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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 $[Cd(SCN)_2Ni(en)(NCS)_2(EtOH)]_2$ **1** (en = ethylenediamine) was obtained by reaction of $Cd(NO_3)_2{\cdot}4H_2O$, KSCN, $Ni(NO_3)_2{\cdot}6H_2O$ and en in a mole ration 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, $\alpha = 113.116(6)°$, $\beta = 106.550(6)°$, $\gamma = 101.622(4)°$, $V = 749.0(5)$ Å^3. 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 $[Cd_2Ni_2(\mu\text{-}1,3\text{-}SCN)_4]$ 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.

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 thiocyanate 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, $[Cd(SCN)_2Ni(en)(NCS)_2(EtOH)]_2$ **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 $Cd(NO_3)_2{\cdot}4H_2O$ (0.31 g, 1 mmol), KSCN (0.29 g, 3 mmol) and $Ni(NO_3)_2{\cdot}6H_2O$ (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 $0.25 \times 0.22 \times 0.20\ mm^3$ 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 $2.40° < \theta < 25.50°$. All diffraction measurements were performed at room temperature using graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å). A total of 4035 (2318 independent, $R_{int} = 0.0145$) 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 υNH 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 $[Cd(SCN)_2Ni(en)(NCS)_2(EtOH)]_2$ **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 coordination 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 chelate 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 × 0.22 × 0.20
Radiation (Å)	MoKα 0.71073
Theta min–max (°)	2.40–25.50
Tot., uniq. data, *R*(int)	4035, 2761, 0.0145
Observed data [*I* > 2.0 sigma(*I*)]	2318
N_{ref}, N_{par}	2761, 160
R, wR_2, *S*	0.0268, 0.0586, 1.012
Min. and max. resd. dens. [e/Å^3]	−0.637, 0.385

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) $x, y, 1+z$.

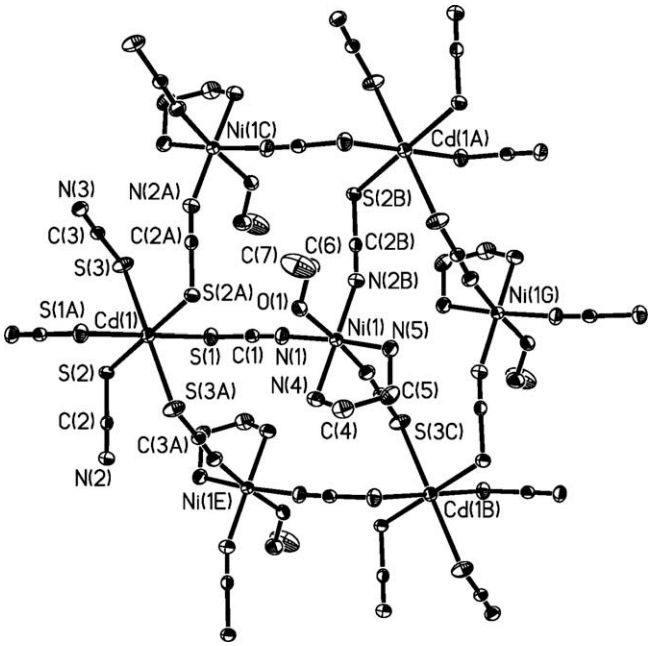

Fig. 1. A fragment structure of complex **1** with the atomic labeling scheme as 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry operation: (A) $1-x, 2-y, 1-z$; (B) $x, -1+y, z$; (C) $x, y, 1+z$; (E) $1-x, 2-y, 2-z$; (G) $1-x, 1-y, 2-z$.