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Synthesis, Crystal Structure, and Magnetic Property of a Cyano Involved Ion-Pair Complex Based on Macrocyclic Metallic Tecton and $[Ni(CN)_4]^{2-}$ [1]

G. X. Zhou, Y. H. Wang*, and H. Xia**

Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan, 430074 P.R. China
e-mail: 909098173@qq.com; caihua223@gmail.com***

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Abstract—A cyano-bridged nickel(II) complex $[NiL]_2\{[NiL][Ni(CN)_4]_2\}_2 \cdot H_2O$ (III) (L = 1,3,10,12,15,18-hexaazatetracyclo[16,2,1,$1^{12.15}$,$0^{4.9}$]docosane), based on macrocyclic metallic tecton and diamagnetic $[Ni(CN)_4]^{2-}$ has been synthesized and characterized by physico-chemical methods, as well as single crystal X-ray determination (CIF file CCDC no. 1038635). The crystal belongs to orthorhombic, space group: $P2_12_12_1$, with $a = 15.410(3)$, $b = 15.752(3)$, $c = 19.134(4)$ Å, $Mr = 2137.74$ g mol^{-1}, $Z = 2$, $V = 4644.6(16)$ $Å^3$ (CIF file CCDC no. 1038635). Single X-ray diffraction analysis reveals that complex **I** shows a ion-pair type structure which consists of two fragments $[NiL]^{2+}$ and $\{[NiL][Ni(CN)_4]_2\}^{2-}$. In this complex, each $\{[NiL][Ni(CN)_4]_2\}^{2-}$ binds two $[NiL]^{2+}$, resulting a hydrogen-bonded 1D chain. In additional, the magnetic properties were studied.

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INTRODUCTION

In recent years, the design and synthesis of cyano-bridged complexes become an interesting area because of their rich and interesting structure, magnetic properties and strong tendency to construct sophisticated coordination bonding networks [1–4]. The most popular approach to the synthesis of cyano-bridged magnetic materials is the use of an anionic building-block $[M(CN)_x]^{n-}$ in conjunction with cationic units of the type $[M'(Ligand)_y]^{m+}$ [5], forming heterometallic hybrid cyano-bridged complexes $[M'(Ligand)_y]_n[M(CN)_x]_m$. Anionic building block $[M(CN)_x]^{n-}$ can be diamagnetic parts, such as $[Ag(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Au(CN)_4]^-$, $[Fe(CN)_6]^{4-}$ or paramagnetic parts, such as $[Fe(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Mo(CN)_8]^{4-}$, etc. Recent years, our group are especially interested in the diamagnetic $[Ni(CN)_4]^{2-}$ [6–8]. The tetracyano-nickel anion $[Ni(CN)_4]^{2-}$ possesses the ability to link various central atoms to form molecules with 1D, 2D and 3D structures by using two or for –CN gropus [9–12].

Macrocyclic complexes containing transition metal ions, which can be used as building blocks to construct polymers with bridging ligands. The resulting polymers show intriguing network topologies and potential applications in magnetism, luminescence, catalysis, etc. [13–15]. To date, most of these complexes contain tetraaza-macrocyclic ligands, whereas the studies of macrocyclic complexes containing six nitrogen atoms are relatively rare. Therefore, the combination of $[Ni(CN)_4]^{2-}$ and macrocyclic complex will produce some interesting structure to study. It is should noted that, very recently, we utilized the $[Ni(CN)_4]^{2-}$ to react with macrocyclic complex to generate a unprecedented porous structure [8]. Along with this line, we modified the macrocyclic complex precursor by adding a cyclohexane side group on macrocyclic ligand, interestingly, resulting an entire different structure. In this paper, we reported the synthesis and structures a cyano involved ion-pair complex $[NiL]_2\{[NiL][Ni(CN)_4]_2\}_2 \cdot H_2O$ (**I**) (L = 1,3,10,12, 15,18-hexaazatetracyclo[16,2,1,$1^{12.15}$,$0^{4.9}$]docosane), based on macrocyclic metallic tecton and $[Ni(CN)_4]^{2-}$. In additional, the magnetic properties were studied.

EXPERIMENTAL

Materials and methods. All reagents were purchased commercially and used without further purification. The precursor complex $[NiL](ClO_4)_2$ was prepared as described [16]. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Vario ELIII CHNS/O elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet Avatar 370 Fourier Transform Infrared spectrometer. X-ray powder diffraction (**XRPD**) patterns were recorded on a Shimadzu D/MAX-3BX diffractometer with CuK_α radiation.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should

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[1] The article is published in the original.

Table 1. Crystallographic data and structural refinement details of complex **I**

Parameter	Value
M	2137.74
Crystal size, mm	0.22 × 0.35 × 0.41
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, Å	15.410(3)
b, Å	15.752(3)
c, Å	19.134(4)
V, Å^3	4644.6(16)
Z	2
ρ_{calcd}, g cm^{-3}	1.527
$\mu(MoK_\alpha)$, mm^{-1}	1.653
$F(000)$	2240
Limiting indices	$-22 \le h \le 22$, $-19 \le k \le 22$, $-28 \le l \le 28$
Reflections measured	46773
Reflections unique, R_{int}	15243 (0.048)
Reflections with $I > 2\sigma$, I	13858
Reflections refined	603
GOOF (F^2)*	0.99
$R(F)/wR(F^2)$* ($I > 2\sigma(I)$)	0.0615/0.1157
$R(F)/wR(F^2)$* (all data)	0.0546/0.1106
$\Delta\rho_{max}/\Delta\rho_{min}$), e Å^{-3}	0.71 and –0.68
Flack	0.026(16)

* GOOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obc} - n_{param})]^{1/2}$; $R_1 = |F_o| - |F_c|/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

be handled with care and prepared only in small quantities.

Synthesis of complex I. A solution of $K_2[Ni(CN)_4]$ (0.3 mmol, 72 mg) in 10 mL water was added to a solution of $[NiL](ClO_4)_2$ (0.3 mmol, 166 mg) in 10 mL DMF with stirring. Filtration and slow evaporation of the resulting solution gave orange crystals after four weeks. The yield was 40% based on $K_2[Ni(CN)_4]$.

IR (KBr; ν, cm^{-1}): 2127 m, 2117 s (for –CN group).

For $C_{80}H_{130}N_{40}Ni_8O$

anal. calcd., %:	C, 44.95;	H, 6.13;	N, 26.21.
Found, %:	C, 45.32;	H, 6.09;	N, 26.41.

X-ray structure determination. Single crystal X-ray diffraction data for complex was collected on a Bruker Apex CCD diffractmeter with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 293(2) K. Data reductions and absorption corrections were performed using the SAINT and SADABS programs respectively [17]. The structures were solved by direct methods using SHELXS-97 program [18] and refined with full-matrix least squares on F^2 using SHELXL-97 program [19]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The details of crystallographic data for these four structures are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Supplementary material for structure I has been deposited in the Cambridge Crystallographic Data Centre (CCDC no. 1038635; deposit@ccdc.cam.ac.uk or http://www.ccde.cam.ac.uk).

RESULTS AND DISCUSSION

The crystal structure of complex I is entire different from similar complexes based on macrocyclic complexes and $[Ni(CN)_4]^{2-}$. Complex I shows a ion-pairs structure which contains one $[NiL]^{2+}$ cation and one $\{[NiL][Ni(CN)_4]_2\}^{2-}$ anion (Fig. 1a). In $\{[NiL][Ni(CN)_4]_2\}^{2-}$ fragment, the center nickel atom is coordinated by four nitrogen atoms from macrocyclic ligand and two nitrogen atoms from two axial $[Ni(CN)_4]^{2-}$ anions with an octahedral geometry. Both bond lengths and bond angles are located in normal range. Essentially, the $\{[NiL][Ni(CN)_4]_2\}^{2-}$ links to discrete $[NiL]^{2+}$ by electrostatic attraction (distance Ni(3)–N(2) 3.033 Å). Every $\{[NiL][Ni(CN)_4]_2\}^{2-}$ binds two $[NiL]^{2+}$ segments, resulting a 1D hydrogen-bonded chain (Fig. 1b). Furthermore, those chains are connected by hydrogen-bonds to a wave-like 3D supramoleculer network (Fig. 1c).

It is should noted that, very recently, we utilized the $[Ni(CN)_4]^{2-}$ to react with macrocyclic complex to generate a unprecedented porous structure (Fig. 2). Along this line, we modified the macrocyclic complex precursor by adding a cyclohexane side group on macrocyclic ligand, however, resulting an entire different structure. The comparison clearly indicates the steric hindrance of cyclohexane lead to the different framework.

Table 2. Selected bond lengths and angles for complex **I**

Bond	*d*, Å	Bond	*d*, Å
N(4)–Ni(1)	2.142(4)	C(8)–Ni(2)	1.860(4)
N(5)–Ni(1)	2.163(4)	C(1)–Ni(4)	1.866(5)
N(9)–Ni(1)	2.060(3)	C(2)–Ni(4)	1.863(4)
N(10)–Ni(1)	2.070(3)	C(3)–Ni(4)	1.872(5)
N(12)–Ni(1)	2.100(3)	C(4)–Ni(4)	1.867(4)
N(20)–Ni(1)	2.093(3)	N(15)–Ni(3)	1.942(4)
C(5)–Ni(2)	1.874(4)	N(17)–Ni(3)	1.943(3)
C(6)–Ni(2)	1.867(5)	N(14)–Ni(3)	1.944(3)
C(7)–Ni(2)	1.869(5)	N(18)–Ni(3)	1.950(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(4)Ni(1)N(5)	170.25(18)	C(5)Ni(2)C(7)	175.2(2)
N(4)Ni(1)N(9)	84.28(15)	C(5)Ni(2)C(8)	93.57(19)
N(4)Ni(1)N(10)	88.87(15)	C(6)Ni(2)C(7)	90.7(2)
N(4)Ni(1)N(12)	94.86(14)	C(6)Ni(2)C(8)	177.1(2)
N(4)Ni(1)N(20)	91.37(15)	C(7)Ni(2)C(8)	87.5(2)
N(5)Ni(1)N(9)	89.06(16)	C(1)Ni(4)C(2)	87.4(2)
N(5)Ni(1)N(10)	83.56(16)	C(1)Ni(4)C(3)	91.5(2)
N(5)Ni(1)N(12)	92.73(16)	C(1)Ni(4)C(4)	175.7(2)
N(5)Ni(1)N(20)	95.27(16)	C(2)Ni(4)C(3)	175.7(2)
N(9)Ni(1)N(10)	86.09(12)	C(2)Ni(4)C(4)	93.63(19)
N(9)Ni(1)N(12)	94.25(12)	C(3)Ni(4)C(4)	87.8(2)
N(9)Ni(1)N(20)	175.65(14)	N(17)Ni(3)N(18)	86.96(13)
N(10)Ni(1)N(12)	176.28(14)	N(14)Ni(3)N(18)	92.16(13)
N(10)Ni(1)N(20)	93.95(12)	N(14)Ni(3)N(15)	87.76(15)
N(12)Ni(1)N(20)	85.99(12)	N(14)Ni(3)N(17)	174.02(16)
C(5)Ni(2)C(6)	88.5(2)	N(15)Ni(3)N(17)	93.49(15)

The IR spectra show features attributable to the CN triple bond stretching vibrations of the complexes. The presence of split signals in the range of 2120–2150 cm^{-1} indicates the different form of CN on $[Ni(CN)_4]^{2-}$. High frequency attributes the bridging mode and low frequency correspond the vacant mode, which are consistent of crystal structure analyses. X-ray powder diffraction patterns of the complex were recorded to confirm purity of the as-synthesized bulk materials. The experimental XRD patterns match with the calculated lines from the crystal structures, confirming the purity of the sample.

The variable-temperature magnetic susceptibility of complex I were investigated at $H = 0.2$ T and $T = 2.0$–300 K. As shown in Fig. 3, the $\chi_m T$ value is 2.05 emu K mol^{-1} at 300 K, which is close to the value for two spin-only Ni^{2+} ion with $S = 1$. Magnetic of complex I also obeys the Curie-Weiss law $\chi_m = C/(T - \theta)$ with $C = 2.04$ emu K mol^{-1} . The Weiss temperature $\theta = 0.245$ K shows it exists weak ferromagnetic inter-

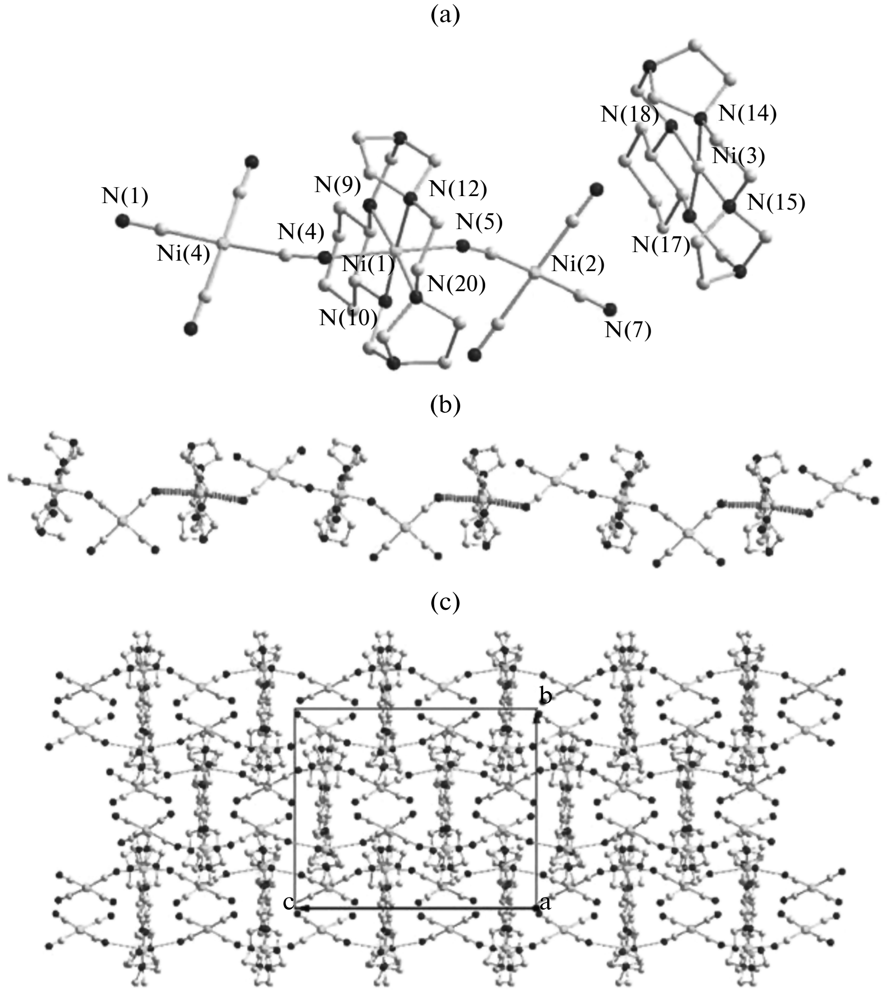

Fig. 1. Diagram of molecular (a), water molecule is omitted for clarity; hydrogen-bonded 1D chain (b); wave-like 3D supramoleculer network (c).

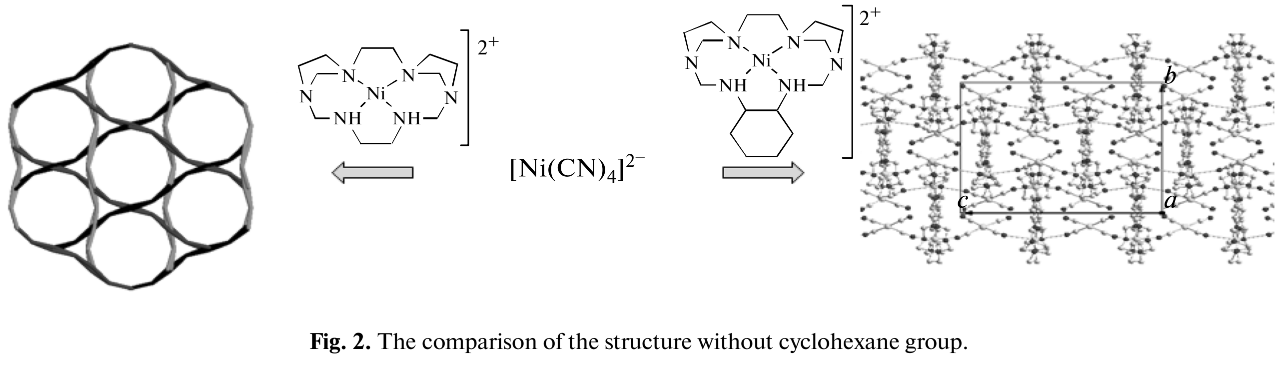

Fig. 2. The comparison of the structure without cyclohexane group.

actions. As the temperature decrease, the $\chi_m T$ value is keep constant until 10 K, then, below the 10 K, the $\chi_m T$ value is sharply fall to a minimum value of 1.29 emu K mol^{-1} at 2 K. Such behaviors may result from the competition of zero-field splitting of Ni^{2+} ions and ferromagnetic intermoleculer interaction. The magnetic data can be fitted according to an $S = 1$ spin state for Ni(II) with a zero-field splitting effect and an intermoleculer interaction by Equation (1) [20]. The best fits were obtained with $D = 5.15$ cm^{-1}, $zJ' = 0.16$ and $g = 2.02$. The value of D is comparable to that observed for similar mononuclear complexes.

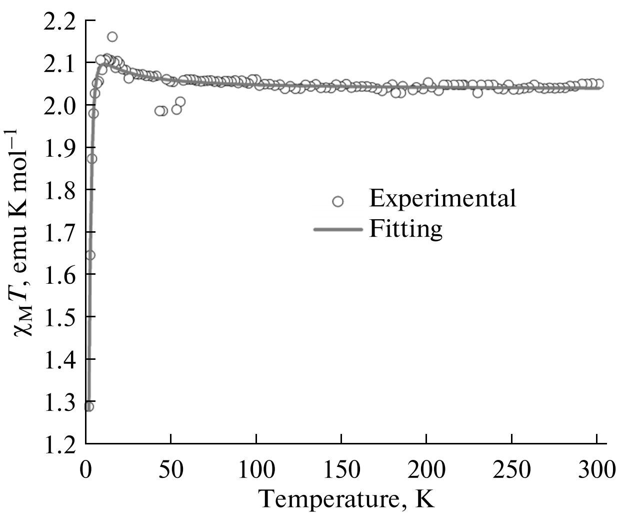

Fig. 3. Temperature dependence of $\chi_m T$ for complex **I**, the solid line represents the theoretical values and the dotted line the fitting.

Positive zJ' confirmed the weak ferromagnetic intermolecular interaction.

$$\begin{aligned}\chi_{\text{chain}} &= 2Ng^2\beta^2(2KT/D)/3KT(2KT/D)\\ &\quad\times\{[1-\exp(-D/KT)]\\ &\quad+\exp(-D/KT)\}/[1+2\exp(-D/KT)],\\ \chi_{\text{m}} &= \chi_{\text{chain}}/[1-\chi_{\text{chain}}(zJ'/Ng^2\beta^2)].\end{aligned} \tag{1}$$

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