Polyhedron 29 (2010) 1575-1582

Contents lists available at ScienceDirect

Polyhedron

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

Four divalent metal thiocyanate coordination compounds containing a rigid functional pyridine ligand

Lin Kong^a, Wei-Jie Li^a, Xian-Lei Li^a, Wen-Qian Geng^a, Fu-Ying Hao^a, Jie-Ying Wu^{a,*}, Hong-Ping Zhou^{a,*}, Jia-Xiang Yang^a, Yu-Peng Tian^{a,b,c}, Bao-Kang Jin^a

^a Department of Chemistry, Key Laboratory of Inorganic Chemistry Materials, Anhui University, Hefei 230039, PR China ^b State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China ^c State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history: Received 21 December 2009 Accepted 11 February 2010 Available online 16 February 2010

Keywords: Coordination molecule π -Conjugated system Crystal structure Optical property

ABSTRACT

A series of new coordination compounds $Zn(SCN)_2L_2$ (1), $Co(SCN)_2L_2$ (2), $[Cd(SCN)_2L_2\cdot 2L]_n$ (3) and $[CdHg(SCN)_4L_2]_n$ (4) have been prepared by self-assembly of a rigid functional pyridine ligand, *trans*-4-[4'-(N-methyl-N-hydroxyethyl)amimo]styryl pyridine (abbreviated as L) with $M(SCN)_x$ (M: Zn, Co, Cd, CdHg; x: 2, 4). The crystal structures indicate that 1 and 2 are mononuclear compounds while 3 and 4 are coordination polymers. O-H···N, C-H···O, O-H··· π and C-H··· π hydrogen bonds play significant roles in the final crystal structures. The solid-state luminescence properties have been measured. The results indicate that the photoluminescence spectra of all the compounds can be changed by the frameworks and introducing of different metal ions.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The crystal engineering of hybrid inorganic-organic framework materials lies at the interface of coordination and supramolecular chemistry and is center of interest in materials research, owing to their potential applications in the fields of molecular absorption, catalysis, host-guest chemistry, electrical conductivity and molecular magnetism [1]. These coordination molecules can be specially designed by careful selection of metal cations with preferred coordination geometries, the nature of the anions, the structure of the connecting ligands, and the reaction conditions [2]. Among these, the selection of cations is extremely important because changing the preferred coordination geometries of the cations can control and adjust the topologies of coordination frameworks, even for structures containing the same spacer ligand and anion [3]. Additionally, in construction of the infinite supramolecular networks, multidentate ligand thiocyanate is usually employed to bridge between metal centers to form polymeric structures. SCN⁻ is a highly versatile ambidentate ligand with a polarizable π system and two different donor atoms, which can coordinate to metals through either the nitrogen or the sulfur atom, or both [4]. The various bridging modes of SCN⁻ anion not only generate new types of network structures but also offer the opportunity for forming heterometallic complexes involving various combinations of metal ion node points. Such combinations could lead to the formation of materials with useful properties driving from the presence of the heterometallic arrays [5].

To design and prepare molecular crystals with desired and predictable structures, it requires an understanding of the intermolecular interactions that link molecules together. Successful noncovalent assembly of individual entities into complex structures normally relies on a toolbox containing intermolecular weak interactions such as hydrogen bonds [6] and π - π interactions [7], which are observed frequently in solid state.

Up to now, it has become increasingly apparent that the coordination networks with interesting structure alone are not sufficient to sustain the rapid growth in the fields of materials. The important aspect which has greatly affected the field of supramolecular chemistry is the design and synthesis of new functional ligands, which play an important role in determining the properties of materials. As far as we know, there are a few reports on the compounds containing unidentate pyridine ligand with functional groups [8]. More efforts may be focused on the field.

Considering all the aspects above, we have designed rationally and synthesized readily a rigid functional pyridine ligand with satisfactory electron donor and acceptor through a conjugated bridge. Based on the bridging potential of the hard and soft coordination centers of the ambidentate SCN⁻ anion, we are able to obtain different compounds with functional structures. The combination of inorganic and functional organic moieties leads to both new structural architectures and excellent luminescence properties. Therefore, in this article, synthesis, structure and photoluminescence property of the four new compounds are reported.





^{*} Corresponding authors. Tel.: +86 551 5108151; fax: +86 551 5107342. *E-mail addresses:* jywu1957@163.com (J.-Y. Wu), zhpzhp@263.net (H.-P. Zhou).

Table 1

Crystal data and structure refinement for compound 1, 2, 3 and 4.

Compound	1	2	3	4
Formula	$C_{34}H_{36}ZnN_6O_2S_2$	$C_{34}H_{36}CoN_6O_2S_2$	C ₆₆ H ₇₂ CdN ₁₀ O ₄ S ₂	C ₃₆ H ₃₆ CdHgN ₈ O ₂ S ₄
Formula weight	690.18	683.74	1245.86	1053.96
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	Pccn	Pccn	ΡĪ	P2(1)/n
a (Å)	11.420(5)	11.404(2)	11.002(5)	6.906(4)
b (Å)	27.483(5)	27.574(4)	17.281(7)	19.171(9)
c (Å)	10.477(5)	10.445(2)	7.940(8)	30.158(2)
α (°)	90.000(5)	90.000	106.020(1)	
β (°)	90.000(5)	90.000	99.446(1)	96.318(4)
γ (°)	90.000(5)	90.000	105.180(1)	
V (Å ³)	3288(2)	3284.4(8)	3059.3(2)	3968.3(4)
Ζ	4	4	2	4
$D_{\text{Calc}} (\text{mg/m}^{-3})$	1.394	1.383	1.352	1.764
F (0 0 0)	1440	1428	1300	2064
Crystal size (mm)	$0.20 \times 0.10 \times 0.09$	$0.20\times0.10\times0.10$	$0.20\times0.10\times0.10$	$0.20\times0.10\times0.10$
Reflection collected	21 824	25 277	35 306	23 697
Goodness of fit (GOF) on F^2	0.897	0.953	1.021	1.008
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0488, wR_2 = 0.1297$	$R_1 = 0.0478, wR_2 = 0.0583$	$R_1 = 0.0590, wR_2 = 0.1481$	$R_1 = 0.0373, wR_2 = 0.0634$
R indices (all data)	$R_1 = 0.0948, wR_2 = 0.1599$	$R_1 = 0.1052, wR_2 = 0.1722$	$R_1 = 0.1067, wR_2 = 0.1822$	$R_1 = 0.0735, wR_2 = 0.0748$

2. Experimental

2.1. General

All commercially available chemicals are of analytical grade and used without further purification. The solvents were purified by conventional methods before use. IR spectra were recorded on a Nicolet FT-IR instrument by using KBr discs in the 4000–400 cm⁻¹ range. Elemental analyses were carried out on Perkin–Elmer 240 analyzer. ¹H and ¹³C NMR spectra were performed on Bruker 400 MHz Ultrashield spectrometer and reported as parts per million (ppm) from TMS (δ). Electrospray ionization mass spectra (ESI-MS) were acquired using a model LCQ ion trap mass spectrometer (Finnigan) equipped with a Finnigan MAT electrosprayion source. UV–Vis spectra were recorded on an U-4100 UV–Vis spectrophotometer. Luminescence spectra were recorded on a Hitachi F-3500 fluorescence spectrophotometer at room temperature.

2.2. Synthesis

4-(N-methyl-N-hydroxyethyl)amimo)benzaldehyde was synthesized according to the reported method [9].

2.2.1. Synthesis of trans-4-[4'-(N-methyl-Nhydroxyethyl)amimo]styryl pyridine (**L**)

The mixture of 4-(N-methyl-N-hydroxyethyl)amimo)benzaldehyde (3.58 g, 20.00 mmol), 4-methylpyridine (2.05 g, 22.00 mmol) and t-BuOK (5.61 g, 60.00 mmol) were placed in a mortar, ground for 10 min, and then poured into distilled water (300 mL). The product was extracted twice with CH₂Cl₂, and the organic layer was dried overnight with anhydrous MgSO₄. Next, the solvent was removed by rotary evaporator to give crude product, and then the residue was purified by recrystallization from ethanol to give 4.06 g yellow powder with yield 80%. ¹H NMR (DMSO- d_6 , 400 MHz) ppm: 2.96 (s, 3H), 3.43-3.46 (t, J = 6 Hz, 2H), 3.55-3.56 (t, J = 4.8 Hz, 2H), 6.72-6.74 (d, J = 8.4 Hz, 2H), 6.93-6.97 (d, J = 16.4 Hz, 1H), 7.45–7.49 (t, J = 6.4 Hz, 3H), 7.53–7.55 (d, J = 5.2 Hz, 2H), 8.48–8.49 (d, J = 5.2 Hz, 2H); Anal. Calc. for C₁₆H₁₈N₂O: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.41; H, 6.98; N, 11.43%. MS: *m/z* (%): 254 (M⁺), 223, 209, 194; IR (KBr, cm⁻¹): $v = 3340 (v_{O-H}, m)$, 1589 (v_{-ring} , s), 1523 (v_{-ring} , m), 1381 (v_{C-N} , m), 1052 (δ_{C-O} , m).

2.2.2. Preparation of $Zn(SCN)_2L_2$ (1)

L (0.51 g, 2.00 mmol) and Zn(SCN)₂ (0.18 g, 1.00 mmol) were dissolved in 100 mL of methanol, refluxed for 2 h at 60 °C, cooled to give a clear yellow solution. Yellow crystals suitable for X-ray diffraction were obtained after 10 days by slow evaporation of the methanol solution at room temperature. Yield: 0.48 g (70%). *Anal.* Calc. for C₃₄H₃₆ZnN₆O₂S₂. C, 59.16; H, 5.26; N, 12.18. Found: C, 58.92; H, 5.03; N, 12.49%. IR (KBr, cm⁻¹): v = 2923 (v_{CH2} , w), 2075 (s, v_{as-SCN}), 1590 (v_{-ring} , vs), 1523 (v_{-ring} , m), 1380 (v_{C-N} , w), 1079 (δ_{C-O} , w).

2.2.3. Preparation of $Co(SCN)_2L_2$ (2)

L (0.025 g, 0.10 mmol) and Co(SCN)₂ (0.018 g, 0.10 mmol) were dissolved in 20 mL of methanol. After refluxed for 2 h at 70 °C, the solution was cooled to give a clear yellow solution. Yellow crystals suitable for X-ray diffraction were obtained after two weeks by slow evaporation of the methanol solution at room temperature. Yield: 0.028 g (82%). *Anal.* Calc. for C₃₄H₃₆CoN₆O₂S₂: C, 59.72; H, 5.31; N, 12.29. Found: C, 59.60; H, 5.13; N, 12.03%. IR (KBr, cm⁻¹): v = 2872 (v_{CH2} , w), 2064 (s, v_{as-SCN}), 1580 (v_{-ring} , vs), 1506 (v_{-ring} , s), 1370 (v_{C-N} , w), 1070 (δ_{C-O} , w).

2.2.4. Preparation of $[Cd(SCN)_2L_2 \cdot 2L]_n$ (3)

Compound **3** was synthesized by layering method at room temperature. A clear methanol solution (15 mL) of Cd(SCN)₂ (0.023 g, 0.10 mmol) was carefully layered onto a solution of **L** (0.025 g, 0.10 mmol) in chloroform (10 mL). Yellow needle-shaped crystals suitable for X-ray diffraction were obtained by slow interlayer diffusion. Yield: 0.024 g (77%). *Anal.* Calc. for $[C_{66}H_{72}CdN_{10}O_4S_2]_n$: C, 63.63; H, 5.82; N, 11.24. Found: C, 63.02; H, 5.55; N, 11.61% IR (KBr, cm⁻¹): $v = 2873 (v_{CH2}, w)$, 2084 (s, v_{as-SCN}), 1590 (v_{-ring} , vs), 1520 (v_{-ring} , s), 1373 (v_{C-N} , w), 1079 (δ_{C-O} , w).

2.2.5. Preparation of $[CdHg(SCN)_4L_2]_n$ (4)

Methanol solution of CdHg(SCN)₄ was prepared by reaction of Cd(NO₃)₂·6H₂O (0.034 g, 0.10 mmol), Hg(NO₃)₂·H₂O (0.034 g, 0.10 mmol) and KSCN (0.002 g, 0.20 mmol) in 20 mL of absolute methanol. The white precipitate of KNO₃ was removed by filtration. The methanol solution of CdHg(SCN)₄ was carefully layered onto a solution of L (0.025 g, 0.10 mmol) in chloroform (15 mL). Yellow needle crystals suitable for X-ray diffraction were obtained by slow interlayer diffusion. Yield: 0.037 g (70%). Anal. Calc for $[C_{36}H_{36}CdHgN_8O_2S_4]_n$: C, 41.02; H, 3.44; N, 10.63. Found: C,

Compound 1					
Zn(1) - N(1)	1.933(4)	S(1)-C(19)	1.606(5)	C(19) - N(1)	1.147(5)
Zn(1)-N(2)	2.025(3)	C(7) - C(8)	1.326(5)	C(6) - C(7)	1.452(6)
C(9)-C(8)	1.458(6)				
N(1)-Zn(1)-N(2)	104.5(1)	N(1)-Zn(1)-N(2A)	110.0(2)	N(1)-Zn(1)-N(1A)	119.1(2)
N(1A)-Zn(1)-N(2)	109.4(2)	N(1)-C(19)-S(1)	178.1(4)		
Compound 2					
Co(1)-N(3)	1.938(4)	Co(1)-N(2)	2.015(3)	S(1)-C(17)	1.607(5)
C(17)-N(3)	1.152(6)				
N(3)-Co(1)-N(3)	118.7(2)	N(2)-Co(1)-N(2)	111.0(2)	N(3)-Co(1)-N(2)	104.0(2)
Compound 3					
Cd(01) - N(9)	2,298(5)	Cd(01)-S(2)	2.705(2)	Cd(01)-S(1)	2.750(2)
Cd(01) - N(3)	2.369(4)	Cd(1) - N(2)	2.357(2)	Cd(1) - N(10)	2.316(5)
N(10)-Cd(01)-S(1)	101.4(1)	N(10)-Cd(01)-S(2)	85.1(1)	N(10)-Cd(01)-N(2)	86.4(2)
N(10) - Cd(01) - N(3)	87 2(2)	N(9) - Cd(01) - N(2)	94 8(2)	N(9) - Cd(01) - S(2)	90.7(1)
N(9) - Cd(01) - N(3)	91 7(2)	N(9) - Cd(01) - S(1)	82 8(1)	N(3) - Cd(01) - S(2)	92 6(1)
N(3) - Cd(01) - S(1)	878(1)	N(2) - Cd(01) - S(1)	91 8(1)	N(2) - Cd(01) - S(2)	89 3(1)
	0/10(1)		0110(1)		0010(1)
Compound 4	2 512(2)		2 516 (2)	11-(1) ((2)	2 502(2)
Hg(01)-S(1)	2.513(2)	Hg(01) - S(4)	2.516(2)	Hg(1)-S(3)	2.583(2)
Hg(01) - S(2)	2.518(2)	Cd(1) - N(6)	2.435(5)	Cd(1) - N(2)	2.331(5)
Cd(1)–N(8)	2.336(5)	Cd(1)-N(7)#1	2.322(5)		
S(1)-Hg(01)-S(4)	108.6(5)	C(34)-S(1)-Hg(01)	97.3(2)	N(8)-Cd(1)-N(6)	94.2(2)
N(2)-Cd(1)-N(6)	83.7(2)	N(2)-Cd(1)-N(8)	91.2(2)		

Table 2

 Table 3

 Weak interaction parameters for 1, 2, 3 and 4.

Bond lengths (Å) and angles (°) for compound 1, 2, 3 and 4.

D−H…A	Ring	d(D-H) (Å)	d(H–A) (Å)	d(D–A) (Å)	<dha (°)</dha
$\begin{array}{c} \textit{Compound} \\ \textit{O}-\textit{H}\cdots \pi^{a} \\ \textit{C}-\textit{H}\cdots \textit{O}^{b} \end{array}$	1	0.819	2.740	3.400	139.1
	C9, C10, C11, C12, C13, C14	0.930	2.588	3.504	168.5
Compound $.0 - H \cdots \pi^{c}$	2	0.819	2.730	3.396	139.6
C-H $\cdots 0^{d}$	C4, C5, C6, C7, C8, C9	0.930	2.576	3.494	169.3
Compound .	3	0.820	1.995	2.770	157.3
O−H···N ^{e,f}		0.821	2.058	2.744	140.7
C−H···O ^g		0.959	2.508	3.456	169.7
$\begin{array}{c} \textit{Compound} \\ \textit{C-H}{\cdots}\pi^h \end{array}$	4 C4, C5, C6, C7, C8, C9	0.928	3.762	4.445	132.8

^a x 0.5 - y z

^b 1.5 - x 1.5 - y z

 $^{\rm c}_{.}$ 0.5 – x 1.5 – y z

d x 1.5 - y 0.5 + z

e -x + 1 - y - z + 1

f -x -y + 2 -z + 1

 $f^{g} x 1 - y z$ $h^{h} 1 + x y z$

40.60; H, 3.64; N, 11.03%. IR (KBr, cm⁻¹): $v = 2900 (v_{CH2}, w)$, 2120 (s, v_{as-SCN}), 1580 (v_{-ring} , vs), 1520 (v_{-ring} , s), 1370 (v_{C-N} , w), 1065 (δ_{C-O} , w).

2.3. X-ray crystallography

The X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 298(2) K. Intensity data were collected in the variable ω -scan mode. The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with the SHELXTL-97 program package [10]. All crystallographic data for the four compounds are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. Weak interaction parameters are listed in Table 3, involving distance, angle and symmetry code.

3. Results and discussion

3.1. Synthesis

The new organic ligand, trans-4-[4'-(N-methyl-N-hydroxyethyl)amimo|styryl pyridine (L) is a unidentate pyridine derivative with π -conjugated system and functional group. Synthetic details of L are summarized in Scheme 1. The ligand has been synthesized by solid-state reaction at room temperature, and is found to proceed efficiently in excellent yield (80%) in short reaction time (10 min). During the synthesis, the product is obtained without any organic solvent, which agrees with the principles of 'green chemistry'. The four compounds with different coordination geometries are prepared through self-assembly of the same ligand with four divalent metal thiocvanate salts. Compound 1 and 2 are only mononuclear compounds, while **3** is a coordination polymer and a hetero-metallic polymer is gotten for CdHg(SCN)₄. The four compounds are insoluble in water or in common organic solvents. High yields of the products indicate that these compounds are thermodynamically stable under the prevailing reaction conditions.

3.2. Crystal structures

3.2.1. Crystal structure of $Zn(SCN)_2L_2$ (1)

The metal coordination molecule, $Zn(SCN)_2L_2$, crystallizes in orthorhombic form with space group *Pccn* as shown in Fig. 1a. The coordination geometry of zinc atom is a distorted tetrahedron with two nitrogen atoms from **L** and two nitrogen atoms from SCN^- anions, where the bond angles around Zn^{2+} are in the range of 104.5° – 119.1° , and the Zn–N bond lengths are between



Scheme 1. The synthetic routes for ligand L.



Fig. 1. (a) Coordination environments of Zn with the atom numbering scheme. (b) The 1D framework showing the weak O–H···π (orange) interactions along *c* axis at a distance of 2.740 Å. (c) Packing diagram of **1**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1.933(4) Å and 2.025(3) Å. The strong distortion in the tetrahedral environment of the four donor atoms can be induced by strong stereo interactions between the ligands. The bond lengths of C6–C7 (1.452(6) Å) and C8–C9 (1.458(6) Å) are located between normal C–C single-bond distance of 1.54 Å and C=C double-bond distance of 1.34 Å, respectively. In the compound, the molecular structure of **L** is almost planar, least-square plane calculation shows that the dihedral angle between benzene ring and pyridine ring is 3.8°, indicating they are nearly coplanar. Excellent coplanarity of conjugated moiety enables the compound to be a high delocalized-electron system.

From Table 2, it can be seen that the S–C–N bond angle is 178.1(4)°, that is to say, the SCN⁻ anion is a perfect linear group. The S–C and C–N distances in SCN⁻ anion are 1.606(5) and 1.147(5) Å, respectively, indicating a π -delocalization along the metal-thiocyanate chain [1]. This observation is consistent with the fact that the SCN⁻ anion is easily polarizable (⁻S–C \equiv N \leftrightarrow S–C \equiv N⁻).

The adjacent molecules are stacked through $O-H\cdots\pi$ (ring C9, C10, C11, C12, C13, C14) interactions along the same direction (*c* axis) at a short intermolecular distance of 2.740 Å (the angle of $O-H\cdots\pi$ is 139.1°) to form 1D structure as shown in Fig. 1b. There is also a $C-H\cdotsO$ intermolecular hydrogen bond with the $H\cdotsO$



Fig. 2. (a) Coordination environments of Cd with the atom numbering scheme, H atoms are omitted for clarity. (b) 1D zigzag chain fragment showing Cd-S and Cd-N interactions along a axis. (c) The 2D architecture is connected by O-H. N hydrogen bonds at distance of 1.995 Å-2.058 Å.

distance of 2.588 Å (C–H \cdots O = 168.5°), which is very important in supramolecular self-assembly to form 2D sheets in the *ab* plane. Then the as-assembled 2D planes are stacked through $O-H\cdots\pi$ interactions to form 3D structure (Fig. 1c).

3.2.2. Crystal structure of $Co(SCN)_2L_2$ (2)

The crystal structure of **2** is very similar to that of **1**. Compound 2 is also a mononuclear compound. The molecules are stacked through O–H $\cdots\pi$ interactions to form 1D chain. There also exists C-H···O hydrogen bond to generate 2D sheets. The details of the structure are described in Supplementary material.

3.2.3. Crystal structure of $[Cd(SCN)_2L_2?2L]_n$ (3)

Compared to mononuclear compounds 1 and 2, the polymer 3 can be synthesized when $Cd(SCN)_2$ is introduced. Compound **3** crystallizes in triclinic with space group $P\overline{1}$. More interesting, each independent cell contains a compound molecule and two free L molecules as shown in Fig. 2a. Cd²⁺ ion, being in between soft and hard acid, exhibits both bonding modes with S and N [11]. Each Cd²⁺ ion lies in a center of symmetry surrounded by six related atoms, two are sulfur atoms and the other four are nitrogen atoms. The two sulfur atoms are from SCN⁻ anions (the Cd–S bond length is 2.705(2)Å), and four nitrogen atoms, two of which are from two **L** molecules occupying the axial positions with Cd-N(2)bond length of 2.357(2) Å, other two are from SCN⁻ anions (the Cd–N bond length is 2.316(5)Å). Therefore, the polyhedron can be described as a distorted octahedron.

Adjacent Cd²⁺ ions are linked by two bridging SCN⁻ anions with the Cd···Cd distance of 5.520 Å (Fig. 2b), creating 1D $[Cd(SCN)_2]_n$ zigzag polymeric chain along the *a* axis comprising eight-membered (N-C-S-Cd)₂ rings, which have been well documented in Cd–SCN systems [12].

Interestingly, it is noted that each compound molecule is accompanied by two free ligand molecules. The dihedral angle between benzene ring and pyridine ring of the compound is 11.7° , while that in the free ligand to be 2.1° , showing a severe distortion due to some weak interactions with adjacent molecules. The two free ligand molecules are stabilized by forming two types of intermolecular hydrogen bonds. One is $O-H\cdots N$ hydrogen bond between the free ligand and the metal compound with the $H\cdots N$ distance of 1.995 and 2.058 Å, $(O-H\cdots N = 157.3^{\circ} \text{ and } 140.7^{\circ})$, the other is $C-H\cdots O$ hydrogen bond between two free ligands with the $H\cdots O$ distance of 2.508 Å ($C-H\cdots O = 169.7^{\circ}$). These weak interactions play vital role in determining the crystal packing and in the construction of the extended 2D sheets in the *ab* plane (Fig. 2c).

3.2.4. Crystal structure of $[CdHg(SCN)_4L_2]_n$ (4)

As mentioned above, the various bridging modes of the thiocyanate ligand not only generate new types of network structures but also offer the opportunity for forming hetero-metallic compounds. Such combinations could lead to the formation of materials with useful properties driving from the presence of the heterometallic arrays. To get hetero-metallic polymer, Hg²⁺ ions are added to prepare **4**. The hetero-metallic polymer crystallizes in monoclinic with space group P2(1)/n. The coordination modes of **4** can be rationalized in terms of the hard-soft acid-base concept (HSAB). Hg²⁺ ion, being a soft acid, is preferentially coordinated by the soft base (S) terminus of the SCN⁻ anion [9]. Cd²⁺ ion, therefore, coordinates by the hard base (N) atoms from SCN⁻ anion and **L**. As shown in Fig. 3, each Hg²⁺ ion is in a distorted tetrahedral geometry, being coordinated by four sulfur atoms from SCN⁻ anions. The Hg–S bond lengths are between 2.513(2) and 2.583(2) Å. The Hg-S-C angles vary from 93.6(2) to 97.3(2)°. The SCN⁻ anions are virtually linear with average S–C and N–C bond length of 1.645(8) and 1.140(3) Å, respectively. Each Cd²⁺ ion places in a distorted octahedral environment, coordinated by six N atoms, two of which are from two L and others are from SCN⁻ anions. The Cd–N bond lengths are between 2.322(5) and 2.435(5) Å. The Cd–N–C angles are in the range of 83.7(2)°-179.6(2)°. The dihedral angle between benzene ring and pyridine ring of the polymer molecule is 8.2°.



Fig. 3. (a) Coordination environments of Cd and Hg with the atom numbering scheme; H atoms are omitted for clarity. (b) 1D zigzag chain fragment along *a* axis. (c) 2D polymeric sheet in the *ab* plane.

Adjacent Cd^{2+} ions are linked by two bridging SCN^- anions and two Hg^{2+} ions with the $Cd\cdots Cd$ distance of 6.906 Å (Fig. 3b) and $Cd\cdots Hg$ distance ranging from 5.340 to 5.908 Å, which further form 1D polymeric chain along the *a* axis.

Cd²⁺ and Hg²⁺ ions are also linked by bridging SCN⁻ anions to form 2D sheets in the *ab* plane, containing 24-membered [Cd₃Hg₃(SCN)₆] cycles as subunits, which adopt pseudo-chair configuration, as shown in Fig. 3c. The 2D layers link each other through C-H··· π (ring C4, C5, C6, C7, C8, C9) interaction (H··· π distance of 3.762 Å, C-H··· π = 132.8°) to form 3D frameworks.

Comparing the four compounds, we have observed the differences in coordination mode, geometries and dimensions with variation of the center metals. The SCN⁻ anion links the center metals in various fashions to form different constructions. Compound 1 and **2** are mononuclear compounds, whose metal atom adopts distorted tetrahedral coordination geometry. The adjacent molecules are stacked through $O-H\cdots\pi$ interactions to form 'A' type 1D structure. Compound **3** is an infinite coordination molecule. Cd²⁺ ions are linked by bridging SCN⁻ groups to create 1D zigzag polymeric chain comprising eight-membered (N-C-S-Cd)₂ rings. The structure displays 'pupa' type with two free ligands attached through hydrogen bonds to enhance the stability of the whole structure, which is just like a Chinese 'dragon' with two wings flying in the sky. For CdHg-L heteropolymer, each Cd²⁺ ion is in a distorted octahedral environment and each Hg²⁺ ion is in a distorted tetrahedral geometry. Cd²⁺ and Hg²⁺ ions are linked by bridging SCN⁻ groups to form 1D polymer chain and 24-membered [Cd₃Hg₃(SCN)₆] cycles, which then create 2D polymeric plane. All these further verify that the selection of metal cations can definitely adjust the topologies of coordination frameworks, even for structures containing the same spacer ligand and anion.

3.3. Optical properties

The linear absorbance and photoluminescence properties for **L** and four compounds in solid state have been studied at room temperature. The electronic spectra of the compounds are very close to that of free **L**. The longest wavelength UV absorption peaks are located at about 375 nm for the compounds and 372 nm for free **L** (Fig. S4), presumably arisen from π - π ^{*} transitions [13]. Compared to that of free **L**, there is a slight red shift in $\lambda_{abs-max}$ when metals are introduced. The detailed data are listed in Table 4.

Metal complexes are promising luminescent materials with potential applications as light-emitting materials owing to their ability to enhance, quench, and shift luminescent emission of organic ligands by metal coordination. Free **L** and the four compounds **1– 4** show emission in solid state at room temperature (Fig. S5). The excitation spectra are very similar to their absorption spectra. The nanosecond range of lifetime reveals that the emission is fluorescent in nature. As shown in Fig. S5, the maxima emissions observed in the four compounds are all red-shifted compared with that of **L**. The maximum wavelengths of **1**, **2** and **4** are red-shifted by 33 nm, 30 nm and 46 nm from 501 nm to 534 nm, 531 nm and 547 nm, respectively. However, for **3**, it is red-shifted by 15 nm from 501 nm to 516 nm, which is closer to **L** than that of **1**, **2** and **4**. The outcome of synergy effect of compound and free ligand may be responsible for the solid luminescence. The results indicate

Table 4					
Absorbance ar	d fluorescence	data for L,	1, 2,	3 and	4

Table 4

Compound	L	1	2	3	4
$\lambda_{abs-max}$ (nm) λ_{em-max} (nm)	372 501	375 534	374 531	373 516	375 547
t (IIS)	0.95	3.29	3.30	2.63	3.91

that photoluminescence properties of the compounds can be changed by the frameworks and different center metals.

Owing to the excellent optical properties, these compounds may be used as potential lighter-emitting materials, chemical sensing and biological applications.

4. Conclusions

Compounds **1–4** are synthesized by self-assembly of the flexible ligand, *trans*-4-[4'-(N-methyl-N-hydroxyethyl) amimo]styryl pyridine) with M(SCN)_x (M: Zn, Co, Cd, CdHg; x: 2, 4). By supramolecular self-assembly of different metals with the same ligand, different types of framework can be obtained. Compound **1** and **2** are only mononuclear compounds, while **3** is a polymer and **4** is a heteropolymer. The result shows that the choice of metal ion is critical in determining the architecture of the compound. O-H…N, C-H…O, O-H… π and C-H… π hydrogen bonds also play significant roles in the final crystal structures. The emission wavelength of the compounds can be changed by the frameworks and introducing of different metals. These compounds have potential usage as lighter-emitting materials, chemical sensing, and biological applications.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (20771001, 50703001 and 50873001), Young Teacher Foundation of Institution of High Education of Anhui Province (2006jq1030), Education Committee of Anhui Province (KJ2009A52) and Foundation for Scientific Innovation Team of Anhui Province (2006KJ007TD).

Appendix A. Supplementary data

CCDC 741841, 737174, 707972 and 737173 contain the supplementary crystallographic data for compound **1**, **2**, **3** and **4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223– 336–033; or E–mail: deposit@ccdc.cam.au.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.02.018.

References

- J. Pasán, J. Sanchiz, L. Cañadillas-Delgado, O. Fabelo, M. Déniz, F. Lloret, M. Julve, C. Ruiz-Pérez, Polyhedron 28 (2009) 1802.
- [2] H. Zhang, X.M. Wang, K. Zhang, B.K. Teo, Coord. Chem. Rev. 183 (1999) 157.
 [3] (a) F. Jin, H.P. Zhou, X.C. Wang, Z.J. Hu, J.Y. Wu, Y.P. Tian, M.H. Jiang,
- Polyhedron 26 (2007) 1338;
 (b) F. Jin, J. F Li, H.P. Zhou, J.Y. Wu, J.X. Yang, Y.P. Tian, M.H. Jiang, J. Mol. Struct. 829 (2007) 202.
- [4] (a) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319;
 - (b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, Acc. Chem. Res. 38 (2005) 217;

(c) D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, Acc. Chem. Res. 38 (2005) 273;

(d) R.J. Hill, D.L. Long, N.R. Champness, P. Hubberstey, M. Schröder, Acc. Chem. Res. 38 (2005) 335;

- (e) M.W. Hosseini, Acc. Chem. Res. 38 (2005) 313;
- (f) N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176.
- [5] H.P. Zhou, J.H. Yin, L.X. Zheng, P. Wang, F.Y. Hao, W.Q. Geng, X.P. Gan, G.Y. Xu, J.Y. Wu, Y.P. Tian, X.T. Tao, M.H. Jiang, Y.H. Kan, Cryst. Growth Des. 9 (2009) 3789.
- [6] (a) C.B. Aakeröy, D.J. Salmon, Cryst. Eng. Commun. 7 (2005) 439;
 (b) J.M. Lehn, Science 295 (2002) 2400;
 - (c) G.R. Desiraju, Acc. Chem. Res. 35 (2002) 565;
 - (d) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
 - (e) M. Wenger, J. Bernstein, Angew. Chem., Int. Ed. 45 (2006) 7966;
 - (f) S.L. Childs, K.I. Hardcastle, Cryst. Eng. Commun. 9 (2007) 364.

- [7] (a) N. Barooah, R.J. Sarma, J.B. Baruah, Cryst. Eng. Commun. 8 (2006) 608; (b) N. Motobiro, Cryst. Eng. Commun. 6 (2004) 130
- (b) N. Motohiro, Cryst. Eng. Commun. 6 (2004) 130.
 [8] (a) H.J. Liu, X.T. Tao, J.X. Yang, Y.X. Yan, Y. Ren, H.P. Zhao, Q. Xin, W.T. Yu, M.H. Jiang, Cryst. Growth Des. 8 (2008) 259;
 (b) Y.P. Tian, L. Li, J.Z. Zhang, J.X. Yang, H. P Zhou, J.Y. Wu, P.P. Sun, L.M. Tao, Y.H. Guo, C.K. Wang, H. Xing, W.H. Huang, X.T. Tao, M.H. Jiang, J. Mater. Chem. 17 (2007) 3646.
- [9] X.M. Wang, Y.F. Zhou, W.T. Yu, C. Wang, Q. Fang, M.H. Jiang, H. Lei, H.Z. Wang, J. Mater. Chem. 10 (2000) 2698.
 [10] G.M. Sheldrick, SHELXTL V5.1 Software Reference Manual Bruker, AXS Inc.,
- [10] G.M. Sheldrick, SHELXTL V5.1 Software Reference Manual Bruker, AXS Inc., Madison, Wisconsin, USA, 1997.
- [11] (a) F.H. Allen, C.M. Bird, R.S. Rowland, P.R. Raithby, Acta Crystallogr., Sect. B 53 (1997) 696;

- (b) A.D. Bond, W. Jones, J. Chem. Soc., Dalton Trans. (2001) 3045;
- (c) H.P. Zhou, Y.M. Zhu, J.J. Chen, Z.J. Hu, J.Y. Wu, X. Yi, M.H. Jiang, Y.P. Tian, Inorg. Chem. Commun. 9 (2006) 90.
- [12] (a) M. Taniguchi, Y. Sugita, A. Ouchi, Bull. Chem. Soc. Jpn. 60 (1987) 179;
 (b) M. Taniguchi, A. Ouchi, Bull. Chem. Soc. Jpn. 62 (1987) 424;
 (c) H.J. Chen, G. Yang, X.M. Chen, Acta Crystallogr., Sect. C 55 (1999) 2012;
 (d) G. Yang, H.G. Zhu, B.H. Liang, X.M. Chen, J. Chem. Soc., Dalton Trans. (2001) 580;

(e) H. Zhang, D.E. Zelmon, G.E. Price, B.K. Teo, Inorg. Chem. 39 (2000) 1868.

[13] (a) C.M. Che, C.W. Wan, K.Y. Ho, Z.Y. Zhou, New J. Chem. 25 (2001) 63;
 (b) C.M. Che, C.W. Wan, W.Z. Lin, W.Y. Yu, Z.Y. Zhou, W.Y. Lai, S.T. Lee, Chem. Commun. (2001) 721.