



Influence of the anion on the coordination mode of an unsymmetrical N-heterocyclic ligand in Cd(II) complexes: From discrete molecule to one- and two-dimensional structures

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ABSTRACT

Five new 0D–2D Cd(II) complexes, $[\text{Cd}_2(\text{Hbimt})_2\text{I}_4]$ (**1**), $[\text{Cd}(\text{bimt})(\text{Hbimt})\text{Br}]_n$ (**2**), $[\text{Cd}(\text{Hbimt})\text{Cl}_2(\text{H}_2\text{O})]_n$ (**3**), $\{[\text{Cd}(\text{Hbimt})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**4**) and $[\text{Cd}(\text{Hbimt})(\text{SCN})_2]_n$ (**5**) (Hbimt = 2-((benzimidazol-yl)methyl)-1H-tetrazole) have been synthesized by the reactions of Hbimt with suitable cadmium salts. Employment of different anions can influence the coordination modes of the Hbimt ligand, and accordingly result in different structures ranging from 0D to infinite 1D and 2D networks. Complex **1** displays a dimeric structure in which two Cd(II) ions are bridged through two iodine atoms. Complex **2** was caused by deprotonation of the Hbimt ligand, resulting in a 1D helical chain. While in complexes **3** and **4**, Hbimt acts as a bidentate bridging ligand which joins two Cd(II) ions, leading to 1D stair-like chains. Complex **5** exhibits a 2D network structure with infinite 1D $[\text{Cd}_2(\text{SCN})_2]_n$ chains. The distinct structures of **1**, **2**, **3**, **4** and **5** reveal that the anions and the versatile coordination modes of the ligand play an important role in the structures of the complexes. In addition, the luminescent properties of complexes **1–5** have been investigated in the solid state at room temperature.

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1. Introduction

In recent years, the construction of complexes with specific structures is becoming increasingly popular by virtue of the possible design of materials with specific electronic, optic, magnetic and catalytic properties [1–12]. Although a variety of metal complexes have been successfully synthesized, true rational control in constructing complexes with desired structures and physical properties still remains a distant prospect in crystal engineering because various factors are involved in the formation of the complexes, such as the metal and its coordinating possibilities, the nature of the counterions, the metal-to-ligand ratio, the flexibility of the organic building blocks, the number and orientation of the coordinating sites in the organic spacers, and the solvent of recrystallization, and so forth [13–19]. Among those factors mentioned above, the selection of anions is extremely important because changing the geometry and size of the corresponding anions can control and adjust the structures of complexes, even for complexes containing neutral ligands [20]. Nowadays, the study of the influence of anions on the final structures of complexes has become a rapidly emerging field [21–24]. For example, Raju Mondal and coworkers have reported on the influence of different anions on the structures of Zn(II) complexes constructed from a flexible neutral ligand in the presence of

various anions, and indicated that the employment of different anions can lead to diverse structures, from discrete 0D structures to infinite 1D chains, 2D bilayer networks and 3D metal–organic frameworks [1]. Other relevant examples showing the influence of the anionic counterions on the final structures of the assembly have been reported by Vilar and co-workers [22], Brisse and co-workers [15], Morsali and co-workers [25], Kim and co-workers [26] and Sun and co-workers [27,28], among others [23,29,30].

2-((Benzimidazol-yl)methyl)-1H-tetrazole (Hbimt) has a flexible methylene group, which allows Hbimt to have flexible conformations and better adaptability, and thus can provide various possible self-assemblies and construction of complexes. So we selected Hbimt as a ligand to react with Cd(II) salts in the presence of various anions and we have obtained one 0D binuclear complex $[\text{Cd}_2(\text{Hbimt})_2\text{I}_4]$ (**1**), three 1D complexes $[\text{Cd}(\text{bimt})(\text{Hbimt})\text{Br}]_n$ (**2**), $[\text{Cd}(\text{Hbimt})\text{Cl}_2(\text{H}_2\text{O})]_n$ (**3**), $\{[\text{Cd}(\text{Hbimt})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (**4**), and one 2D complex $[\text{Cd}(\text{Hbimt})(\text{SCN})_2]_n$ (**5**). The results indicate that the nature of the anions has great influence on the coordination modes of the Hbimt ligand, and thus influences the architectures of the complexes.

2. Experimental

2.1. Materials and instruments

All chemicals were of reagent grade quality, obtained from a commercial source and used without further purification. IR spectra

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were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region 400–4000 cm^{-1} . Carbon, hydrogen and nitrogen analyses were carried out on a Flash EA 1112 elemental analyzer. Steady state fluorescence measurements were performed using a Hitachi F-4500 spectrofluorimeter at ambient temperature in the solid-state. The Mulliken atomic charge distributions and the contributive percentages of nitrogen atoms in the frontier molecular orbitals of the free ligand were calculated by the B3LYP/6-31G (d, p) level of theory.

2.2. Synthesis of the ligand 2-((benzimidazol-yl)methyl)-1H-tetrazole

O-phenylenediamine (10.8 g, 0.1 mol) and tetranitrazoleacetic acid (15.4 g, 0.12 mol) were dissolved in 60 ml 4 M hydrochloric acid. The solution was heated to 100–120 °C and refluxed for 6 h. After slow cooling to room temperature, the mixture was poured into 0–10 °C iced-water. The pH value was adjusted to 8–9 with concentrated ammonia, stirred acutely, which gave a voluminous precipitate. The precipitate was filtered and washed with distilled water. Then needle crystals were obtained by recrystallization with distilled water. Yield: 17.4 g, 87%. M.p: 189–191 °C. A crystal of the ligand Hbimt, suitable for crystallography, was selected and its structure was determined. *Anal. Calc.* For $\text{C}_9\text{H}_8\text{N}_6$: C, 53.99; H, 4.03; N, 41.98. Found: C, 53.94; H, 4.05; N, 41.96%. IR (KBr, cm^{-1}): 3263(m), 3117(m), 1706(w), 1600(w), 1529(w), 1484(w), 1459(s), 1429(s), 1335(m), 1225(w), 1191(s), 1104(m), 982(w), 765(s), 649(m), 472(w).

2.3. Synthesis of the complexes

2.3.1. Preparation of $[\text{Cd}_2(\text{Hbimt})_2\text{I}_4]_n$ (**1**)

A methanol (5 mL) solution of Hbimt (10 mg, 0.05 mmol) was added dropwise into a methanol solution (3 mL) of CdI_2 (18.3 mg, 0.05 mmol) to give a clear solution. The reaction mixture was left to stand at room temperature. Colorless block crystals, suitable for X-ray diffraction, were obtained about a month later by slow evaporation of the solvent. Yield: 62%. *Anal. Calc.* for $\text{C}_{18}\text{H}_{16}\text{Cd}_2\text{I}_4\text{N}_{12}$: C, 19.08; H, 1.42; N, 14.84. Found: C, 19.12; H, 1.49; N 14.73%. IR (KBr, cm^{-1}): 3115(m), 2941(w), 1599(w), 1527(w), 1483(m), 1458(m), 1426(s), 1332(m), 763(s).

Table 1
Crystallographic data for complexes 1–5.

Complexes	1	2	3	4	5
Formula	$\text{C}_{18}\text{H}_{16}\text{Cd}_2\text{I}_4\text{N}_{12}$	$\text{C}_{18}\text{H}_{15}\text{BrCdN}_{12}$	$\text{C}_9\text{H}_{10}\text{CdCl}_2\text{N}_6\text{O}$	$\text{C}_9\text{H}_{15}\text{CdN}_6\text{O}_{7.5}\text{S}$	$\text{C}_{11}\text{H}_8\text{CdN}_8\text{S}_2$
Formula weight	1132.83	591.73	401.53	471.73	428.77
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	C2/c	Cc	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	22.181(4)	18.327(4)	7.102(1)	7.660(2)	8.252(2)
b (Å)	7.494(2)	12.534(3)	8.586(2)	8.536(2)	8.572(2)
c (Å)	16.573(3)	10.911(2)	11.326(2)	13.028(3)	10.786(2)
α (°)	90	90	102.57(3)	74.12(3)	92.46(3)
β (°)	92.61(3)	121.59(3)	92.56(3)	88.94(3)	94.20(3)
γ (°)	90	90	109.14(3)	72.10(3)	101.94(3)
V (Å ³)	2752.1(9)	2135.0(7)	631.8(2)	777.6(3)	743.0(3)
Z	4	4	2	2	2
D_{calc} (g/cm ³)	2.734	1.841	2.111	2.015	1.916
μ (mm ⁻¹)	6.065	2.929	2.151	1.591	1.758
Reflections collected	13840	12995	6820	9542	9095
Unique reflections	2632	4907	2781	3683	3501
R_{int}	0.0296	0.0350	0.0193	0.0179	0.0245
Data/restraints/parameters	2632/0/164	4907/2/290	2781/0/181	3683/0/223	3501/0/199
Goodness of fit (GOF)	0.871	0.990	1.049	0.946	0.843
R_1 [$I > 2\sigma(I)$]	0.0281	0.0335	0.0188	0.0274	0.0245
wR_2 [$I > 2\sigma(I)$]	0.0808	0.0748	0.0463	0.0733	0.0588
R_1 (all data)	0.0298	0.0371	0.0198	0.0299	0.0276
wR_2 (all data)	0.0833	0.0775	0.0468	0.0834	0.0619

2.3.2. Preparation of $[\text{Cd}(\text{bimt})(\text{Hbimt})\text{Br}]_n$ (**2**)

A water solution (2 mL) of potassium bromide (11.9 mg, 0.1 mmol) was added dropwise into a methanol solution (3 mL) of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (13.4 mg, 0.05 mmol) and then a methanol (3 mL) solution of Hbimt (10 mg, 0.05 mmol) was added dropwise into the above mixture to give a clear solution. The reaction mixture was left to stand at room temperature. Colorless needle crystals suitable for X-ray diffraction were obtained about two months later by slow evaporation of the solvent. Yield: 55%. *Anal. Calc.* for $\text{C}_{18}\text{H}_{15}\text{BrCdN}_{12}$: C, 36.54; H, 2.56; N, 28.41. Found: C, 36.49; H, 2.52; N, 28.47%. IR (KBr, cm^{-1}): 3122(m), 2979(w), 1604(w), 1537(w), 1445(s), 1345(m), 755(s).

2.3.3. Preparation of $[\text{Cd}(\text{Hbimt})\text{Cl}_2(\text{H}_2\text{O})]_n$ (**3**)

A methanol solution (6 mL) of Hbimt (10 mg, 0.05 mmol) was added dropwise into a water solution (2 mL) of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (11.4 mg, 0.05 mmol) to give a clear solution. The reaction mixture was left to stand at room temperature. Colorless block crystals suitable for X-ray diffraction were obtained about a month later by slow evaporation of the solvent. Yield: 58%. *Anal. Calc.* for $\text{C}_9\text{H}_{10}\text{CdCl}_2\text{N}_6\text{O}$: C, 26.92; H, 2.51; N, 20.93. Found: C, 26.88; H, 2.53; N, 20.82%. IR (KBr, cm^{-1}): 3427(m), 3327(s), 3107(m), 1612(w), 1528(w), 1444(s), 1318(w), 756(s).

2.3.4. Preparation of $[\{\text{Cd}(\text{Hbimt})(\text{SO}_4)(\text{H}_2\text{O})_2\} \cdot 1.5\text{H}_2\text{O}]_n$ (**4**)

The procedure followed was similar to that of **3** except that $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ (12.8 mg, 0.05 mmol) was used instead of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$. Colorless prism crystals suitable for X-ray diffraction were obtained about a month later by slow evaporation of the solvent. Yield: 55%. *Anal. Calc.* for $\text{C}_9\text{H}_{15}\text{CdN}_6\text{O}_{7.5}\text{S}$: C, 22.92; H, 3.21; N, 17.82. Found: C, 22.84; H, 3.18; N, 17.86%. IR (KBr, cm^{-1}): 3288(m), 3118(w), 1625(w), 1528(w), 1488(w), 1440(m), 1337(m), 1224(w), 1110(s), 1030(w), 986(m), 768(m), 652(w), 620(s), 592(w), 474(w).

2.3.5. Preparation of $[\text{Cd}(\text{Hbimt})(\text{SCN})_2]_n$ (**5**)

A water solution (2 mL) of KSCN (9.7 mg, 0.1 mmol) was added dropwise into a methanol solution (3 mL) of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (15.4 mg 0.05 mmol), and then a methanol (3 mL) solution of Hbimt (10 mg, 0.05 mmol) was added dropwise into the above mixture to give a clear solution. The reaction mixture was left to

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