



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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ARTICLE INFO

Article history:

Received 25 April 2009

Received in revised form 13 June 2009

Accepted 14 June 2009

Available online 21 June 2009

Keywords:

Heteronuclear complex

Thiocyanato-bridged

Crystal structure

Luminescent properties

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 materials 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, $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2$ **1**.

2. Experimental

2.1. Materials and physical measurements

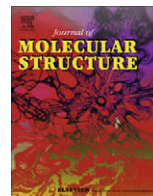
All the chemicals were of analytical grade and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{−1} region. The UV–vis 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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硫氰酸桥接的二维镉(II)-镍(II)杂核聚合物复合物的合成、晶体结构及发光性能

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文章信息

文章历程: 2009年4月25日收到 2009年6月13日修订后收到 2009年6月14日接受 2009年6月21日在线发布

关键词: 异核配合物 硫氰酸桥接 晶体结构 发光性质

摘要

通过在乙醇溶液中以1:3:1:0.1的摩尔比反应 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 、 KSCN 、 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和乙二胺(en), 获得了异核配位聚合物 $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2 \cdot 1$ (en = 乙二胺)。该复合物通过红外光谱、电子光谱及单晶X射线衍射分析进行表征。晶体结构分析表明, 所述复合物属于三斜晶系空间群 $P\bar{1}$, 晶胞参数为 $a = 8.922(3) \text{ \AA}$, $b = 9.860(3) \text{ \AA}$, $c = 10.333(5) \text{ \AA}$, $\alpha = 113.116(6)^\circ$, $\beta = 106.550(6)^\circ$, $\gamma = 101.622(4)^\circ$, 晶体体积 $V = 749.0(5) \text{ \AA}^3$ 。Cd(II)和Ni(II)中心通过双 μ -1,3-硫氰酸盐桥连形成二维网络, 该网络包含三种类型的16元 $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ 大环。每个Cd(II)中心通过六个 μ -1,3-SCN $^-$ 桥连六个Ni(II)中心, 每个Ni(II)中心通过三个 μ -1,3-SCN $^-$ 桥连三个Cd(II)中心。1的发光性质于

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1. 介绍

在过去的十年中, 异核配位聚合物因其有趣的网络拓扑结构以及独特的电学、磁学、催化和光学性质, 在配位化学和材料科学领域引起了极大的关注[1–4]。在配位聚合物的设计和自组装中, 关键因素是合理选择桥联配体, 将金属离子组装成所需的框架结构[5]。线性三原子拟卤素 SCN^- 是最佳桥联配体之一, 它可以同时与不同的金属中心形成配位键[6]。大量研究致力于硫氰酸盐桥联配位聚合物的设计[7]。在这些结构中, 硫氰酸根离子必须作为刚性桥联配体, 通过1,1- μ -SCN $^-$ 、1,1- μ -NCS $^-$ 或1,3- μ -SCN $^-$ 构型连接一对金属中心, 以满足金属离子的配位数要求。与同核硫氰酸盐配位聚合物相比[8],

并获得具有新型堆积结构和有趣光学性质的配合物[11]。作为我们在配位聚合物组装与性质研究工作的延续[12], 本文报道了新型杂核1,3-硫氰酸盐桥联配位聚合物 $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2 \cdot 1$ 的合成、晶体结构及发光性质。

2. 实验

2.1. 材料和物理测量

所有化学品均为分析纯, 使用前未进行进一步纯化。元素分析(C、H和N)在Perkin-Elmer 240C分析仪上进行。红外光谱在KBr片中用Nicolet 170 SXFT-IR分光光度计在4000–400 cm^{-1} 范围内记录。紫外-可见光谱用HITACHI U-4100分光光度计测定, 发光光谱在Hitachi F-7000荧光分光光度计上测得。

2.2. 目标配合物的制备

将40 mL乙醇溶液中的 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.31 g, 1 mmol)、 KSCN (0.29 g, 3 mmol)和 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1 mmol)混合。然后将滤液加入0.1 mmol无水乙二胺中, 并搅拌0.5小时。将蓝色溶液放置在室温下缓慢蒸发, 得到适用于X射线结构测定的蓝色块状晶体。产率:

我们目前关注的是含有阴离子 SCN^- 配体和 d^{10} 金属离子Cd(II)的异金属硫氰酸配合物的构建, 预计这一策略将影响晶体结构

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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 $0.25 \times 0.22 \times 0.20 \text{ mm}^3$ 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 $2.40^\circ < \theta < 25.50^\circ$. All diffraction measurements were performed at room temperature using graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). 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 ν_{NH} 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 ($^\circ$) 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 ($^\circ$)			
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) $x, y, 1 + z$.

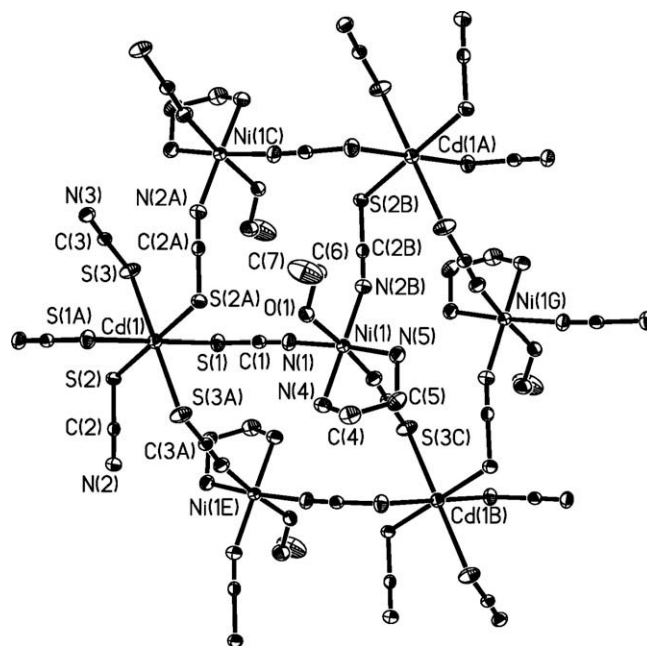


Fig. 1. A fragment structure of complex **1** with the atomic labeling scheme as 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry operation: (A) $1 - x, 2 - y, 1 - z$; (B) $x, -1 + y, z$; (C) $x, y, 1 + z$; (E) $1 - x, 2 - y, 2 - z$; (G) $1 - x, 1 - y, 2 - z$.

tion geometry. The average distances of Cd(II)–S is 2.716 \AA . 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 $2.041(3)$ – $2.087(3) \text{ \AA}$, 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 \AA for Cd(1)···Ni(1), 6.19 \AA for Cd(1)···Ni(1C) and 6.16 \AA 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 \AA and 1.142 \AA 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, $P\bar{1}$
<i>a</i> (Å)	8.922(3)
<i>b</i> (Å)	9.860(3)
<i>c</i> (Å)	10.333(5)
α ($^\circ$)	113.116(6)
β ($^\circ$)	106.550(6)
γ ($^\circ$)	101.622(4)
Volume (Å ³)	749.0(5)
<i>Z</i>	1
<i>D_c</i> (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 ($^\circ$)	2.40–25.50
Tot., uniq. data, <i>R</i> (int)	4035, 2761, 0.0145
Observed data [$I > 2.0 \sigma(I)$]	2318
<i>N_{ref}</i> , <i>N_{par}</i>	2761, 160
<i>R</i> , <i>wR₂</i> , <i>S</i>	0.0268, 0.0586, 1.012
Min. and max. resd. dens. [e/Å ³]	−0.637, 0.385

72%。分析计算，基于 $C_{14}H_{28}CdN_{10}Ni_2O_2S_6$ (%)：C 21.27, H 3.57, N 17.72。实测：C 21.21, H 3.61, N 17.70。

2.3. 晶体学研究

选择了尺寸为 $0.25 \times 0.22 \times 0.20 \text{ mm}^3$ 的合适样品进行晶体学研究，然后将其安装在 Bruker APEX II CCD 衍射仪上，使用 ω 和 φ 扫描模式，范围为 $2.40^\circ < 2\theta < 25.50^\circ$ 。所有衍射测量均在室温下使用石墨单色化的 MoK α 辐射 ($k = 0.71073 \text{ \AA}$) 进行。共测量了 4035 个衍射点 (其中 2318 个独立点， $R_{\text{int}} = 0.0145$)。结构通过直接方法求解，并使用 SHELXL-97 程序 [13] 在 F^2 上进行全矩阵最小二乘精修。所有非氢原子均进行了各向异性热因子精修。氢原子则放置在计算位置。结构求解和精修基于 1863 个信号强度 $I > 2\sigma(I)$ 的独立衍射点。空间群、晶格参数及其他相关信息列于表 1。部分键长和键角列于表 2。

3. 结果与讨论

3.1. 红外光谱

1号化合物的红外光谱清楚地证明了亚乙二胺分子的配位，表现在 3345 cm^{-1} 处有一个强烈的 --NH 吸收峰。与自由亚乙二胺分子的胺基 3400 cm^{-1} 吸收峰相比，其向低波数移动了 55 cm^{-1} ，这强烈表明胺基与1号化合物中的镍原子发生了配位。观察到的 2123 cm^{-1} 的 $\text{C}\equiv\text{N}$ 伸缩振动频率清楚地显示了 SCN $^-$ 的配位方式为 M--SCN--M 桥联模式，这与相关化合物 [10a,14] 一致。其结构最终通过X射线晶体学得到确认。

3.2. 复合物1的晶体结构

复合物 $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})]_2$ 1 结晶于三斜晶系空间群 $P\bar{1}$ 。Cd(II) 和 Ni(II) 原子的配位几何如图 1 所示。与金属离子相关的键参数列于表 2。Cd(II) 原子位于反演中心，由六个来自六个 $\mu\text{--}1,3$ -硫氰酸盐桥的 S 原子包围，以形成畸变的八面体配位结构。

表 1 复合物 1 的晶体数据及结构精修参数。

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, $P\bar{1}$
<i>a</i> (Å)	8.922(3)
<i>b</i> (Å)	9.860(3)
<i>c</i> (Å)	10.333(5)
α (°)	113.116(6)
β (°)	106.550(6)
γ (°)	101.622(4)
Volume (Å ³)	749.0(5)
<i>Z</i>	1
<i>D_c</i> (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, <i>R</i> (int)	4035, 2761, 0.0145
Observed data [<i>I</i> > 2.0 σ (<i>I</i>)]	2318
<i>N_{ref}</i> , <i>N_{par}</i>	2761, 160
<i>R_w</i> , <i>wR₂</i> , <i>S</i>	0.0268, 0.0586, 1.012
Min. and max. resd. dens. [e/Å ³]	−0.637, 0.385

表2 复合物1的选定键长 (Å) 和角度 (°)。

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)		

对称代码: (A) 1 − *x*, 2 − *y*, 1 − *z*; (B) *x*, −1 + *y*, *z*; (C) *x*, *y*, 1 + *z*。

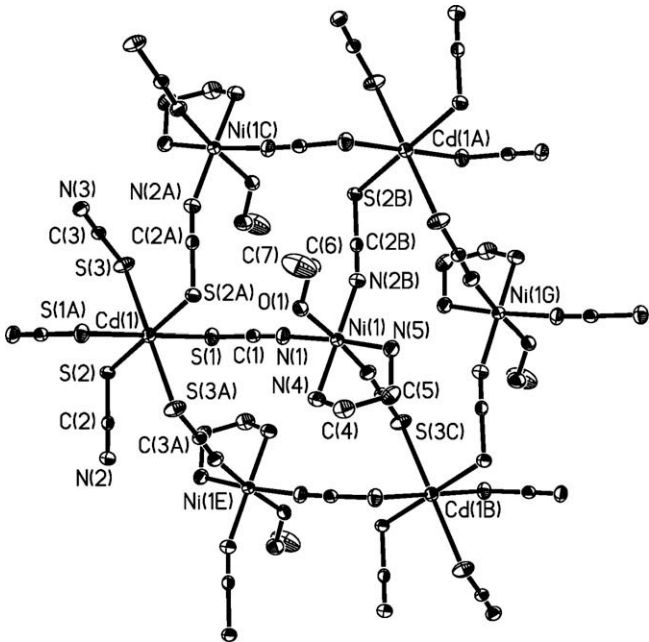


图1. 复合物1的部分结构及其原子标记方案，以30%概率的热椭球表示。为清晰起见省略了氢原子。对称操作: (A) 1 − *x*, 2 − *y*, 1 − *z*; (B) *x*, −1 + *y*, *z*; (C) *x*, *y*, 1 + *z*; (E) 1 − *x*, 2 − *y*, 2 − *z*; (G) 1 − *x*, 1 − *y*, 2 − *z*。

几何构型。Cd(II)–S的平均距离为2.716 Å。镍(II)原子也位于反转中心上，具有八面体环境，其配位为 N_5O ，其中赤道位置上由来自两个 $\mu\text{--}1,3$ -硫氰酸盐桥的四个氮原子 N(1)、N(2B)、N(4) 和 N(5) 以及一个乙二胺双齿螯合配体占据，Ni–N 的距离在 2.041(3)–2.087(3) Å 范围内，属于正常范围。乙醇分子的 O 原子与 $\mu\text{--}1,3$ -硫氰酸根离子的 N 原子互为反位。 $\mu\text{--}1,3$ -硫氰酸根阴离子将一个铜和一个镍原子连接在一起，Cd(1)··Ni(1) 的铜与镍距离为 5.92 Å，Cd(1)··Ni(1C) 为 6.19 Å，Cd(1)··Ni(1E) 为 6.16 Å。硫氰酸基几乎呈线性，N–C–S 的平均键角为 178°。平均 S–C 和 C–N 的距离分别为 1.645 Å 和 1.142 Å，与其他硫氰酸盐中观察到的值一致。

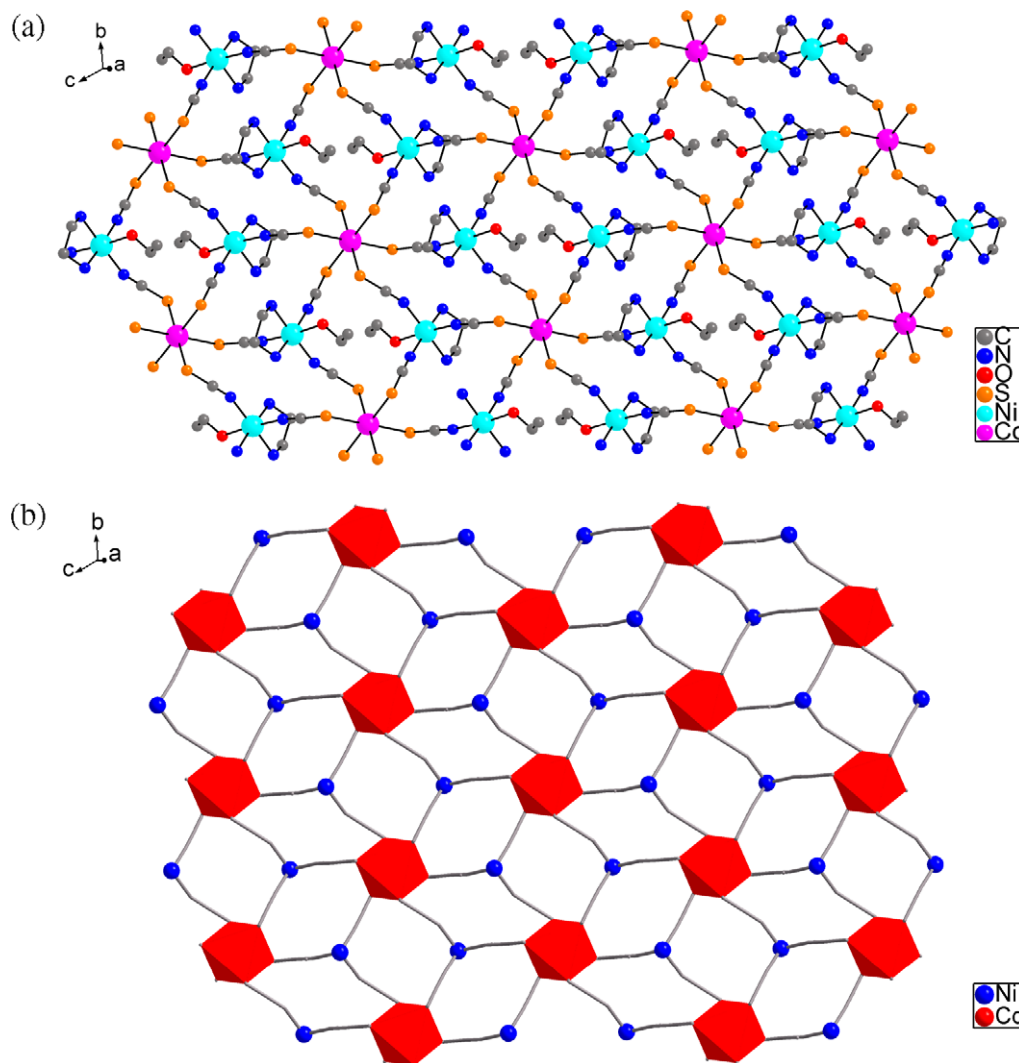


Fig. 2. 2D sheet of in the complex **1** comprising three type of 16-membered $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ rings. Hydrogen atoms have been omitted for clarity (a). EtOH, SCN^- and en molecules and hydrogen atoms have been omitted for clarity (b).

As the distance of $\text{Cd} \cdots \text{Ni}$ 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 $\mu\text{-}1,3$ -thiocyanate bridges and each nickel(II) center links three cadmium(II) centers by three $\mu\text{-}1,3$ -thiocyanate bridges. The $\text{Cd} \cdots \text{Cd}$ and $\text{Ni} \cdots \text{Ni}$ distances are 9.86 Å and 7.04 Å for $\text{Cd}(1) \cdots \text{Cd}(1A)$ and $\text{Ni}(1) \cdots \text{Ni}(1C)$, 10.33 Å and 6.26 Å for $\text{Cd}(1) \cdots \text{Cd}(1B)$ and $\text{Ni}(1) \cdots \text{Ni}(1E)$ and 11.14 Å and 5.34 Å for $\text{Cd}(1A) \cdots \text{Cd}(1B)$ and $\text{Ni}(1) \cdots \text{Ni}(1G)$, respectively. Furthermore, $\text{O-H} \cdots \text{S}$ 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 $\text{O}(1) \cdots \text{S}(2A)$ separation is 3.30 Å and $\text{O}(1)\text{-H}(1A) \cdots \text{S}(2A)$ 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 polynuclear 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

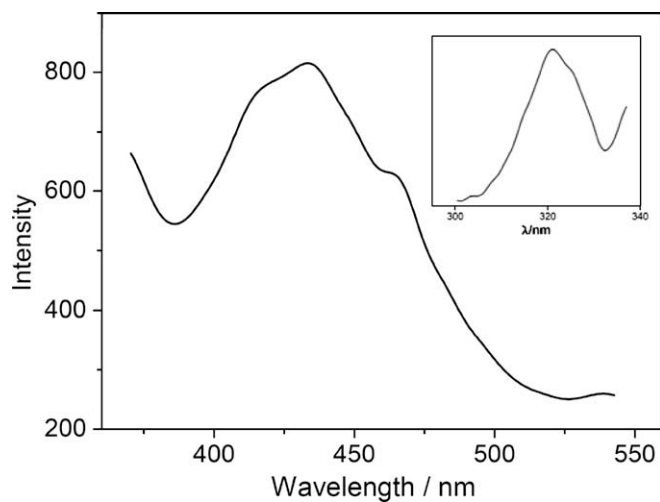


Fig. 3. The emission spectrum ($\lambda_{\text{ex}} = 321 \text{ nm}$) and excitation spectrum (inset, $\lambda_{\text{em}} = 434 \text{ nm}$) of complex **1** in solid state at room temperature.

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

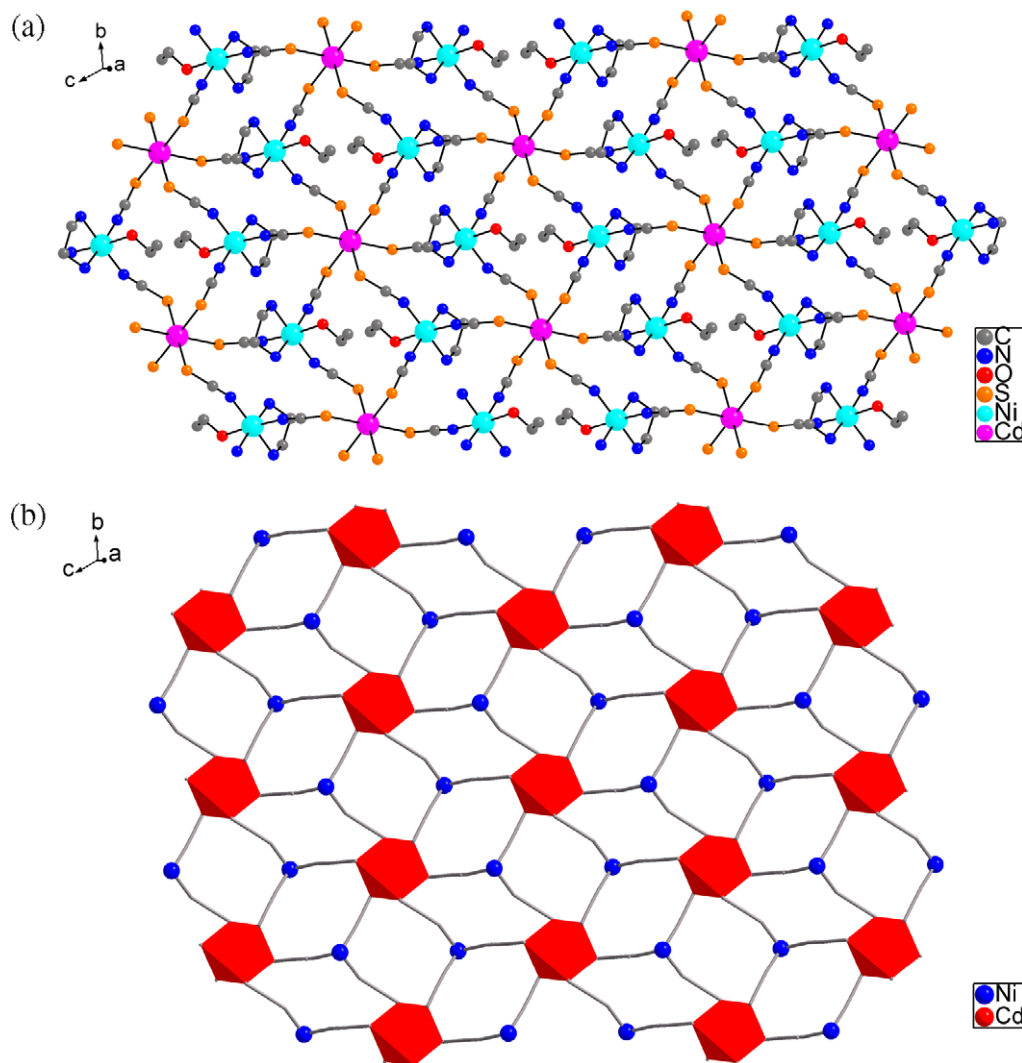


图2. 复合物1中的二维片层, 由三种类型的16元 $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ 环组成。为了清楚起见, 省略了氢原子 (a)。为了清楚起见, 省略了 EtOH 、 SCN^- 和 en 分子及氢原子 (b)。

由于 $\text{Cd}\cdots\text{Ni}$ 的距离不同, 有三种类型的16元 $[\text{Cd}_2\text{Ni}_2(\mu\text{-}1,3\text{-SCN})_4]$ 大环, 它们有助于增加化合物的维度, 从而形成二维片状结构 (图2)。每个镉(II)中心通过六个 $\mu\text{-}1,3$ -硫氰酸桥连接六个镍(II)中心, 每个镍(II)中心通过三个 $\mu\text{-}1,3$ -硫氰酸桥连接三个镉(II)中心。 $\text{Cd}\cdots\text{Cd}$ 和 $\text{Ni}\cdots\text{Ni}$ 的距离分别为: $\text{Cd}(1)\cdots\text{Cd}(1\text{A})$ 和 $\text{Ni}(1)\cdots\text{Ni}(1\text{C})$ 为9.86 Å和7.04 Å, $\text{Cd}(1)\cdots\text{Cd}(1\text{B})$ 和 $\text{Ni}(1)\cdots\text{Ni}(1\text{E})$ 为10.33 Å和6.26 Å, $\text{Cd}(1\text{A})\cdots\text{Cd}(1\text{B})$ 和 $\text{Ni}(1)\cdots\text{Ni}(1\text{G})$ 为11.14 Å和5.34 Å。此外, 在乙醇分子的 $\text{O}(1)$ 原子与硫氰酸阴离子的 $\text{S}(2)$ 原子之间发现了 $\text{O}\cdots\text{H}\cdots\text{S}$ 氢键, 以稳定二维网络。 $\text{O}(1)\cdots\text{S}(2\text{A})$ 的距离为3.30 Å, $\text{O}(1)\text{--H}(1\text{A})\cdots\text{S}(2\text{A})$ 的角度为123°。

3.3. 发光与紫外-可见-近红外光谱

金属-有机配合物的设计和研究是一个活跃且有趣的领域, 涉及荧光特性及其作为发光材料的潜在应用。在这些配合物中, 一些多核 d^{10} 过渡金属配合物, 如 $\text{Cd}(\text{II})$ 和 $\text{Zn}(\text{II})$ 配合物, 显示出有趣的发光特性。因此, $\text{Cd}(\text{II})$ 配合物的合成可以是一种有效的方法来

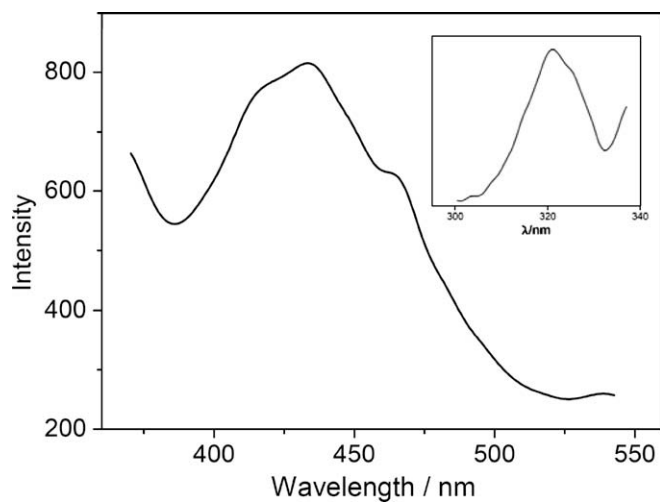


图3. 复合物1在室温固态下的发射光谱 (λ_{em} 321 nm) 和激发光谱 (插图, λ_{ex} 434 nm)。

获得新型发光材料 [16,17]。在此, 复合物1在固态下的发射和激发光谱

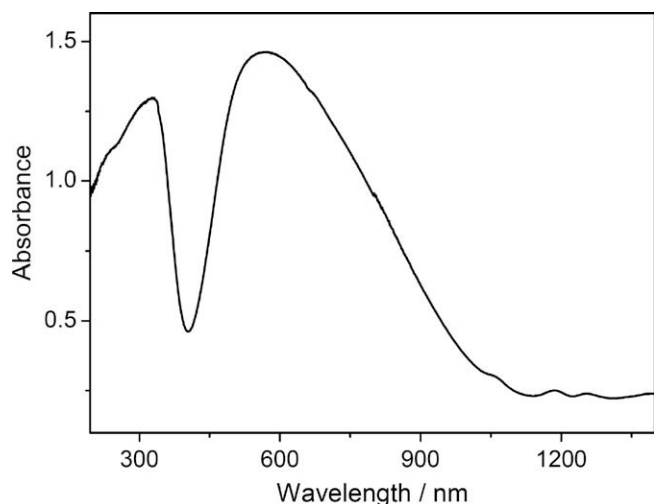


Fig. 4. The electronic absorption spectrum of complex **1** in the solid state at room temperature.

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 Cd^{2+} , Zn^{2+} and Hg^{2+} ions, therefore, 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 $[\text{Cd}(\text{SCN})_2\text{Ni}(\text{en})(\text{NCS})_2(\text{EtOH})_2]$ 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 $[\text{Cd}_2\text{Ni}_2(\mu\text{-1,3-SCN})_4]$ 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).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20701012), the Foundation of the Education

Ministry of China (No. 207068), the Education Department of Henan Province of China (Nos. 2007150011 and 2008B150002) and the Foundation for University Youth Key Teacher of Henan Province of China.

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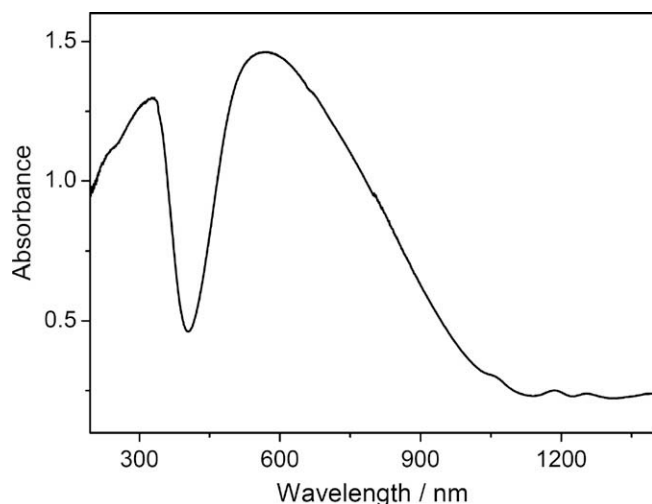


图4. 复合物1在室温下固态的电子吸收光谱。

在室温下进行了研究(见图3)。虽然该配位聚合物包含八面体几何结构的顺磁性镍(II),但在321 nm激发下,该配合物显示出在434 nm的单一发射峰。该结果与相关化合物[18]的发现相似。如图4所示,对于固态下1的电子光谱,分别在328和566 nm处出现两个吸收带,可归因于配体-金属电荷转移和d-d跃迁带。SCN基团是良好的电子供体,电子能够从SCN⁻转移到Cd²⁺、Zn²⁺和Hg²⁺离子上,因此,配合物1在434 nm的发射带可能归因于LMCT(配体到金属的电荷转移),这一现象在其他多核d¹⁰金属聚合物中也有观察到[16,17]。使用硫氰酸根配体的其他Cd(II)聚合物中也观察到了类似的发射[19]。

4. 结论

总之,制备了[Cd(SCN)₂Ni(en)(NCS)₂(EtOH)]₂异核配位聚合物。通过单晶X射线衍射分析确定了该配合物的结构,并通过红外光谱、元素分析、紫外光谱及荧光性质进行了表征。Cd(II)和Ni(II)中心通过二-μ-1,3-硫氰酸盐桥连接,形成包含三种16元[Cd₂Ni₂(μ-1,3-SCN)₄]大环的二维网络。对1的荧光测量显示出在434 nm处的强峰。关于该主题的进一步研究正在进行中。

5. 补充材料

CCDC-705912 包含本文的补充晶体学数据。这些数据可以在 www.ccdc.cam.ac.uk/conts/retrieving.html 免费获取(或通过剑桥晶体学数据中心(CCDC),地址:12 Union Road, Cambridge CB2 1EZ, 英国;传真: +44 (0) 1223 336033; 电子邮件: deposit@ccdc.cam.ac.uk)。

致谢

本工作得到了中国国家自然科学基金(编号20701012)和教育基金的资助

中国教育部(编号207068)、中国河南省教育厅(编号2007150011和2008B150002)以及中国河南省大学青年骨干教师基金会。

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