Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Syntheses and structures of three novel coordination compounds assembled with 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-imidazole)

ABSTRACT

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ARTICLE INFO

Article history: Received 21 January 2008 Received in revised form 6 March 2008 Accepted 10 March 2008 Available online 1 April 2008

Keywords: Coordination compounds Flexibility N ligand Photoluminescence

1. Introduction

The self-assembly of metal-organic frameworks (MOFs) have attracted much attention, due to their elegant structural topologies and wide potential applications as functional materials [1]. Studies in this field have been focused on the design and preparation, as well as the structure-property relationships. Significant progress have been achieved [2], however, it is still a great challenge to rationally prepare and predict the exact structures and composition of target products in crystal engineering. The resulting MOF structures are determined by several factors, including the coordination nature of metal ions, ligand structure, counterions, and so on. The design of ligand is usually a useful way of manipulating the generation of the molecular architecture.

Up to now, a large number of beautiful MOFs of ingenious design based on flexible bis(imidazole) ligands, such as $(N-im)_2(CH_2)_n$ (n = 1-4) [3,4], have been constructed. These ligands bearing alkyl spacers are good choices of N-donor ligands, because the flexible nature of spacers allows the ligands to bend and rotate when it coordinates to metal centers. The structures and properties also can be modified by changing the spacer groups, for an instance, the length of the spacer. We designed and prepared a long ligand, [1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-imidazole)] (L) (Scheme 1), which is longer than 1,4-bis(imidazol-1-yl)-butane (bimb) due to the introduction of an O atom into the methylene ($-CH_2-$)₄ skeleton. The increasing length may control the physical dimensions of the crystalline architecture and, accordingly, affect the internal chemistry of the coordination polymers. Therefore, the exploration of this ligand is necessary to enrich and develop this field. In this paper, we report our efforts in the design and synthesis of the long flexible organic ligand, L, combined with different metal cations to assemble into diverse architectures consisting of 0D, 1D and 2D structures. Three new compounds were obtained: $[Cu_2(HCOO)_4 (L)_2]\cdot 2H_2O(1), [Cd(L)_2(NO_3)_2](2)$ and [Ni(BDC)(L)](3) ($H_2BDC = 1,4$ -benzenedicarboxylic acid). All compounds are characterized by elemental analysis, IR spectrum, thermogravimetric analyses and X-ray crystallography. In addition, compound **2** exhibit strong blue photoluminescence.

2. Experimental

2.1. Materials and general procedures

A new long flexible ligand, 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-imidazole) (L), has been prepared.

The hydrothermal reactions of L with various metal ions (M(II) = Cu(II), Cd(II) and Ni(II)) yielded three

new coordination compounds consisting of 0D, 1D and 2D structures. Compound 1 is a dinuclear M₂L₂

metallocycle. Compound **2** is a double-stranded chain running along b axis direction. Compound **3** affords

highly undulated 2D (4,4) layers. In addition, complex 2 exhibits strong blue photoluminescence.

Solvents and starting materials for synthesis were purchased commercially and used as received. The ligand L was prepared according to reported procedures [5]. The IR spectrum was recorded as KBr pellets on a Nicolet Magna-FT-IR 560 spectrometer in the 4000–400 cm⁻¹ region. Elemental analysis for C, H and N was performed on a Perkin-Elmer 240 analyzer. The photolumines-cence measurements were carried out on crystalline samples at room temperature and the spectra were collected with a Hitachi F-2500FL spectrophotometer. The thermogravimetric analyses were investigated on a standard TG analyzer under a nitrogen flow at a heating rate of 5 °C/min for all measurements.

2.2. Preparation

Synthesis of $[Cu_2(HCOO)_4(L)_2]$ - $2H_2O(1)$. An aqueous solution (15 mL) of formic acid (0.10 g, 0.2 mmol) was added slowly with





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Scheme 1. 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1H-imidazole) (L).

constant stirring to a solution of $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ (0.12 g, 0.5 mmol) in water (15 mL). After the precipitation was dissolved completely, L ligand (0.21 g, 1.0 mmol) also in water was added in drops. The resulting mixture was stirring for 5 h at room temperature. About one month later blue block-shaped crystals were obtained. Yield: 48% (based on Cu). Elemental analysis (%): Calcd. for (1): C 38.14, H 4.80, N 14.83. Found: C 38.08, H 4.85, N 14.86. IR (KBr): v (cm⁻¹) = 3430(s), 3130(s), 2918(m), 1609(s), 1523(m), 1405(m), 865(m), 657(m).

Synthesis of $[Cd(L)_2(NO_3)_2](2)$. An aqueous solution (15 mL) of Cd(NO₃)₂·4H₂O (0.31 g, 1.0 mmol) was added slowly with constant stirring to a solution of L (0.21 g, 0.1 mmol) in water (20 mL). The reaction mixture was then heated to reflux for 3 h. The resulting mixture was left to stand at room temperature for three weeks. Colorless crystalline product was obtained. Yield: 51% (based on Cd). Elemental analysis (%): Calcd. for (2): C 37.02, H 4.35, N 21.59. Found: C 37.09, H 4.40, N 21.51. IR (KBr): v (cm⁻¹) = 3130(s), 3037(m), 2906(m), 1528(m), 1380(s), 1085(m), 840(m), 825(s), 656(m).

Synthesis of [Ni(BDC)(L)](3). The mixture of NiSO₄·6H₂O (0.26 g, 1.0 mmol), 1,4-H₂BDC (0.17 g, 1.0 mmol) and L (0.21 g, 1.0 mmol) was dissolved in 8 mL of distilled water. The pH value was then adjusted to 5.5 with 1 M NaOH solution and the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel. This was then heated to 160 °C for 2 days. After the reactor was slowly cooled to room temperature, green block-shaped crystals were filtered off and dried in air. Yield: 42% (based on Ni). Elemental analysis (%): Calcd. for (3): C 50.39, H 4.23, N 13.06. Found: C 50.48, H 4.19, N 13.13. IR (KBr): v (cm⁻¹) = 3126(s), 3040(s), 2915(m), 1585(s), 1548(m), 1469(m), 1405(m), 1085(m), 840(m), 656(m).

2.3. Crystallographic data collection and refinement

X-ray Crystallographic Measurements for 1-3. Accurate unit cell parameters were determined by a least-squares fit of 2θ values, and intensity data were measured on a rigaku r-axis rapid IP area detector with MoK α radiation (λ = 0.71073 Å) at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan technique. All structures were solved by direct methods and refined by fullmatrix least-squares fitting on F^2 by SHELX-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data for the three compounds are summarized in Table 1 and selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Descriptions of the structures

3.1.1. $[Cu_2(HCOO)_4(L)_2] \cdot 2H_2O(1)$

X-ray crystallographic analysis provides direct evidence of M₂L₂ metallocyclic structure of compound 1, as shown in Fig. 1A. Each Cu(II) atom exhibits a trigonal-bipyramidal (CuO₃N₂) coordination environment with three O atoms from three formate anions and two N atoms from two L ligands, respectively. The Cu-O bond distances vary from 1.983(5) to 2.322(5) Å, while Cu–N bond lengths

Table 1	

Т

Crystallographic data and structure refinement details for 1-3

Compound	1	2	3
Formula	C24H36Cu2N8O12	C ₂₀ H ₂₈ CdN ₁₀ O ₈	C72H72N16Ni4O20
Fw	755.69	648.92	1716.30
Cryst. syst.	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	ΡĪ	Cc
a (Å)	15.799(3)	8.7924(18)	6.9627(14)
b (Å)	15.952(3)	8.8320(18)	19.317(4)
c (Å)	14.885(3)	10.444(2)	13.806(3)
α (°)	90	84.20(3)	90
β (°)	115.36(3)	68.23(3)	95.51(3)
γ (°)	90	61.91(3)	90
V (Å ³)	3389.9(11)	661.8(2)	1848.3(7)
Ζ	4	1	1
D (mg cm ⁻³)	1.481	1.628	1.542
T (K)	293(2)	293(2)	293(2)
F(000)	1560	330	888
R _{int}	0.1298	0.0347	0.0333
GOF	0.992	1.012	1.045
R_1 , $wR_2 [I > 2\sigma(I)]$	0.0872, 0.2416	0.0312, 0.0807	0.0253, 0.0643

Table 2			
Selected bond lengths (Å) and	angles (°) fe	or complexes	1-3

1			
Cu(1)-O(3)	1.974(5)	Cu(1)3-N(1)	1.978(6)
Cu(1)–N(4)#1	1.982(6)	Cu(1)-O(1)	1.983(5)
Cu(1)-O(1)#1	2.322(5)		
O(3) - Cu(1) - N(1)	90.2(2)	O(3)-Cu(1)-N(4)#1	89.7(2)
N(1)-Cu(1)-N(4)#1	167.5(2)	O(3)-Cu(1)-O(1)	171.1(2)
N(1)-Cu(1)-O(1)	90.8(2)	N(4)#1-Cu(1)-O(1)	91.3(2)
O(3)-Cu(1)-O(1)#1	93.2(2)	O(1)-Cu(1)-O(1)#1	77.9(2)
2			
Cd(1)-N(4)	2.286(2)	Cd(1)-N(2)#3	2.3173(19)
Cd(1)-O(1)	2.405(3)		
N(4)-Cd(1)-N(4)#2	180.000(1)	N(4)-Cd(1)-N(2)#3	91.15(8)
N(4)-Cd(1)-N(2)#4	88.85(8)	N(2)#3-Cd(1)-N(2)#4	180.000(1)
N(2)#4-Cd(1)-O(1)	86.60(10)	N(4)-Cd(1)-O(1)	94.63(9)
N(4)#2-Cd(1)-O(1)	85.37(9)	N(2)#3-Cd(1)-O(1)	93.40(10)
O(1)-Cd(1)-O(1)#2	180.00(11)		
3			
N(1)-Ni(1)	2.0348(14)	Ni(1)-O(2)	2.0815(11)
Ni(1)-O(1)	2.1661(11)		
N(1)#5-Ni(1)-N(1)	88.23(8)	N(1)-Ni(1)-O(2)	95.93(5)
N(1)-Ni(1)-O(2)#5	97.63(5)	O(2)#5-Ni(1)-O(2)	161.08(6)
N(1)#5-Ni(1)-O(1)#5	158.03(5)	N(1)-Ni(1)-O(1)#5	93.05(5)
O(2)#5-Ni(1)-O(1)#5	62.16(4)	O(2)-Ni(1)-O(1)#5	104.04(5)
O(1)#5-Ni(1)-O(1)	93.84(6)		

^a Symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z for **1**; #2 -x, -y + 2, -z + 2; #3 -x, -y + 1, -z + 2; #4 x, y + 1, z for **2**; #5 -x + 1, y, -z + 1/2for 3.

are 1.978(6) and 1.982(6) Å. The L ligands exhibit *cis* configuration with a pair of imidazole groups inclined by 16.19°. Two L ligands connect two Cu(II) atoms to achieve a 24-numbered M₂L₂ metallacyclic ring. The formate anions adopt two coordination modes. One occupies terminal positions as unidentate ligand, the other bridges two Cu ions through one oxygen atom only, which results in Cu---Cu separation of 3.354 Å. The distances from 2.716 to 3.013 Å between the O atoms of the free water molecules and the O atoms of formate anions indicate the formation of O-H···O hydrogen bonds, although the hydrogen atoms of water molecules could not be found [4c]. These hydrogen bonds connected the adjacent Cu₂L₂ metallacycles to form a 1D supramolecular chain running along caxis direction (Fig. 1B).

3.1.2. [Cd(L)₂(NO₃)₂](2)

Polymer **2** crystallizes in triclinic space group of $P\overline{1}$. As shown in Fig. 2A, each Cd(II) atom is coordinated by four N atoms from four L



Fig. 1. (A) Copper coordination environment with major atom numbering scheme in **1** showing 24-numbered metallocyclic Cu₂L₂ unit (the free water molecule is omitted for clarity). (B) 1D supramolecular chain formed by O-H···O hydrogen bonds indicated by blue dashed lines.



Fig. 2. (A) Cadmium coordination environment with major atom numbering scheme in **2**showing 24-numbered metallocyclic Cd₂L₂ unit in the 1D chain. (B) View along *b* axis direction of 1D double-stranded chain.

ligands in the equatorial positions and two O atoms from two NO₃⁻ anions at the axial positions to give octahedral environment. The Cd–N bond lengths are 2.286(2) and 2.3173(19) Å and Cd–O bond length is 2.405(3) Å, which fall in the normal range found in other Cd complexes [6]. Comparing to those in **1**, the L ligands exhibit *cis* configuration with a pair of imidazole groups inclined by 81.77° and link two adjacent Cd atoms to form a 24-numbered M₂L₂ metallocyclic ring with Cd…Cd distance being 8.832 Å. In contrast to **1**, the metallacycles of **2** are repeated to generate a 1D double-stranded chain running along the *b* axis direction (Fig. 2B).

3.1.3. [Ni(BDC)(L)](3)

Single-crystal X-ray structural analysis of 3 shows that each Ni(II) atom exhibits a distorted octahedral environment, composed of four carboxylic O atoms from two 1,4-BDC anions (Ni-O = 2.0815(11) and 2.1661(11) Å) and two N atoms from two L ligands (Ni–N = 2.0348(14) Å), as shown in Fig. 3A. The L ligand adopts a cis configuration with two imidazole rings inclined by 54.63° and gives a Ni…Ni separation of 6.963 Å. Different from the structures mentioned earlier, only one L ligand connects two adjacent Ni atoms. Ni atoms are arranged in left- and right-handed helices running along a axis direction (Fig. 3B) instead of 24-membered M₂L₂ metallocycles. Each 1,4-BDC anion coordinates to two Ni atoms in the μ_2 - η^3 -chelation mode [7]. Thus, the 1,4-BDC anions bridge two adjacent left- and right-handed helical chains to afford highly undulated 2D (4,4) layers that contain 42-membered rings with metal ions at each corner and a molecule L and a 1,4-BDC anion at each edge, respectively (Fig. 3C). The lengths of the opposite edges are equal, with the distances being 10.672 Å and 6.963 Å, respectively, and the diagonal distances are 15.814 Å and 8.639 Å. The (4,4) networks of 3 stack in a parallel fashion. It is surprisingly, no interpenetration occurs.

Through comparison of the structures of 1-3, it is apparent that the steric geometry of the flexible L ligand has a significant influ-

ence on the formation of resulting structure. The chemical nature of the long spacer tends to favour *cis* conformation due to the orientation of C–O–C bond, which facilitates the formation of metallocyclic structures, as found in complexes **1** and **2**. On the other hand, a twist of the two imidazole rings relative to the N– $(CH_2)_2$ –O– $(CH_2)_2$ –N chain can lead to helical chains, as found in complex **3**. Such helical chains may be formed by the ring-opening polymerization of M₂L₂ metallocycle [8].

3.2. Photoluminescent properties

Photoluminescent measurements of the compound **2** were carried out in the solid state at room temperature. The solid-state photoluminescent spectra of **2** is depicted in Fig. 4. It can be seen that the intense photoluminescence emission at 448 nm (λ_{ex} = 350 nm) is exhibited. The emission of **2** may be due to σ -donation from the coordination environment of the Cd(II) centers and thus be assigned as ligand-to-metal charge-transfer (LMCT) [9]. The emission in the blue region indicates that compound **2** appears to be good candidate for promising blue-light emitting material.

3.3. Thermogravimetric analyses

To study the stability of these polymers, thermogravimetric analyses (TGA) of complexes **1–3** were performed (Fig. 5). The TGA curve of complex **1** indicates two main weight losses. The first one from 34 to 152 °C corresponds to the loss of two lattice water molecule and one L ligand. The observed weight loss of 33.28% is in agreement with the calculated one (32.35%). The second weight loss can be detected from 212 to 529 °C that is attributed to the complete decomposition of the other L ligand and formate anions. The remaining residue is presumed to be CuO (calcd: 21.17%; found: 21.58%). In comparison with **1**, compound **2** is more stable



Fig. 3. (A) Nickle coordination environment with major atom numbering scheme in 3. (B) The 1D left- and right-helical structure constructed by nickel centers and L ligands. (C) Front (left) and side (right) view of the highly undulated 2D (4,4) network.



100 80 TG /% 60 40 20 0 200 400 600 0 800 T/°C

Fig. 4. Solid-state emission spectra of compound 2 at room temperature.

Fig. 5. Thermogravimetric analyses (TGA) curve of compounds 1-3.

up to 260 °C, where the decomposition of the framework starts. A rapid weight loss of 66.12% from 247 to 385 °C corresponds to the burning of the L ligand (calcd: 66.57%) and the resulting residue remains as CdO (calcd: 19.79%; found: 18.49%). The framework of compound **3** begins to collapse from 393 to 440 °C and the remaining residue is presumed to be NiO (calcd: 17.41%; found: 14.89%). Therefore, compound **3** is the most stable one among three compounds.

4. Conclusion

The use of the new flexible bis(imidazole) ligand (L) and divalent transitional metal ions [Cu(II), Cd(II) and Ni(II)] affords three interesting architectures, demonstrating again the aesthetic diversity of coordination chemistry. The results of this study not only illustrate that the nature of the neutral ligands play an important role in the construction of coordination polymers but also indicates that the introduction of a heteroatom into the methylene $(-CH_{2}-)_n$ skeleton of bis(imidazole) spacers is an efficient method for construction of novel MOFs. It is believed that more metal complexes containing flexible N-donor ligands with interesting structures as well as physical properties will be synthesized.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (50572040).

Appendix A. Supplementary data

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-674675 (1), 674676 (2) and 674677 (3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/</u><u>data_request/cif</u>. Table S1 (hydrogen-bond geometry for compound 1), Fig. S1 (Fluorescence emission spectrum of L ligand at room temperature) and Fig. S2 (the measured and simulated XRPD patterns for compound 2) in the Supplementary material. Supplementary data associated with this article can be found, in the on-line version, at doi:10.1016/j.molstruc.2008.03.034.

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