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一个由多元羧酸和含氮配体构成的二维 Mn(Ⅱ)配合物的合成、表征和发光性能研究

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摘要:本文采取水热合成方法,利用二元羧酸和含氮杂环配体作为混合配体设计合成了一个二维 Mn(Ⅱ)配合物[Mn(mip)(NDC)]$_n$ (**1**)(mip=2-(3-methoxyphenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline, NDC=naphthalene-1,4-dicarboxylic acid),并对其进行元素分析、红外光谱分析、热失重分析、紫外–可见光谱分析和 X-射线单晶衍射表征。配合物 **1** 属于单斜晶系,$P2_1/n$ 群,其晶胞参数如下:a=1.245 80(7) nm,b=1.474 50(9) nm,c=1.365 44(8) nm,β=97.644 0(1)°。在 **1** 中,金属锰(Ⅱ)与来自 3 个 NDC 配体的 4 个 O 原子和来自 1 个 mip 配体的 2 个 N 原子配位,形成扭曲的八面体构型。配合物 **1** 呈现二维(4,4)拓扑构型。热重分析表明配合物 **1** 的分解经历了两个阶段,并且该配合物的结构是比较稳定的。我们初步研究了配体和配合物 **1** 的荧光性能,结果表明配合物 **1** 可以做为潜在的发光材料。

关键词:晶体结构;热稳定性分析;荧光性能

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One 2D Mn(Ⅱ) Complex Constructed by Poly-Carboxylate and N-heterocyclic Ligands: Syntheses, Characterizations and Photoluminescent Properties

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Abstract: One coordination complex constructed from dicarboxylate acid and N-heterocyclic ligand as mixed ligands, namely, [Mn (mip) (NDC)]$_n$ (**1**) (mip =2-(3-methoxyphenyl)-1*H*-imidazo [4,5-f] [1,10]phenanthroline, NDC = naphthalene-1,4-dicarboxylic acid) has been synthesized by hydrothermal reaction. Complex **1** was characterized by elemental analysis, infrared spectrum (IR), single crystal X-ray diffraction, UV-Vis spectrum, and thermogravimetric analysis (TGA). Complex 1 crystallizes in monoclinic, space group $P2_1/n$ with a=1.245 80(7) nm, b=1.474 50(9) nm, c=1.365 44(8) nm, β=97.6440(1)°. In **1**, the metal ions Mn(Ⅱ) act as distorted octahedral geometry, being surrounded by four carboxylate oxygen atoms from three NDC ligands and two donor nitrogen atoms from one mip molecule. Complex **1** shows 2D (4,4) sheet topology. TG analysis shows two clear courses of weight loss, which corresponds to the decomposition of different ligands. The structure-related solid-state uorescence spectra of free ligands and complex **1** have been determined, and the result displays that complex **1** should be acted as potential luminescent material. CCDC: 919758.

Key words: crystal structures; thermal stability; fluorescence

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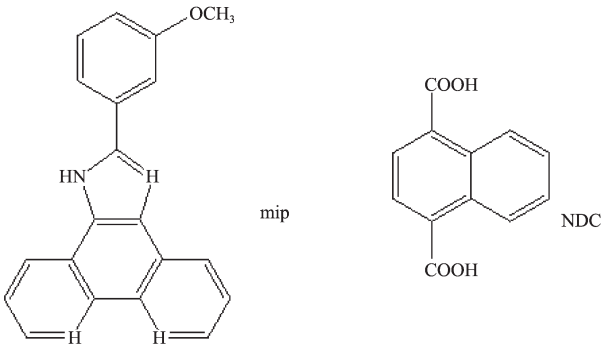
0 Introduction

Design and construction of metal-involved supra-molecular architectures based on crystal engineering are currently of interest. The increasing interest in this eld is justied not only by their intriguing structural motifs, but also their potential applications as various fields such as ion exchange, microelectronics, catalysis, nonlinear optics, porous materials, etc.[1-7]. These complexes can be specially designed by the careful selection of metal centers with preferred coordination geometries, the nature of the anions, template, the structure of the connecting ligands, and the reaction conditions. In addition, H-bonds and π-π interactions also affect the results. A successful approach to build these supra-molecular frameworks is to select suitable multi-dentate ligands as building blocks. Among them, multidentate ligands such as poly-carboxylate and N-heterocyclic ligands are widely used in the rational design and controlled synthesis of complexs [8-10]. As for the N-heterocyclic ligands, we chose one long-conjugated unsymmetrical aromatic N-heterocyclic ligands mip (2-(3-methoxyphenyl)-1H-imidazo [4,5-f] [1,10] phenanthroline) in the construction of complexes. Multi-carboxylate ligands have been demonstrated as top-rank candidates, owing to their versatile coordination modes, for the formation of 1D, 2D or 3D frameworks. In order to investigate the effect of the flexibility on the formation, particularly the carboxylate anions, we selected polycarboxylic acid: naphthalene-1,4-dicarboxylic acid (NDC), using N-heterocyclic and carboxyl ligands as mixed ligands to obtain the expected results.



Scheme 1　Ligands used in the paper

For the past several years, we studied the synthesis of the similar ligands [11-13]. However, the investigation for this type of N-heterocyclic ligand is not enough. Manganese complexs with carboxylate are known to exist at the active sites of some Mn(Ⅱ)-containing metalloenzymes [14-15]. Multidentate ligands have been used to coordinate to metal atoms by the N donors on the heterocyclic rings and O donors on the carboxyl groups. As proton donors and acceptors, the carboxylic oxygen atoms and nitrogen atoms in heterocyclic carboxylic acids can not only coordinate as monodentate or multidentate ligands, but also provide intermolecular hydrogen bonds for assembling the complex into high-dimensional supramolecular networks. It is noteworthy that the existence of hydrogen bonds reinforces the structural stability of complex. For above reasons, in this paper, we design and synthesis one novel complex, namely: $[Mn(mip)(NDC)]_n$. Non-covalent intermolecular interactions (hydrogen bonds and π-π interactions) play an important role in the architectures in reinforcing the structural stability. The research shows that the title complex is good luminescent material.

1 Experimental

1.1 Materials and physical measurements

The ligand mip was prepared by the method according to the description in the literature procedures[16]. All the other chemicals from commercial sources were of AR grade and used without further purification. The FTIR spectrum was recorded on an Alpha Centauri FTIR spectrophotometer using KBr discs in the 400~4 000 cm^{-1} region. TG analysis was performed with a Diamond DSC thermal analyzer at the rate of 10 ℃·min^{-1} rise of temperature in nitrogen atmosphere. Crystal structures were determined on a Bruker SMART APEX II CCD X-ray diffractometer. Elemental analyses of C, H and N were performed on a PE-2400 elemental analyzer. Melting points were obtained on an X-6 microscopic melting point apparatus and are uncorrected. Fluorescence spectra were recorded on a FLSP 920 Edinburgh fluorescence

spectrometer. ^{1}H NMR spectra of mip ligand were carried out with Bruker AV 300 MHz spectrometers and chemical shifts are referenced to internal TMS. Mass spectrometric measurements were carried out at the ICIQ mass spectrometric facility. UV spectra were obtained on a JASCO V-570 spectrometer.

1.2 Syntheses

Ligand mip: A mixture of 3-methoxybenzaldehyde, 1,10-phenanthroline-5,6-dione (0.525 g, 2.5 mmol), ammonium acetate (3.88 g, 50 mmol) and glacial acetic acid was reuxed for 4 h, then cooled to room temperature. Yellow precipitate was obtained when addition of concentrated aqueous ammonia to neutralize, which was collected and washed with water. The crude product dissolved in ethanol was puried by ltration on silica gel. The principal yellow band was obtained. Then evaporation of the solution gave yellow products. Yield 0.57 g, 70%. m.p. 314~322 ℃. ^{1}H NMR ($CDCl_3$, ppm): 3.25 (s, 3H, CH_3-O-Ar), 3.58 (s, 1H, NH), 6.73~7.65 (m, 4H, Ar-H), 7.90-9.10 (m, 6H, aromatic protons in the moiety of phenanthroline, Ar-H). MS (ESI): m/z=327.1 $[M+1]^+$, 349.1 $[M+Na]^+$. $C_{20}H_{14}N_4O$ (326.35): Calcd. (%): C 73.61, H 4.32, N 17.17; Found (%): C 73.49, H 4.26, N 17.25.

$[Mn(mip)(NDC)]_n$ (**1**): A mixture of mip (0.100 g, 0.3 mmol), $Mn(SO_4)_2\cdot H_2O$ (0.051 g, 0.3 mmol), NDC (0.130 g, 0.6 mmol)in distilled H_2O (18 mL) was stirred at room temperature and adjusted the pH value to about 7.0 with NaOH. We put the cloudy solution into a 30-mL Teon-lined stainless vessel at 170 ℃ for 3 d and afterwards cooled to room temperature at a rate of 5 ℃·h^{-1}. The yellow crystals of complex **1** were obtained in 78% yield based on Mn. $C_{32}H_{20}MnN_4O_5$: Calcd.(%): C 64.54, H 3.38, N 9.41; Found (%): C 64.42, H 3.34, N 9.29%. IR (KBr, cm^{-1}): 3199(s), 1 566 (vs), 1 511 (vs), 1479 (s), 1 405 (s), 1 349(vs), 1 101(s), 885(s), 803(s), 701(m), 614(m), 531(m).

1.3 X-ray structure determination

Single-crystal X-ray diffraction data for complex **1** was collected at 292 (2) K with a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 (2) K in the range of 2.04° ≤θ ≤26.05°. Absorption corrections were applied using multi-scan technique and the structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the programs SHELXS-97 [17] and SHELXTL-97 [18]. Non-hydrogen atoms were refined with anisotropic temperature parameters and all hydrogen atoms were refined isotropically. Experimental details for crystallographic data and structure refinement parameters for complex **1** are listed in Table 1. The final cycle of refinement converged to R=0.077 8, and wR=0.150 1 (for all data). All the hydrogen atoms attached to carbon were generated geometrically.

CCDC: 919758.

Table 1 Crystal data and details of structure refinement parameters for 1

Complex	**1**	Absorption coefficient / mm^{-1}	0.586
Empirical formula	$C_{32}H_{20}MnN_4O_5$	F(000)	1 220
Formula weight	595.46	Crystal size / mm	0.43×0.32×0.25
Crystal system	monoclinic	θ range / (°)	2.04~26.05
Space group	$P2_1/n$	Reflections collected	15 638
a / nm	1.245 80(7)	Unique reflections (R_{int})	4 904(0.0441)
b / nm	1.474 50(9)	Goodness-of-fit on F^2	1.039
c / nm	1.365 44(8)	Final R indices ($I>2\sigma(I)$)	R_1=0.057 8
β / (°)	97.644 0(1)		wR_2=0.137 3
Volume / nm^3	2.485 9(3)	R indices (all data)	R_1=0.077 8
Z	4		wR_2=0.150 1
D_c / (g·cm^{-3})	1.591	Largest difference peak and hole / (e·nm^{-3})	1 198, –447

2 Results and discussion

2.1 IR spectra

In complex **1**, the strong characteristic absorption peaks at 1 566 and 1 511 cm^{-1} are attributed to the antisymmetric stretching vibration of the coordinated carboxyl groups, and the peak at 1 349 cm^{-1} corresponds to the symmetric stretching of carboxyl. The separations $\Delta\nu$ ($\nu_{as}(COO^-)$-$\nu_s(COO^-)$) are 217 and 162 cm^{-1}, indicating that the carboxyls groups adopt monodentate and bidentate coordination modes to coordinate Mn (Ⅱ) atoms. The results of IR spectra could be confirmed by the X-ray single-crystal diffraction.

2.2 Description of the structure

The asymmetric unit and coordination environment of Mn(Ⅱ) in complex **1** is shown in Fig.1, and the simplified 2D (4,4) layer structure of complex **1** is suggested in Fig.2. Selected bond lengths and bond angles are given in Table 2. Hydrogen bond lengths and angles for the complex **1** are shown in Table 3.

Table 2　Selected bond lengths (nm) and bond angles (°) for 1

Mn(1)-O(1)	0.2219(3)	Mn(1)-N(1)	0.2291(3)	Mn(1)-O(4)	0.2133(2)
Mn(1)-O(3)	0.2229(2)	Mn(1)-O(2)	0.2214(2)	Mn(1)-N(2)	0.2237(3)
O(2)-Mn(1)-O(1)	58.96(9)	O(4)-Mn(1)-N(1)	94.63(9)	O(1)-Mn(1)-O(3)	103.51(1)
O(4)-Mn(1)-O(2)	145.89(9)	O(1)-Mn(1)-N(1)	92.41(10)	O(2)-Mn(1)-N(2)	93.21(10)
O(2)-Mn(1)-O(3)	86.77(9)	N(2)-Mn(1)-N(1)	72.47(10)	O(3)-Mn(1)-N(2)	92.48(9)
O(4)-Mn(1)-N(2)	120.70(9)	O(4)-Mn(1)-O(1)	89.75(9)	O(2)-Mn(1)-N(1)	99.55(10)
O(1)-Mn(1)-N(2)	146.28(1)	O(4)-Mn(1)-O(3)	88.05(8)	O(3)-Mn(1)-N(1)	163.88(10)

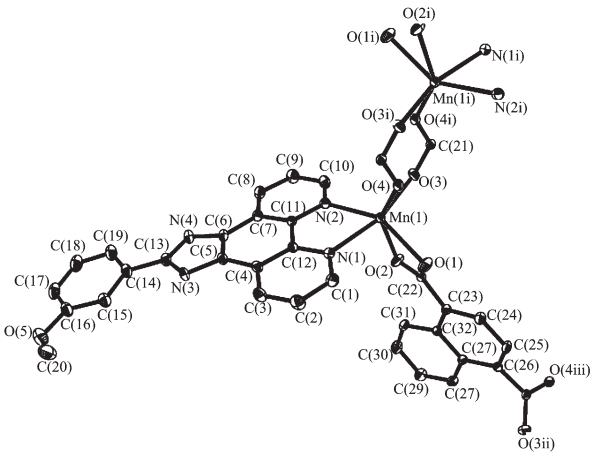
Table 3　Hydrogen bond lengthsand anglesfor the complex 1

D-H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA /(°)
N3-H3B···O3^{i}	0.086 0	0.226 0	0.298 8	143
C28-H28A···O4^{ii}	0.093 0	0.260 0	0.349 7	163

Symmetry transformations used to generate equivalent atoms: i: 0.5+*x*, 0.5−*y*, 0.5+*z*; ii: −0.5−*x*, 0.5+*y*, 0.5−*z*

As shown in Fig.1, the asymmetric unit of complex **1** consists of one Mn(Ⅱ) atom, one mip ligand, and one NDC ligand. The Mn (Ⅱ) atom is hexa-coordinated with two nitrogen atoms (N(1), N(2)) from one chelating mip ligand and four oxygen atoms (O(1), O(2) atom from one chelating bidentate NDC, O(3), O (4) atom from two distinct bridging monodentate NDC ligand), forming a distorted octahedral geometry. The angle of O(1)-Mn(1)-O(3), O(3)-Mn(1)-N(2), N(2)-Mn(1) -N (1), O (1)-Mn (1)-N (1) is 103.51 (1)°, 92.48 (9)°, 72.47(1)°, 92.41(1)°, and the sum is 360.87°. For the coordination environment of Mn (1), the Mn1, O (1), O(3), N(1), N(2) atoms define the basal plane, and the O(2) and O(4) atoms occupy the apical axial positions. The bond distances of Mn-O in complex **1** are from 0.213 3(2) to 0.222 9(2) nm, and those of Mn-N bond distances fall in the 0.2237(3) to 0.229 1(3) nm range, which are similar with the values reported[19-22].

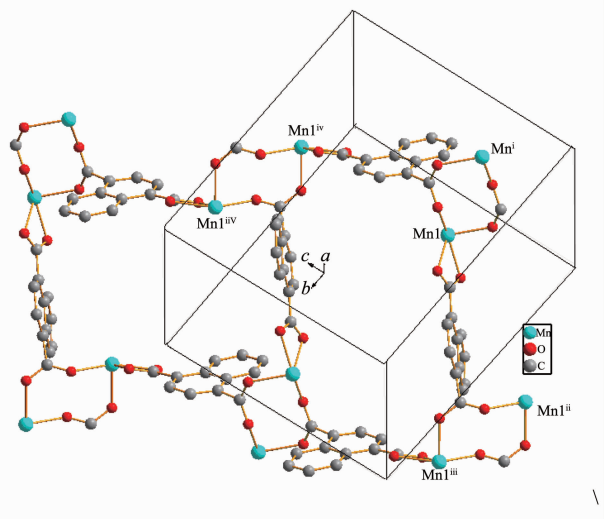
The NDC ligands take bis-chelating and monodentate bridging coordination modes to link three metal Mn(Ⅱ) atoms, and this lead to the formation of 2D (4,4) layer network. There are two types of rings in the 2D network: (1) 8-membered ring which contains which contains Mn(1)-O(3)-C(21)-O(4A)-Mn(1A)-O(3A) -C(21A)-O(4) atoms (A: 0.5−*x*, −0.5+*y*, 1.5−*z*), and the angle of O(4)-C21-O (3) is 124.778°. Two Mn atoms



Hydrogen atoms were omitted, displacement ellipsoids are drawn at the 30% probability level; Symmetry transformations used to generate equivalent atoms: i: $-x$, $-y$, $1-z$; ii: $-0.5-x$, $0.5+y$, $0.5-z$; iii: $-0.5+x$, $0.5-y$, $-0.5+z$

Fig.1 the asymmetric unit and coordination environment of Mn(Ⅱ) in complex **1**

are bridged by two carboxylate groups to give a binuclear molecular building block with shorter separation of Mn ⋯ Mn is 0.504 9 nm; (2) 36-membered ring which contains four Mn atoms with the diagonal distances are 1.022 47 and 1.730 44 nm. In order to get better insight into the framework, we omit the mip ligands to obtain the simplified 2D (4,4) network if considering these dimeric motifs as single



The mip ligand and hydrogen atoms were omitted for clarity; Symmetry transformations used to generate equivalent atoms: i: $-x$, $-y$, $1-z$; ii: $-0.5+x$, $0.5-y$, $-0.5+z$; iii: $-0.5-x$, $0.5+y$, $0.5-z$; iv: $0.5+x$, $0.5-y$, $0.5+z$; iiv: $0.5-x$, $0.5+y$, $1.5-z$.

Fig.2 Simplified 2D (4,4) layer structure of complex **1**

nodes (Fig.2). Moreover, there are π-π interactions between the aryl ring of mip ligands and the aryl ring of the NDC ligands with distances between Cg (1)→Cg(2) ring centroid is 0.3697 nm. Cg(1): C27→C28→C29→C30→C31→C32, Cg(2): C7→C8→C9→C10→C11 →N2. There are two types of H-bond intersections: C-H⋯O(H(28A)⋯O(4) 0.260 nm, C(28)⋯O(4) 0.349 7 nm and C(28)-H(28A)⋯O(4) 163°) and N-H⋯O(H(3B)⋯O(3) 0.226 nm, N(3)⋯O(3) 0.2988 nm and N(3)-H(3B)⋯O(3) 143°) interactions. The existence of hydrogen bond and π-π interactions reinforce the structural stability of complex **1**.

2.3 UV-Vis absorption spectra

The UV-Vis absorption spectra of mip ligand and complex **1** are determined in the solid state at room temperature (Fig.3). The result suggests that complex **1** exhibits absorption bands at 405 nm. The ligand MIP shows two absorption bands at 233 and 275 nm. The absorption band of complex **1** is red-shifted by 130~172 nm relative to that of free ligand MIP. After coordination, the formation of more large conjugated system may be the reason for the strong red-shift. The above analyses for UV-Vis spectral are in agreement with the determined crystal structure of complex **1**.

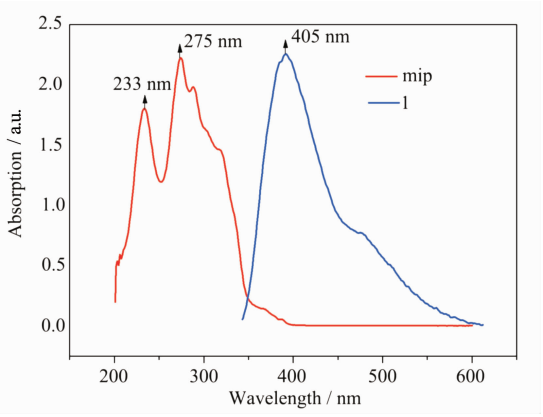


Fig.3 UV-Vis spectra of the ligand and complex **1** at room temperature

2.4 Thermal analysis

To further fully characterize the complex **1**, we examined its thermal stability using thermal gravimetric analysis (TG-DTA). TG curve has been obtained from crystalline samples of the complex in the flowing nitrogen atmosphere with a heating rate of

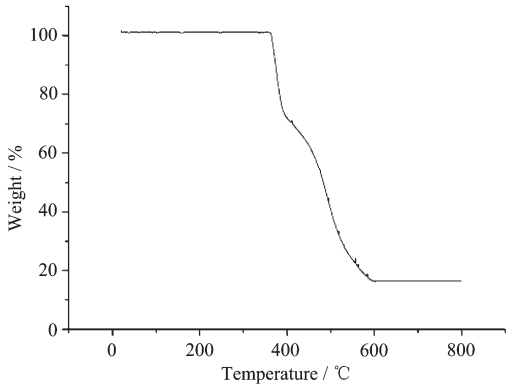


Fig.4　TGA curves of complex **1**

10 ℃·min^{-1} (Fig.4), as expected, complex **1** exhibits two steps of weight losses: the first weight loss corresponding to the removal of NDC ligand is 31.05% (Calcd. 33.25%) from 361 to 408 ℃, and the second weight loss corresponding to the removal of mip ligand is 54.61% (Calcd. 54.80%) from 408 to 604 ℃.The final formation of the complex is metal oxide MnO (Calcd. 11.91%). The thermal analysis result suggests the two-dimensional sheet structure of anhydrous complex **1** is stabile before 361 ℃.

2.5　Photoluminescent properties

Luminescent complexes are currently of great interest because of their various applications in photochemistry and photophysics. So in this study, we research the luminescence of the free ligands, as well as the complex **1** (Fig.5). The free ligand mip exhibits one emission band at 539 nm upon excitation at 325 nm, and the free ligand exhibit emissions at 490 nm for NDC (excitation at 380 nm). Complex **1** shows one strong emission band at 582 nm (excitation at 325 nm), which is red-shifted by 43 nm relative to that of free ligand mip. The red-shift suggests that the Mn(II) ions coordinate to ligand mip, which evokes ligand-to-metal charge transfer (LMCT) [23]. The results of luminescence suggest the emission bands of the complexes are the result of poly-carboxylate and N-heterocyclic ligands interact on each other. Our complex exhibits strong emissions, which may be attributed to the rigidity of complexes. The rigidity is favor of energy transfer and reduces the loss of energy through a radiationless pathway. However, the effect of the microenvironment between ligands and complex on the luminescence properties still needs further investigations. Complex **1** may be good candidate for potential photoluminescence materials, because it is highly thermally stable and insoluble in water and common organic solvents.

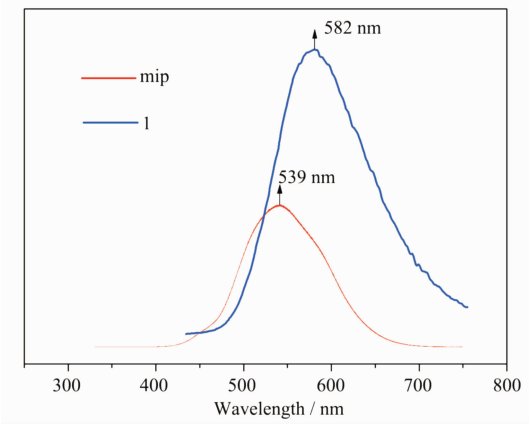


Fig.5　Luminescent spectrum of ligand mip and complex **1** in solid state at room temperature

3　Conclusions

In complex **1**, The NDC ligands function in bridging bidentate-chelating bidentate coordination modes, and this lead to the formation of a 2D sheet network in the title complex. This material will give new impetus to the construction of novel functional material with potentially useful physical properties.

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