研究简报

一个二维梯状化合物[Ni($\mu_{1,5}$-dca)$_2$(en)]$_n$ 的合成，结构和磁性

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Synthesis, Structure and Magnetic Property of a Two-dimensional Stair-like Framework: [Ni($\mu_{1,5}$-dca)$_2$(en)]$_n$

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A new nickel(II)-dicyanamide compound, [Ni(dca)$_2$(en)]$_n$ (**1**) (dca=dicyanamide anion, [N(CN)$_2$]$^-$; en=ethylene diamine), has been synthesized and its structure has been determined by single crystal X-ray diffraction analysis. The crystal is monoclinic, space group $P2_1/n$ with unit cell dimensions: a=0.694 3(1) nm, b=1.041 5(2) nm, c=1.413 2(2) nm, and β=90.381°, Z=4, V=1.011 0(3) nm^3. In this compound, the adjacent nickel atoms are connected by dca all in $\mu_{1,5}$-bridging mode to form ladder-like units, which are linked with double dca bridges to generate a regular infinite stair-like structure. Temperature-dependent magnetic susceptibility was also characterized for this compound. CCDC: 208276.

Keywords:　　**nickel compound**　　　**coordination polymer**　　　**stair-like structure**　　　**magnetism**

0　Introduction

The dicyanamide anion, [N(CN)$_2$]$^-$, has gained much interest in recent years. A great deal of attention has focused on the structural and magnetic properties of dca-bridged polymers[1~3]. This anion shows the versatility of coordinating to metal ions in various modes. For instance, Zn(dca)$_2$ is a layer compound with μ_2-bridging dca[4], whereas Mn(dca)$_2$ adopts a 3-D rutile-type structure containing μ_3-dca bridges[5,6]. The potential of dca for the preparation of extended frameworks is illustrated by the great deal of recent attention on coordination polymers containing this ligand[7].

Previously we introduced en (ethylene diamine) in the dca-containing metal complex, and obtained a novel 1D five-coordinated copper(II) coordination polymer with both $\mu_{1,5}$-dca and pseudo-$\mu_{1,3}$-dca bridges[8]. A further step in our synthetic strategy consists of increasing the coordination number of the central metal so as to obtain multidimensional network. With this aim, we selected nickel(II) ion instead of copper(II). As a result, a new 2D nickel(II) compound with the formula [Ni($\mu_{1,5}$-dca)$_2$(en)]$_n$ (**1**) has now been synthesized and performed single crystal X-ray structure analysis. The dicyanamide anion in **1** bridges the metal atoms in $\mu_{1,5}$-

bridging mode in two different directions. A ladder-like moiety can be proposed as a structural unit whose repetition leads to a 2D stair for this compound.

1　Experimental

1.1　Materials and Physical Measurements

All commercially available chemicals were of reagent grade and were used without further purification. Elemental analyses were determined on an Elemental Vario ELIII elemental analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT IR spectrometer in the range of $200 \sim 4\,000$ cm^{-1}. Variable-temperature ($2.2 \sim 273.0$ K) magnetic susceptibility measurements were carried out on a MPMS/C magnetometer in a magnetic field of 1 T. And the diamagnetic corrections were evaluated by using Pascal's constants.

1.2　Synthesis of the Title Compound

To a methanol solution (25 mL) of $NiCl_2 \cdot 6H_2O$ (118 mg, 0.50 mmol), ethylene diamine (0.03 mL) was added. After stirring the mixture for about 20 min, sodium dicyanamide (0.090 g, 1 mmol) was added. The above mixture was stirred and heated for about 30 min, then filtered when it was still hot. The light-blue solution was allowed to stand in air at room temperature until deep blue diamond-shaped single crystals of $[Ni(dca)_2(en)]_n$ were obtained. Yield 58%. Found (%): C, 28.71; H, 2.90; N, 43.82. Anal. Calc. for $C_6H_8N_8Ni$ (%): C, 28.72; H, 3.19; N, 44.67.

1.2.1　X-ray Crystallography

A single crystal with approximate dimensions 0.18 mm × 0.16 mm × 0.06 mm for **1** was coated with epoxy glue and mounted on a glass fiber in a random orientation for data collections. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ=0.071 073 nm) at room temperature in the ω-2θ scan mode. An empirical absorption correction was applied to the data using the SADABS program[9]. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated in idealized positions. All calculations were performed using the SHELXTL program[10]. Crystal data and structure refinement parameters for **1** are listed in Table 1. Selected bond lengths and angles are presented in Table 2.

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2　Results and discussion

A labeled ORTEP plot for the structure section of the compound $[Ni(dca)_2(en)]_n$ is shown in Fig.1. The coordination geometry of Ni(II) ion can be regarded as distorted octahedral coordinated by six nitrogen atoms, among which four come from dca ligands and two from a bidentate coordination en ligand. Since each Ni(II) atom links to four $[N(CN)_2]^-$ and each of four $[N(CN)_2]^-$ furthers $\mu_{1,5}$-bridges to other Ni centers, the combination of metal atoms and dca ligands gives rise to two Ni(II) array parallelograms with dimensions 0.823 3 nm × 0.832 6 nm and cornerwise distance in range 1.001 3~

Table 1　Crystal Data and Structure Refinement Parameters for 1

empirical formula	$C_6H_8N_8Ni$
formula weight	250.91
temperature / K	293(2)
wavelength / nm	0.071 073
crystal system	monocline
space group	$P2_1/n$
a / nm	0.694 3(1)
b / nm	1.041 5(2)
c / nm	1.413 2(2)
α / (°)	90
β / (°)	98.381(3)
γ / (°)	90
volume / nm³	1.011 0(3)
Z	4
calculated density / (Mg·m⁻³)	1.648
absorption coefficient / mm⁻¹	1.899
$F(000)$	512
crystal size / mm	0.18 × 0.16 × 0.06
θ range for data collection / (°)	2.44 to 22.50
limiting indices	$-7 \leqslant h \leqslant 3$,
	$-11 \leqslant k \leqslant 6$,
	$-15 \leqslant l \leqslant 14$
reflections collected / unique	2 334 / 1 317 [R(int)=0.049 3]
completeness to θ=22.50°	99.5%
refinement method	full-matrix least-squares on F^2
data / restraints / parameters	1 317 / 0 / 136
goodness-of-fit on F^2	1.148
final R indices [$I>2\sigma(I)$]	R_1=0.066 1, wR_2=0.124 1
R indices (all data)	R_1=0.114 3, wR_2=0.152 9
largest diff. peak and hole / (e·nm⁻³)	459 and −409

Table 2　Bond Lengths (nm) and Angles (°) for Title Compound

a. selected bond length

bond length	
Ni-N(3)#1	0.203 8(9)
Ni-N(7)	0.207 4(7)
Ni-N(4)	0.207 4(9)
Ni-N(6)#2	0.208 3(8)
Ni-N(8)	0.210 0(8)
Ni-N(1)	0.212 1(1)

#1: $-x-1/2$, $y+1/2$, $-z+3/2$; #2: $x+1/2$, $-y+1/2$, $z-1/2$

b. selected angles

bond angles	
N(8)-Ni-N(1)	174.5(4)
N(4)-Ni-N(6)#2	175.4(3)
N(3)#1-Ni-N(7)	176.0(3)
C(1)-N(1)-Ni	154.2(9)
C(3)-N(4)-Ni	166.6(8)
C(5)-N(7)-Ni	109.2(6)
C(6)-N(8)-Ni	108.0(7)
N(1)-C(1)-N(2)	171.9(1)
N(6)-C(4)-N(5)	174.4(1)
N(4)-C(3)-N(5)	173.9(2)
C(1)-N(2)-C(2)	120.1(9)
C(4)-N(5)-C(3)	125.9(0)
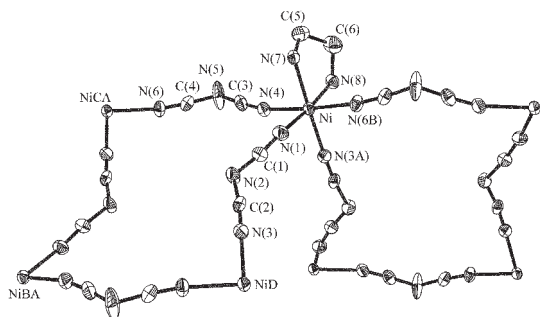
Fig.1　Local coordination around metal ion in **1**

Fig.2　(a) A side-on view of the stair-like sheet of **1** ignored en

(b) Scheme of the stair-like sheet of **1** ignored en

1.217 9 nm. Approximate C_{2v} symmetry is also observed for the dca ligand with typical bond lengths of C(1)-N(1), C(2)-N(3), C(3)-N(4) and C(4)-N(6) being 0.117 0(2) nm, 0.115 4(2) nm, 0.116 3(2) nm and 0.113 7(2) nm, respectively[11~13].

Ignored en unit, the crystal structure consists of an extended 2D layer network shown in Fig.2(a). One of above-mentioned Ni(Ⅱ) array parallelograms is described as the step of the ladder structure. The step extends by double dca bridges along *ob* direction to 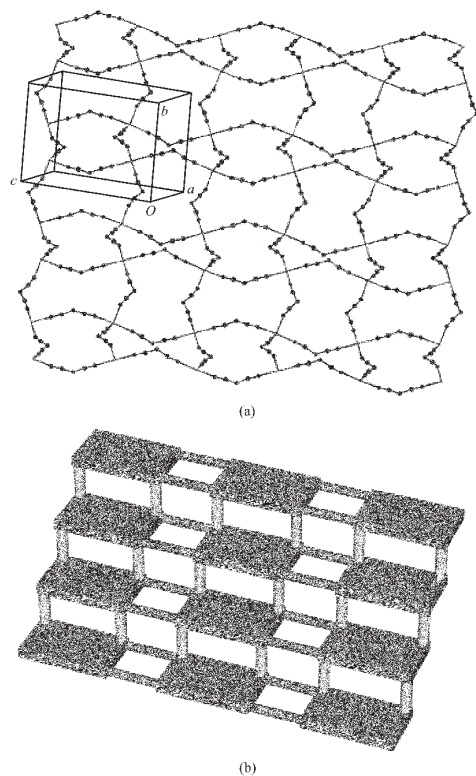form the ladder unit. And these units are connected also through double single-dca-bridges along ac direction, which lead to a regular infinite stair-like molecular structure as the scheme Fig.2(b) shows us. In a word, one of the Ni(Ⅱ) array parallelograms functions as the step of the ladder, and the other as the connectivity of steps. It seems like ladders and stair in this compound.

At room temperature, the solid state infrared spectrum of this compound was performed. The strong and sharp absorptions at 2 306 cm^{-1}, 2 256 cm^{-1}, 2 189 cm^{-1} are corresponding to $\nu_{sym} + \nu_{asym}(C \equiv N)$, $\nu_{sym}(C \equiv N)$ and $\nu_{asym}(C \equiv N)$ of the dca ligand, which are comparable to those of related compounds[14~17]. In addition, the above bands differ from those of Na(dca)$_2$, observed at 2 286, 2 232 and 2 179 cm^{-1} [16]. The shift towards higher frequencies of these peaks reflects the bridging coordination mode of dca in **1**. The bands at 3 350 and 2 939 cm^{-1} are assigned to the N-H and C-H stretching vibrations, respectively. And bands at 1 352 cm^{-1} are assigned to the in plane bending vibration of the N-H bonds of **1**.

The temperature-dependence of χ_m and $\chi_m T$ are depicted in Fig.3. At 273.0 K, the measured magnetic moment μ_{eff} for **1** is 3.159 μB, which is slightly larger than the spin-only value for an uncoupled Ni(II) ion (g=2.0, 2.830 μB). On cooling the temperature, the $\chi_m T$ decreases smoothly from 273.0 to 56.8 K, and then increases gradually to 1.298 $cm^3 \cdot mol^{-1} \cdot K$ at 3.7 K before abruptly reaching the minimum value of 1.199 $cm^3 \cdot mol^{-1} \cdot K$ at 2.2 K.
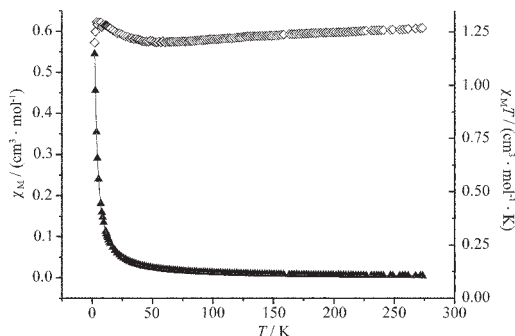

Fig.3　Plots of χ_m vs T (▲) and $\chi_m T$ vs T (◇) for compound **1**, respectively

　　　The solid line shows the best fits to the model.

The data can be fitted by an expression for S=1 systems with dominant zero field splitting effects, D. But taking into account of the molecular field approximation, zJ is added to the Zeeman term, as is shown is expression (**1~4**).

$$\chi_z = \frac{2Ng^2\beta^2}{kT}\frac{\exp(-D/kT)}{1+2\exp(-D/kT)} \tag{1}$$

$$\chi_x = \frac{2Ng^2\beta^2}{D}\frac{1-\exp(-D/kT)}{1+2\exp(-D/kT)} \tag{2}$$

$$\chi' = \frac{\chi_z + 2\chi_x}{3} \tag{3}$$

$$\chi = \frac{\chi'}{1-(\frac{2zJ}{Ng^2\beta^2})\chi'} \tag{4}$$

The best parameters were g=2.192, D=4.095 cm^{-1}, J=0.038 cm^{-1}, and R=5.50 × 10^{-8}, where $R = \sum_{i=1}^{m}(\chi_i^{calc} - \chi_i^{exp})^2 / \sum_{i=1}^{m}(\chi_i^{exp})^2$ respectively. The small positive J shows very weak ferromagnetic coupling between the Ni(II) ions. According to the structural data, only $\mu_{1,5}$-dca bridge can act as the effective super-coupling exchange media. It confirms that the dca ligand is a very poor magnetic exchange mediator between metal ions[7,18]. The positive J also confirms the hypothesis E. Colatcio et al. postulated recently[18].

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