第 24 卷第 9 期 无 机 化 学 学 报 Vol.24 No.9
2008 年 9 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 1461~1467

超分子 2,2′-联咪唑镉(Ⅱ)配聚物的合成与结构表征

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摘要: 以硫氰酸根、叠氮基、二氰胺为桥联配体,分别与 2,2′-联咪唑和硝酸镉反应,获得配聚物[Cd(SCN)$_2$(H$_2$biim)]$_n$ (**1**), [Cd(N$_3$)$_2$(H$_2$biim)]$_n$ (**2**)和[Cd$_2$(NO$_3$)(dca)$_3$(H$_2$biim)$_{2.5}$]$_n$ (**3**),3 个化合物通过元素分析、IR、TGA 等表征,并测定了它们的晶体结构。结果表明:化合物 **1** 和 **2** 分别是以 $\mu_{1,3}$-SCN$^-$和 $\mu_{1,1}$-N$_3^-$双桥连接的一维链状结构, 化合物 **3** 是以 $\mu_{1,5}$-dca$^-$和 $\mu_{3,3'}$-H$_2$biim 交叉桥连的二维网状结构。对它们的荧光性质也进行了初步分析。

关键词: 镉; 配合物; 2,2′-联咪唑; 荧光性质
中图分类号: O614.24$^+$2 **文献标识码**: A **文章编号**: 1001-4861(2008)09-1461-07

Synthesis and Structural Characterization of Supramolecular Cadmium(Ⅱ)-2,2′-biimidazole Coordination Polymers

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Abstract: Three polymeric compounds [Cd(SCN)$_2$(H$_2$biim)]$_n$ (**1**), [Cd(N$_3$)$_2$(H$_2$biim)]$_n$ (**2**) and [Cd$_2$(NO$_3$)(dca)$_3$(H$_2$biim)$_{2.5}$]$_n$ (**3**) (H$_2$biim=2,2′-H$_2$biimidazole, dca=dicyanamide), have been synthesized and characterized. Compound **1** forms a 1D chain where [CdS$_2$N$_4$] octahedra are doubly bridged by two $\mu_{1,3}$-SCN$^-$ ligands. These chains are stacked together through hydrogen bonds and π-π interactions forming a 2D supermolecular network. In compound **2**, the [CdN$_6$] octahedra are doubly bridged by two $\mu_{1,1}$-N$_3^-$ bridges to form a chain. These chains are stacked together through hydrogen bonding interactions forming a 3D supermolecular structure. In compound **3**, the Cd2 ions are alternately bridged by two $\mu_{1,5}$-dca$^-$ and one $\mu_{3,3'}$-H$_2$biim bridge along b-axis and form a chain. These chains are bridged by $\mu_{1,5}$-dca$^-$ to form a plane. Cd1 and Cd2 atoms are bridged by one dca$^-$ with Cd1 locate at either side of the plane. The luminescent properties of these compounds were studied. CCDC: 657894, **1**; 657895, **2**; 657896, **3**.

Key words: cadmium; complex; 2,2′-biimidazole; luminescent properties

0 Introduction

Biimidazole and its derivatives have received much attention in material science, such as electron transport materials, catalytic materials and anticancer agents[1~3]. Recently, biimidazole was used to build supermolecular hybrid materials for its versatile coordination modes and the ability to construct hydrogen bonds[4,5]. As far as we know, the most reported compounds with H$_2$biim as ligands are mononuclear and via

收稿日期:2008-04-14。收修改稿日期:2008-06-04。
江苏省自然科学基金(No.BK2006044)、江苏省教育厅重大基金(No.06KJA43014)和江苏省新型功能材料重点建设实验室开放基金(No.07KFJJ007)资助项目。
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hydrogen bonding interactions to form a 3D supermolecular structure[6~10]. Using Cl^-, Br^-, dca^- or isonicotinic acid as coligands, coordination polymers were constructed[4,11~13]. To study the influences of coligands in the construction of coordination polymers, we employed SCN^-, N_3^- and dca^- as counter-anions, as well as Cd^{2+} as cation. Here, we report the syntheses and characterization of two one-dimensional polymeric complexes $[Cd(SCN)_2(H_2biim)]_n$ (**1**) and $[Cd(N_3)_2(H_2biim)]_n$ (**2**), and a two-dimensional polymeric complex $[Cd(NO_3)(dca)_3(H_2biim)_{2.5}]_n$ (**3**).

1 Exerimental

1.1 Physical measurements

IR spectra were recorded on a Nicolet MagNa-IR 550 instrument with KBr pellets in the range 4 000~400 cm^{-1}. The elemental analyses for C, H and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. Thermogravimetric analyses (TGA) were performed with a SDT 2960 thermoanalyzer under N_2 (25~1 000 ℃ range) at a heating rate of 5 ℃·min^{-1}. The luminescent spectra were performed on a Perkin-Elmer LS55 spectrofluorometer.

1.2 Synthesis of $[Cd(SCN)_2(H_2biim)]_n$ (1)

To a methanol solution (2 mL) of H_2biim (0.005 4 g, 0.04 mmol) and Cd $(NO_3)_2·4H_2O$ (0.012 3 g, 0.04 mmol) was added an aqueous solution (1 mL) containing NH_4SCN (0.006 1 g, 0.08 mmol). The mixture was stirred at room temperature for 10 min and then filtered. The resulting solution was allowed to evaporate slowly at room temperature. After 2 weeks, colorless crystals of compound **1** were formed. Yield: 84%, based on Cd. Anal. Calcd. for $C_8H_6CdN_6S_2$ (%): C 26.49; H 1.67; N 23.17. Found (%): C 26.38; H 1.69; N 23.25. IR (KBr, cm^{-1}): 2 069s, 1 637s, 1 618s, 1 524s, 1 421m, 1 311m, 1 174m, 1 094s, 986w, 937w, 858m, 764m, 683m, 617m.

1.3 Synthesis of $[Cd(N_3)_2(H_2biim)]_n$ (2)

The colorless crystals of compound **2** were prepared similar to **1** except that NaN_3 (0.005 2 g, 0.08 mmol) was used instead of NH_4SCN. Yield: 71%, based on Cd. Anal. Calcd. for $C_6H_6N_{10}Cd$ (%): C 21.80; H 1.83; N 42.34. Found (%): C 21.58; H 1.78; N 42.65. IR (KBr, cm^{-1}): 2 064s, 2 019s, 1 647w, 1 635w, 1 616s, 1 525s, 1 508w, 1 424m, 1 094s, 702m, 667s, 640w, 619m.

1.4 Synthesis of $[Cd_2(NO_3)(dca)_3(H_2biim)_{2.5}]_n$ (3)

The colorless crystals of compound **3** were prepared similar to **1** except that Na-dca (0.007 1 g, 0.08 mmol) was used instead of NH_4SCN. Yield: 79%, based on Cd. Anal. Calcd. for $C_{21}H_{15}N_{20}Cd_2O_3$ (%): C 30.75; H 1.84; N 34.15. Found (%): C 30.58; H 1.89; N 34.25. IR (KBr, cm^{-1}): 2 287s, 2 251m, 2 230s, 2 178s, 1 617m, 1 524s, 1 499m, 1 423s, 1 344s, 1 13m, 1 177m, 1 126m, 1 093s, 998m, 932m, 850m, 752s, 669s, 519s.

1.5 Crystal structure determination

Single crystals with dimensions 0.30 mm × 0.20 mm × 0.20 mm for **1**, 0.38 mm × 0.16 mm × 0.13 mm for **2**, 0.20 mm × 0.15 mm × 0.10 mm for **3** were selected for indexing and intensity data collection at 193(2) K on a Rigaku Mercury CCD X-ray single crystal diffractometer using graphite-monochromatized Mo $K\alpha$ (λ = 0.071 070 nm). The data was collected in the θ range 3.2°~25.3° for **1**, 3.3°~25.3° for **2** and 3.1°~25.3° for **3** using mode. Numbers of observed and unique reflections are 5 490 and 1 069 (R_{int}=0.027) for **1**, 8 550 and 896 (R_{int}=0.028) for **2**, 27 108 and 5 120 (R_{int}=0.083) for **3**. The crystal structures of **1**, **2** and **3** were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atom. All hydrogen atoms were introduced at the calculated positions and included in the structure-factor calculations. Neutral atom scattering factors were taken from Cromer and Waber[14]. Anomalous dispersion effects were included in F_{calc}[15]. A summary of the key crystallographic information for complexes **1**, **2** and **3** are listed in Table 1. Selected bond lengths and angles are given in Table 2~4.

CCDC: 657894 , **1**; 657895, **2**; 657896, **3**.

Table 1 Crystallographic data for complexes 1, 2 and 3

Compound	1	2	3
Formula	$C_8H_6N_6CdS_2$	$C_6H_6N_{10}Cd$	$C_{21}H_{15}N_{20}Cd_2O_3$
Formula weight	362.71	330.61	820.33

Continued Table 1

Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*2/*c*	*Pbcn*	$P2_1/c$
a / nm	1.331 6(3)	1.039 1(2)	1.432 5(2)
b / nm	0.852 16(15)	1.498 8(3)	1.400 80(19)
c / nm	1.095 2(2)	0.625 56(14)	1.503 0(2)
β / (°)	105.105(4)	90	111.308(3)
V / nm^3	1.174 3(4)	0.974 3(4)	2.809 8(7)
Z	4	4	4
T / K	193(2)	193(2)	193(2)
D_{calcd} / ($g\cdot cm^{-3}$)	2.052	2.254	1.939
μ (Mo *K*α) / mm^{-1}	2.2	2.237	1.580
F(000)	704	640	1604
No. observations ($I>2\sigma(I)$)	995	858	4253
R_1[a], wR_2[b] ($I>2\sigma(I)$)	0.018 1, 0.045 0	0.022 8, 0.053 5	0.068 4, 0.151 2
GOF[c]	1.07	1.12	1.01
$(\Delta\rho)_{max}$ / ($e\cdot nm^{-3}$)	400	320	1 560
$(\Delta\rho)_{min}$ / ($e\cdot nm^{-3}$)	−350	−510	−1 390

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, [c] $GOF=[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obsrevation}-N_{parameter})]^{1/2}$.

Table 2　Selected bond lengths (nm) and angles (°) for compound 1

Cd(1)-N(3)	0.230 8(2)	Cd(1)-N(1)	0.233 8(2)	Cd(1)-S(1B)	0.274 7(1)
N(3)-Cd(1)-N(3A)	99.51(9)	N(3)-Cd(1)-N(1)	167.17(6)	N(3A)-Cd(1)-N(1)	93.27(6)
N(1)-Cd(1)-N(1A)	73.99(8)	N(3)-Cd(1)-S(2B)	89.42(5)	N(3A)-Cd(1)-S(1B)	88.75(75)
N(1)-Cd(1)-S(1B)	89.65(5)	N(1A)-Cd(1)-S(1B)	92.62(5)	S(1B)-Cd(1)-S(1C)	177.16(3)

Symmetry codes: A: 1−*x*, *y*, 3/2−*z*; B: 1−*x*, −*y*, 1−*z*; C: *x*, −*y*, 1/2+*z*.

Table 3　Selected bond lengths (nm) and angles (°) for compound 2

Cd(1)-N(3)	0.230 5(2)	Cd(1)-N(1)	0.234 9(2)	Cd(1)-N(3B)	0.244 6(2)
N(3)-Cd(1)-N(3A)	147.92(12)	N(3)-Cd(1)-N(1A)	94.70(9)	N(3)-Cd(1)-N(1)	111.16(9)
N(1A)-Cd(1)-N(1)	73.43(12)	N(3)-Cd(1)-N(3B)	84.62(7)	N(3A)-Cd(1)-N(3B)	78.36(9)
N(1A)-Cd(1)-N(3B)	157.80(8)	N(1)-Cd(1)-N(3B)	86.08(8)	N(3B)-Cd(1)-N(3C)	115.33(12)

Symmetry codes: A: 1−*x*, *y*, 1/2−*z*; B: *x*, 1−*y*, *z*−1/2; C: 1−*x*, 1−*y*, 1−*z*.

Table 4　Selected bond lengths (nm) and angles (°) for compound 3

Cd(1)-N(1)	0.229 9(7)	Cd(1)-N(11)	0.228 7(8)	Cd(1)-N(3)	0.230 2(7)
Cd(1)-N(5)	0.229 3(7)	Cd(1)-N(7)	0.231 9(7)	Cd(1)-O(1)	0.282 0(6)
Cd(2)-N(12)	0.227 9(7)	Cd(2)-N(17)	0.228 2(7)	Cd(2)-N(14)	0.234 9(7)
Cd(2)-N(19)	0.238 1(7)	Cd(2)-N(18A)	0.228 3(7)	Cd(2)-N(15B)	0.239 0(7)
N(11)-Cd(1)-N(5)	103.6(3)	N(11)-Cd(1)-N(1)	94.6(3)	N(11)-Cd(1)-N(7)	92.0(3)
N(11)-Cd(1)-O(1)	163.9(2)	N(11)-Cd(1)-N(3)	109.8(2)	N(5)-Cd(1)-N(1)	161.8(3)
N(5)-Cd(1)-N(3)	98.2(2)	N(5)-Cd(1)-N(7)	74.8(2)	N(5)-Cd(1)-O(1)	76.6(2)
N(1)-Cd(1)-N(3)	74.6(2)	N(1)-Cd(1)-N(7)	105.6(2)	N(1)-Cd(1)-O(1)	86.2(2)
N(3)-Cd(1)-N(7)	158.2(2)	N(3)-Cd(1)-O(1)	85.8(2)	N(7)-Cd(1)-O(1)	72.4(2)
N(12)-Cd(2)-N(17)	175.6(3)	N(12)-Cd(2)-N(18A)	89.3(3)	N(17)-Cd(2)-N(18A)	91.4(3)

Continued Table 4

N(12)-Cd(2)-N(14)	89.4(3)	N(17)-Cd(2)-N(14)	95.0(3)	N(18A)-Cd(2)-N(14)	88.8(3)
N(12)-Cd(2)-N(19)	83.7(2)	N(17)-Cd(2)-N(19)	91.9(2)	N(18A)-Cd(2)-N(19)	93.2(3)
N(14)-Cd(2)-N(19)	172.7(3)	N(12)-Cd(2)-N(15B)	93.5(3)	N(17)-Cd(2)-N(15B)	86.4(3)
N(18A)-Cd(2)-N(15B)	172.0(3)	N(14)-Cd(2)-N(15B)	83.7(3)	N(19)-Cd(2)-N(15B)	94.5(2)

Symmetry codes: A: x, 1/2−y, z−1/2; B: −x, −y, −z+1.

2 Results and discussions

2.1 Crystal structure description

Compound **1** crystallizes in monoclinic space group *C*2/*c*. The asymmetric unit consists of 1/2 H_2biim ligand, 1/2 Cd atoms and one SCN^- ion (Fig.1). Cd1 locates at an inversion center and has an octahedron environment with six positions occupied by [N(1), N(1A)] from one H_2biim ligand and [N(3), N(3A), S(1B), S(1C)] from four equivalent SCN^- ions. The Cd1-N1 bond length is 0.233 8(2) nm. Cd1-N3 bond length 0.230 8(2) nm is shorter than the Cd1-S1B bond length 0.274 7(1) nm and is consistent with the corresponding values of Cd-SCN system[16]. The [CdS_2N_4] octahedral are doubly bridged by two $\mu_{1,3}$-SCN^- bridges to form a chain with Cd⋯Cd distance of 0.566 3 nm. The adjacent polymeric chains in **1** were linked through the interchain N−H⋯N hydrogen bonding interactions [N2⋯N3 (1−x, 1+y, 3/2−z) 0.298 2(2) nm] and the π-π interactions between imidazole rings of neighboring chains with distances 0.361 1 nm and dihedral angle of 0.1°, thereby forming a two-dimensional supermolecular network extending along the *bc* plane (Fig.2).

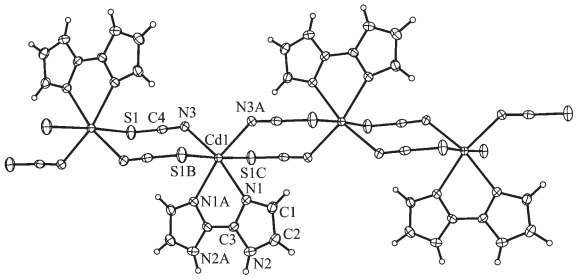

Fig.1 An ORTEP drawing of compound **1** with atomic labeling scheme

Complex **2** crystallizes in orthorhombic space group *Pbcn*. The asymmetric unit consists of 1/2 H_2biim ligand, 1/2 Cd atoms and one N_3^- ion (Fig.3). Cd1 locates at an inversion center and has an octahedron environment with six positions occupied by [N(1), N(1A)]

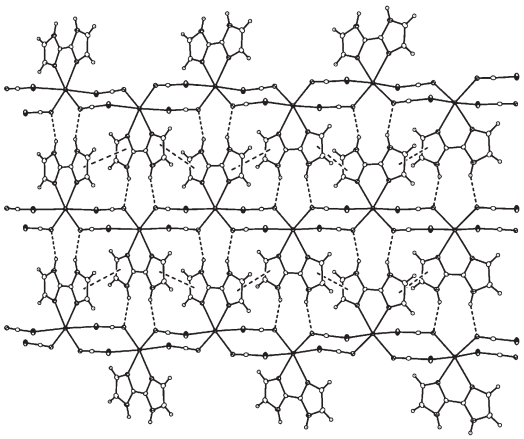

Fig.2 2D layer structure of compound **1** through hydrogen bonding and π-π interactions between adjacent chains

from one H_2biim ligand and [N(3), N(3A), N(3B), N(3C)] from four equivalent N_3^- ions. The Cd1-N1 bond length is 0.234 9(2) nm close to the corresponding value of compound **1**. Cd1-N3 and Cd1-N3B bond lengths are 0.230 5(2) nm and 0.244 6(2) nm, respectively. The [CdN_6] octahedra are doubly bridged by two $\mu_{1,1}$-N_3^- ions to form a chain with Cd1⋯Cd1C distance of 0.368 3 nm. The Cd1-N3-Cd1C bond angle is 101.64(9)° in accordance with the value of other Cd-N_3 compounds[16]. These chains are stacked together through H-bond interactions: [N2⋯N5 (1/2−x, 3/2−y, −1/2+z) 0.311 1(4) nm; N2⋯N5 (1/2+x, 1/2+y, 1/2−z) 0.308 0(4) nm] to

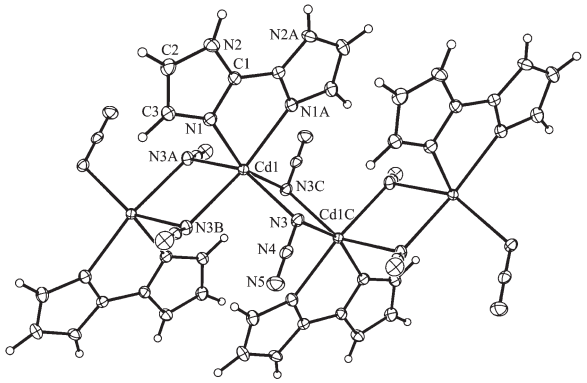

Fig.3 An ORTEP drawing of compound **2** with atomic labeling scheme

form a 3D supermolecular structure (Fig.4).

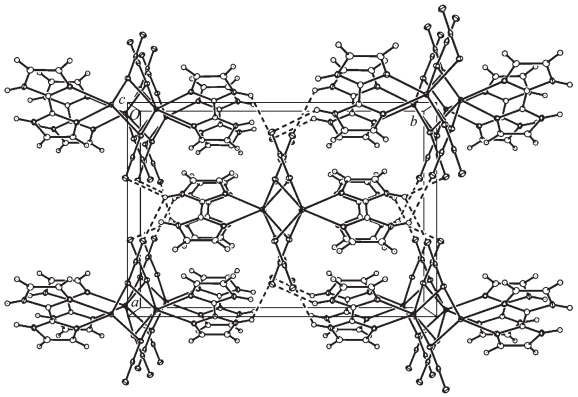

Fig.4　Packing diagram of compound **2** in a cell viewed along the *c*-axis

Compound **3** crystallizes in monoclinic space group $P2_1/c$. The asymmetric unit consists of two types of Cd atoms, 3 dca^- ions, 2.5 H_2biim and one NO_3^- ion (Fig.5). Cd1 has a distorted octahedron environment and coordinate to [N1, N3, N5, N7] from two H_2biim ligands, N11 from one dca ion and O1 from NO_3^- ion. The Cd1-N bond lengths are normal and in the range of 0.228 7(8)~0.231 9(7) nm. The Cd1-O1 bond length is 0.282 0(6) nm, indicates that the interaction is very weak. Cd2 has an octahedron environment and coordinate to [N12, N14, N17, N18A, N15B] from five equivalent dca^- ions and N19 from one H_2biim ligand. The Cd2-N distances are in the range of 0.227 9(7)~0.239 0 (7) nm. In the structure, the Cd2 ions are alternately bridged by two $\mu_{1,5}$-dca^- and one $\mu_{3,3'}$-H_2biim bridge along *b*-axis and form a chain. These chains are bridged by $\mu_{1,5}$-dca^- to form a plane (Fig.6). The Cd⋯Cd distances are 0.751 6(1), 0.772 9(1) and 0.755 5(1) nm, respectively, bridged by one $\mu_{1,5}$-dca^- bridge, two $\mu_{1,5}$-dca^- bridges and one H_2biim bridge. Cd1 and Cd2 atoms are bridged by one dca- with Cd1 locate at either side of the plane with Cd1⋯Cd2 distance 0.883 5(1) nm (Fig.7). Unlike that in complex **1** and **2**, the H_2biim ligand in complex **3** have two coordination modes: one acts as bridging bidentate ligand to coordinate to Cd atoms, the other acts as chelating bidentate ligand to coordinate to Cd1 atom. The adjacent layers are stacked together by hydrogen bonding interactions [N(2)⋯O(2) (1−*x*, −*y*, −*z*) 0.285 2(9) nm; N(4)⋯O(2) (1−*x*, 1−*y*, −*z*) 0.285 5(9) nm; N(6)⋯O(1) (1−*x*, 1−*y*, −*z*) 0.295 2(10) nm; N(8)⋯O(1) (1−*x*, 1−*y*, −*z*) 0.327 3(10) nm; N(8)⋯O(3) (1−*x*, 1−*y*, −*z*) 0.290 7(10) nm; N8⋯N9(1−*x*, 1−*y*, −*z*) 0.345 8(10) nm; N20⋯N15 (*x*, *y*+1, *z*) 0.297 1(10) nm; N(4)⋯N(11) (1−*x*, −1/2+*y*, 1/2−*z*) 0.316 3(10) nm] to afford a 3D supermolecular structure (Fig.8).

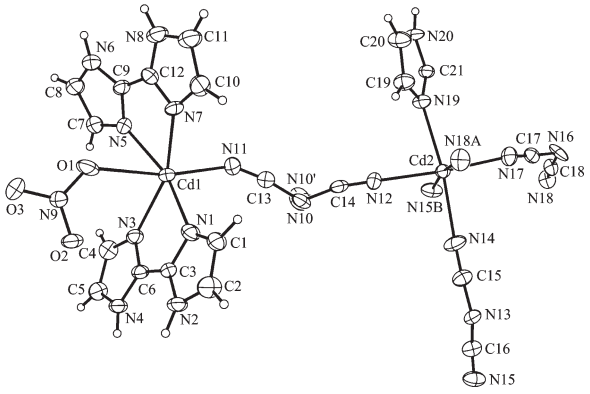

Fig.5　An ORTEP drawing of compound **3** with atomic labeling scheme

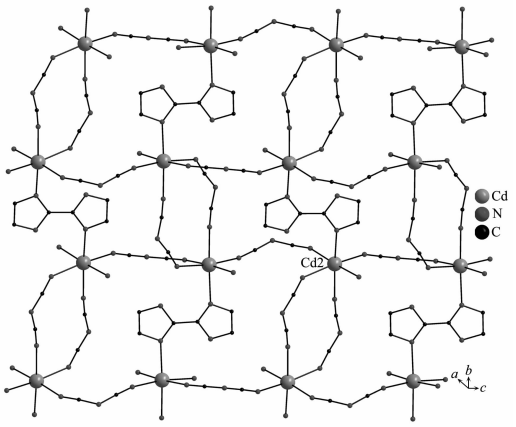

Fig.6　2D structure of compound **3** built by Cd2 atoms

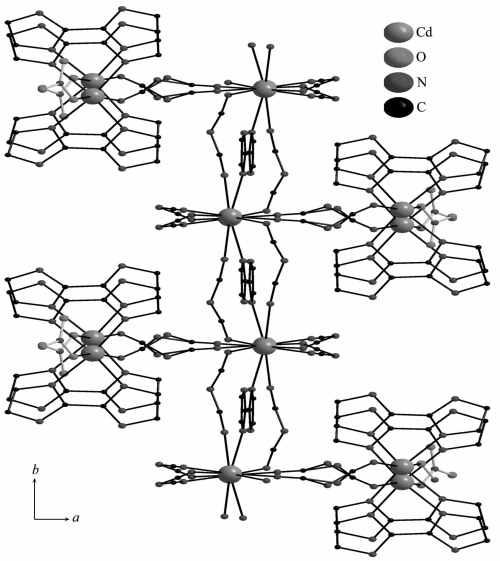

Fig.7　2D structure of compound **3**, viewed along *c*-axis

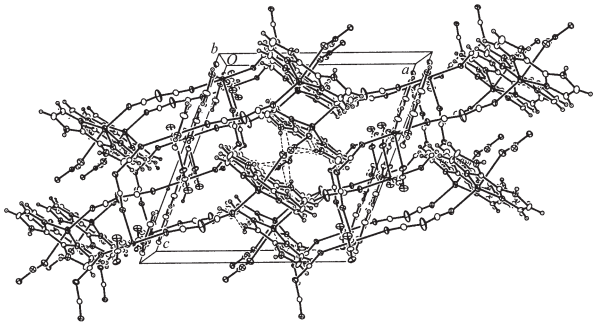

Fig.8 Packing diagrams of compound **3** in a cell viewed along *b*-axis

2.2 Thermogravimetric analysis

The TG curves exhibited that **1**, **2** and **3** are stable up to their decomposition temperatures of 250, 240 and 290 ℃, respectively (Fig.9). In compound **1**, the first weight loss of 31.72% in the region of 250~390 ℃ corresponds to the loss of SCN^- ligands (calculated 32.03%). In compound **2**, the first weight loss of 25.44% from 240 to 380 ℃ is consistent with the loss of N_3^- ligands (calculated 25.42%). As for compound **3**, the first weight loss of 7.38% between 290 and 380 ℃ corresponds to the loss of NO_3^- ligands (calculated 7.56%), and the second weight loss of 24.04% between 380 and 470 ℃ corresponds to the loss of dca ligands (calculated 24.15%). The loss of H_2biim ligands begines at 500 ℃ for **1**, 530 ℃ for **2** and 470 ℃ for **3**.

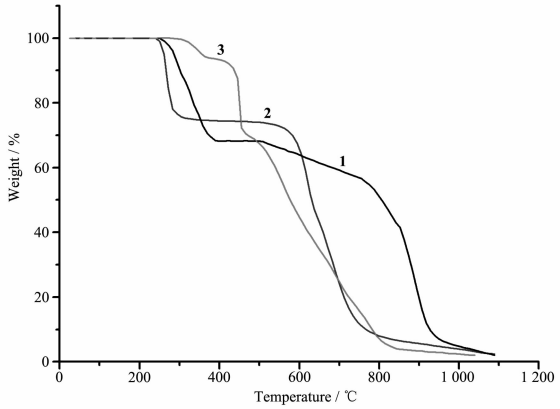

Fig.9 TG view of compounds **1**, **2** and **3**

2.3 Fluorescent spectra analysis

The emission spectra of H_2biim and compounds **1**~**3** in the solid state at room temperature are shown in Fig.10. Compounds **1**~**3** have the same metal centers and the measurements were carried out under the same experimental conditions (λ_{ex}=336 nm), thus a comparison of the fluorescence spectra can be made. The maximum emission wavelength of H_2biim is 425 nm. The maximum emission wavelengths of **1**~**3** are 427, 428 and 435 nm, respectively, are assigned to the $\pi \rightarrow \pi^*$ transitions of the H_2biim ligands[17]. The difference of the emission wavelengths presumably attribute to the difference of the crystal structure.

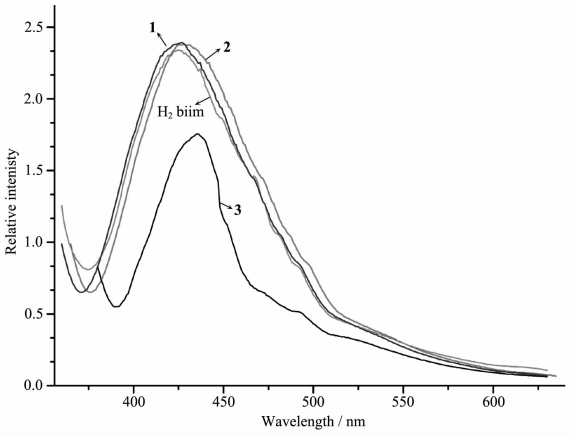

Fig.10 Fluorescent emission spectra of compounds **1**~**3** and H_2biim ligand (λ_{ex}=336 nm)

3 Conclusion

In summary, complexes **1**~**3** were isolated from the reaction of $Cd(NO_3)_2$ and H_2biim with NH_4SCN, NaN_3 and $Na[N(CN)_2]$, respectively. Complex **1** and **2** have a 1D chain structure, while complex **3** has a 2D layered structure. Photoluminescence studies reveal that complex **1**, **2**, and **3** exhibit strong blue fluorescent emissions at 427, 428 and 435 nm, upon excitation at 336 nm, respectively. These emissions are assigned to the H_2biim intraligand emission.

References:

[1] Mao F, Mano N, Heller A. *J. Am. Chem. Soc.*, **2003**,**125**:4951~4957

[2] Esteruelas M A, Garcia M P, Lopez A M, et al. *Organometallics*, **1992**,**11**:702~705

[3] Bloemink M J, Engelking H, Karentzopoulos S, et al. *Inorg. Chem.*, **1996**,**35**:619~627

[4] Sang R L, Xu L. *Inorg. Chim. Acta*, **2006**,**359**:525~532

[5] Ghoshal D, Ghosh A K, Ribas J, et al. *Cryst. Growth & Des.*, **2005**,**5**:941~947

[6] Ye B H, Ding B B, Weng Y Q, et al. *Inorg. Chem.*, **2004**,**43**:6866~6868

[7] Ohrstrom L, Larsson K, Borg S, et al. *Chem. Eur. J.*, **2001**,**7**:

4805~4810

[8] Atencio R, Chacon M, Gonzalez T, et al. *Dalton Trans.*, **2004**: 505~513

[9] Mohamadou A, Albada G A, Driessen W L, et al. *Polyhedron*, **2004**,**23**:1969~1973

[10]Ghosh A K, Jana A, Ghoshal D D, et al. *Cryst. Growth & Des.*, **2006**,**6**:701~707

[11]Hu M L, Cai X Q, Chen J X. *Acta Cryst.*, **2005**,**C61**:m403~m405

[12]Hester C A, Collier H L, Baughman R G. *Polyhedron*, **1996**, **15**:4255~4258

[13]Marshall S R, Incarvito C D, Shum W W, et al. *Chem. Commun.*, **2002**:3006~3007

[14]Cromer D T, Waber J T. *International Tables for X-ray Crystallography*. Birmingham Englang: The Kynoch Press, **1974**, Ⅳ:Table 2.2 A

[15]Ibers J A, Hamilton W C. *Acta Cryst.*, **1964**,**17**:781~782

[16](a)Banerjee S, Wu B, Lassahn P G, et al. *Inorg. Chim. Acta*, **2005**,**358**:535~544

(b)Chand B, Ray U, Mostafa G, et al. *Polyhedron*, **2004**,**23**: 1669~1676

[17]Sang R L, Xu L. *Polyhedron*, **2006**,**25**:2167~2174