ²) ^a	1.101	1.028
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.872/-0.361	0.477/-0.362

^aThe structure was solved by direct methods and refined by full-matrix least-squares fitting on *F*² by SHELXL-97.

C, 66.30; H, 3.78; N, 11.05. Found: C, 66.22; H, 3.85; N, 11.12. IR data for **1** (KBr, cm⁻¹): 3670(s), 3070(s), 1445(m), 1359(s), 1322(v), 1287(m), 986(s), 791(s), 745(s).

Synthesis [Cu(H₂bbbz)(tp)-2(C₂H₅OH)·H₂O]*n* (2**):** To an aqueous solution (5 mL) of Cu(NO₃)₂·1.5H₂O (45.67 mg, 0.2 mmol) was added an ethanol solution (10 mL) of H₂bbbz (38.24 mg, 0.1 mmol), and then added H₂tp (16.60 mg, mmol) to the mixture. After stirring for 20 min, the mixture was left for evaporating at room temperature to obtain purple hexagon crystal after ten days. (yield *ca.* 10% based on Cu^{II}). Anal. Calcd for C₆₂H₅₈Cu₂N₈O₁₃ (%): C, 59.60; H, 4.68; N, 8.96. Found: C, 59.67; H, 4.60; N, 9.01. IR data for **2** (KBr, cm⁻¹): 3682(s), 3073(m), 1580(s), 1503(v), 1446(s), 1379(s), 988(m), 837(m), 744(s).

X-ray Crystallography. The X-ray diffraction intensity data for the crystals was collected using Mo K α radiation (λ = 0.71073 Å) on a Bruker SMART CCD diffractometer in the *h* scan mode at 296(2) K. Structure solution and refinement were carried out using the programmes SHELXS 97 and SHELXL97.²² The hydrogen atoms associated with carbon and nitrogen atoms were generated geometrically, and the hydrogen atoms attached to H₂O were located from difference Fourier syntheses. The crystal data and structure refinement details for complex **1** and **2** are given in Table 1. Selected bond lengths

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**

Complex 1			
Cu1-O8	2.354(4)	Cu2-N10	1.985(4)
Cu1-N1	1.982(4)	Cu2-N11	1.991(4)
Cu1-N4	2.009(4)	Cu2-N14	1.983(4)
Cu1-N5	1.990(4)	Cu2-N15	1.985(4)
Cu1-N8	2.001(4)	Cu2-O13	2.426(4)
O8-Cu1-N1	90.64(13)	O8-Cu1-N4	91.70(13)
O8-Cu1-N5	101.93(13)	O8-Cu1-N8	97.08(13)
N1-Cu1-N4	91.73(15)	N1-Cu1-N5	167.21(14)
N1-Cu1-N8	91.70(15)	N4-Cu1-N5	90.28(15)
N4-Cu1-N8	170.53(14)	N5-Cu1-N8	84.47(15)
N10-Cu2-N11	90.54(16)	N10-Cu2-N14	171.11(14)
N10-Cu2-N15	91.63(16)	N11-Cu2-N14	84.96(16)
N11-Cu2-N15	168.70(19)	N14-Cu2-N15	91.34(17)
O13-Cu2-N14	97.19(13)	O13-Cu2-N15	89.73(16)
O13-Cu2-N10	91.20(13)	O13-Cu2-N11	101.32(16)
Complex 2			
Cu1-O6	2.399(3)	Cu1-O7	1.940(2)
Cu1-O5	2.001(2)	Cu1-N3	1.967(2)
Cu1-N1	1.950(3)		
O5-Cu1-O6	58.53(9)	O5-Cu1-O7	88.98(9)
O5-Cu1-N1	92.08(10)	O5-Cu1-N3	165.94(11)
O5-Cu1-C28	29.24(10)	O6-Cu1-O7	90.94(10)
O6-Cu1-N1	98.03(10)	O6-Cu1-N3	107.41(10)
O6-Cu1-C28	29.30(9)	O7-Cu1-N1	170.07(11)
O7-Cu1-N3	91.52(10)	O7-Cu1-C28	89.42(10)
N1-Cu1-N3	89.85(10)	N1-Cu1-C28	96.31(11)
N3-Cu1-C28	136.71(12)		

(Å) and angles (°) are listed in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-777823 for **1**, CCDC-777824 for **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

Results and Discussion

Single-crystal X-ray diffraction measurement (Table 1) reveals that compound **1** crystallizes in the triclinic space group *P*-1. In the asymmetry unit, there are two crystallographic-independent mononuclear Cu(H₂bbbz)₂(pt) molecules and two H₂pt guest molecules (Fig. 1). In each molecule, the Cu(II) ion is five-coordinated by four nitrogen atoms from two protonated H₂bbbz ligands and one oxygen atom from pt molecule. The τ value of 0.055 (τ = 0 for an ideal square-pyramid and τ = 1 for an ideal trigonal bipyramid) indicates the geometry is a slightly distorted square pyramid with the axial site occupied by O(8).²³ The H₂bbbz in **1** acts as a bidentate ligand via its benzimidazole nitrogen atoms. The Cu-N and Cu-O bonds lengths in the two mononuclear molecules are close and the average Cu-N bonds lengths are comparable with the corresponding ones of reported CuN4O coordinated compound while the Cu-O bonds lengths are slightly longer.²⁴ The two benzimidazolyl rings of the H₂bbbz in the complex form a dihedral angle of 73.8°, larger than the angle in the ligand (67.2°).^{21(b)}

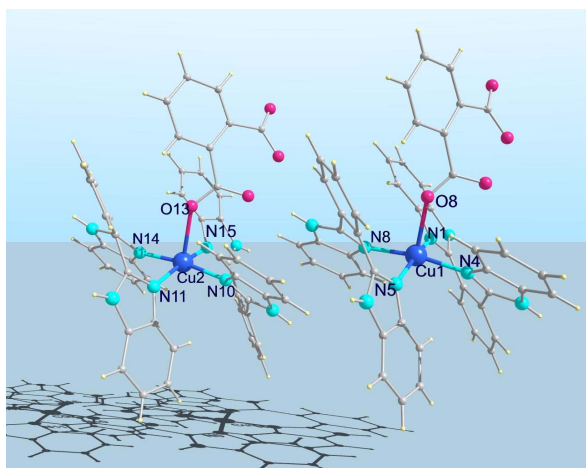


Figure 1. The metal coordination environment in **1**. The uncoordinated molecules were omitted for clarity.

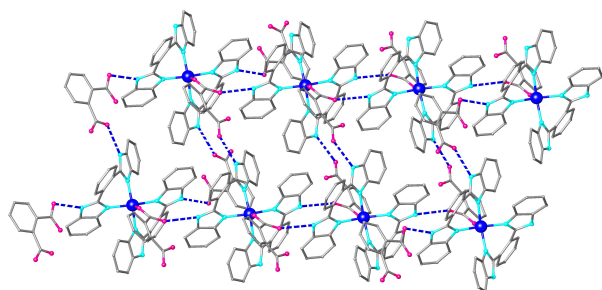


Figure 2. 1D double-strand chains formed by hydrogen bonds in complex **1**.

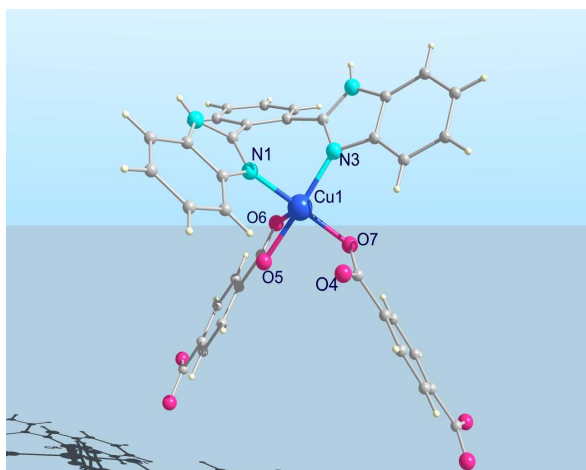


Figure 3. The metal coordination environment in **2**. The uncoordinated molecules were omitted for clarity.

The molecules are connected through the N-H \cdots O hydrogen bonds (Table S1) to form 1D supramolecular double-stranded chains (Fig. 2), the chains are further connected through C-H \cdots O interaction (Table S2) to construct a three-dimensional architectures (Fig. S1). The uncoordinated H₂tp ligands fill in the remaining unoccupied space, making additional contribution to the stabilization of the structure.

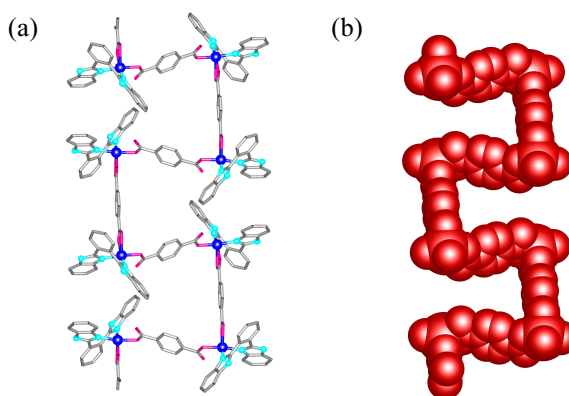


Figure 4. (a) The 1D chains are linked by the monodentate and bidentate bridging tp ligands. (b) The space filling model of **2** showing zipper-like chain, some atoms were omitted.

Differently, when the secondary ligand H₂tp was used, the similar reaction gives a zipper-like coordination polymer of **2**. As shown in Fig. 3. The crystal of **2** conforms to the space group *C2/c*. Each independent crystallographic unit contains a Cu^{II} atom, a tp molecule, a H₂bbbz ligand, two ethanol molecules and a lattice water molecule. Each Cu^{II} atom is primarily coordinated by two nitrogen atoms from a chelate H₂bbbz and three oxygen atoms from one bidentate tp and one monodentate tp ligand to furnish a distorted square pyramidal coordination geometry, of which the τ value is 0.069, slightly larger than **1**, which may be attributed to the small bite angle of chelating carboxylate.²³ The analogous bond lengths in each benzimidazole ring are not significantly different. The dihedral angle between the two benzimidazolyl rings is 111.9°. The dihedral angles between benzimidazole rings with the benzene ring are 132.3° and 41.8°, respectively. The Cu-N bond lengths fall into the range 1.950(3) to 1.967(2) Å, comparable with Cu-N bond lengths of reported complex,²⁵ while the Cu-O bond lengths (1.940(2) to 2.399(3) Å) are longer than the corresponding ones. The tp²⁻ anion adopts chelating-bidentate and monodentate modes to link Cu(II) cations to form one-dimensional zipper-like chain running along the *a*-axis, as depicted in Fig. 4, the H₂bbbz phenyl rings at each side of the zipper-like chain are arranged in an off-set fashion; adjacent chains are connected through N-H \cdots O and O-H \cdots O hydrogen bonds (N(2)-H(2A) \cdots O(3) 2.710, O(1)-H(1A) \cdots O(6) 2.721 and O(3)-H(3WA) \cdots O(7) 2.856 Å) (Table S3), each pair of polymeric chains are linked together through face to face π - π stacking interactions between the benzimidazole ligands (3.535 Å), indicating a strong aromatic π - π stacking interaction (Fig. S2).²⁶

The UV-vis spectra of free H₂bbbz and the complexes **1** and **2** are studied in the ethanol solution at room temperature (Fig. S3). The ligand H₂bbbz and complex **1** display similar absorption bands ranging from 220 to 320 nm, indicating the intraligand $\pi \rightarrow \pi^*$ electronic transitions, originating from the imidazole groups.²⁷ The maximum absorption of complex **2** has a strong band at *ca.* 220 nm, which can be assigned to metal-to-ligand charge transfer (MLCT).

In ethanol solution, the emission spectra of free ligand and complexes **1** and **2** were measured at room temperature (Fig. 5). The ligand H₂bbbz displays a strong emission band at 403 nm

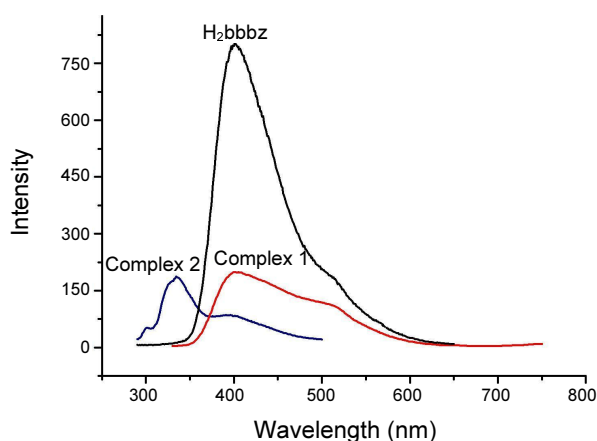


Figure 5. Fluorescence spectra of the H₂bbbz ligand, complex **1** and **2** in the ethanol solution.

upon excitation at 282 nm and the maximum emission peak is 120 nm red-shifted compared to the related absorption band, similar to other compounds containing benzimidazole group,^{27,28} which could be attributed to the $\pi \rightarrow \pi^*$ transition. The emission band of complex **1** is similar to that of the ligand (upon excitation at 275 nm), this phenomenon may be ascribed to the typical intraligand charge transfer (ILCT) which has also been observed in a series of imidazole-metal analogues.²⁹ The compound **2** displays a maximum emission at 334 nm upon excitation at 275 nm. Compared to the free H₂bbbz ligand, compound **2** has a blue shift of ca. 70 nm which can be attributed to metal-to-ligand charge transfer (MLCT),³⁰ while the shoulder peaks at 400 nm may be attributable to intraligand charge transfer (ILCT).³¹ Significant difference of emission between **1** and **2** is probably due to the differences of anions and coordination environment around central metal ions, because photoluminescence behavior is closely associated with the local environments around metal ions.³²

Conclusion

In summary, taking advantage of dicarboxylate organic molecules as secondary ligands, we have prepared and characterized two new metal-organic coordination complexes [Cu(H₂bbbz)(pt)]·(H₂pt) and [Cu(H₂bbbz)(tp)]·2(C₂H₅OH)·H₂O]_n, which contain discrete 0D molecule and infinite 1D zipper chain, respectively. The crystal structures show that the secondary ligands have an important influence on the resulting structures. The new compounds exhibit different luminescence in the ethanol solution which may be attributed to the different coordination effect.

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