

带有水簇(H₂O)₄的四氰合镍配合物的合成与磁性研究

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摘要: 一个四氰合镍配合物 $[\text{Ni}(\text{i-Pr}_3\text{TACN})][\text{Ni}(\text{CN})_4]_2 \cdot 2\text{H}_2\text{O}(\mathbf{1})$ 通过 $\text{K}_2[\text{Ni}(\text{CN})_4]$ 和 $[\text{NiPr}_3\text{TACN}]\text{Cl}_2$ 自组装的方法合成, 单晶解析表明其配合物中存在一个由 4 个分子水组成的水簇。4 个水分子在一个平面上, 每个水分子即是氢键的给体也是氢键的受体。磁化率测定表明配合物中 Ni(II) 间为反铁磁作用且 J 值为 -1.09 cm^{-1} 。

关键词: 四氰合镍; 晶体结构; 水簇; 磁性特征

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Synthesis and Magnetic Property of a Novel Tetracyanonickelate(II) Complex with Discrete Water Cluster (H₂O)₄

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Abstract: A tetracyanonickelate-nickel complex $\{[\text{Ni}(\text{i-Pr}_3\text{TACN})][\text{Ni}(\text{CN})_4]\}_2 \cdot 2\text{H}_2\text{O}(\mathbf{1})$ has been synthesized by self-assembly using $\text{K}_2[\text{Ni}(\text{CN})_4]$ and $[\text{NiPr}_3\text{TACN}]\text{Cl}_2$, ($\text{i-Pr}_3\text{TACN} = 1,4,7\text{-Triisopropyl-1,4,7-Triazacyclononane}$). The X-ray character shows there is a discrete tetramer water clusters in $\mathbf{1}$. Within the cluster, the four water molecules are fully coplanar and each water monomer acts as both single hydrogen bond donor and acceptor. The magnetic susceptibility shows an antiferromagnetic interaction between the Ni(II) ions and the J values is -1.09 cm^{-1} . CCDC: 727702.

Key words: tetracyanonickelate; crystal structure; water cluster; magnetic property

Much attention has been paid to assemble cyanide-bridged coordination complexes in recent years in light of their promising properties for an assortment of applications including electronics, magnetism and catalysis^[1-10], in which tetracyanonickelate is also been pay attention. On the one hand, diamagnetic $[\text{Ni}(\text{CN})_4]^{2-}$ is excellence model for magnetic studies which bridge paramagnetic ions, but on the other hand the tetracyanonickelate anion, as a bridging ligand, can be constructed 1D, 2D and 3D

structures^[11-23]. low-dimensional cyanide-bridged complexes based on $[\text{Ni}(\text{CN})_4]^{2-}$ form a new family of molecular magnetic materials. However, the research that using macrocyclic ligand as terminal group to control the structure still remains relatively undeveloped. On the other hand, water clusters can play an important role in the stabilization of supramolecular systems both in solution and in the solid state, and there is clearly a need for a better understanding of how such water aggregations are inuenced by the overall

structure of their surroundings^[24-27]. In the past several decades, considerable attention has been focused on theoretical and experimental studies of small water clusters to understand the structures and characteristics of liquid water and ice^[28-29].

In this study, we report a complex **1** in which [Ni(CN)₄]²⁻ as bridging ligand to construct a low-dimensional complex. Complex **1** can be synthesized by the reaction of [Ni(*i*-Pr₃TACN)]Cl₂ with K₂ [Ni(CN)₄], which is a cyanide bridged [2+2] type of molecular square.

1 Experimental

1.1 Materials and measurements

The ligand **1**, 4, 7-Triisopropyl-1, 4, 7-Triazacyclononane (*i*-Pr₃TACN) was synthesized according to the literature^[30-32].

1.2 Preparation of **1**

A water solution (20 mL) of K₂Ni(CN)₄·2H₂O (0.111 g, 0.4 mmol) was layered with an acetonitrile solution (20 mL) of [Ni(*i*-Pr₃TACN)]Cl₂ (0.150 g, 0.4 mmol). After about 2 weeks, block-shaped blue crystals of **1** formed from the solution. The crystals were collected, washed with water and methanol, and dried

in the air. Yield: 51%. (based on tetracyanonickelate salts) Anal. Calcd. for C₁₉H₃₇N₇Ni₂O₂: C, 44.36; H, 7.27; N, 19.03. Found (%): C, 44.49; H, 7.27; N, 19.12. IR (KBr): 3 456s, 2 974s, 2165 (CN, coordinated) and 2 138 cm⁻¹ (CN, uncoordinated), 1 652s.

1.3 X-ray crystallography

Diffraction data for complex **1** were collected at 293 K, with a Bruker SMART 1000 CCD diffractometer using Mo *K*α radiation (λ=0.071 073 nm) with the ω-2θ scan technique. An empirical absorption correction (SADABS) was applied to raw intensities^[33]. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on *F*² using SHELXL-97^[34-35]. H atoms of the water molecule were located in a difference Fourier map and the O-H distances were normalized to 0.085 nm. All other hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Crystallographic data and refinement details are given in Table 1 and the selected bonds lengths and bonds angles of the complex **1** are listed in Table 2.

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Table 1 Crystal data and structure refinement for **1**

Empirical formula	C ₁₉ H ₃₇ N ₇ Ni ₂ O ₂	Absorption coefficient / mm ⁻¹	1.588
Formula weight	512.98	<i>F</i> (000)	1 088
Temperature / K	113(2)	Crystal size / mm	0.20×0.20×0.20
Wavelength / nm	0.071 07	θ range for data collection	1.73 to 27.87°
Crystal system,	Monoclinic,	Limiting indices	-10≤ <i>h</i> ≤11, -23≤ <i>k</i> ≤23, -19≤ <i>l</i> ≤20
Space group	<i>P</i> 2 ₁ / <i>c</i>	Reflections collected/unique	30 246/5 755 (<i>R</i> _{int} =0.069 5)
Unit cell dimensions	<i>a</i> =0.855 3(2) nm; α=90° <i>b</i> =1.823 3(5) nm; β=95.492(4)° <i>c</i> =1.555 2(4) nm; γ=90°	Max. and min. transmission	0.741 9 and 0.741 9
Volume / nm ³	2.414 3(11)	Data/restraints/parameters	5 755/4/295
<i>Z</i>	4	Goodness of fit on <i>F</i> ²	1.102
<i>D</i> _c / (Mg·m ⁻³)	1.411	Final <i>R</i> indices [<i>I</i> >2θ(<i>I</i>)]	<i>R</i> ₁ =0.052 2, <i>wR</i> ₂ =0.109 1
		<i>R</i> indices (all data)	<i>R</i> ₁ =0.065 6, <i>wR</i> ₂ =0.116 7
		Largest diff. peak and hole / (e·nm ⁻³)	850 and -579

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

Ni(1)-N(4)	0.201 3(3)	Ni(1)-N(2)	0.208 8(3)	Ni(2)-C(17)	0.187 0(3)
Ni(1)-N(7) ⁱ	0.204 4(2)	Ni(2)-C(18)	0.186 2(3)	Ni(1)-N(3)	0.212 6(2)
Ni(1)-N(1)	0.207 1(2)	Ni(2)-C(16)	0.186 8(3)		

Continued Table 2

N(4)-Ni(1)-N(7) ⁱ	87.17(10)	N(4)-Ni(1)-N(3)	93.29(9)	C(16)-Ni(2)-C(17)	89.72(13)
N(4)-Ni(1)-N(1)	111.54(11)	N(7)i-Ni(1)-N(3)	178.95(10)	C(18)-Ni(2)-C(19)	87.71(12)
N(7)i-Ni(1)-N(1)	93.44(9)	N(1)-Ni(1)-N(3)	87.27(9)	C(16)-Ni(2)-C(19)	92.79(12)
N(4)-Ni(1)-N(2)	160.24(10)	N(2)-Ni(1)-N(3)	84.22(9)	C(17)-Ni(2)-C(19)	177.49(13)
N(7)i-Ni(1)-N(2)	95.03(9)	C(18)-Ni(2)-C(16)	172.89(13)		
N(1)-Ni(1)-N(2)	87.96(10)	C(18)-Ni(2)-C(17)	89.79(13)		

Symmetry transformations used to generate equivalent atoms: i: -x, 1-y, 1-z

Table 3 Hydrogen bonds for shelxl [nm and deg.]

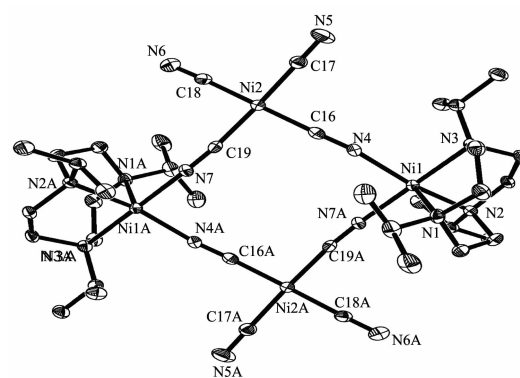
D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
O(1)-H(1D)···N(6) ⁱⁱ	0.085 4(10)	0.199 1(13)	0.283 9(4)	172(5)
O(2)-H(2D)···O(1) ⁱⁱⁱ	0.085 3(10)	0.192 3(19)	0.273 8(4)	159(4)
O(2)-H(2C)···N(5) ^{iv}	0.085 3(10)	0.204 5(15)	0.288 8(4)	170(6)
O(1)-H(1C)···O(2) ^v	0.085 9(10)	0.191 2(12)	0.276 9(4)	175(6)

Symmetry transformations used to generate equivalent atoms:ii: x+1, y, z; iii: -x+1, -y+1, -z+1; iv: x+1, -y+1/2, z+1/2; v: x, y, z-1

2 Results and discussion

2.1 Crystal structures of 1

The structure of the complex **1** is shown in Fig.1. The symmetric unit in this crystal contains two [Ni(CN)₄]²⁻ bridge two *cis*-[Ni(pr₃TACN)]²⁺ in *cis*-positions to form a [2+2] type of discrete molecular square. The distance of Ni(1)-N(macrocycle) (0.2068-0.2215 nm) are close to the Ni(1)-N(cyano) distances (0.199 3 and 0.197 8 nm) and they are longer than the Ni(2)-C(cyano) distances (0.1849 (5)-0.1881 (5) nm). Furthermore the C-N (coordinated) distances of the cyano groups are close to the C-N (uncoordinated) distances. Interestingly, a cyclic water tetramer is located in complex **1**. Within the cluster, the four water molecules are fully coplanar and each water monomer acts as both single hydrogen bond donor and acceptor. The hydrogen bond distances and angles within the water tetramer are as follows: O (1)-O (2)=2.774(5), O(1)-O(2A)=2.745(6), ∠O(1)-O(2)-O(1A)=100.06(5), ∠O(2)-O(1)O(2A)=79.94 (5) (Table 1). The average hydrogen bond distance within the water tetramer is 2.758, which is slightly shorter than 2.78 estimated in the udud water tetramer of (D₂O)₄ in the gas phase^[28]. The most remarkable feature in **1** is that the cyclic water tetramer connects the [2+2] molecular



Symmetry code: A: -x, 1-y, 1-z

Fig.1 An ORTEP drawing of **1** with thermal ellipsoids drawn at the 30% probability level. (H₂O have been cancelled for clarity)

square through hydrogen bond to form a 2D structure (Fig.2).

2.2 Electronic spectra of 1

The electronic spectra of complex **1** show absorption bands at 604 nm and 374 nm, which can be attributed to Ni(II) (3d⁸) permission spin state ³A_{2g}-³T_{1g} (F), ³A_{2g}-³T_{1g} (P) *d-d* transition band in octahedral eld^[36].

2.3 Magnetic property of 1

The magnetic property data were obtained using a Quantum Design PPMS 6000 magnetometer in the temperature range 2 to 300 K at an applied magnetic

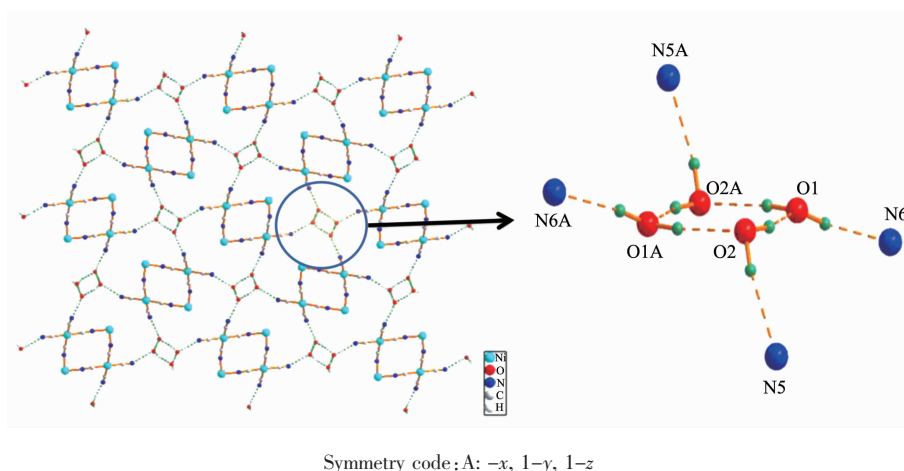


Fig.2 Stacking diagram of **1** along the a axis showing the hydrogen bond, ipr3tacn ligands were omitted for clarity

field of 2 kG. The magnetic susceptibility χ_m and the magnetic moment μ_{eff} is show in Fig.3 The effective magnetic moment μ_{eff} value of is close to 4.63 B.M. at room temperature, and a little larger than the spin-only value of 4.00 B.M. for Ni(II) ($S=1$, $g=2$). With the temperature decreases μ_{eff} slowly decrease, after the temperature reach 30 K, μ_{eff} increase rapidly and get minimum at 2 K. This indicates a weak antiferromagnetic interaction between Ni (II) ions, because $[\text{Ni}(\text{CN})_4]^{2-}$ ions is diamagnetic. The plot of $1/\chi_m$ versus T in the range 2~300 K obeys the Curie-Weiss law with a small negative Weiss constant of $\theta=-3.45$ K, and we have simulated the μ_{eff} vs T data using equation

$$\chi_m = \frac{N\beta^2 g^2}{KT} = \frac{10 + 2\exp[-4J/(KT)]}{5 + 3\exp[-4J/(KT)] + \exp[-6J/(KT)]} + N\alpha$$

Where N is Avogadro constant, K represent Boltzmann constant and β stand for Bohr magnetron. The minimization of the agreement factor $R = \sum [(\chi_{\text{obs}} - \chi_{\text{calc}})^2 /$

$(\chi_{\text{obs}})^2] = 4.1 \times 10^{-4}$ lead to the best fit parameter $J = -1.09$ cm^{-1} , $g = 2.29$.

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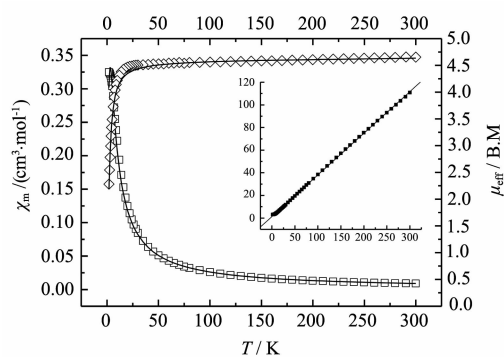


Fig.3 Plots of the magnetic susceptibility of complex **1**

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