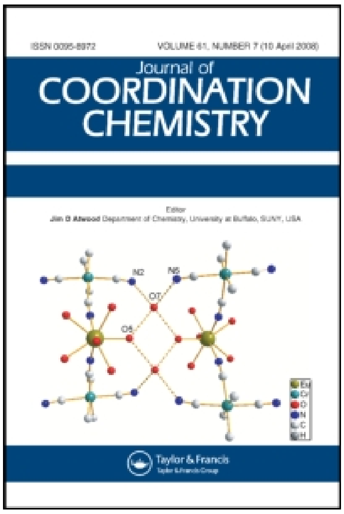

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Synthesis, crystal structure and fluorescence of a two-dimensional coordination polymer with 1-(pyrazin-2-yl) pyridine-2(1H)-one and thiocyanate as mixed bridge ligands

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A two-dimensional sheet coordination polymer, $[Cd(\mu\text{-}C_9H_7N_3O)(\mu\text{-}NCS)_2]_n$, ($C_9H_7N_3O$=1-(pyrazin-2-yl)pyridin-2(1H)-one), has been synthesized with 1-(pyrazin-2-yl)pyridin-2(1H)-one and thiocyanate anion as bridging ligands, and its crystal structure determined by X-ray crystallography. The crystal belongs to monoclinic system with space group $P2_1/c$, and its relevant crystal parameters are: $a = 7.5392(16)$ Å, $b = 18.343(4)$ Å, $c = 10.155(2)$ Å, $\beta = 106.362(3)°$, $Z = 4$, $V = 1347.4(5)$ Å^3, $C_{11}H_7CdN_5OS_2$, $D_{Calcd} = 1.980$, $R = 0.0516$. The crystal structure reveals that both 1-(pyrazin-2-yl)pyridin-2(1H)-one and thiocyanate anion connect adjacent Cd(II) ions resulting in a two-dimensional sheet structure in the *bc* plane. There are weak π–π stacking interactions between adjacent pyridine rings. The coordination polymer has weaker fluorescent emission in the solid state than 1-(pyrazin-2-yl)pyridin-2(1H)-one compound, attributed to the π–π stacking interaction and the coordination effect.

Keywords: Coordination polymer; Mixed bridge ligand; Cadmium; Crystal structure

1. Introduction

Azacycloaromatic compounds and thiocyanate play pivotal roles in bridging coordination polymers [1–5], some of which exhibit special physical properties [6, 7]. We are interested in designing and synthesizing new complexes with bridging ligands and studying their fluorescence properties, and especially the effects of intermolecular solid-state interactions on the fluorescence emission intensity. Here we report the synthesis, crystal structure and solid fluorescence of the title coordination polymer.

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2. Experimental

2.1. *Preparation*

1-(pyrazin-2-yl)pyridin-2(1H)-one was synthesized with a published method [8]; other chemicals are analytical grade and used without further purification. Methanol solution (10 mL) of 1-(pyrazin-2-yl)pyridin-2(1H)-one (0.0627 g, 0.362 mmol) was added to 20 mL H_2O solution containing $Cd(ClO_4)_2 \cdot 6H_2O$ (0.3036 g, 0.724 mmol) and NaSCN (0.1174 g, 1.45 mmol), and the mixed solution was stirred for a few minutes. Yellow single crystals were obtained after allowing the mixed solution to stand at room temperature for one week. Yield 65% (based on 1-(pyrazin-2-yl)pyridin-2(1H)-one). Anal. Calcd for $C_{11}H_7CdN_5OS_2$ (Fw: 401.74): C, 32.88; H, 1.76; N, 17.43; Cd, 27.98%. Found: C, 33.05; H, 1.98; N, 17.02; Cd, 28.65%.

2.2. *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.

2.3. *X-ray crystal structure determination*

A suitable single crystal with dimensions of $0.22 \times 0.19 \times 0.12\,mm^3$ was selected and glued on the tip of a glass fiber. The crystal structure determination was carried out at 25°C on a Bruker Smart-1000 CCD using a graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range $4.44 < 2\theta < 53.96°$. A total of 7773 reflections were collected, of which 2872 were independent ($R_{\text{int}} = 0.051$) and 2238 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. 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 cycle of refinement using a riding model. The programs for structure solution and refinement were SHELXTL (Bruker, 2001).

3. Results and discussion

3.1. *Infrared spectrum*

The IR spectrum displays strong and sharp peaks at 2098 cm^{-1} for vibration of thiocyanate and 1653 cm^{-1} for C=O; sharp peaks at 1557 cm^{-1}, 1540 cm^{-1} and 1411 cm^{-1} arise from vibrations of C=C and C=N.

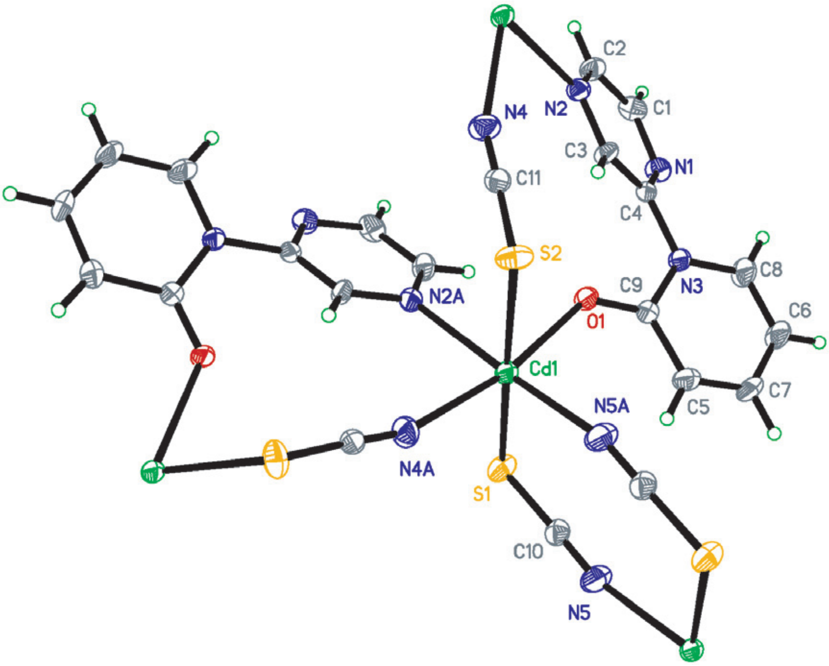

Figure 1. Atom numbering scheme of the title complex.

3.2. *Crystal structure*

3.2.1. Crystal data. $a = 7.5392(16)$ Å, $b = 18.343(4)$ Å, $c = 10.155(2)$ Å, $\beta = 106.362(3)^\circ$, $V = 1347.4(5)$ Å^3, $Z = 4$, $D_c = 1.980$, $F(000) = 784$, μ(Mo-Kα) = 1.931 mm^{-1}; goodness-of fit on F^2, 1.060; final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0516$, $wR_2 = 0.0971$; R indices (all data): $R_1 = 0.0718$, $wR_2 = 0.1040$; completeness to $\theta = 26.97^\circ$, 98.1%; largest difference peak and hole: 0.733 (e Å^{-3}) and –0.624 (e Å^{-3}), respectively.

3.2.2. Crystal structure description. Figure 1 shows the asymmetric unit and symmetry-related fragments of the complex with numbering scheme. The data of table 1 indicate that Cd(II) is a distorted octahedral CdN_3OS_2. In the crystal each Cd(II) atom is surrounded by three other symmetry-related Cd(II) atoms, and pairs of Cd(II) atoms are connected by two $\mu_{1,3}$-SCN$^-$ bridging ligands with Cd···Cd separation of 5.7360(13) Å, creating an eight-membered ring. Another pair of Cd(II) atoms are bridged by both $\mu_{1,3}$-SCN$^-$ and $\mu_{1,6}$-[1-(pyrazin-2-yl)pyridin-2(1H)-one], with a Cd···Cd separation of 6.3746(11) Å, forming a binuclear 11-membered ring. Figure 2 shows the two-dimensional coordination structure for the crystal. In the two-dimensional structure there is a 24-membered ring that is fabricated by six $\mu_{1,3}$-SCN$^-$ bridging ligands and six Cd(II) atoms. A 16-membered ring constructed by four Cd(II) atoms and four thiocyanate bridges was reported [9]. The 24-membered ring

Table 1. Selected bond distances (Å) and angles (°) for the complex.

Cd1–O1	2.369(4)	Cd1–S1	2.6522(16)	Cd1–S2	2.7246(16)
Cd1–N2A	2.403(4)	Cd1–N4A	2.322(5)	Cd1–N5A	2.280(5)
N5A–Cd1–N4A	91.62(18)	N5A–Cd1–O1	98.42(17)		
N4A–Cd1–O1	169.02(15)	N5A–Cd1–N2A	172.44(16)		
N4A–Cd1–N2A	86.23(16)	O1–Cd1–N2A	83.24(14)		
N5A–Cd1–S1	96.22(12)	N4A–Cd1–S1	94.35(13)		
O1–Cd1–S1	89.00(10)	N2A–Cd1–S1	91.17(11)		
N5A–Cd1–S2	85.61(12)	N4A–Cd1–S2	88.46(13)		
O1–Cd1–S2	87.88(10)	N2A–Cd1–S2	87.08(11)		
S1–Cd1–S2	176.59(5)				

Symmetry codes: N2A, N4A: x, $-y+3/2$, $z-1/2$; N5A: $-x$, $-y+1$, $-z+1$.

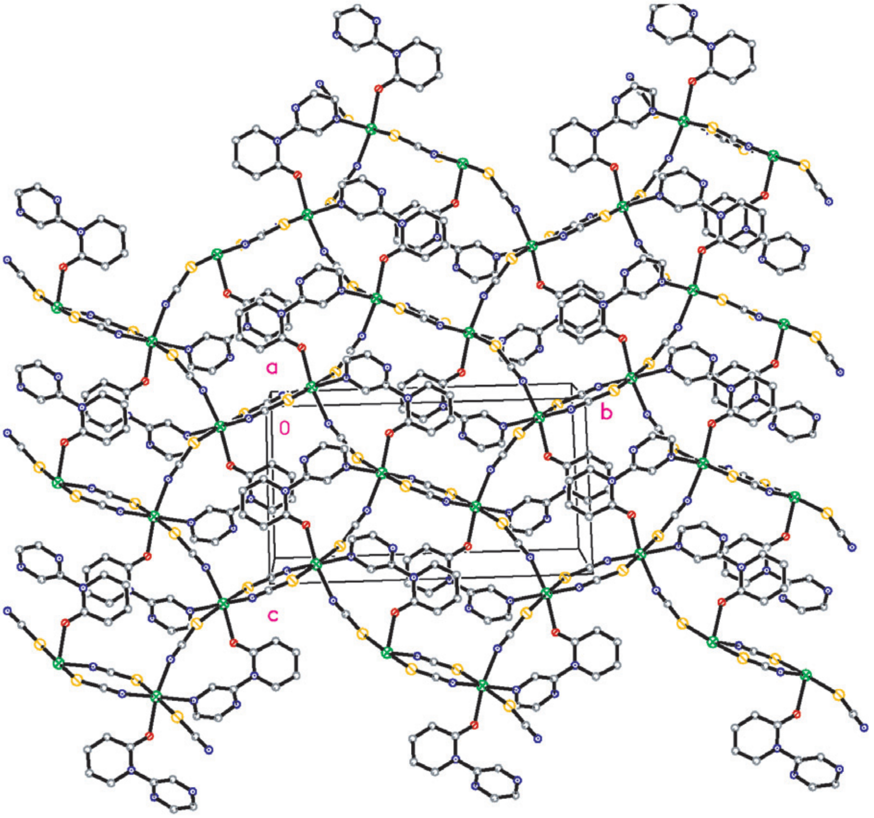

Figure 2. Unit cell and two-dimensional structure (hydrogen atoms were omitted for clarity).

in our complex is the maximum ring in complexes of Cd(II) and thiocyanate to our knowledge; the magnitude of the rings is dominated by the second ligand [9]. In the two-dimensional sheet 1-(pyrazin-2-yl)pyridin-2(1H)-one plays a role of consolidating component for the 24-membered ring. In the sheet there is a weak π–π stacking interaction between neighboring pyridine rings; the relevant distances are $Cg1 \cdots Cg1^{i} = 3.662(4)$ Å and $Cg1 \cdots 1^{i}_{perp} = 3.640$ Å [symmetry codes: (i) $-x$, $1-y$, $2-z$; Cg1 is the centroid of the N3/C5–C9 ring; $Cg1 \cdots 1_{perp}$ is the perpendicular

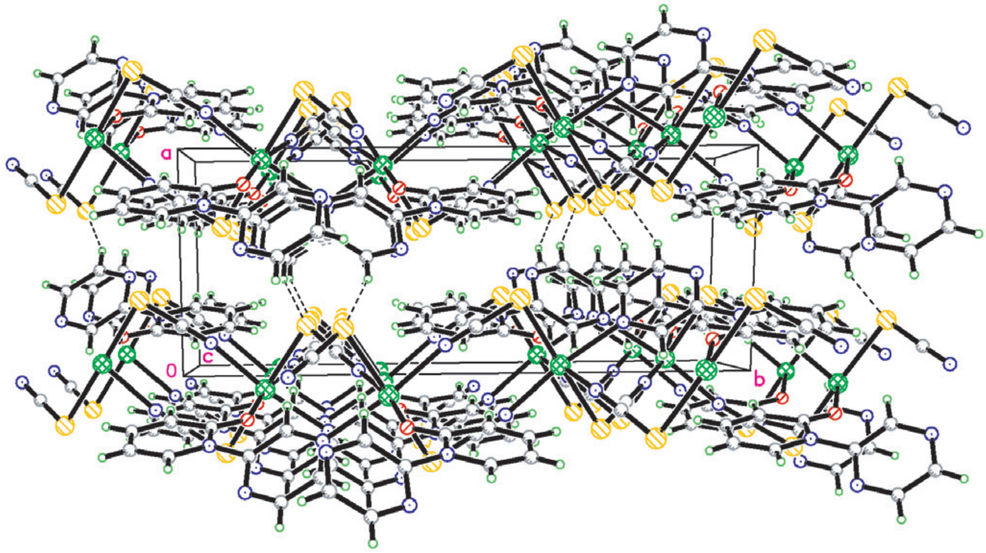

Figure 3. Unit cell and the stacking of the sheets.

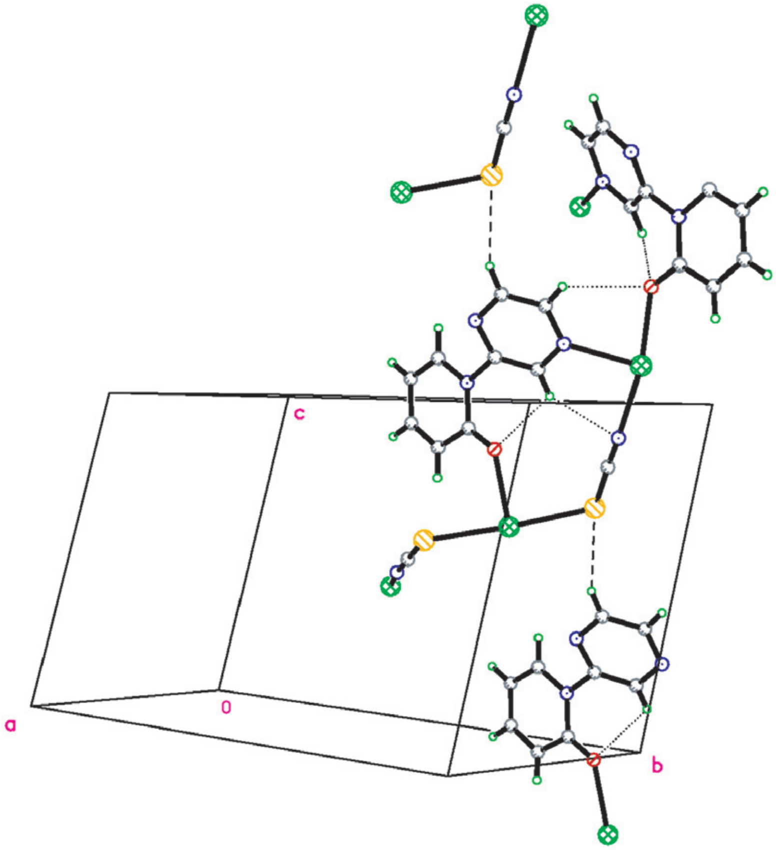

Figure 4. Unit cell and the hydrogen bonds.

Table 2. Hydrogen bond distances (Å) and angles (°).

D–H···A	D–H	H···A	D···A	∠D–H···A
C1–H1···S2^{i}	0.93	2.81	3.690(6)	157
C2–H2···O1^{ii}	0.93	2.57	3.154(7)	121
C3–H3···O1	0.93	2.30	2.767(6)	110
C3–H3···N4	0.93	2.58	3.193(7)	123

Symmetry codes: (i) $1+x$, y, $1+z$; (ii) x, $3/2-y$, $1/2+z$.

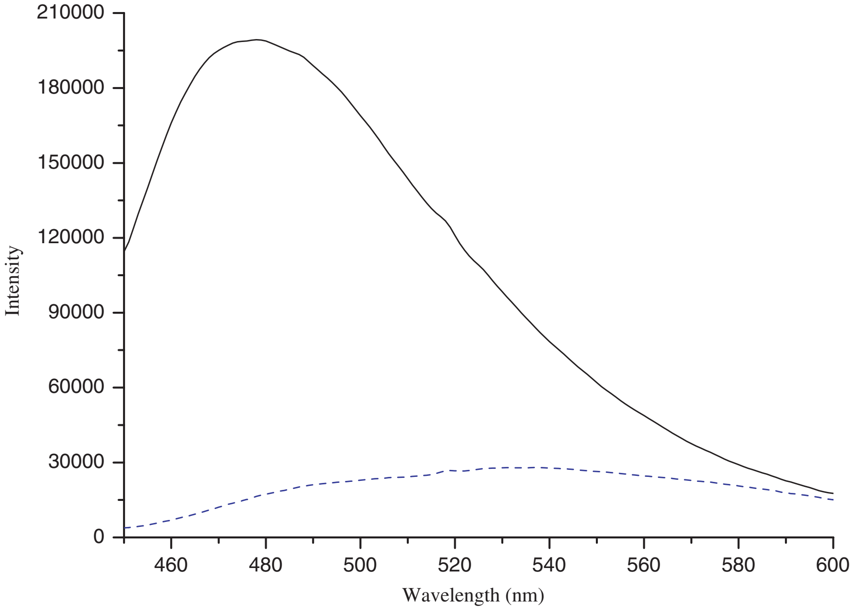

Figure 5. The fluorescence spectra of the complex (blue dashes) and 1-(pyrazin-2-yl)pyridin-2(1H)-one (solid line).

distance from Cg1 to ring 1]. Figure 3 reveals that the sheets stack along the *a* axis leading to formation of a super-molecular three-dimensional structure. Figure 4 and table 2 show the non-classic C–H···O and C–H···N hydrogen bonds in sheet and C–H···S hydrogen bond between sheets; these hydrogen bonds consolidate the crystal packing. The dihedral angle between pyrazine ring and pyridine ring of 1-(pyrazin-2-yl)pyridin-2(1H)-one ligand is 33.3(3)°, smaller than that of uncoordinated 1-(pyrazin-2-yl)pyridin-2(1H)-one ligand [46.45(14)°] [10]. This may be attributed to the balance between the coordination effect and stereo-exclusion between atoms H3 and O1.

3.3. *Fluorescence property*

Figure 5 shows the fluorescence spectra of the complex and 1-(pyrazin-2-yl)pyridin-2(1H)-one; both spectra were obtained when the excitation wavelength is 408 nm in the solid state. The maximum emission peaks are at 478 nm and 534 nm for 1-(pyrazin-2-yl)pyridin-2(1H)-one compound and the coordination polymer, respectively, and the emission intensity of the coordination polymer is weaker than its organic ligand. The fluorescent emission of the complex is from 1-(pyrazin-2-yl)pyridin-2(1H)-one, and the smaller dihedral angle between pyrazine ring and the pyridine ring of 1-(pyrazin-2-yl)pyridin-2(1H)-one in the complex may cause the bathochromic shift of the maximum emission peak position. The weaker emission intensity of the complex may arise from the coordination effect of 1-(pyrazin-2-yl)pyridin-2(1H)-one and the π–π stacking interaction of the neighboring pyridine rings [11–13].

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