

Synthesis, crystal structure and luminescent properties of a thiocyanato-bridged two-dimensional heteronuclear polymeric complex of cadmium(II) and nickel(II)

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ABSTRACT

The heteronuclear coordination polymer $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2$ **1** (en = ethylenediamine) was obtained by reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KSCN , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and en in a mole ratio of 1:3:1:0.1 in ethanol solution. The complex is characterized by IR spectroscopy, electronic spectroscopy and single-crystal X-ray diffraction analysis. Crystal structure analyses show that the title complex belongs to the triclinic space group $P\bar{1}$ with $a = 8.922(3)$, $b = 9.860(3)$, $c = 10.333(5)$ Å, $\alpha = 113.116(6)^\circ$, $\beta = 106.550(6)^\circ$, $\gamma = 101.622(4)^\circ$, $V = 749.0(5)$ Å³. Cd(II) and Ni(II) centers are linked by di- μ -1,3-thiocyanate bridges to form a 2D network containing three types of 16-membered $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ macrocycles. Each Cd(II) center links six Ni(II) centers by six μ -1,3-SCN[−] bridges and each Ni(II) center links three Cd(II) centers by three μ -1,3-SCN[−] bridges. The luminescent properties of **1** in the solid state were investigated.

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1. Introduction

During the past decade, heteronuclear coordination polymers have attracted great interest in coordination chemistry and material science with regard to their intriguing network topologies and interesting electric, magnetic, catalytic and optical properties [1–4]. In the design and self-assembly of coordination polymers, the key factor is the rational selection of bridging ligands for assembling metal ions to construct a desired framework [5]. The linear triatomic pseudohalide, SCN[−], is one of the best bridging ligands, which may form bonds with different metal centers simultaneously [6]. Much effort has been devoted to the design of thiocyanato-bridged coordination polymers [7]. In these structures a thiocyanate ion must act as a rigid bridged ligand which may link a pair of metal centers through 1,1- μ -SCN[−], 1,1- μ -NCS[−] or 1,3- μ -SCN[−] configuration to satisfy the coordination number of the metal ion. Compared with homonuclear thiocyanate coordination polymers [8], the crystal engineering of heteronuclear thiocyanate polymeric complexes is inherently flexible and particularly attractive for the preparation of new network types. As this greater structural ambivalence will lead to the synthesis of unprecedented structures which may cause difficulty in controlling the synthetic reactions and the structures of the products [9,10].

Our current interest is the construction of heterometal thiocyanato complexes containing anionic SCN[−] ligand and d^{10} metal ions Cd(II) and this strategy is anticipated to affect the crystal structure

and obtain complexes with a new type of stacking structure and interesting optical properties [11]. As a continuance of our research work in the assemblies and properties of coordination polymers [12], here we report the synthesis, crystal structure and luminescent properties of the new heteronuclear μ -1,3-thiocyanato-bridged coordination polymer, $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2$ **1**.

2. Experimental

2.1. Materials and physical measurements

All the chemicals were of analytical grade and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{−1} region. The UV-vis spectra were measured with a HITACHI U-4100 spectrophotometer and the luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer.

2.2. Preparation of the title complex

A 40 mL ethanol solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.31 g, 1 mmol), KSCN (0.29 g, 3 mmol) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1 mmol) were mixed. Then the filtrate was added to 0.1 mmol ethylenediamine anhydrous and the solution was stirred for 0.5 h. The blue solution was left for slowly evaporating at room temperature to obtain blue block crystals suitable for X-ray structure determination. Yield:

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72%. Anal. Calcd. for $C_{14}H_{28}CdN_{10}Ni_2O_2S_6$ (%): C 21.27, H 3.57, N 17.72. Found: C 21.21, H 3.61, N 17.70.

2.3. Crystallographic studies

A suitable sample of size $0.25 \times 0.22 \times 0.20$ mm³ 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 $2.40^\circ < \theta < 25.50^\circ$. All diffraction measurements were performed at room temperature using graphite monochromatized MoK α radiation ($\lambda = 0.71073$ Å). A total of 4035 (2318 independent, $R_{\text{int}} = 0.0145$) reflections were measured. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 program [13]. 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 $I > 2\sigma(I)$. Space group, lattice parameters and other relevant information are listed in Table 1. Select bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. IR spectra

The IR spectra of **1** gave clear evidences of the coordination of en molecule by the existence of a strong νNH absorption centered at 3345 cm⁻¹. Compared with 3400 cm⁻¹ assigned to the amine group of free en molecule, a 55 cm⁻¹ shift to low wavelength number strongly suggest coordination of the amine group with Ni atoms in the complex **1**. The stretching CN frequencies observed at 2123 cm⁻¹ clearly indicate a coordination mode of the SCN⁻ with a M-SCN-M bridge mode, which agree well with the relevant compounds [10a,14]. Its identity was finally confirmed by X-ray crystallography.

3.2. Crystal structure of complex **1**

Complex $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2$ **1** crystallizes in the triclinic space group $P\bar{1}$. The coordination geometry of Cd(II) and Ni(II) atoms are depicted in Fig. 1. The bond parameters associated with the metal ions are listed in Table 2. The Cd(II) atom lies on an inversion center and is surrounded by six S atoms from six di- μ -1,3-thiocyanate bridges to attain a distorted octahedral coordina-

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

Bond length (Å)			
Cd(1)–S(1)	2.6658(10)	Cd(1)–S(2)	2.7151(9)
Cd(1)–S(3)	2.7668(13)	Ni(1)–N(1)	2.040(3)
Ni(1)–N(2B)	2.048(3)	Ni(1)–N(3C)	2.054(3)
Ni(1)–N(4)	2.082(2)	Ni(1)–N(5)	2.087(2)
Ni(1)–O(1)	2.170(2)		
Bond angle (°)			
S(1)–Cd(1)–S(2)	82.67(3)	S(1A)–Cd(1)–S(2)	97.33(3)
S(1)–Cd(1)–S(3)	84.28(4)	S(1A)–Cd(1)–S(3)	95.72(4)
S(2)–Cd(1)–S(3)	80.67(3)	S(2A)–Cd(1)–S(3)	99.33(3)
N(1)–Ni(1)–N(2B)	91.66(11)	N(1)–Ni(1)–N(3C)	91.65(11)
N(2B)–Ni(1)–N(3C)	94.64(11)	N(1)–Ni(1)–N(4)	91.27(11)
N(2B)–Ni(1)–N(4)	174.46(10)	N(3C)–Ni(1)–N(4)	89.97(10)
N(1)–Ni(1)–N(5)	173.76(11)	N(2B)–Ni(1)–N(5)	93.96(11)
N(3C)–Ni(1)–N(5)	90.59(11)	N(4)–Ni(1)–N(5)	82.91(10)
N(1)–Ni(1)–O(1)	87.48(10)	N(2B)–Ni(1)–O(1)	89.93(10)
N(3C)–Ni(1)–O(1)	175.37(9)	N(4)–Ni(1)–O(1)	85.50(10)
N(5)–Ni(1)–O(1)	89.82(10)		

Symmetry code: (A) $1 - x, 2 - y, 1 - z$; (B) $x, -1 + y, z$; (C) $x, y, 1 + z$.

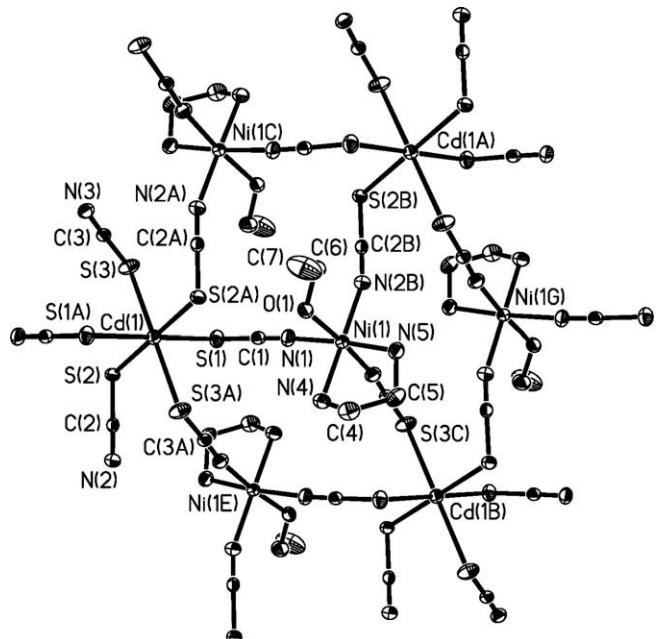


Fig. 1. A fragment structure of complex **1** with the atomic labeling scheme as 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry operation: (A) $1 - x, 2 - y, 1 - z$; (B) $x, -1 + y, z$; (C) $x, y, 1 + z$; (E) $1 - x, 2 - y, 2 - z$; (G) $1 - x, 1 - y, 2 - z$.

tion geometry. The average distances of Cd(II)–S is 2.716 Å. The nickel(II) atom, which is also lies on an inversion center, has an octahedral environment with an N_5O donor set, in which the equatorial positions are occupied by four nitrogen atoms N(1), N(2B), N(4) and N(5) from two di- μ -1,3-thiocyanate bridges and one ethylenediamine bidentate ligand with Ni–N distances in the rang $2.041(3)$ – $2.087(3)$ Å, which is located in the normal range. The O atom of ethanol molecule and N atom of a di- μ -1,3-thiocyanate ion are *trans* to each other. The di- μ -1,3-thiocyanate anion links one cadmium and one nickel atoms together with the cadmium and nickel distance of 5.92 Å for Cd(1)–Ni(1), 6.19 Å for Cd(1)–Ni(1C) and 6.16 Å for Cd(1)–Ni(1E), respectively. The thiocyanate groups are almost linear with the average N–C–S bond angles of 178° . The average S–C and C–N distances at 1.645 Å and 1.142 Å are in accordance with the values observed in other thiocyanato bridges metal complexes [14,15].

Table 1
Crystal data and structure refinement parameters for complex **1**.

Crystal data	
Chemical formula	$C_{14}H_{28}CdN_{10}Ni_2O_2S_6$
Color	Blue
Formula weight	790.64
Cell setting, space group	Triclinic, $P\bar{1}$
a (Å)	8.922(3)
b (Å)	9.860(3)
c (Å)	10.333(5)
α (°)	113.116(6)
β (°)	106.550(6)
γ (°)	101.622(4)
Volume (Å ³)	749.0(5)
Z	1
D_c (mg m ⁻³)	1.753
Crystal size (mm)	$0.25 \times 0.22 \times 0.20$
Radiation (Å)	MoK α 0.71073
Theta min–max (°)	2.40–25.50
Tot., uniq. data, $R(\text{int})$	4035, 2761, 0.0145
Observed data [$I > 2.0 \sigma(I)$]	2318
$N_{\text{ref}}, N_{\text{par}}$	2761, 160
R, wR_2, S	0.0268, 0.0586, 1.012
Min. and max. resid. dens. [e/Å ³]	-0.637, 0.385

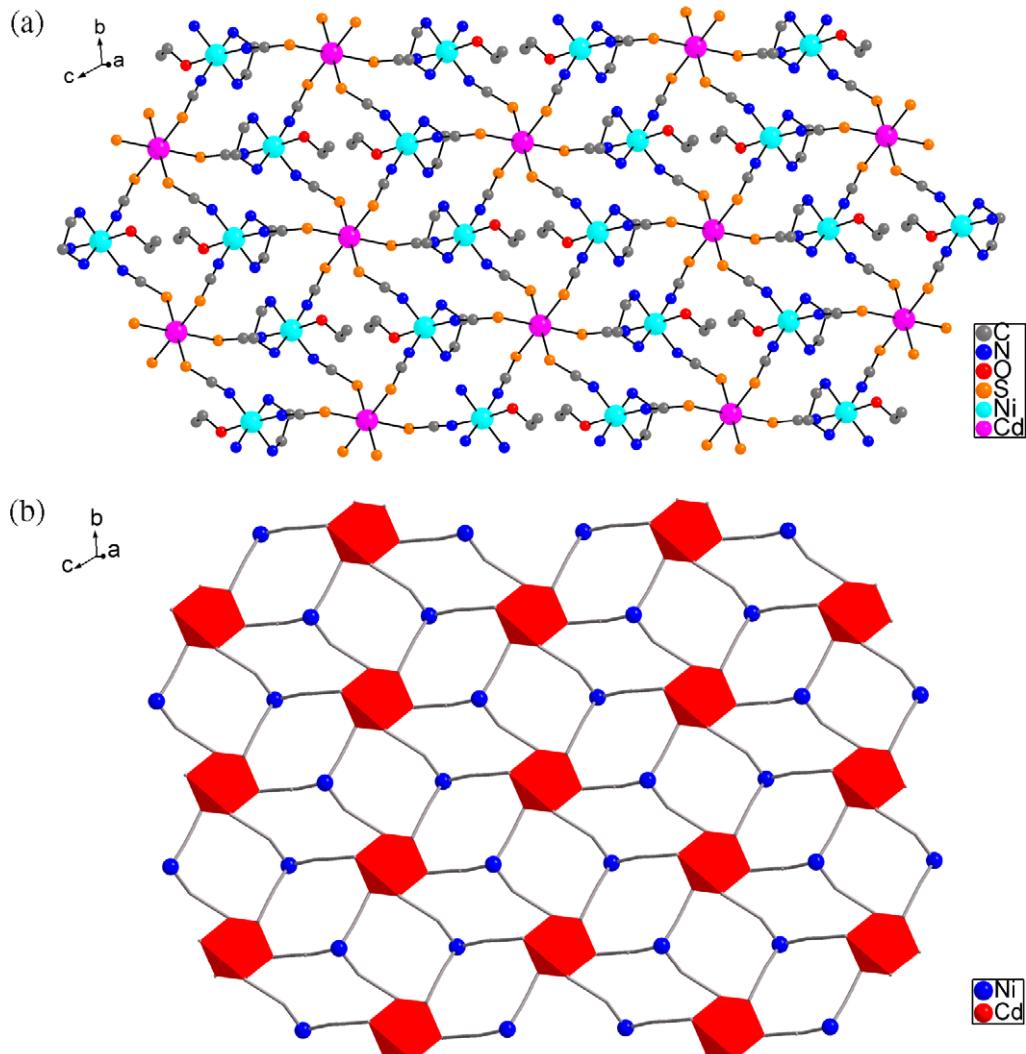


Fig. 2. 2D sheet of in the complex **1** comprising three type of 16-membered $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ rings. Hydrogen atoms have been omitted for clarity (a). EtOH, SCN⁻ and en molecules and hydrogen atoms have been omitted for clarity (b).

As the distance of Cd···Ni is different, there are three types of 16-membered $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ macrocycles and serve to increase the dimensionality of the compound to form a 2D sheet (Fig. 2). Each cadmium(II) center links six nickel(II) centers by six μ -1,3-thiocyanate bridges and each nickel(II) center links three cadmium(II) centers by three μ -1,3-thiocyanate bridges. The Cd···Cd and Ni···Ni distances are 9.86 Å and 7.04 Å for Cd(1)···Cd(1A) and Ni(1)···Ni(1C), 10.33 Å and 6.26 Å for Cd(1)···Cd(1B) and Ni(1)···Ni(1E) and 11.14 Å and 5.34 Å for Cd(1A)···Cd(1B) and Ni(1)···Ni(1G), respectively. Furthermore, O-H···S hydrogen bonds were found between the O(1) atom of the ethanol molecule and S(2) atom of the thiocyanate anion to stabilize the 2D network. The O(1)···S(2A) separation is 3.30 Å and O(1)-H(1A)···S(2A) angle is 123°.

3.3. Luminescence and UV-vis-NIR spectra

The design and study of metal-organic complexes is an active and interesting area for fluorescence properties and potential applications as emissive materials. Among them, a number of poly-nuclear d^{10} transition metal complexes, such as Cd(II) and Zn(II) complexes, exhibit interesting luminescence properties. Thus, the syntheses of Cd(II) complexes can be an efficient method for

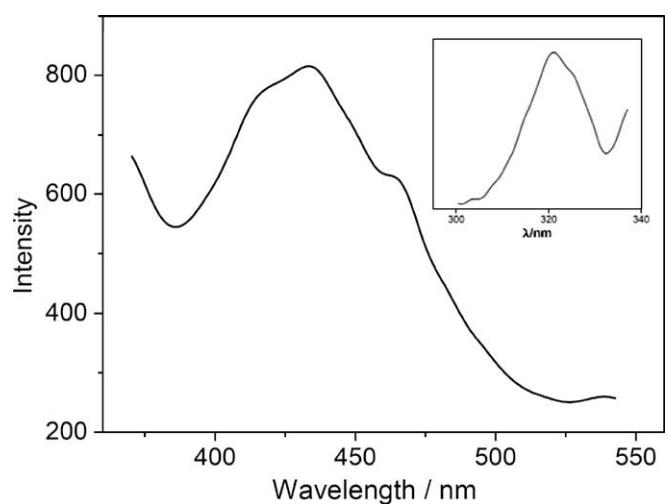


Fig. 3. The emission spectrum ($\lambda_{\text{ex}} = 321 \text{ nm}$) and excitation spectrum (inset, $\lambda_{\text{em}} = 434 \text{ nm}$) of complex **1** in solid state at room temperature.

obtaining new types of luminescent materials [16,17]. Herein, the emission and excitation spectra of the complex **1** in the solid state

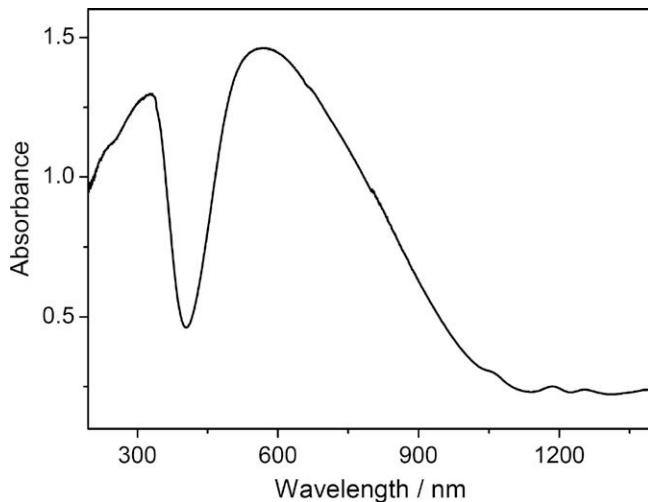


Fig. 4. The electronic absorption spectrum of complex **1** in the solid state at room temperature.

at room temperature have been examined (in Fig. 3). Although the title coordination polymer contains the paramagnetic nickel(II) in and octahedral geometry, upon excitation at 321 nm, the complex shows one emission peak at 434 nm. This result is similar to those found in a related compound [18]. As depicted in Fig. 4, for the electronic spectrum of **1** in the solid state, two absorption bands at 328 and 566 nm can be assigned to ligand–metal charge transfer and *d*-*d* transition bands, respectively. The SCN group is a good electron supplier and the electron transfer from SCN[−] to Cd²⁺, Zn²⁺ and Hg²⁺ ions, therefor, the emission band at 434 nm for the complex **1** might be attributed to LMCT (ligand-to-metal charge transfer), which has been observed in other polynuclear *d*¹⁰ metal polymers [16,17]. Similar emission has also been observed in other Cd(II) polymers using thiocyanate ligand [19].

4. Conclusion

In summary, the [Cd(SCN)₂Ni(en)(NCS)₂(EtOH)]₂ heteronuclear coordination polymer was prepared. The structure of the complex has been established by single-crystal X-ray diffraction analysis and also characterized by IR, elemental analysis, UV and luminescent properties. Cd(II) and Ni(II) centers are linked by di- μ -1,3-thiocyanate bridges to form a 2D network containing three types of 16-membered [Cd₂Ni₂(μ -1,3-SCN)₄] macrocycles. The fluorescence measurement of **1** showed a strong band with a maximum at 434 nm. Further work on this theme is in progress.

5. Supplementary material

CCDC-705912 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223 336033; email: deposit@ccdc.cam.ac.uk).

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