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Journal of Molecular Structure 789 (2006) 128-132

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

Luminescent 2D supramolecular network constructed from tubular coordination polymer based on H-bonding and π - π interactions

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Received 14 November 2005; received in revised form 19 December 2005; accepted 20 December 2005 Available online 14 February 2006

Abstract

A novel cadmium(II) coordination polymers, $[Cd(bitmb)_2 \cdot H_2O]_n$ (1) (Hbitmb=4-(2-benzimidazolethiomethyl)benzoic acid) has been synthesized under hydrothermal conditions, and characterized by elemental analysis and IR spectra. X-ray diffraction analyses show that 1 is a 1D tubular structure, which is further assembled to 2D supramolecular network by H-bonding and π - π interactions. 1 is luminescent and displays an emissive maximum at 450 nm in the solid state at room temperature. © 2006 Elsevier B.V. All rights reserved.

Keywords: Coordination polymer; Cd(II) complex; Crystal structure; Luminescence

1. Introduction

Luminescent coordination polymers have recently attracted much research interest primarily because of their potential applications in photoactive materials [1–3]. Compared with the luminescent organic polymers, the emission wavelength of most metal-organic coordination polymers can be tuned or changed by adjusting the length or conjugation of ligand since luminescent emission is mostly dominated by the coordinated ligand transition. In addition, luminescent metal-organic coordination polymers have many more advantages-such as high thermal stability, good mechanical properties and relatively high emitting intensity—over pure organic materials. Attempts to control the dimensionality and topology of these materials have focused on judicious selection of functional ligands with metal ions of the appropriate coordination geometry [4-8]. Recently, the use of flexible ligands with multiple donor sites to engineer coordination polymer arrays encounters a number of inherent challenges, such as difficult to predict and to form high dimensionality [9,10]. However, the propensity toward structural diversity in such systems brings opportunities to probe their conditions of formation and to gain

a greater understanding of the factors leading to this structural variety.

We have been investigating the use of flexible ligands based on aromatic spacers linked to thioether-pyridine arms to build coordination polymer arrays. Assembly of these type ligands and d10 transition metal ions produced some interesting luminescent complexes [11-13]. In our continuous investigations on self-assembly with flexible bridging ligands, herein, we wish to report on the exploitation of a new bridging ligand, 4-(2-benzimidazolethiomethyl)benzoic acid (Hbitmb) (Scheme 1). This ligand is designed and synthesized partly because the asymmetrical feature of it containing the twisted binding sites that can induce the formation of novel structures when linked by advisable metal nodes; but more importantly, our new strategy lies in the recognition that the Hbitmb ligand with a benzimidazole ring and a carboxylate group can serve as a strong N-H···O hydrogen bonding donor-acceptor site, and generate secondary chain-to-chain interaction in addition to the coordination and π - π interaction. In nature, the protein that is found in silk fibers epitomizes this strategy: the primary polypeptide chains are further linked by a secondary interchain hydrogen bonding interaction to generate a β -pleated sheet topology, which provides the flexibility yet very strong and resistant to stretching [14]. Thus, the assembly of Hbitmb with Cd^{2+} ions under hydrothermal conditions afforded a luminescent 1D tubular coordination polymer, $Cd(bitmb)_2 \cdot H_2O]_n$ (1), which is further assembled to 2D supramolecular network by H-bonding and π - π interactions.

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2.1. Materials and measurements

All the reagents for syntheses were commercially available and employed without further purification or with purification by standard methods prior to use. Elemental analyses (C, H, N) were performed on a Perkin–Elmer model 240C automatic instrument. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer with KBr pellet. ¹H NMR was measured on a Bruker AM500 spectrometer with SiMe₄ as the internal reference. Thermogravimetric analysis was performed on a NETZSCH STA 449C thermai analyzer under flowing N₂ with a heating rate of 10 °C/min. Emission spectra were recorded on a Perkin–Elmer LS55 Luminescence spectrometer.

2.2. Synthesis of 4-(2-benzimidazolethiomethyl)benzoic acid (Hbitmb)

2-Mercaptobenzimidazole (1.502 g, 10 mmol) was added to a stirred solution of KOH (0.56 g, 10 mmol) in H₂O (20 mL). The mixture was warmed to reflux, then α -bromo-*p*-toluic acid (2.15 g, 10 mmol) was added and the mixture was refluxed for about 10 h with vigorous stirring. After being cooled, the mixture was left to stand overnight. The precipitate was filtered off and washed with water, giving a fine white powder in 95% yield. Anal. Calcd. for C₁₅H₁₂N₂O₂S: C 63.36, H 4.25, N 9.85; found: C 63.31, H 4.21, N 9.89. IR (KBr) v: 3065 (w), 2984 (m), 2916 (m), 2668 (m), 1704 (vs), 1609 (s), 1520 (s), 1423 (s), 1368 (vs), 1247 (s), 1176 (s), 1020 (m), 842 (m), 745 (vs), 601 (m) cm⁻¹; ¹H NMR (500 MHz, DMSO- d_6): δ 4.631 (s, 2H, CH₂), 4.762 (s, 1H, NH), 7.118–7.134 (t, $J_1 = 3$ Hz, $J_2 =$ 5 Hz, 2H, bi), 7.556–7.571 (d, J=7.5 Hz, 2H, ph), 7.862–7.878 (d, J=8 Hz, 2H, ph), 7.919–7.934 (d, J=7.5 Hz, 2H, bi), 12.616 (s, 1H, COOH).

2.3. Synthesis of $[Cd(bitmb)_2 \cdot H_2O]_n$ (1)

A mixture of $CdCl_2 \cdot 2.5H_2O$ (23 mg, 0.1 mmol) with Hbitmb (57 mg, 0.2 mmol) in 10 mL of H₂O was sealed in a stainless-steel reactor with a Teflon liner and heated at 110 °C for 72 h. A quantity of colorless single crystals was obtained after the solution was cooled to room temperature at a rate of 10 °C/h. The yield of **1** is ca. 70% based on Hbitmb. Anal. Calcd. for [C₃₀H₂₄CdN₄O₅S₂]: C 51.69, H 3.47, N 8.04; found: C 51.62, H 3.42, N 8.01. IR (KBr) ν : 3377 (m), 3112 (w), 3097 (w), 1609 (s), 1587 (vs), 1533 (vs), 1404 (vs), 1276 (s), 1227 (s), 1017 (m), 861 (m), 743 (s), 639 (m) cm⁻¹.

2.4. Crystal structural determination

A colorless single crystal of 1 was mounted on a glass fiber and used for data collection, respectively. All intensity data were collected on a Bruker CCD diffractometer by ω scan technique at room temperature using graphite-monochromated Mo K α (λ =0.71073 Å) radiation. All empirical absorption corrections were applied by using the SADABS program [15]. The structures were solved by direct methods and refined using the shelxl-97 program package [16]. Metal atoms in each complex were located from E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix leastsquares methods with anisotropic thermal parameters for nonhydrogen atoms on F^2 . The positions of H atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The important crystal data are summarized in Table 1, and the selected bond lengths and angles for the complexes are given in Table 2. Crystallographic data for the complex 1 have been deposited at the Cambridge Crystallographic Data Center with CCDC Number 256264. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 122 333 6033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1 Crystallographic data for **1**

1	
Empirical formula	$C_{30}H_{24}CdN_4O_5S_2$
FW	697.05
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	8.631
b (Å)	10.814
<i>c</i> (Å)	15.833
α (°)	89.86
β (°)	77.12
γ (°)	76.25
$V(\text{\AA}^3)$	1397.3
Z	2
D_c , (g cm ⁻³)	1.657
$\mu (\mathrm{mm}^{-1})$	0.980
F(000)	704
Crystal size (mm)	$0.15 \times 0.12 \times 0.05$
θ range (°)	1.94-25.03
Limiting indices	$-10 \le h \le 9, -12 \le k \le 12,$
	$-18 \le l \le 17$
Reflections collected/unique	8659/4892 [<i>R</i> (int)=0.0327]
Completeness to $\theta = 25.03$	99.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4892/0/379
Goodness-of-fit on F^2	1.105
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0503, wR_2 = 0.0831$
R indices (all data)	$R_1 = 0.0690, wR_2 = 0.0916$
Largest diff. peak and hole	$0.718 \text{ and } -0.483 \text{ e } \text{\AA}^{-3}$

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

1 ^a			
Cd(1)-O(2)	2.228(3)	Cd(1)-O(4B)	2.290(4)
Cd(1)-N(3)	2.278(4)	Cd(1)-O(3B)	2.409(4)
Cd(1)-N(1A)	2.290(4)	Cd(1)–O(1)	2.628(4)
O(2)-Cd(1)-N(3)	100.42(13)	N(3)-Cd(1)-O(3B)	83.90(13)
O(2)-Cd(1)-N(1A)	90.47(14)	N(1A)-Cd(1)-O(3B)	144.44(15)
N(3)-Cd(1)-N(1A)	99.94(13)	O(4B)-Cd(1)-O(3B)	54.89(14)
O(2)-Cd(1)-O(4B)	130.38(15)	O(2)-Cd(1)-O(1)	52.71(12)
N(3)-Cd(1)-O(4B)	125.87(15)	N(3)-Cd(1)-O(1)	127.22(14)
N(1A)-Cd(1)-O(4B)	97.27(13)	N(1A)-Cd(1)-O(1)	121.47(13)
O(2)-Cd(1)-O(3B)	123.87(16)	O(4B)-Cd(1)-O(1)	82.57(14)
O(3B)-Cd(1)-O(1)	80.16(14)		

^a Symmetry transformations used to generate equivalent atoms are: A: -x + 1, -y+2, -z; B: x+1, y-1, z; C: x-1, y+1, z.

3. Results and discussion

3.1. Synthesis and crystal structure of 1

The ligand Hbitmb was conveniently prepared from the substitution reaction between 2-mercaptobenzimidazole and α -bromo-*p*-toluic acid under strong alkaline (KOH) conditions with higher yield. The resulting white powder was characterized by elemental analyses, IR and ¹H NMR. The complex **1** was obtained as colorless needle crystals by hydrothermal reaction (110 °C, 72 h) between Hbitmb and Cd²⁺ salts and characterized by spectroscopic data as well as X-ray crystallography. It is interestingly noted that **1** could also be isolated according to the same synthetic procedure, however, using Cd(X)₂ (X=NO₃, Cl, OAc) as the source of metals, which indicates that the final products are independent of the counter-anions of the metal salts. Furthermore, **1** is air stable and insoluble in water or common organic solvents.

The complex 1 crystallizes in the triclinic unit cell space group P-1 consisting of neutral Cd(bitmb)₂ asymmetric unit and a dissociative water molecule. As shown in Fig. 1, each Cd(II) center binds to four carboxylate oxygen atoms and two nitrogen atoms from four bitmb ligands to form a severely



Fig. 1. The asymmetric unit representation of **1** showing the local geometry around the metal center and ligand. Thermal ellipsoids were drawn at the 50% probability level.



Fig. 2. The 1D structure of 1 with 2×2 and 4×4 grids in its backbone.

distorted octahedral geometry. The average Cd-O and Cd-N distances are 2.388 and 2.278 Å, respectively, which are similar to normal Cd–O and Cd–N coordination bonds [17]. Each ligand coordinates to two Cd(II) atoms and the carboxylate group adopts a chelating mode. Owing to the ligand is flexible by way of sp³ configurations of -CH₂Sspacer, the dihedral angles between phenyl and benzimidazole groups are 97.9 and 88.1°, respectively. The array of ligands linked by Cd centers gives a 1D polymer, as shown in Fig. 2. The structural characteristic of this chain is that there are two kinds of grids $(2 \times 2 \text{ and } 4 \times 4)$ within its backbone. Furthermore, these 2×2 grids form a 1D channel which results in tubular coordination polymer for 1 (Fig. 3). As expected, these chains are parallel each other and further assembled to 2D supramolecular network via hydrogen bonding and $\pi - \pi$ interactions. Fig. 4 indicates the 2D H-bonding network with two types: N-H····Ocarboxylate and N–H···O_{water} (Table 3). Fig. 5 displays two types of weak π – π interactions: $\pi_{phenyl} – \pi_{benzimidazole}$ and $\pi_{benzimidazole} –$ $\pi_{benzimidazole}$ (Table 4). It can be concluded that the designed chain-to-chain strong H-bonding and π - π interaction play an important role on the formation and stability of supramolecular network. Thermogravimetric analysis (TGA) shows that compound 1 undergoes two-step weight losses. As shown in Fig. 6, the first step occurs from 100 to 150 °C where the weight loss is 2.62%, which corresponds to the loss of water molecules (expected, 2.58%). The weight remains almost unchanged in the plateau from 150 to 310 °C. The second occurs at the range from 340 to 510 °C, and a weight loss of 42.1% showing that the compound begins to decompose.



Fig. 3. View of 1D tubular structure of 1.



Fig. 4. View of H-bondings in the 2D supramolecular network of 1.

Table 3 Hydrogen bond lengths (Å) and bond angles (°) for 1 $\!\!\!\!\!\!$

D–H···A	D-H (Å)	H····A (Å)	D····A (Å)	∠DHA (°)	Symmetry code
N(2)- $H(2A)\cdots O(1)$	0.88	1.96	2.827(6)	167	$\begin{array}{c} 2-x,\\ 2-y,-z \end{array}$
O(5)- $H(5A)\cdots O(4)$	0.88	1.99	2.767(6)	147	x, 1+y, z

3.2. Luminescent spectrum

The emission spectrum of compound 1 in the solid state at room temperature was measured. Excitation of solid samples of 1 at 330 nm produces a strong blue emission with peak maximum at 450 nm, as shown in Fig. 7. According to the luminescent Cd(II) coordination polymers reported in literatures [4,17,18], the emission band might be attributable to the ligand-to-metal charge transfer (LMCT). This observation indicates that compound 1 may be candidate for blue photoactive materials.



Fig. 5. View of π - π interactions in the 2D supramolecular network of 1.

Table	e 4				
$\pi - \pi$	interaction	parameters	for	1	

	Distance between ring centroids (Å)	Dihedral angle (°)	Symmetry code
Ring(1)-ring(4)	3.711(3)	7.07	2-x, 2-y, -z
Ring(3)-ring(3)	3.785(3)	0.00	2-x, 2-y, -z
Ring(3)-ring(4)	3.668(3)	0.00	1 - x, 3 - y, -z
Ring(2)-ring(2)	3.680(3)	6.10	2-x, 2-y, -z





Fig. 6. The TG curve of 1.

4. Conclusion

In conclusion, we have successfully demonstrated a feasible way in obtaining luminescent 2D supramolecular network from tubular polymer by employing strong chain-to-chain hydrogen bonding and π - π interactions to enhance the framework rigidity. Other results based on the Hbitmb ligand are in progress and will be published very soon.



Fig. 7. The emission spectrum of 1 in the solid state at room temperature.

Acknowledgements

We are thankful for the financial support of the National Nature Science Foundation of China (No. 20231020) and the Nature Science Foundation of Fujian Province.

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