

Preparation of N,N,N',N'-tetrakis-(2-benzimidazolylmethyl)-1,2-ethanediamine and crystal assemblies of the relative complexes

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ABSTRACT

N,N,N',N'-tetrakis-(2-benzimidazolylmethyl)-1,2-ethanediamine (TBIMEDA), was prepared by reaction of ethylenediamine tetra-acetic acid disodium salt (EDTA) with 1,2-diaminobenzene in a refluxed glycol solution, and furthermore, three allomeric complexes [(M^{II} TBIMEDA) SO₄·5H₂O, M = Cd, Co, Ni] were self-assembled by solvothermal method based on reaction of this ligand with the relative sulfates respectively. These allomeric complexes were characterized by elemental analysis and IR spectroscopy and their crystal structures were determined by single crystal X-ray structural analysis. In the crystal architecture of these complexes, every metal(II) ion is chelated by one neutral TBIMEDA ligand to form an octahedral core with configuration of five heterocyclic rings (five-member ring). These cores then were linked together by multi hydrogen bond interactions with sulfate ions and water molecules to construct their 3D crystal architectures.

Keywords: Benzoimidazolmethyl Ethane Diamine; Solvothermal; Complex; Crystal Architecture

1. INTRODUCTION

Azaheterocyclic compounds, with strong coordination ability during complex preparations and as better acceptors in hydrogen bonding formation, were more frequently selected in coordination research [1-4]. After self-assemblies, the conjugated π bonds in the heterocyclic ligands provided abounding information on electromagnetism and photoelectrochemistry, and these special complex's aggregation was well known as functionalized material in future applications [5-9]. Meanwhile EDTA (ethylenediamine tetra-acetic acid) was regard as the

most useful multidentate ligand using in analytic chemistry. In this work, based on reaction of EDTA with benzene-1,2-diamine, a multidentate ligand with four benzoimidazole groups, N,N,N',N'-tetrakis-(2-benzimidazolylmethyl)-1,2-ethanediamine (TBIMEDA), was prepared according to the reported method (Scheme 1) [10-13]. Furthermore, by self-assembly of TBIMEDA reacting with different sulfates, three single-nuclear complexes with same crystal configuration were constructed by solvothermal methods, and their crystal structures were well defined by X-ray analysis.

2. EXPERIMENTAL

2.1. Materials and Physical Measurements

All chemicals and solvents were of analytical reagent grade and used as received. Elemental analysis was performed in a Perkin-Elmer 240 elemental analyzer. IR spectrum was obtained using a Nicolet IR200 infrared spectrometer. The fluorescence spectra were taken on an Edinburgh Instruments FLS920 fluorescence spectrometer respectively.

2.2. Synthesis of Ligand

Preparation of the ligand, N,N,N',N'-tetrakis-(2-benzimidazolylmethyl)-1,2-ethanediamine (TBIMEDA) was described as below [10-13]: A solution of EDTA (2.92 g, 0.01 mol) and 1,2-diaminobenzene (4.32 g, 0.04 mol) in 100 mL of glycol was heated to boiling and kept in reflux for 16 h. After cooling down to room temperature, the mixture was added to water (ac. 400 mL) for precipitation over night. The crude product was separated by filtration, purified by recrystallization with small volume of ethanol for three times and dried in air. A white powder product in yield of 70% was obtained with m. p. = 156°C - 158°C. IR data (KBr, cm⁻¹): 3186 vs (ν_{N-H}), 2966 w, 2823 w, 1617 s, 1535 s, 1486 w (σ_{N-H}), 1454 s, 1433 vs, 1348 s, 1311 m, 1274 vs, 1245 m, 1217 w, 1094

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s, 1049 m, 1021 m, 996 m, 963 w, 845 m, 747 vs, 616 w, 485 m. Calc. (found) for $C_{34}H_{32}N_{10}$: C 72.88 (72.90), H 3.84 (3.82), N 7.08 (7.12). This IR data were similar to the reported values. [10] The preparation of TBIMEDA was described as **Scheme 1**.

2.3. Synthesis of Complexes

2.3.1. $Co(TBIMEDA) \cdot SO_4 \cdot 5H_2O(1)$

Keeping under stirring, TBIMEDA (0.0706 g, 0.1 mmol), $CoSO_4 \cdot 7H_2O$ (0.0422 g, 0.15 mmol) are mixed with water (8 mL). The mixture was sealed in an autoclave and the autoclave was placed in an oven at 120°C for 60 h. After cooling down to room temperature at rate of 5°C/h, filtrating and washing, several large and transparent orange crystals were collected (in yield of 34%). Found (Calc.) for $CoC_{34}H_{42}N_{10}O_9S$: C, 49.44(49.45); H, 5.11 (5.13); N, 16.98(16.96)%. IR data(KBr, cm^{-1}): 3415 s, 3101 w, 3056 w, 2917 w, 2774 w, 2643 w, 1621 m, 1540 m, 1470 m, 1450 vs, 1392 m, 1274 vs, 1119 vs, 1029 m, 939 m, 910 w, 910 w, 857 w, 743 vs, 620 vs, 555 w, 514 w.

2.3.2. $Ni(TBIMEDA) \cdot SO_4 \cdot 5H_2O(2)$

Keeping under stirring, TBIMEDA (0.0706 g, 0.1 mmol), $NiSO_4 \cdot 6H_2O$ (0.0262 g, 0.1 mmol) were mixed with water (8 mL). The mixture was sealed in an autoclave and the autoclave was placed in an oven at 140°C for 60 h. After cooling down to room temperature at rate of 5°C/h, filtrating and washing, several large and transparent blue crystals were collected (in yield of 45%). Found (Calc.) for $NiC_{34}H_{42}N_{10}O_9S$: C, 46.48(46.47); H, 5.13(5.11); N, 16.97(16.99)%. IR data (KBr, cm^{-1}): 3415 s, 3105 m, 3064 w, 2913 w, 2765 w, 2639 w, 1544 m, 1405 vs, 1392 s, 1331 vs, 1278 vs, 1221 w, 1115 vs, 1029 s, 988 w, 939 s, 906 m, 849 m, 743 vs, 616 vs, 545 w, 518 w.

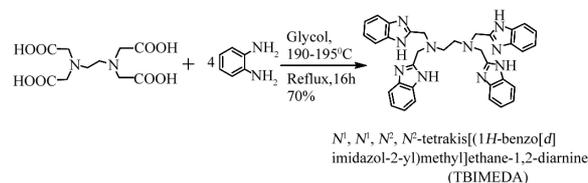
2.3.3. $Cd(TBIMEDA) \cdot SO_4 \cdot 5H_2O(3)$

Similar to the assembly of **1**, when $NiSO_4 \cdot 6H_2O$ was replaced by $CdSO_4 \cdot 8H_2O$ (0.0385 g, 0.05 mmol), large and transparent blue crystals were obtained in yield of 45% by the same hydrothermal method. Found(Calc.) for $CdC_{34}H_{42}N_{10}O_9S$: C, 49.44(49.45); H, 5.07(5.09); N, 15.95(15.93)%. IR data (KBr, cm^{-1}): 3395 s, 3096 m, 2761 w, 1621 m, 1540 m, 1446 vs, 1384 s, 1335 m, 1278 s, 1094 vs, 1025 s, 755 s, 620 m.

2.4. Single Crystal X-Ray Diffraction Analysis

The X-ray data collections and structure determinations were performed on a Bruker SMART CCD. The data were collected using graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was solved by direct methods and refined by full-matrix least-square calculation on F^2 with SHELX-97 program package.

[14]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were placed in calculated positions. The crystallographic data for **1-3** are summarized in **Tables 1** and **2**.



Scheme 1. Preparation of N,N,N,N-tetrakis-(2-benzimidazolylmethyl)-1,2-ethanediamine (TBIMEDA).

Table 1. Crystallographic data for **1-3**.

Crystalline data empirical formula	1	2	3
	$C_{34}H_{42}CdN_{10}O_9S$	$C_{34}H_{40}CoN_{10}O_8S$	$C_{34}H_{40}Ni_{10}NiO_8S$
Mr/g mol ⁻¹	879.24	807.75	807.53
T/K	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
<i>a</i> /Å	11.2807(16)	11.366(2)	11.3360(13)
<i>b</i> /Å	14.980(2)	14.872(3)	14.2121(17)
<i>c</i> /Å	23.081(3)	22.655(5)	23.605(3)
<i>V</i> /Å ³	3900.2(10)	3829.7(14)	3802.9(8)
<i>Z</i>	4	4	4
$\rho_c/g \cdot cm^{-3}$	1.497	1.401	1.410
μ/mm^{-1}	0.679	0.565	0.628
<i>S</i>	1.042	0.969	1.026
Reflections collected	24451	21215	21583
Unique collected	7645	7492	7453
<i>R</i> _{int}	0.0303	0.0925	0.0375
<i>R</i> ₁ ^a (<i>I</i> > 2(<i>I</i>))	0.0484,	0.0814	0.0590
<i>wR</i> ₂ ^b (all data)	0.1357	0.2417	0.1663

$$^a R_1 = \frac{\sum \|F_o - |F_c|\|}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

3. RESULTS AND DISCUSSION

3.1. Crystal Analyses for 1 - 3

Complexes **1** - **3** are alloisomers with each other, **1** is therefore selected as a typical example for discussing their crystal configurations. The view of the single core of **1** is depicted in **Figure 1**. Some selected bond distances and angles are listed in **Table 1**, and the hydrogen bonding data are listed in **Table 2**. **1** adopted orthorhombic system with $P2_12_12_1$ space group (unit cell parameters: $a = 11.2807(16)$ Å, $b = 14.980(2)$ Å, $c = 23.081(3)$ Å, $\beta = 90.00^\circ$, $V = 3900.2(10)$ Å³, $Z = 4$, $D_c = 1.497$ mg/cm³). Cadmium(II) ion in the core of complex **1** is coordinated by one neutral TBIMEDA ligand, forming five of five-member rings (**Figure 1**). The octahedral coordination core around cadmium(II) ion includes six N atoms, two of them originate from the chain of ethanediamine and the others originate from the unsaturated N atoms in imidazole rings. All distances of Cd-N described above are near to or shorter than the sum of Van der Waals radii for Cd and N, and the effective chelations result in distorted octahedron around Cd(II) ions. However, the saturated N atoms in imidazoles, include N3, N5, N11 and N12, are protonated and without any coordination contribution.

3.2. Hydrogen Bond Interactions in 1

In the crystal structure of complex **1**, the Cd(II) coordination cores are linked through intermolecular N-H...O and O-H...O hydrogen bonds with sulfate ions and water molecules (**Figure 2**), forming a complicate 3D architecture. If all water molecules are omitted, the Cd(II)

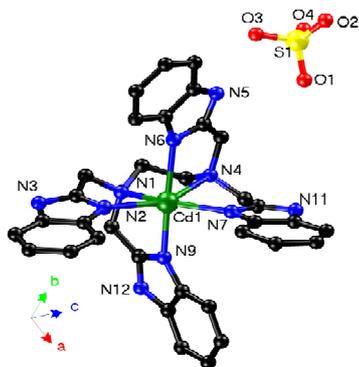


Figure 1. Diagram of single core in crystal architecture of **1**. All H atoms and 5 water molecules (O5-O9) are omitted for clarity. Just like the chelation of EDTA with metal ion, Cd^{II} in **1** adopting an octahedral configuration is chelated by five of 5-membered rings, where the two positive charges are counteracted by the sulfate anion.

Table 2. Select bond lengths (Å) and angles (°) for **1** - **3**.

1			
Cd(1)-N(7)	2.234(5)	Cd(1)-N(2)	2.251(5)
Cd(1)-N(9)	2.312(5)	Cd(1)-N(1)	2.480(5)
Cd(1)-N(6)	2.311(5)	Cd(1)-N(4)	2.526(4)
N(7)-Cd(1)-N(2)	141.56(19)	N(7)-Cd(1)-N(6)	91.0(2)
N(7)-Cd(1)-N(9)	92.50(19)	N(2)-Cd(1)-N(9)	93.55(18)
N(7)-Cd(1)-N(1)	143.9(2)	N(2)-Cd(1)-N(1)	73.72(18)
N(9)-Cd(1)-N(1)	73.5(2)	N(7)-Cd(1)-N(4)	72.87(18)
N(6)-Cd(1)-N(4)	71.84(17)	N(9)-Cd(1)-N(4)	90.07(18)
N(2)-Cd(1)-N(6)	96.09(17)	N(2)-Cd(1)-N(4)	144.97(18)
N(6)-Cd(1)-N(9)	159.6(2)	N(1)-Cd(1)-N(4)	74.01(17)
N(6)-Cd(1)-N(1)	92.1(2)		
2			
Co(1)-N(3)	2.142(7)	Co(1)-N(8)	2.148(7)
Co(1)-N(1)	2.169(7)	Co(1)-N(10)	2.292(8)
Co(1)-N(6)	2.165(6)	Co(1)-N(9)	2.337(6)
N(3)-Co(1)-N(8)	131.9(3)	N(3)-Co(1)-N(6)	91.1(3)
N(3)-Co(1)-N(1)	92.7(3)	N(8)-Co(1)-N(1)	93.4(3)
N(3)-Co(1)-N(10)	151.1(3)	N(8)-Co(1)-N(10)	76.0(3)
N(1)-Co(1)-N(10)	93.1(3)	N(3)-Co(1)-N(9)	75.2(3)
N(6)-Co(1)-N(9)	93.4(2)	N(1)-Co(1)-N(9)	76.5(2)
N(8)-Co(1)-N(6)	92.7(2)	N(10)-Co(1)-N(9)	78.7(3)
N(6)-Co(1)-N(1)	167.8(3)	N(10)-Co(1)-N(9)	78.7(3)
N(10)-Co(1)-N(9)	78.7(3)		
3			
Ni(1)-N(7)	2.078(4)	Ni(1)-N(1)	2.085(4)
Ni(1)-N(3)	2.098(4)	Ni(1)-N(9)	2.158(4)
Ni(1)-N(5)	2.088(4)	Ni(1)-N(10)	2.173(4)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)
N(9)-Ni(1)-N(10)	82.91(15)	N(9)-Ni(1)-N(10)	82.91(15)

coordination water molecules are omitted, the Cd(II) coordination cores and sulfate ions will be linked by hydrogen bonding interactions to form a metal organic framework (MOF, as describing in **Figure 3**), and this MOF can be simplified as a topologic diagram with characters of 3×7^2 around Cd cores and $3^2 \times 7^5 \times 8^3$ around sulfate cores (**Figure 4**). Meanwhile, if all Cd cores were ignored, the sulfate ions and water molecules will be linked together to construct a 2D chain running along the *a* axis (**Figure 5**).

3.3. Photoluminescence

Excitation under $\lambda_{\text{Ex}} = 341$ nm, ligand TBIMEDA gave a emission at $\lambda_{\text{Em}} = 375$ nm, which was contributed from its conjugated configuration with $\pi-\pi^*$ electron transition (**Figure 6**). After crystal assembly using the ligand with the metal ions with d^{10} configuration, such as Cd(II) in **1**, its crystal state also presented a strong emission peaks at $\lambda_{\text{Em}} = 417$ nm ($\lambda_{\text{Ex}} = 339$ nm). Obviously, compared with

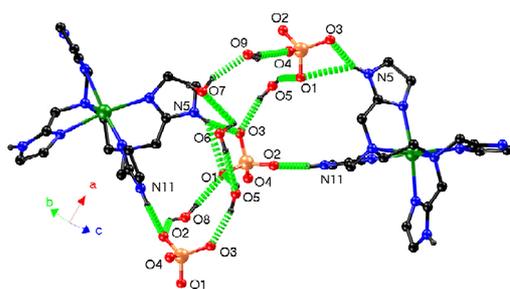


Figure 2. Hydrogen bonding interactions in **1**'s crystal architecture.

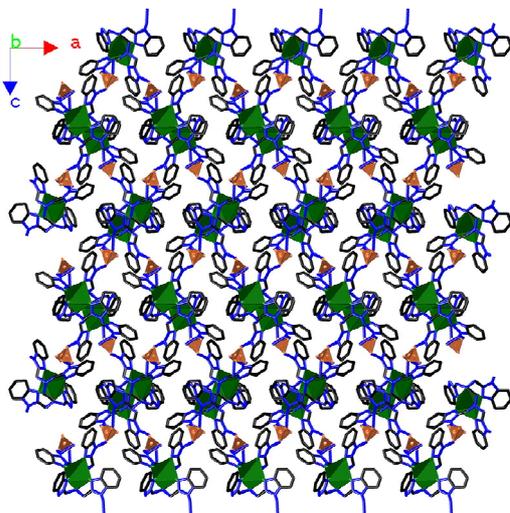


Figure 3. Crystal architecture of **1** constructed by hydrogen bonding interactions. Cd^{II} cores and SO₄²⁻ ions are linked together to form a network stretched in the *ac* plane. All H₂O molecules and H atoms without hydrogen bonding contributions are omitted for clarity.

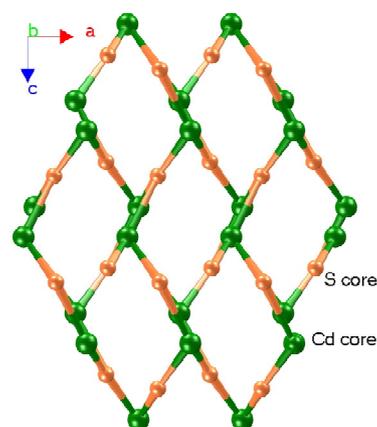


Figure 4. Simplified graph of for complex **1** with topologic characters of $3 \times 7 \times 8$ around Cd(II) cores and $3^2 \times 7^5 \times 8^4$ around sulfate anions.

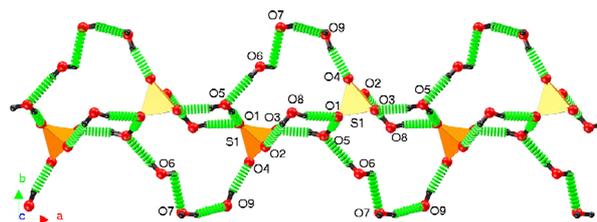


Figure 5. Simplified graph of for **1** only with water molecules and sulfate anions.

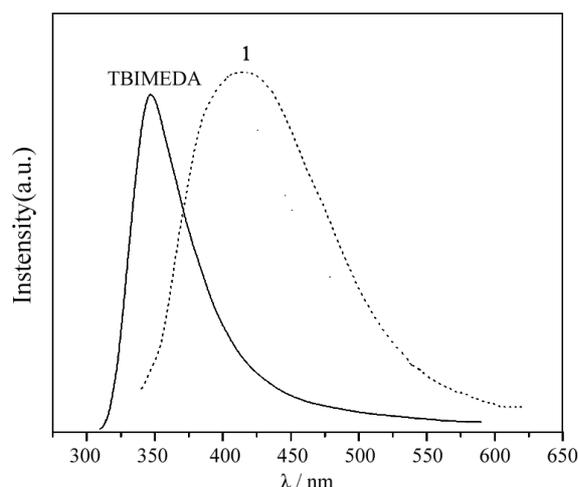
the ligand's emission, the fluorescent peaks of **1** emerged with red shift. This photoluminescence mechanism originated from ligand-metal charge transition (LMCT) [15], and its emission peak position was decided by the coordination situation of ligand with metal ion [16].

4. CONCLUSION

Ligands of diamine with imidazole group exhibited potentially application in biodegradation. In this work, after preparation of N,N,N',N'-tetrakis-(2-benzimidazolylmethyl)-1,2-ethanediamine(TBIMEDA), and using it as ligand reacting with different salts, three crystal architectures were self-assembled under solvothermal conditions. In crystal assembly, beside coordination between metal and ligands, the crystal architectures were also sustained by multi hydrogen bonding interactions from the complex cores with sulfate anions and water molecules. Three crystal architectures of M(TBIMEDA) SO₄·5H₂O (M = Cd^{II}, Co^{II}, Ni^{II}) all adopted orthorhombic crystalline with *P2₁2₁2₁* space group. The metal center was chelated by three TBIMEDA to construct an octahedral configuration with five 5-numbered chelating rings, where the coordinating atoms were unsaturated N in imidazole ring and saturated N from ethylenediamine chain. These complexes can be used as a model to study

Table 3. Typical hydrogen bonding interactions in **1-3**.

1				
Donor-H...Acceptor	D-H/Å	H...A/Å	D-A/Å	D-H-A/°
N11-H11...O2	0.86	1.83	2.68	171
N5-H5...O3	0.86	1.98	2.77	152
O5-H5a...O1	0.85	2.00	2.81	159
O8-H8e...O1	0.85	1.98	2.81	166
O5-H5b...O3	0.85	1.91	2.74	166
O7-H7a...O9	0.85	1.97	2.78	158
2				
Donor-H...Acceptor	D-H/Å	H-A/Å	D-A/Å	D-H-A/°
N4-H4...O4	0.86	1.97	2.86	153
O2w-H2wa...O1	0.85	1.96	2.81	176
N7-H7a...O2w	0.86	1.91	2.77	177
O3w-H3wa...O3	0.85	1.90	2.74	168
O5w-H5wa...O4w	0.85	1.60	2.45	179
3				
Donor-H...Acceptor	D-H/Å	H-A/Å	D-A/Å	D-H-A/°
N4-H4...O2	0.86	1.86	2.70	162
N2-H2...O3	0.86	1.85	2.70	172
O1w-H1wa...O3	0.85	1.97	2.80	165
O1w-H1wb...O4w	0.85	1.99	2.82	164
O3w-H3wa...O1	0.85	1.87	2.72	178
O3w-H3wb...O4	0.85	2.33	3.18	178
N8-H8...O1w	0.86	1.87	2.72	166

**Figure 6.** Emission spectra of ligand TBIMEDA ($\lambda_{\text{exa}} = 341$ nm) and **1** ($\lambda_{\text{exa}} = 339$ nm).

the effect of stereochemistry on the coordination polyhedron of M(II) ions. Although these M(II) ions were coordinated by six atoms, their coordination bonds were different in length, and therefore they may use different hybrid orbitals to form inner orbital or outer orbital coordination compounds. Obviously, these conclusions should be supported by magnetic determination and thermal gravimetric analysis. Further study should be intensively investigated.

5. ACKNOWLEDGEMENTS

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