



# Synthesis, crystal structure and luminescent properties of one coordination polymer of cadmium(II) with mixed thiocyanate and hexamethylenetetramine ligands

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## ABSTRACT

A novel Cd(II) coordination polymer  $[\text{Cd}(\text{SCN})_2(\text{hmt})_{1/2}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (hmt = hexamethylenetetramine) has been synthesized and characterized by IR, elemental analysis, TG technique and X-ray crystallography. Cd(II) atom has an distorted octahedral environment with an  $\text{N}_3\text{S}_2\text{O}$  donor set. Every six Cd(II) centers are linked by hmt and thiocyanato bridges to form a planar 2D coordination polymer containing hexagonal metallocyclic rings  $[\text{Cd}_6(\text{SCN})_8(\text{hmt})_2]$ . A 2D layer structure is held together with its neighboring ones via a set of hydrogen-bonding interactions to form a 3D supramolecular structure. The luminescent properties of the title complex in the solid state were investigated.

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## 1. Introduction

Much interest at present is focused on the deliberate construction of coordination polymers by self-assembly of the component metal complexes [1]. These solid materials are attractive to chemists not only for the variety of topologies and intriguing frameworks, but also for their interesting electric, magnetic, catalytic and optical properties [2]. Among them, the incorporation of Cd(II) in the fascinating metal-based supramolecular architectures is of great interest in view of their appealing structures and photoluminescent properties, which should lead to new functional materials [3]. Much effort has been devoted to the design of Cd(II)-containing coordination polymers owing to the ability to form bonds with different donors simultaneously, the large radius, various coordination modes and special physical properties of Cd(II) ion [4,5]. These complexes display a variety of different structural motifs, such as one dimensional helical ribbon or molecular zippers, two dimensional molecular squares or triangular grids, and penetrating and non-penetrating three-dimensional networks [6].

As we know, the crystal engineering of coordination polymers are usually achieved by the reactions of metal ions with organic molecules such as bi-, tri- and multidentate neutral or anionic organic linkers such as 4,4-bipyridine (BPY), hexamethylenetetramine (hmt) and thiocyanate, benzene-1,3,5-tricarboxylate (BTC) [7–9]. Hexamethylenetetramine, a potential tetradentate neutral

organic ligand, has been used to assemble new supramolecular architectures with metal ions via various possible coordination modes, namely, involving one to four N atoms of hmt in coordination [10–12]. Among the anionic ligands, one of the best bridging ligands is ambidentate  $\text{SCN}^-$ , which tends to link metal ions such as Cd(II) with both N and S atoms to form dimensional structures [13]. Herein it is attempted to synthesize a Cadmium complex containing the hmt and  $\text{SCN}^-$  multiligands, we report the synthesis, crystal structure and the luminescent properties of a novel two-dimensional coordination polymer  $[\text{Cd}(\text{SCN})_2(\text{hmt})_{1/2}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (1).

## 2. Experimental

### 2.1. Physical measurements

Elemental analyses (C, H and N) were carried out on a PerkinElmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the  $4000\text{--}400\text{ cm}^{-1}$  region. The thermogravimetric analysis was carried out under nitrogen condition on a PerkinElmer-7 thermal analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$  from 25 to  $1000^\circ\text{C}$ , and the luminescent spectra were performed on an F-7000 spectrometer.

### 2.2. Materials

All the chemicals were reagent grade and used without further purification.

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**Table 1**  
Crystallographic data and structure refinement for complex **1**.

Crystal data	
Chemical formula	2(C <sub>5</sub> H <sub>8</sub> CdN <sub>4</sub> OS <sub>2</sub> )H <sub>2</sub> O
Color	Colourless
Formula weight	651.36
Cell setting, space group	Orthorhombic, <i>Aba2</i>
<i>a</i> (Å)	15.174(3)
<i>b</i> (Å)	10.707(2)
<i>c</i> (Å)	12.854(3)
Volume (Å <sup>3</sup> )	2088.4(7)
<i>Z</i>	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	2.072
Crystal size (mm)	0.20 × 0.15 × 0.10
Radiation (Å)	Mo Kα 0.71073
Theta Min.–Max. (°)	2.82–25.49
Tot., Uniq. Data, <i>R</i> (int)	4832, 1879, 0.0362
Observed data [ <i>I</i> > 2.0 σ( <i>I</i> )]	1863
<i>N</i> ref, <i>N</i> par	1879, 125
<i>R</i> , <i>wR</i> 2, <i>S</i>	0.0362, 0.1003, 1.02
Flack <i>x</i>	0.06(5)
Min. and Max. Resd. Dens. [e/Ång <sup>3</sup> ]	–1.46, 0.90

### 2.3. Preparation of the title complex

A 10-mL aqueous solution of 3CdSO<sub>4</sub>·8H<sub>2</sub>O (0.513 g, 0.67 mmol) and KSCN (0.388 g, 4 mmol) were mixed, and was slowly added to a 3-mL aqueous solution of hmt (0.140 g, 1 mmol). After stirring for 30 min, the mixture was filtrated and left for slowly evaporating at room temperature to obtain colorless block crystals suitable for X-ray structure determination. Yield: 60%. Anal. Calcd. for C<sub>10</sub>H<sub>18</sub>Cd<sub>2</sub>N<sub>8</sub>O<sub>3</sub>S<sub>4</sub> (%): C, 18.44; H, 2.78; N, 17.20. Found (%): C, 18.26; H, 2.92; N, 17.28.

### 2.4. Crystallographic data collection and refinement

A suitable sample of size 0.20 mm × 0.15 mm × 0.15 mm was chosen for the crystallographic study and then mounted on a Bruker APEX II CCD diffractometer with ω and φ scan mode in the range of 2.82° < θ < 25.49°. All diffraction measurements were performed at room temperature using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). A total of 4832 (1879 independent, *R*<sub>int</sub> = 0.0362) reflections were measured. The structure was solved by direct methods and refined by full-matrix least squares on *F*<sup>2</sup> using SHELXL 97 program [12]. All the non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions. Structure solution and refinement based on 1863 independent reflections with *I* > 2σ(*I*). Space group, lattice parameters and other relevant information are listed in Table 1.

## 3. Results and discussion

### 3.1. Synthesis

In order to extend our research, we vary the hmt concentration keeping other constituents constant. It has been observed that when the cadmium:hmt molar ratio is varied between 1:0.25–1:4 every other 0.25, we obtain these compounds which were revealed by IR spectra and X-ray structure determination. Ultimately, it indicated that they are the same complex **1**. In addition, we also use the triethylamine regulate solution pH between 1 and 12 every other 1 pH, we obtain compounds which are also the same product **1**. In other words, in this synthesis method, the title complex is not influenced by the reaction molar ratio and the pH. It indicated that the title complex is very stable.

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

Bond length (Å)			
Cd(1)–S(2)	2.7098(16)	Cd(1)–O(1)	2.349(4)
Cd(1)–N(1)	2.281(5)	Cd(1)–N(3)	2.447(4)
Cd(1)–S(1A)	2.7059(15)	Cd(1)–N(2A)	2.269(5)
Bond angle (°)			
S(2)–Cd(1)–O(1)	178.32(10)	S(2)–Cd(1)–N(1)	93.32(12)
S(2)–Cd(1)–N(3)	96.19(10)	S(1A)–Cd(1)–S(2)	94.50(6)
S(2)–Cd(1)–N(2A)	94.28(19)	O(1)–Cd(1)–N(1)	86.88(16)
O(1)–Cd(1)–N(3)	85.49(13)	S(1A)–Cd(1)–O(1)	83.83(10)
O(1)–Cd(1)–N(2A)	85.6(2)	N(1)–Cd(1)–N(3)	85.14(17)
S(1A)–Cd(1)–N(1)	88.49(15)	N(1)–Cd(1)–N(2A)	172.3(2)
S(1A)–Cd(1)–N(3)	167.84(10)	N(2A)–Cd(1)–N(3)	92.88(18)
S(1A)–Cd(1)–N(2A)	92.08(17)	Cd(1B)–S(1)–C(1)	98.6(2)
Cd(1)–S(2)–C(2)	99.9(2)	Cd(1)–N(1)–C(1)	159.4(4)
Cd(1B)–N(2)–C(2)	162.5(6)	C(2)–N(2)–Cd(1A)	162.5(6)
S(2)–C(2)–N(2)	177.6(7)	S(1)–C(1)–N(1)	179.5(6)

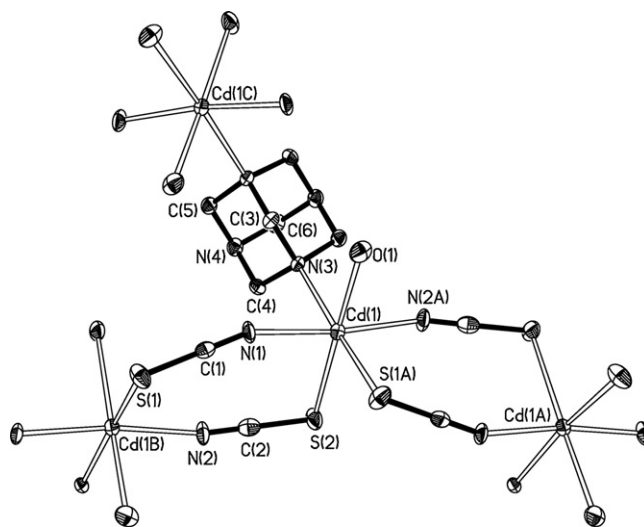
Symmetry code—A: 1/2–*x*, 1/2+*y*, *z*; B: 1/2–*x*, –1/2+*y*, *z*.

### 3.2. IR spectra

In the IR spectrum of the title complex, a sharp and strong (SCN) absorption band at 2100 cm<sup>-1</sup> and a shoulder at 2096 cm<sup>-1</sup> in the complex show the coordination of SCN<sup>-</sup> anion with a 1,3-μ bridge mode, which agrees well with the relevant compounds [7]. The complex **1** shows several bands in the range 2880–2990 cm<sup>-1</sup> which is assigned to the aliphatic (CH) stretching vibrations of hmt [12]. The strong broad band at 3550–3350 cm<sup>-1</sup> are assigned as the (OH) stretching frequency of the coordination water and crystal water molecules.

### 3.3. Description of the crystal structure of compound **1**

Complex **1** crystallizes in the orthorhombic space group *Aba2*. An ORTEP diagram of the complex **1** with the atomic numbering scheme and the coordination geometry of Cd atoms are depicted in Fig. 1. The asymmetry unit consists of a Cd(SCN)<sub>2</sub>(hmt)<sub>1/2</sub>(H<sub>2</sub>O) structure units and one lattice water molecule. The Cd(II) atom is surrounded by two S atoms, three N atoms and one O atom, in which two S atoms and two N atoms from four di-μ-1,3-SCN<sup>-</sup> bridges ligands, one N atom from hmt and the O atom from coordinated



**Fig. 1.** ORTEP drawing of the complex with the atom numbering scheme and the octahedral geometry of Cd1. The atoms are represented by 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity (symmetry codes: A: 1/2–*x*, 1/2+*y*, *z*; B: 1/2–*x*, –1/2+*y*, *z*; C: –*x*, 1–*y*, *z*).

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