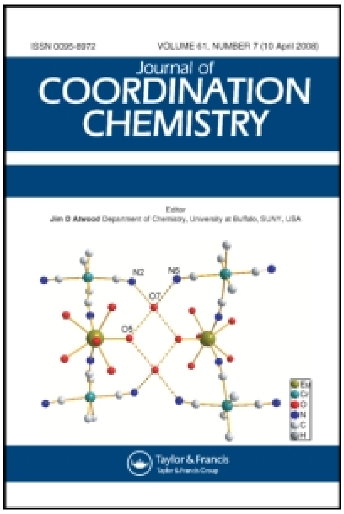

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Synthesis, structure and properties of three one-dimensional coordination polymers $\{[\mathrm{M(II)L(NCS)_2}](\mathrm{DMF})_2\}_{\text{<i>n</i>}}$ (M(II)=cadmium(II), zinc(II), manganese(II); L=1,4-*bis*[2-(2-pyridyl)benzimidazolato]butane)

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Synthesis, structure and properties of three one-dimensional coordination polymers $\{[\mathrm{M(II)L(NCS)_2}](\mathrm{DMF})_2\}_n$ ($\mathrm{M(II)}=$ cadmium(II), zinc(II), manganese(II); $\mathrm{L}=1,4$-*bis*[2-(2-pyridyl)benzimidazolato]butane)

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A tetradentate N-donor ligand 1,4-*bis*[2-(2-pyridyl)benzimidazolato]butane (L) was prepared for construction of a coordination framework. Three one-dimensional coordination polymers $\{[\mathrm{M(II)L(NCS)_2}](\mathrm{DMF})_2\}_n$ ($\mathrm{M(II)}=$ cadmium(II), **1**, zinc(II), **2**, manganese(II), **3**) were obtained by reaction of metal ions and L in the presence of KSCN in DMF/water. The complexes are isostructural and consist of 1D zigzag $[\mathrm{M(II)L(NCS)_2}]_n$ chains and DMF molecules. Within the chains, the metal atoms are each octahedrally coordinated by four N atoms of L and two N atoms of the $\mathrm{SCN^-}$ anions. Complexes **1** and **2** in the solid state at room temperature exhibit intense photoluminescence at 453 and 433 nm, respectively.

Keywords: Cadmium(II) complex; Zinc(II) complex; Manganese(II) complex; Crystal structure; Photoluminescence

1. Introduction

Supramolecular chemistry is a rapidly growing field of research involving construction of molecular assemblies held together by forces such as hydrogen bonding, π–π stacking interactions, and metal-ligand coordination [1, 2]. These assemblies may find utility as new materials with novel catalytic, magnetic, electronic, and optical properties [3–6]. Nitrogen-containing rigid aromatic ligands such as phenanthroline were usually chosen because they can construct supramolecular structure via $\mathrm{C{-}H\cdots O}$ hydrogen bonding and π–π stacking interactions [7–12]. Long flexible chain-like ligands such as α,ω-dicarboxylic acids exhibit conformational and coordination versatility due to single-bonded carbon chains [13–16]. Growing attention was paid to rational design and synthesis of coordination polymers by simultaneous utilization of rigid N-donor ligands and α,ω-dicarboxylate ligands [17–19]. 2-(2-Pyridyl)benzimidazole as a N-donor rigid ligand and its gadolinium complex has been reported by Muller-Buschbaum and

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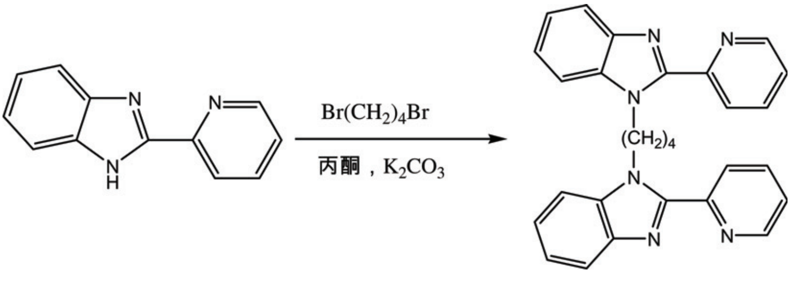
coworkers [20]. However, no example has been reported of using 1,4-*bis*[2-(2-pyridyl)benzimidazolato]butane (L) to construct coordination polymers, in which two 2-(2-pyridyl)benzimidazolato units were linked by a flexible chain-like $(CH_2)_4$ unit. Herein, we report the synthesis and crystal structure of three isostructural 1D zigzag chain-like coordination polymers: $\{[M(II)L(NCS)_2](DMF)_2\}_n$ (M(II) = cadmium(II), **1**, zinc(II), **2**, manganese(II), **3**) and the photoluminescence of **1** and **2**.

2. Experimental

2.1. *Physical measurements*

All chemicals were of analytical reagent grade quality, obtained from commercial sources and used without further purification. Carbon, hydrogen and nitrogen analyses were performed by a Carlo-Erba 1106 elemental analyzer. The infrared spectra in KBr pellets in the range 4000–400 cm^{-1} were recorded using a Shimadzu FTIR-8900 spectrophotometer. ^{1}H-NMR spectra were carried out on Bruker DPX-400 MHz spectrometers at 298 K using TMS as the internal standard. Excitation and emission spectra were recorded on a Hitachi F-3010 spectrophotometer with powder samples.

2.1.1. Preparation of 1,4-*bis*[2-(2-pyridyl)benzimidazolato]butane (L). The ligand L was prepared by the reaction shown in scheme 1; 1.95 g 2-(pyridine-2-yl)-1*H*-benzimidazole (10 mmol), 0.59 mL 1,4-dibromobutane (5 mmol), 2.50 g K_2CO_3 (18 mmol) and KI, which was used as a catalyst, were added to a 100 mL reaction flask with acetone 30 mL and the mixture was magnetically stirred and refluxed for 6 h. After filtration and removing acetone by rotary evaporation, the crude product was obtained and recrystallized in methanol-water (48% yield). M.p. 167–168°C. Anal. Calcd for $C_{28}H_{24}N_6$ (%): C, 75.66; H, 5.44; N, 18.90. Found: C, 75.53; H, 5.38; N, 18.72. IR (cm^{-1}): 3103, 3025, 3000, 2923, 2849 (ν_{C-H}), 1697, 1501, 1493, 1452, 1422 ($\nu_{C=C}$, $\nu_{C=N}$), 1255, 1166 (ν_{C-N}), 842, 796, 760, 735 (δ_{C-H}). ^{1}H-NMR (ppm) (400 MHz, $CDCl_3$, TMS): 8.55–8.56 (d, 2H, ph–H), 8.39–8.41 (d, 2H, ph–H), 7.83–7.85 (m, 4H, ph–H), 7.37–7.39 (m, 2H, ph–H), 7.30–7.32 (m, 6H, ph–H), 4.85–4.88 (t, 4H, $-NCH_2-$), 1.99–2.02 (t, 4H, $-CH_2CH_2-$).



Scheme 1. The synthesized reaction of ligand L.

2.2. *Preparation of the complexes*

The complexes were prepared by the general method,

$$M(NO_3)_2 \cdot xH_2O + L + 2KSCN \xrightarrow{DMF/H_2O} \{[ML(NCS)_2](DMF)_2\}_n + 2KNO_3$$

Details are given here for the cadmium complex:

2.2.1. $\{[CdL(NCS)_2](DMF)_2\}_n$ (1). In a typical synthesis, $Cd(NO_3)_2 \cdot 4H_2O$ (0.077 g, 0.25 mmol) was added to L (0.111 g, 0.25 mmol) and KSCN (0.049 g, 0.50 mmol) in 10 mL of DMF/water (1 : 1, v/v), and the resultant solution was refluxed for 2 h. Colorless block-shape single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature. Anal. Calcd for $C_{36}H_{38}CdN_{10}O_2S_2$ (%): C, 52.78; H, 4.67; N, 17.10. Found: C, 52.66; H, 4.53; N, 16.98.

2.2.2. $\{[ZnL(NCS)_2](DMF)_2\}_n$ (2). Colorless crystals. Anal. Calcd for $C_{36}H_{38}N_{10}O_2S_2Zn$: C, 55.99; H, 4.96; N, 18.14. Found: C, 55.84; H, 4.89; N, 18.02.

2.2.3. $\{[MnL(NCS)_2](DMF)_2\}_n$ (3). Yellow crystals. Anal. Calcd for $C_{36}H_{38}MnN_{10}O_2S_2$: C, 56.76; H, 5.02; N, 18.39. Found: C, 56.53; H, 4.97; N, 18.11.

2.3. *X-ray crystallography*

The reflection intensities for the three complexes were collected at 293 K on a Rigaku RAXIS-IV area detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved with the direct method using the program SHELXS-97 [21]. The refinement and all further calculations were carried out using SHELXL-97 [22]. In all three complexes, the C34 and O2 atoms of one dimethyl formamide are disordered over two positions C34A and O2A, as well as C34B and O2B, which could only be characterized by split positions being equally occupied. Non-hydrogen atoms were refined anisotropically using full-matrix least-squares procedures on F^2. Hydrogen atoms associated with carbon atoms were generated geometrically. Table 1 shows crystallographic crystal data and processing parameters of the complexes. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Structure description*

The new ligand 1,4-*bis*[2-(2-pyridyl)benzimidazolato]butane was prepared by reaction of 2-(pyridine-2-yl)-1*H*-benzo[*d*]imidazole with 1,4-dibromobutane. During the synthesis, two conformational isomers are produced due to single-bond carbon rotation, namely L^1 (N1, N2) and L^2 (N4, N5), respectively. The mean torsion angle of N3–C13–C14–C14^{i} is 163° in L^1 in all three complexes, which is obviously bigger than that of N6–C16–C15–C15^{ii} (58°) in L^2. The torsion angles in L^1 and L^2 of the three

Table 1. Crystal data and structure refinement details.

	1	**2**	**3**
Empirical formula	$C_{36}H_{38}CdN_{10}O_2S_2$	$C_{36}H_{38}N_{10}O_2S_2Zn$	$C_{36}H_{38}MnN_{10}O_2S_2$
Formula weight	819.28	772.25	761.82
Description	Colorless	Colorless	Yellow
Temperature (K)	291(2)	291(2)	291(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions (Å, °)			
a	8.869(1)	11.232(2)	8.840(2)
b	11.278(2)	19.180(4)	11.248(2)
c	19.328(4)	8.784(2)	19.255(4)
α	89.83(3)	90.80(3)	89.55(3)
β	89.52(3)	104.81(3)	89.49(3)
γ	74.28(3)	89.17(3)	74.81(3)
Volume (Å^3)	1860.9(7)	1829.3(6)	1847.5(6)
Z	2	2	2
D_{Calcd} (g cm^{-3})	1.462	1.402	1.369
$F(000)$	840	804	794
μ (mm^{-1})	0.746	0.833	0.518
$T_{\max}$, $T_{\min}$	0.8651, 0.8071	0.7881, 0.8510	0.9035, 0.8602
θ Range (°)	1.05–27.60	1.06–25.99	1.06–26.00
Unique reflections/R_{int}	7250/0.0000	6006/0.0000	5494/0.0000
Observed reflections ($I \geq 2\sigma(I)$)	6039	4467	3896
Data/restraints/parameters	7250/2/467	6006/4/467	5494/4/467
Goodness of fit on F^2	1.063	0.988	1.051
R_1, wR_2 ($I \geq 2\sigma(I)$)^a	0.0532, 0.1413	0.0546, 0.1311	0.0534, 0.1199
R_1, wR_2 (all data)^a	0.0656, 0.1529	0.0755, 0.1412	0.0886, 0.1310
A, B values in weighting scheme^b	0.0984, 0.9757	0.0884, 0.0000	0.0691, 0.0000
$\delta\rho_{\max}$, $\delta\rho_{\min}$ (e Å^{-3})	1.081, −0.827	0.815, −0.571	0.487, −0.470

[a] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

complexes are given in table 2. The carbon–carbon and carbon–nitrogen bonds within L^1 and L^2 are similar, as expected. Although 2-(2-pyridyl)benzimidazolato units in L^1 and L^2 are not planar, the pyridyl rings and benzimidazole rings are nearly coplanar. In the three complexes, L^1 and L^2 are all located on a center of inversion.

Single-crystal X-ray diffraction studies reveal that the three complexes are isostructural and **1** will be described in detail. Complex **1** shows a one-dimensional zigzag-like structure with monomer of $[CdL^1_{1/2} \cdot L^2_{1/2}(NCS)_2] \cdot (DMF)_2$. The asymmetric unit consists of one Cd^{2+} cation, one half of L^1 centered at the 1*c* site and one half of L^2 centered at the 1*b* site and two DMF molecules. As illustrated in figure 1, the Cd atoms are each distorted octahedrons, coordinated by four N (N1, N2; N4, N5) atoms of L^1 and L^2 ligands and two N (N7 and N8) atoms from two SCN^- anions, with the N5 and N7 atoms *trans*. The Cd–N (L) bond distances fall in the range 2.316–2.444 Å, and Cd–N (SCN^- groups) bond distances averaging 2.245 Å are practically identical within the experimental limitation (table 2). The shorter Cd–N (SCN^- groups) bond distances indicate strong interactions between the cadmium ion and SCN^- groups. The *cisoid* and *transoid* bond angles about the central Cd atom are in the regions 69.0–103.7 and 151.9–169.9°, respectively, exhibiting severe deviation from the ideal values of a regular octahedron.

The Cd atoms are alternately interlinked by the L^1 and L^2 ligands to generate 1D zigzag chains along $[01\bar{1}]$ direction (figure 2). The dihedral angle between two adjacent

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2**, and **3**.

	1 (M = Cd)	**2** (M = Zn)	**3** (M = Mn)
Distances			
M1–N1	2.348(2)	2.186(2)	2.264(2)
M1–N2	2.444(3)	2.309(2)	2.370(2)
M1–N4	2.316(2)	2.148(2)	2.239(2)
M1–N5	2.427(3)	2.262(2)	2.336(2)
M1–N7	2.246(3)	2.079(2)	2.158(2)
M1–N8	2.244(3)	2.076(2)	2.152(3)
Angles			
N1–M1–N2	69.52(9)	73.31(7)	71.50(7)
N1–M1–N4	151.9(1)	157.59(6)	154.38(8)
N1–M1–N5	91.76(9)	91.30(7)	91.69(8)
N1–M1–N7	97.8(1)	94.68(8)	96.86(8)
N1–M1–N8	94.6(1)	95.78(7)	94.69(8)
N2–M1–N4	89.38(9)	89.08(7)	88.98(7)
N2–M1–N5	89.70(9)	89.30(7)	88.89(7)
N2–M1–N7	90.4(1)	90.06(7)	90.27(9)
N2–M1–N8	163.3(1)	167.79(7)	164.98(8)
N4–M1–N5	69.00(8)	74.38(7)	70.96(8)
N4–M1–N7	100.8(1)	99.18(8)	99.72(9)
N4–M1–N8	103.7(1)	100.03(8)	102.33(8)
N5–M1–N7	169.8(1)	173.53(8)	170.65(9)
N5–M1–N8	85.4(1)	85.40(7)	85.58(8)
N7–M1–N8	97.2(1)	96.42(8)	97.4(1)
Torsion angles			
N3–C13–C14–C14^{i}	163.2(3)	163.0(2)	163.3(3)
N6–C16–C15–C15^{ii}	61.6(5)	59.0(4)	55.1(7)

Symmetry codes for **1**: i = −*x*, 1 − *y*, −*z*; ii = −*x*, −*y*, 1 − *z*. Symmetry codes for **2**: i = 2 − *x*, 1 − *y*, 1 − *z*; ii = 1 − *x*, 2 − *y*, 1 − *z*. Symmetry codes for **3**: i = 2 − *x*, 1 − *y*, 2 − *z*; ii = 2 − *x*, 2 − *y*, 1 − *z*.

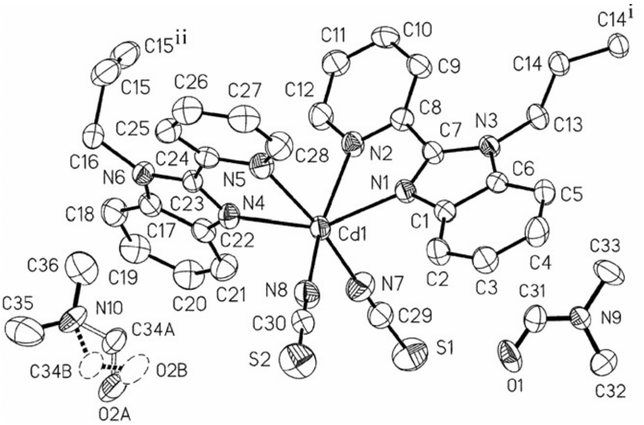


Figure 1. Ortep view of **1** with atomic labelling (the displacement ellipsoids drawn at 35% probability). Symmetry codes: i = −*x*, 1 − *y*, −*z*; ii = −*x*, −*y*, 1 − *z*.

2-(2-pyridyl)benzimidazolato units of L^1 and L^2 is 85.09(5)°. Along [100], the 1D chains are stacked via π–π interactions between two adjacent symmetry related 2-(2-pyridyl)benzimidazolato units of L^2 to generate 2D layers parallel to (011) (the mean interplanar distance: 3.49 Å) (figure 3).

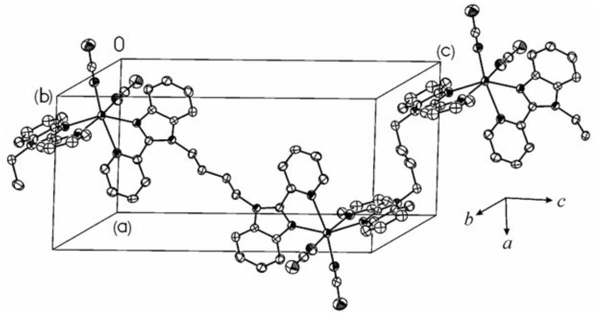


Figure 2. The one-dimensional zigzag-like chain structure of **1**.

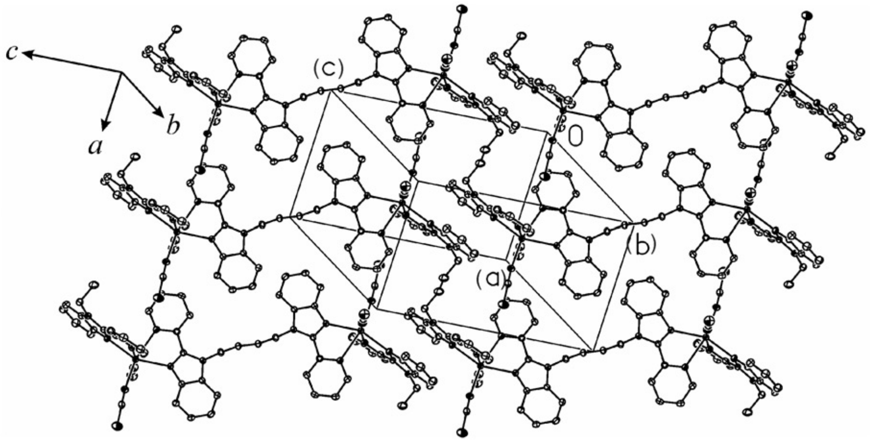


Figure 3. The two-dimensional layer structure of **1**.

Complexes **2** and **3** are almost isostructural with **1**, the metal possesses distorted octahedral coordination geometry, in which the metal–nitrogen bond distances range from 2.076–2.3093 Å in **2** and 2.152–2.370 Å in **3**. The *cisoid* and *transoid* bond angles about the central metal atom are in the region 73.3–100.0 and 157.6–170.7° in **2** and 71.5–102.3 and 154.4–170.7° in **3**. The one-dimensional zigzag chains $^{1}_{\infty}[\mathrm{ML}^1_{1/2} \cdot \mathrm{L}^2_{1/2}(\mathrm{NCS})_2]$ along $[01\bar{1}]$ direction are stacked into 2D layers parallel to (011) via π–π interactions between two adjacent symmetry related 2-(2-pyridyl)benzimidazolato units of L^2 ligands, the mean interplanar distance is 3.49 Å in **2** and 3.43 Å in **3**.

3.2. *Photoluminescence properties*

Another salient feature of the complexes is that complexes $\{[\mathrm{CdL(NCS)_2}](\mathrm{DMF})_2\}_n$ and $\{[\mathrm{ZnL(NCS)_2}](\mathrm{DMF})_2\}_n$ exhibit intense blue photoluminescence when excited with near-UV radiation. Figures 4 and 5 show the excitation and emission spectra of

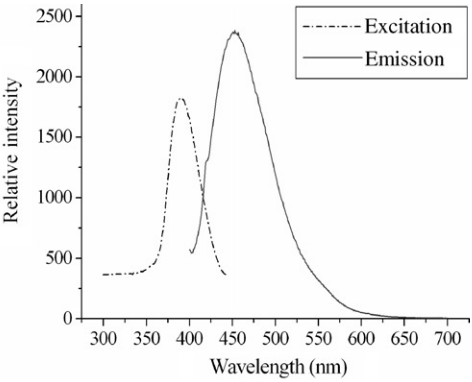


Figure 4. The solid state excitation and emission spectra of **1** at room temperature.

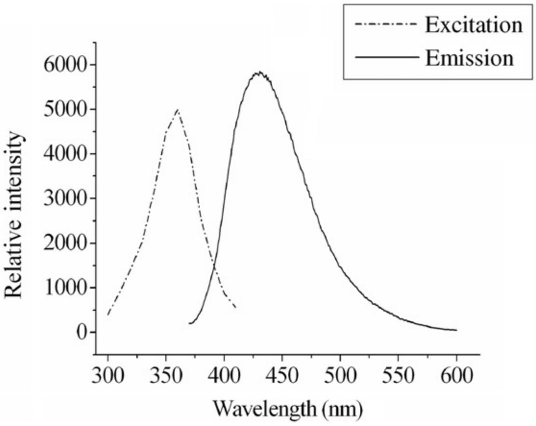


Figure 5. The solid state excitation and emission spectra of **2** at room temperature.

the complexes in the solid state at room temperature. The strong absorption bands at ca 389 nm (figure 4) and 360 nm (figure 5) can be ascribed to metal-perturbed intraligand π–π^* transitions of the pyridyl units, which may be obscured by MLCT transitions. The emission bands of the complexes range from 375 to 650 nm with the maximum peak at 453 and 433 nm; the spectrum profile is independent of the excitation emission wavelength used. The emissions of the complexes are not ligand to metal charge transfer (LMCT) or metal to ligand charge transfer, but likely caused by metal-perturbed π^*–π transitions of the ligand [23, 24] since a similar very weak emission at about 430 nm is also observed for the free ligand. The enhanced luminescence may be attributed to the coordination of the ligand to cadmium and zinc, which increases the rigidity of the ligand and reduces the non-radiative decay through the vibration manifold in the excited state.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 639898 ($C_{36}H_{38}CdN_{10}O_2S_2$), CCDC 639900 ($C_{36}H_{38}N_{10}O_2S_2Zn$) and CCDC 639899 ($C_{36}H_{38}MnN_{10}O_2S_2$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or Email: deposit@ccdc.cam.ac.uk).

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