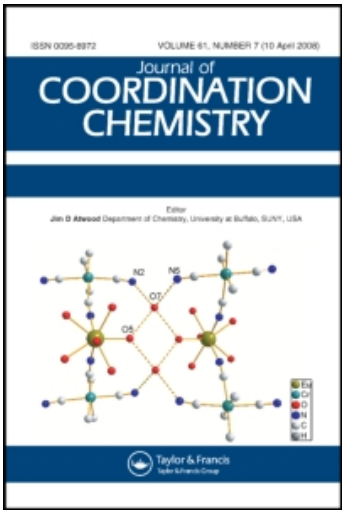

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Synthesis, crystal structure and fluorescence of a two-dimensional Cd(II) coordination polymer with thiocyanato and 4-methylpyridine N-oxide as bridging ligands

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Synthesis, crystal structure and fluorescence of a two-dimensional Cd(II) coordination polymer with thiocyanato and 4-methylpyridine *N*-oxide as bridging ligands

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A two-dimensional coordination complex $[Cd(\mu_{1,3}\text{-}SCN)_2(\mu_2\text{-}mpdo)]_n$ (mpdo = 4-methylpyridine *N*-oxide) has been synthesized and structurally determined by X-ray crystallography. The complex crystallizes in the triclinic space group of $P\bar{1}$ with $a = 8.2589(14)$ Å, $b = 8.5409(14)$ Å, $c = 9.7947(16)$ Å, $\alpha = 70.022(2)^\circ$, $\beta = 74.338(2)^\circ$, $\gamma = 71.530(2)^\circ$. Each Cd(II) is coordinated by four $\mu_{1,3}$-SCN^- forming a zigzag chain and then two μ_2-mpdo monodentate ligands coordinate to two adjacent Cd(II) ions leading to a two-dimensional sheet structure along the *ab* plane, and in the *c* direction the sheets stack parallel through π–π interactions and giving a three-dimensional structure. The complex exhibits a strong fluorescent emission spectrum in the solid state.

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

1. Introduction

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 behavior and so on [2]. In order to synthesize the ideal polymeric complexes judicious choice of bridge ligands is a crucial factor, and many bridge ligands have been designed and used in the syntheses of polymeric complexes. Most reported polymeric complexes deal with a single bridging ligand; only limited numbers of complexes are found with two or more kinds of bridging ligands, but some display interesting properties [3]. Thiocyanate, pyridine *N*-oxide and its derivatives are useful bridging ligands and many complexes [4, 5] with one of them as a bridging ligand exhibit special properties in areas of structure, magnetism [6] and so on. Interest in the structure and properties of complexes with thiocyanate and aromatic *N*-oxide as bridging ligands resulted in the synthesis and characterization of the title complex. To date no complexes with thiocyanate and pyridine *N*-oxide and its derivatives have been reported and no fluorescence spectra have been reported for complexes of aromatic *N*-oxide ligands.

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2. Experimental

2.1. *Preparation*

4-methylpyridine *N*-oxide was prepared according to the literature method [7]. Other chemicals were analytical grade and used without further purification.

$Cd(ClO_4)_2 \cdot 6H_2O$ (0.2263 g, 0.540 mmol), NaSCN (0.0975 g, 1.079 mmol) and 4-methylpyridine *N*-oxide (0.1178 g, 1.079 mmol) were dissolved separately in 15 mL of water and then the three solutions were mixed and stirred for a few minutes. Colorless transparent single crystals were obtained after the mixed solution was allowed to stand for two weeks at room temperature. Yield: 85% (based on mpdo). Anal. Calcd for $C_8H_7CdN_3OS_2$ (1): C, 28.45; H, 2.09; N, 12.45; Cd, 33.29. Found: C, 28.16; H, 2.11; N, 12.10; Cd, 33.65.

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.

2.2.1. Crystal structure determination. A single crystal with dimensions $0.27 \times 0.15 \times 0.12\,mm^3$ was selected and determination of the single crystal was carried out with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.7103$ Å) on a Bruker Smart-1000 diffractometer using the ω scan mode. A total of 4568 reflections were collected in the range of $2.25 \le \theta \le 25.50^\circ$ at 298(2) K, of which 2207 reflections were independent and 2056 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. The absorption correction was made using the program SADABS (Sheldrick, 1996), and corrections for Lorentz and polarization factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was solved by direct methods, and hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The final refinement including hydrogen atoms converged to $R = 0.0228$ and $wR = 0.0611$, $w = 1/[\sigma^2(F_o)^2 + (0.0348P)^2 + 0.1218P]$ where $P = (F_o^2 + 2F_o^2)/3$, $S = 1.059$, $(\Delta\rho)_{max} = 0.532\,e\,Å^{-3}$, $(\Delta\rho)_{min} = -0.477\,e\,Å^{-3}$, $(\Delta/\sigma)_{max} = 0.000$. SHELXTL programs were used for structure solution and refinement. Other structure parameters are given in table 1.

3. Results and discussion

3.1. *Crystal structure*

3.1.1. Crystal data. $C_8H_7CdN_3OS_2$, $M = 337.69$, triclinic, space group $P\bar{1}$, $a = 8.2589(14)$ Å, $b = 8.5409(14)$ Å, $c = 9.7947(16)$ Å, $\alpha = 70.022(2)^\circ$, $\beta = 74.338(2)^\circ$,

Table 1. Crystal data and structure refinement for the complex.

Empirical formula	$C_8H_7CdN_3OS_2$
CCDC deposit number	253348
Formula weight	337.69
Temperature (K)	298
Crystal size (mm^3)	$0.27 \times 0.15 \times 0.12$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.2589(14)
b (Å)	8.5409(14)
c (Å)	9.7947(16)
α (°)	70.022(2)
β (°)	74.338(2)
γ (°)	71.530(2)
Volume ($Å^3$)	605.66(17)
Z	2
Density (calculated) ($Mg\,m^{-3}$)	1.852
Absorption coefficient (mm^{-1})	2.124
θ_{min}, θ_{max} (°)	2.25, 25.50
Completeness to $\theta = 25.50°$ (%)	98.0
Max. and min. transmission	0.7847, 0.5978
Reflections collected	3269
Independent reflections	2207 [$R_{int} = 0.0164$]
Index range	$-10 \le h \le 9$, $-7 \le k \le 10$, $-11 \le l \le 11$
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0228$, $wR_2 = 0.0611$
R indices (all data)	$R_1 = 0.0245$, $wR_2 = 0.0620$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.532, −0.477

Table 2. Selected bond distances (Å) and bond angles (°) for the complex.

Cd1–O1	2.327(2)	Cd1–O1B	2.3531(18)	Cd1–N1A	2.271(3)
Cd1–N3D	2.252(3)	Cd1–S1	2.7444(8)	Cd1–S3	2.6466(9)
O1–Cd1–O1B	70.20(7)	O1–Cd1–S1		81.44(5)	
O1–Cd1–S3	94.55(5)	O1B–Cd1–S1		91.02(5)	
O1B–Cd1–S3	164.44(5)	S1–Cd1–S3		84.42(3)	
N1A–Cd1–O1	91.61(9)	N1A–Cd1–O1B		89.00(8)	
N1A–Cd1–S1	172.59(8)	N3D–Cd1–N1A		94.01(10)	
N3D–Cd1–O1	158.84(10)	N3D–Cd1–O1B		89.50(9)	
N3D–Cd1–S3	105.28(8)	N3D–Cd1–S1		93.40(7)	

Symmetry transformation: A: $-x+2$, $-y+1$, $-z+1$; B: $-x+1$, $-y+1$, $-z+1$; D: $-x+1$, $-y+2$, $-z+1$.

$\gamma = 71.530(2)°$, $Z = 2$, $V = 605.66(17)\,Å^3$, $D_c = 1.852\,g\,cm^{-3}$, $F(000) = 328$, μ (Mo-Kα) $= 2.124\,mm^{-1}$. Selected bond distances and angles are listed in table 2.

3.1.2. Crystal structure. Figure 1 shows the coordination diagram with atom numbering for the complex. The coordination sphere around Cd1 is octahedral through O1, O1B, N1A, N3D, S1 and S3, in which O1 and O1B come from two monodentate μ_2-mpdo bridging ligands, and the other four ligands are four $\mu_{1,3}$-SCN^- bridging ligands. The data of table 2 further confirm that Cd1 atom is in a distorted

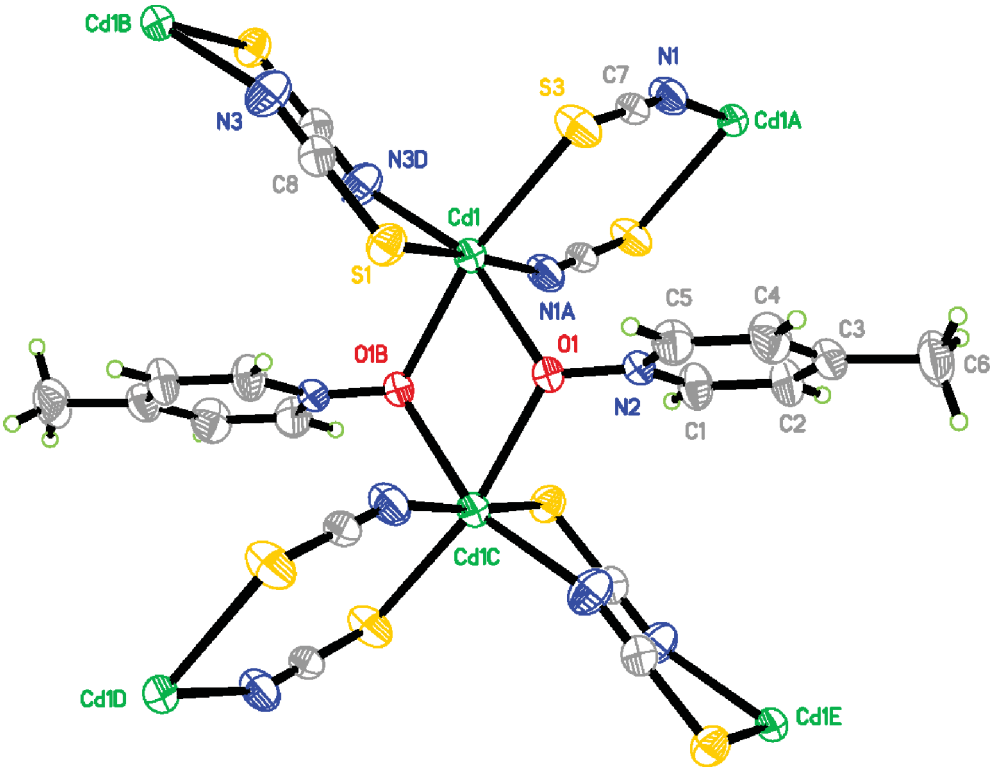

Figure 1. Coordination diagram of the complex with the atom numbering scheme.

octahedral environment. In the crystal there exist two kinds of bridging ligands, $\mu_{1,3}$-SCN^- and μ_2-mpdo. Each Cd(II) has three adjacent Cd(II) ions; adjacent pairs of Cd(II) ions with separation distances 5.7610(10) Å (Cd1 $\cdots$ Cd1A) or 5.7833(10) Å (Cd1 $\cdots$ Cd1B) are connected by coordination of two $\mu_{1,3}$-SCN^- bridging ligands, creating an eight-membered ring structure. Two μ_2-mpdo ligands coordinate adjacent Cd(II) ions with a Cd $\cdots$ Cd separation distance 3.8290(6) Å and form a binuclear four-memberd ring; the four atoms are strictly located in a plane. Figure 2 shows that a 34-membered ring is fabricated by eight $\mu_{1,3}$-SCN^- bridging ligands, four μ_2-mpdo bridging ligands and six Cd(II) ions, and in the ring the maximum distance between the Cd(II) ions is 10.7758(16) Å and the rings as subunits are further assembled into a 2D sheet that is located on the *ab* plane as shown in figure 2. There are weak π–π stacking interactions between neighboring pyridine rings and the relevant distances are Cg1 $\cdots$ Cg1^{i} = 4.720(2) Å and Cg1 $\cdots$ 1^{i}_{perp} = 3.268 Å (symmetry code (i): $1-x$, $-y$, $2-z$; Cg1 is the centroid of the N2/C1–C5 pyridine ring and Cg1 $\cdots$ 1^{i}_{perp} is the perpendicular distance between neighboring pyridine rings Cg1 and Cg1^{i}). Figure 3 shows the adjacent pyridine rings and that the sheets interdigitate and stack up along *c* axis. It is the overlapping of μ_2-mpdo ligands that led to formation of the micro-porous channels (effective cross-section of ca 4.70 × 4.02 Å) in the *a* direction as shown in figure 4.

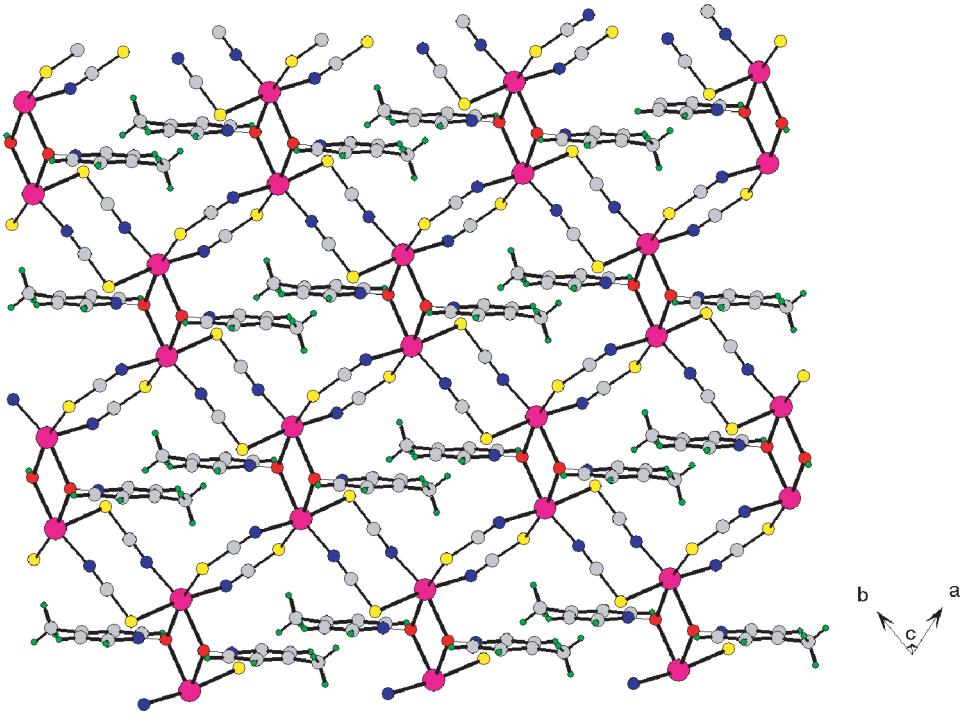

Figure 2. Two-dimensional sheet structure of the complex.

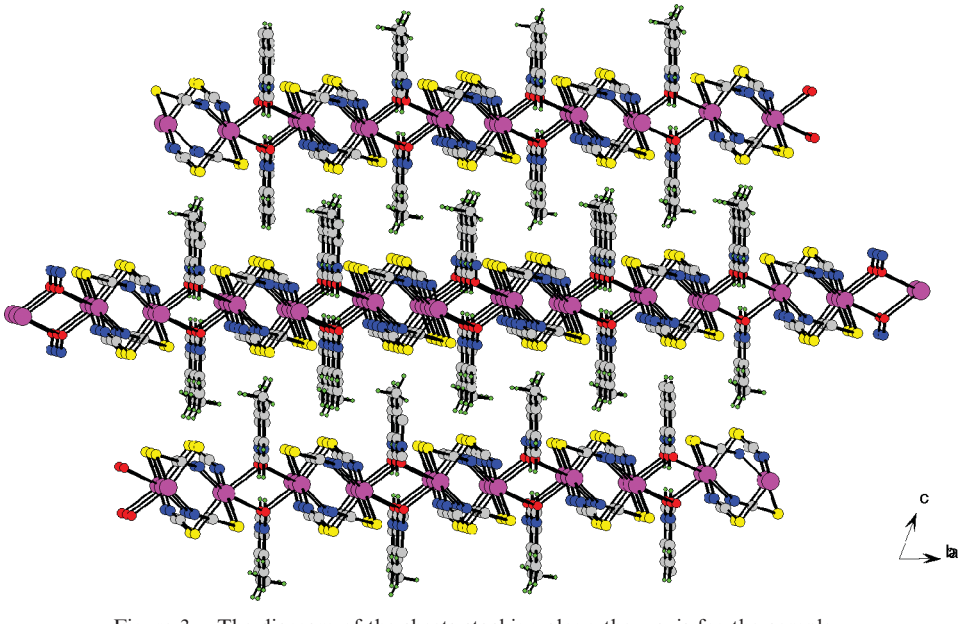

Figure 3. The diagram of the sheets stacking along the *c* axis for the complex.

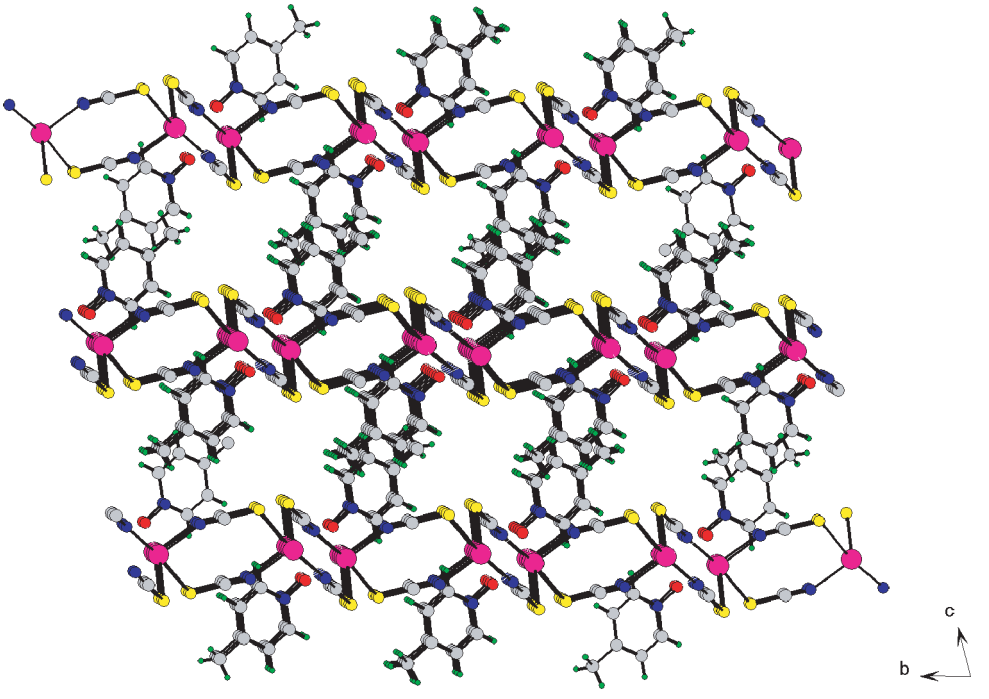

Figure 4. The diagram of the micro-channels viewed from the *a* axis for the complex.

3.2. *Infrared spectrum*

The characteristic absorption of NCS^- appears at 2124 cm^{-1}, and the peaks at 1622(m), 1493(s), 1206(s), 827(s), 757(s) cm^{-1} may be attributed to the vibrations of the C=N and N–O groups.

3.3. *Fluorescence spectrum*

When the excited wavelength was selected at 380 nm the complex exhibits strong fluorescence emission in the solid state and the maximum emission peak is located at 432 nm. The strong fluorescent emission may be attributed to the conjugated π system for mpdo bridging ligands.

Supplementary material

The X-ray crystallographic file, in CIF format, is available from the Cambridge Crystallographic Data Centre on quoting the deposition number CCDC 253348.

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