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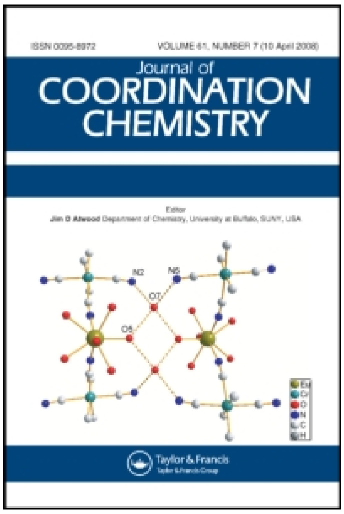

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Synthesis, crystal structures and fluorescence of cadmium(II) coordination polymers with derivatives of pyrazine-1,4-dioxide and thiocyanate as mixed-bridging ligands

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Two Cd(II) coordination polymers have been synthesized with derivatives of pyrazine-1,4-dioxide and thiocyanate anion as bridging ligands and structurally determined by X-ray crystallography. Complex **1**, $[\mathrm{Cd}(\mu_{1,3}\text{-SCN}^-)_2(\mu_{1,6}\text{-L1})]_n$ (L1 = 2,5-dimethylpyrazine-1,4-dioxide), belongs to the triclinic, space group $P\bar{1}$ with $a = 5.7627(18)$ Å, $b = 7.182(2)$ Å, $c = 7.509(2)$ Å, $\alpha = 74.042(3)°$, $\beta = 84.766(4)°$, $\gamma = 88.162(4)°$; complex **2**, $[\mathrm{Cd}_2(\mu_{1,3}\text{-SCN}^-)_4(\mu_4\text{-L2})]_n$ (L2 = 2,3,5,6-tetramethylpyrazine-1,4-dioxide), crystallizes in a monoclinic system with space group $C2/m$ with $a = 10.194(4)$ Å, $b = 13.491(6)$ Å, $c = 8.140(3)$ Å, $\beta = 120.372(4)°$. Complex **1** shows a two-dimensional sheet structure, and in *a* direction the Cd(II) ions were coordinated by $\mu_{1,3}$-SCN$^-$ forming the one-dimensional chain and the L1 bridging ligand made the chains connect in the *c* direction leading to formation of a two-dimensional sheet on the *ac* plane. For **2** the one-dimensional chains in the *a* axis were constructed by coordination of $\mu_{1,3}$-SCN$^-$ bridging ligands with the Cd(II) ions, and in *b* and *c* directions the chains were joined by L2 bridging ligands leading to a three-dimensional structure. In **2** L2 displays a μ_4-bridging coordination mode. Both complexes exhibit strong fluorescence emission.

Keywords: Crystal structure; Cadmium(II) complex; Fluorescence

1. Introduction

Much research has focused on coordination polymeric compounds [1] because new coordination polymers may afford new materials with useful properties such as catalytic activity, micro-porosity, electrical conductivity, non-linear optical activity, magnetic coupling behaviour, etc. [2]. In order to synthesize the ideal polymeric complexes judicious choice of bridge ligands is a crucial factor; many bridging ligands have been designed and used in the synthesis of polymeric complexes. Most polymeric complexes a single kind of bridge ligand is used and limited complexes are found with two or more kinds of bridge ligands; some complexes with mixed bridge ligands display interesting properties [3]. Thiocyanate anion, pyrazine N-oxide and its derivatives are very useful bridge ligands and many complexes [4–5] with one of them as bridge ligand exhibit special properties [6]. Our interest in the structure and properties of complexes with

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thiocyanate and aromatic N-oxide as mixed bridge ligands resulted in the syntheses and characterization of the title complexes. To date no Cd(II) complexes with thiocyanate anion and aromatic N-oxide (or its derivatives) as mixed bridge ligands have been reported.

2. Experimental

2.1. *Reagents*

2,5-Dimethylpyridine-1,4-dioxide and 2,3,5,6-tetramethylpyrazine-1,4-dioxide were prepared according to the literature method [7]. Other chemicals were analytical grade and used without further purification.

2.2. *Preparation of* $[Cd(\mu_{1,3}\text{-}SCN^-)_2(\mu_{1,6}\text{-}L1)]_n$ *(1)*

$Cd(ClO_4)_2 \cdot 6H_2O$ (0.2513 g, 0.599 mmol), NaSCN (0.1056 g, 1.32 mmol) and 2,5-dimethylpyrazine-1,4-dioxide (0.1743 g, 1.24 mmol) were dissolved in 10 mL of water, respectively, and then the three solutions were mixed together and stirred for few minutes. Colourless transparent single crystals were obtained after the mixed solution was allowed to stand for one week at room temperature. Yield: 83% (based on L1). Anal. Calcd for $C_8H_8CdN_4O_2S_2$: C, 26.06; H, 2.19; N, 15.20; Cd, 30.49%. Found: C, 26.53; H, 1.87; N, 14.79; Cd, 30.17%.

2.3. *Preparation of* $[Cd_2(\mu_{1,3}\text{-}SCN^-)_4(\mu_4\text{-}L2)]_n$ *(2)*

The preparation method of **2** is identical with **1** except L1 ligand was replaced by L2 ligand. The yield of the colourless transparent single crystals is 87% (based on L2). Anal. Calcd for $C_{12}H_{12}Cd_2N_6O_2S_4$: C, 23.05; H, 1.93; N, 13.44; Cd, 35.95. Found: C, 23.36; H, 1.68; N, 13.01; Cd, 36.38.

2.4. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000–500 cm^{-1} region using KBr discs. C, H and N elemental analyses were carried out on a Perkin-Elmer 240 instrument. Fluorescence spectra were performed on a FLS920 fluorescence spectrometer.

2.5. *Crystal structures determination*

Suitable single crystals of **1** and **2** were selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structures at 25°C were carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD using

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_8H_8CdN_4O_2S_2$	$C_6H_6CdN_3OS_2$
CCDC deposit no.	257618	254312
Formula weight	368.70	312.66
Temperature (K)	298	298
Crystal size (mm^3)	$0.18 \times 0.15 \times 0.08$	$0.15 \times 0.12 \times 0.09$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/m$
a (Å)	5.7627(18)	10.194(4)
b (Å)	7.182(2)	13.491(6)
c (Å)	7.509(2)	8.140(3)
α (°)	74.042(3)	90.00
β (°)	84.766(4)	120.372(4)
γ (°)	88.162(4)	90.00
Volume (Å^3)	297.55(17)	965.8(7)
Z	1	4
Density (calculated) ($Mg\,m^{-3}$)	2.058	2.150
Absorption coefficient (mm^{-1})	2.179	2.654
θ_{min}, θ_{max} (°)	2.83; 26.00	2.76; 26.95
Completeness (%)	0.976 ($\theta = 26.00°$)	0.984 ($\theta = 26.95°$)
Goodness-of-fit on F^2	1.107	1.096
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0224$, $wR_2 = 0.0597$	$R_1 = 0.0196$, $wR_2 = 0.0499$
R indices (all data)	$R_1 = 0.0224$, $wR_2 = 0.0597$	$R_1 = 0.0208$, $wR_2 = 0.0506$
Largest diff. peak and hole (e Å^{-3})	0.382, −0.482	0.401, −0.466

graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Corrections for Lp factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs for structure solution and refinement were SHELXTL (Bruker 2001). Crystal structures and data collections and refinement parameters for **1** and **2** are listed in table 1, and the selected bond lengths and angles for **1** and **2** are given in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Crystal structure of 1*

Figure 1 shows the coordination diagram with atom numbering scheme. Cd1 is coordinated by O1, O1B, N2A, N2B, S1 and S1B atoms, in which O1 and O1B atoms are from two $\mu_{1,6}$-L1 bridging ligands, and the other four coordinated atoms come from four $\mu_{1,3}$-SCN^- bridging ligands. The data from table 2 indicate that Cd1 lies in a distorted octahedral coordination environment.

In this crystal, the adjacent Cd(II) ions with alternate Cd$\cdots$Cd separation of 5.8650(14) and 5.8543(15) Å are connected by two $\mu_{1,3}$-SCN^- bridging ligands forming a one-dimensional chain in *a* direction, and the chains are further joined by coordination of $\mu_{1,6}$-L1 bridging ligands and Cd(II) ions leading to the formation

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cd1–O1	2.334(2)		
Cd1–S1	2.7194(10)		
Cd1–N2A	2.254(3)		
O1–Cd1–S1	88.20(6)	O1–Cd1–S1B	91.80(6)
O1B–Cd1–S1	91.80(6)	O1B–Cd1–S1B	88.20(6)
N2B–Cd1–O1B	92.32(9)	N2B–Cd1–O1	87.68(9)
N2B–Cd1–S1	92.31(7)	N2B–Cd1–S1B	87.69(7)

Symmetry transformation: N2A: $x-1$, y, z; N2B: $-x+2$, $-y+1$, $-z$; S1B: $-x+1$, $-y+1$, $-z$.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cd1–O1	2.4287(14)		
Cd1–S1	2.6362(11)		
Cd1–N1A	2.279(3)		
S1–Cd1–S1A	112.92(5)	O1A–Cd1–S1	89.71(5)
O1–Cd1–S1	156.18(5)	O1–Cd1–O1A	69.16(9)
N1A–Cd1–O1	96.02(8)	N1A–Cd1–O1A	89.07(8)
N1A–Cd1–S1	94.45(6)	N1B–Cd1–S1	82.12(6)
N1B–Cd1–N1A	173.83(11)		

Symmetry transformation: N1A: $-x+1/2$, $-y+3/2$, $-z$; N1B: $x-1/2$, $-y+3/2$, z; O1A: $-x$, $-y+2$, $-z$; S1A: $-x$, y, $-z$.

of a two-dimensional sheet structure on the *ac* plane as shown in figure 2. The sheets stack up along the *b* direction as shown in figure 3.

3.2. *Crystal structure of 2*

Figure 4 and table 3 indicate that in **2** Cd1 assumes a distorted octahedral geometry. The coordination of L2 is different from that of L1, namely, L2 is a μ_4-bridging ligand, whereas L1 only acts as μ_2-bridging ligand. In the reported complexes with pyrazine-1,4-dioxide and its derivatives as bridging ligands μ_4-bridging has not been observed. The Cd(II) ions with Cd···Cd separation of 5.790 Å connect through $\mu_{1,3}$-SCN$^-$ bridging ligands, forming a one-dimensional chain in the a direction. In *b* and *c* directions the chains are further joined by coordination of L2 with the Cd(II) ions leading to formation of a three-dimensional structure as shown in figure 5.

Comparing coordination modes of L1 and L2, L2 with larger steric hindrance displays a μ_4 coordination mode whereas L1 with smaller steric hindrance has a μ_2 coordination mode, implying that in the solid state coordination modes of ligands are controlled by many factors and steric factors are not dominant.

3.3. *Infrared spectrum*

The characteristic absorption of NCS$^-$ appear at 2106(s) cm^{-1} for **1** and 2112(s) and 2078(s) cm^{-1} for **2**, and the peaks at 1661(s), 1519(w), 1448(s), 1401(s), 1357(s) for **1** and 1622(s), 1441(s), 1384(m), 1350(w) cm^{-1} for **2** may be attributed to the vibrations of the C=N, C=C and N–O groups of pyrazine rings.

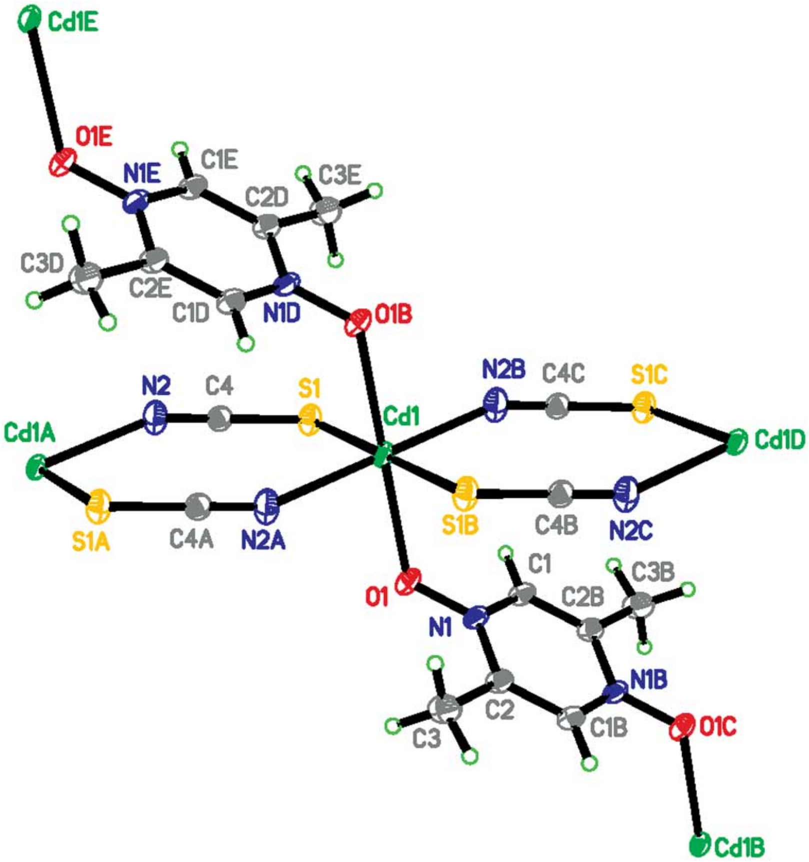

Figure 1. Coordination diagram of **1** with the atom numbering scheme.

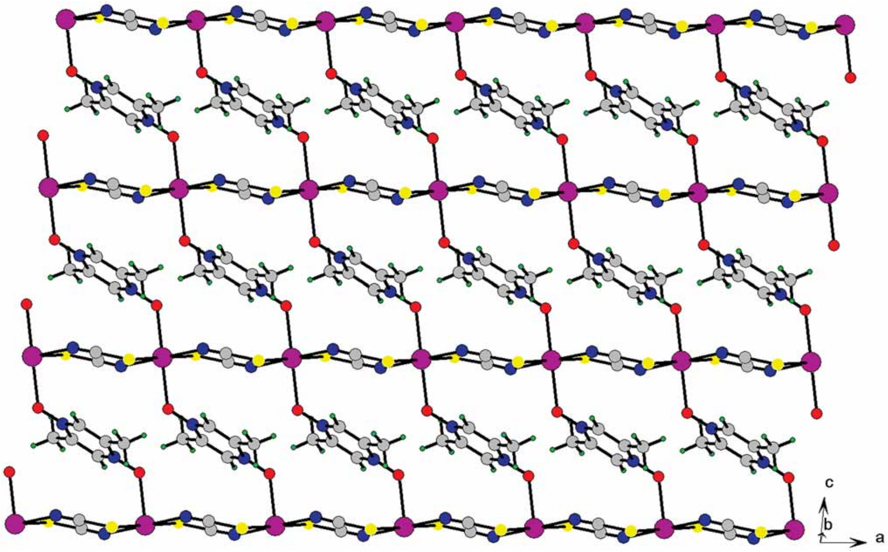

Figure 2. Two-dimensional sheet on the *ac* plane for 1.

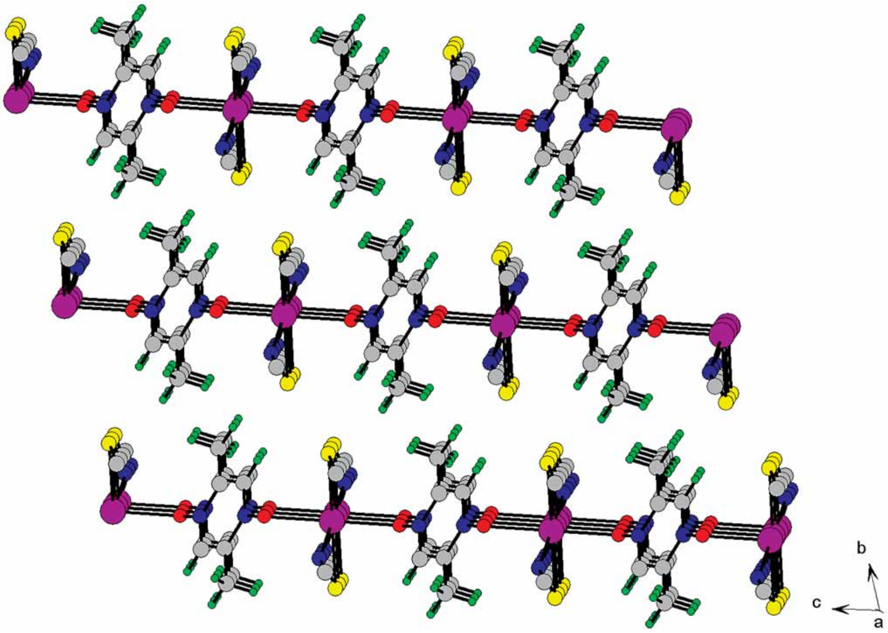

Figure 3. Sheets pile up along the *b* direction for **1**.

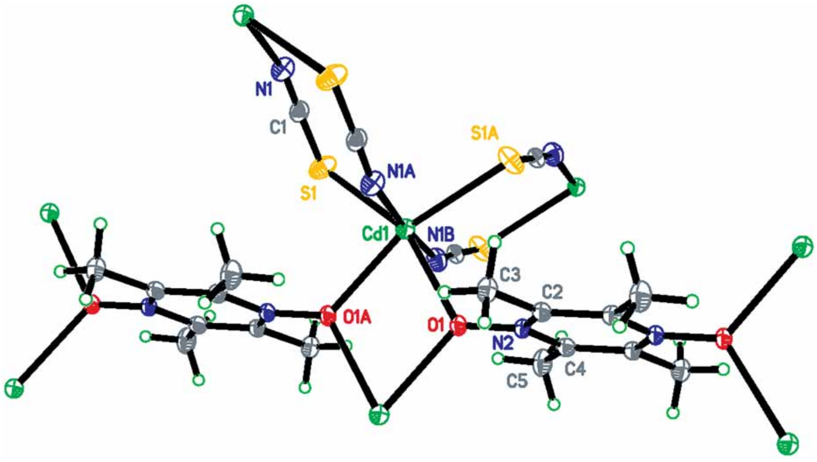

Figure 4. Coordination diagram of **2** with the atom numbering scheme.

3.4. *Fluorescence spectra*

Figure 6 shows the fluorescence spectra of complexes **1** and **2**, and ligands L1 and L2 in the solid state. The four compounds exhibit strong fluorescence emissions and the

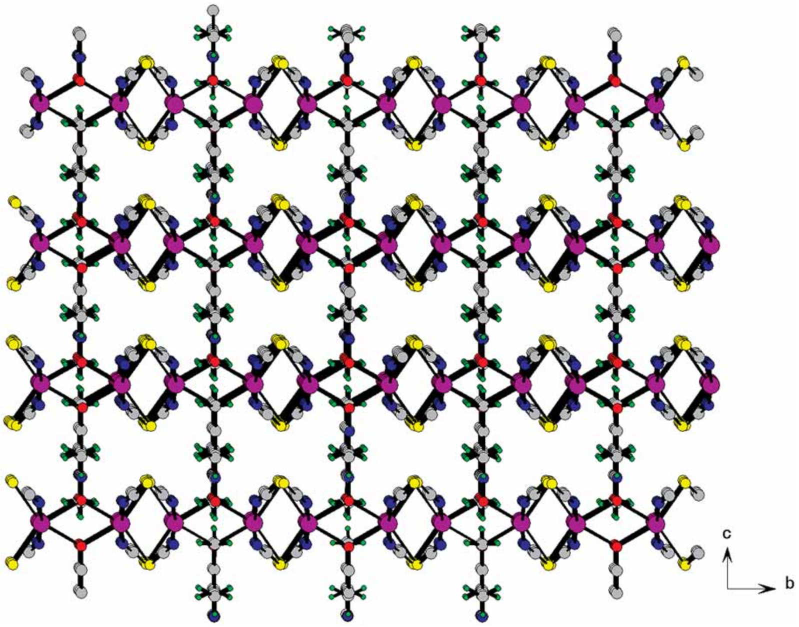

Figure 5. Three-dimensional structure viewed from the *a* direction for **2**.

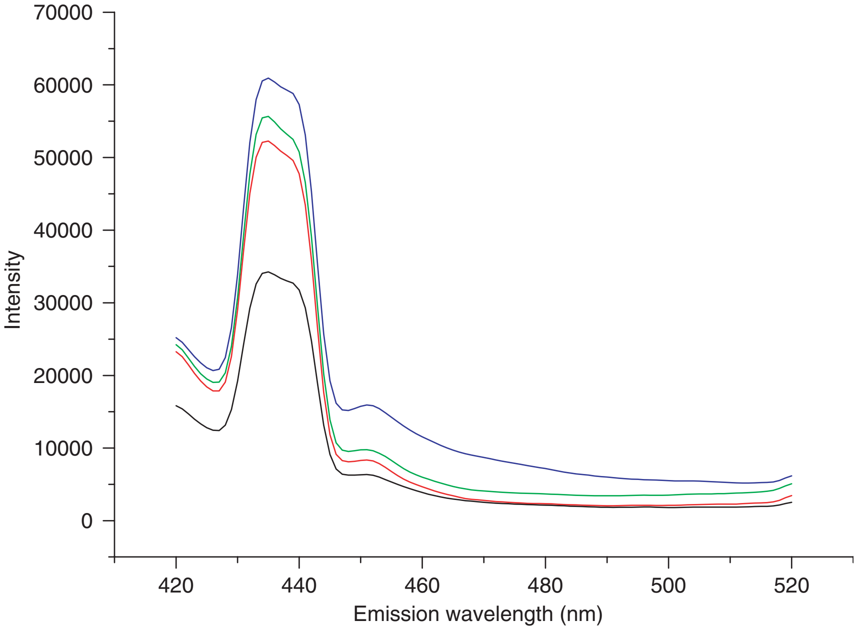

Figure 6. Fluorescence emission spectra for **1** (green line), **2** (red line), L1 (black line) and L2 (blue line).

maximum emission peaks are located at 435 nm when the excitation wavelength was selected at 394 nm. The peak shapes are very similar, which means that the fluorescent emission of the complexes arises from the conjugation of the relevant ligands.

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