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基于[(Tp)Fe(CN)$_3$]$^-$氰根桥联异金属三核配合物的合成、晶体结构及磁性

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摘要: 采用[(Tp)Fe(CN)$_3$]$^-$(Tp=hydrotris(pyrazolyl)borate)与[NiL](ClO$_4$)$_2$(L=3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane)反应,合成了氰根桥联的异金属三核配合物[NiL][(Tp)Fe(CN)$_3$]$_2$·4H$_2$O (**1**),并对其结构和磁性进行了研究。该化合物晶体属于正交晶系,*Pbca* 空间群。配合物 **1** 中,Ni(Ⅱ)大环与 2 个[(Tp)Fe(CN)$_3$]$^-$通过氰根桥联,形成近似直线的三核结构。Ni 原子的配位采取六配位稍畸变的八面体构型,其中大环配体上的 4 个 N 原子占据赤道平面而桥联氰根的 2 个 N 原子占据轴向位置。磁性测定表明在 2~300 K 的温度范围内,Ni(Ⅱ)和 Fe(Ⅲ)之间通过桥联的氰根产生弱的铁磁相互作用。用哈密顿函数 $H=-2J\ (S_{Fe1}\cdot S_{Ni}+S_{Fe2}\cdot S_{Ni})$对其$\chi_M T$-$T$ 曲线进行了拟合,得到 **1** 的朗德因子 g=2.35 和交换常数 J=8.13 cm^{-1}。最后,对配合物的结构与磁性的关系进行了讨论。

关键词: 氰根桥联; 异核配合物; 铁(Ⅲ)配合物; 镍(Ⅱ)配合物; 磁性
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Synthesis, Crystal Structure and Magnetic Properties of Linear Trinuclear Heterometallic Complex Based on [(Tp)Fe(CN)$_3$]$^-$

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Abstract: Using [(Tp)Fe(CN)$_3$]$^-$ (Tp=hydrotris(pyrazolyl)borate) as a building block, one trinuclear complex [NiL][(Tp)Fe(CN)$_3$]$_2$·4H$_2$O (**1**) (L=3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) was prepared and its structure and magnetic properties were studied. Complex **1** crystallizes in the orthorhombic system (*Pbca*), which consists of a neutral Ni^{Ⅱ}Fe$^{Ⅲ}_2$ complex and four H$_2$O molecules. In the compound **1**, the macrocyclic Ni^{Ⅱ} is coordinated by two [(Tp)Fe(CN)$_3$]$^-$ moieties through cyano-bridges in trans positions, resulting in a linear trinuclear structure. The Ni^{Ⅱ} ion adopts a slightly distorted octahedral, with four nitrogen atoms of the macrocyclic ligand L occupying the equatorial plane and two nitrogen atoms of two cyano-bridges situated at the axial sites. Magnetic studies for complex **1** show ferromagnetic coupling between the Ni^{Ⅱ} and Fe^{Ⅲ} ions, giving a S=2 ground state. The best-fit for $\chi_M T$ vs T with a Hamiltonian $H=-2J(S_{Fe1}\cdot S_{Ni}+S_{Fe2}\cdot S_{Ni})$ leads to the parameters g=2.35, J=8.13 cm^{-1} for **1**. The correlations between the structures and the J values are discussed. CCDC: 675244.

Key words: cyano-bridged heterometallic complex; iron(Ⅲ) complex; nickel(Ⅱ) complex; magnetic properties

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In the past decades, much interest has been focused on the applications of using cyanide as a bridge to construct cyano-bridged homo- and heterometallic compounds due to their intriguing structures and remarkable magnetic properties[1]. Hexacyanide anions of the first transition metal elements have been used as useful building blocks to synthesize molecular based magnets possessing the Prussian blue type of structure[2]. To understand the correlation between the crystal structures and magnetic properties, various heterobimetallic complexes with different structures have been extensively investigated by using $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe and Co), $[Mo(CN)_7]^{4-}$ and $[Mo(CN)_8]^{3-}$ as building blocks[3]. In order to extend investigation the relationship between structure and magnetism of the cyano-bridged compounds, we focus on the use of K[(Tp)Fe(CN)$_3$] (Tp= hydrotris(pyrazolyl)borate) as building block to synthesize heterobimetallic complex. Due to bearing a negative charge, $[(Tp)Fe(CN)_3]^-$ is easier to coordinate with metal core with positive charge, which is beneficial in preparation of cyano-bridged compounds[4a]. Herein, we report here the preparation, crystal structure and magnetic properties of one trinuclear complex $[NiL][(Tp)Fe(CN)_3]_2\cdot 4H_2O$ (**1**) (L=3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane).

1 Experimental

1.1 Reagents and physical measurements

K[(Tp)Fe(CN)$_3$] and L were prepared according to the literature methods[4]. All other chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Magnetic susceptibility data were collected in the 2~300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

1.2 Synthesis of $[NiL][(Tp)Fe(CN)_3]_2\cdot 4H_2O$ (1)

A 5 mL aqueous solution of $[NiL](ClO_4)_2$ (55 mg, 0.1 mmol) was added to a stirring solution of K[Fe(Tp)(CN)$_3$] (86 mg, 0.2 mmol) in 15 mL of water. The reaction mixture was stirred for 1 h at room temperature. A red powder was collected by filtration. Orange crystals were obtained after recrystallization from CH_3CN-CH_3OH-H_2O solution. Yield: 75%. Anal. Calcd for $C_{36}H_{58}B_2Fe_2N_{24}NiO_6$(%): C 38.78, H 5.24, N 30.15; Found (%): C 39.05, H 5.41, N 30.47. IR (KBr pellet): ν_{CN} 2 149, 2 123 cm^{-1}.

1.3 Structure determinations

Diffraction data of **1** was collected at 273(2) K on a Bruker Smart Apex 1000 CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm). A total of 41 440 reflections were collected in the range of $1.52° < \theta < 27.05°$ with 5 606 independent ones (R_{int}=0.043 7). The structure was solved using direct method, which yielded the positions of all non-hydrogen atoms. These were refined first with isotropically and then with anisotropically. All the hydrogen atoms (except those of water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of four water molecules were located in the difference Fourier map and refined isotropically; the O-H distances involving the water molecules were refined with a DFIX restraint of 0.086 ~0.091 nm. All calculations were performed using the SHELXTL system of computer program[5]. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 675244.

Table 1 Crystal data for complex 1

Complex	**1**	θ range for data collection / (°)	1.52~27.05
Chemical formula	$C_{36}H_{58}B_2Fe_2NiN_{24}O_6$	Limiting indices	$-18 \leqslant h \leqslant 18, -16 \leqslant k \leqslant 16, -34 \leqslant l \leqslant 32$
Formula weight	1 115.09	Reflections collected / unique (R_{int})	41 440 / 5 606 (0.043 7)
Crystal system	Orthorhombic	Reflections observed [$I>2\sigma(I)$]	3 969
Space group	*Pbca*	D_c / (Mg·cm^{-3})	1.447

Continued Table 1

a / nm	1.479 3(6)	μ / mm^{-1}	0.991
b / nm	1.291 6(5)	Data / restraints / parameters	5 606 / 5 / 322
c / nm	2.679 6(10)	Goodness-of-fit on F^2	1.056
V / nm^3	5.120(3)	Final R indices[$I>2\sigma(I)$] R_1, wR_2	0.051 7, 0.145 9
Z	4	R indices (all data) R_1, wR_2	0.077 6, 0.165 3
F(000)	2 320	Largest diff. peak and hole / (e·nm^{-3})	988 and −609
Crystal size / mm	0.48×0.26×0.18		

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

Fe(1)-C(17)	0.192 3(4)	Fe(1)-C(18)	0.192 2(5)	Fe(1)-C(19)	0.191 5(4)
Fe(1)-N(4)	0.197 3(3)	Fe(1)-N(6)	0.196 6(3)	Fe(1)-N(8)	0.197 3(3)
Ni(1)-N(1)	0.206 6(3)	Ni(1)-N(3)	0.206 4(3)	Ni(1)-N(10)	0.211 6(3)
C(17)-N(10)	0.114 3(5)	C(18)-N(11)	0.114 8(6)	C(19)-N(12)	0.114 7(6)
C(19)-Fe(1)-C(18)	87.6(2)	C(19)-Fe(1)-C(17)	88.27(17)	C(18)-Fe(1)-C(17)	87.37(17)
C(19)-Fe(1)-N(6)	91.53(15)	C(18)-Fe(1)-N(6)	92.66(15)	C(17)-Fe(1)-N(6)	179.80(15)
C(19)-Fe(1)-N(4)	178.82(19)	C(18)-Fe(1)-N(4)	91.29(16)	C(17)-Fe(1)-N(4)	91.44(14)
N(6)-Fe(1)-N(4)	88.76(12)	C(19)-Fe(1)-N(8)	92.77(19)	C(18)-Fe(1)-N(8)	178.90(16)
C(17)-Fe(1)-N(8)	91.60(15)	N(6)-Fe(1)-N(8)	88.38(13)	N(4)-Fe(1)-N(8)	88.38(14)
N(3)-N(1)-N(3A)	180.0	N(3)-Ni(1)-N(1A)	84.74(13)	N(3)-Ni(1)-N(1)	95.26(13)
N(3A)-Ni(1)-N(1)	84.74(13)	N(1A)-Ni(1)-N(1)	180.000(1)	N(3)-Ni(1)-N(10)	91.54(13)
N(3A)-Ni(1)-N(10)	88.46(13)	N(1A)-Ni(1)-N(10)	88.24(13)	N(1)-Ni(1)-N(10)	91.76(13)
N(3)-Ni(1)-N(10A)	88.46(13)	N(1)-Ni(1)-N(10A)	88.24(13)	C(17)-N(10)-Ni(1)	173.8(3)
N(10)-C(17)-Fe(1)	178.5(4)	N(11)-C(18)-Fe(1)	176.9(5)	N(12)-C(19)-Fe(1)	179.0(5)

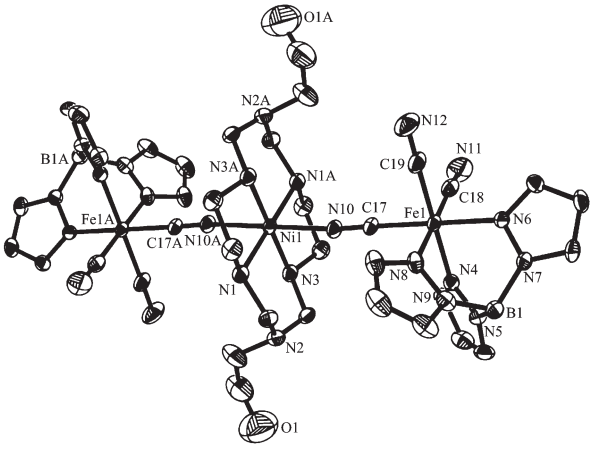
Symmetry transformations used to generate equivalent atoms: A: $-x+2$, $-y+1$, $-z+1$.

2　Results and discussion

2.1　Structure description

The crystal structure of the complex **1** is shown in Fig.1. The [(Tp)Fe(CN)$_3$]$^-$ unit acts as a monodentate ligand through one of its three cyanide groups toward a central [NiL]$^{2+}$ core. Each Fe(Ⅲ) ion is six-coordinated with three Tp nitrogen atoms and three cyanide carbon atoms with a C_{3v} symmetry. The Fe-C (cyano) bond length is 0.192 3(4) nm, which is in good agreement with those observed in other low-spin iron(Ⅲ) complexes[6]. The Fe−C≡N angles for terminal range from 176.9(5)° to 179.0(5)° and the angle for bridging is 178.5(4)°, which departs slightly from strict linearity.

The Ni(Ⅱ) ion is located on an inversion center (Fig.1), and coordinated with two [(Tp)Fe(CN)$_3$]$^-$ moieties through cyano-bridges in trans positions, resulting in a linear trinuclear structure. The Ni^{Ⅱ} ion adopts a slightly distorted octahedral, with four nitrogen atoms of the macrocyclic ligand L [Ni-N$_{eq}$=0.206 4(3)~0.206 6(3) nm] occupying the equatorial plane and two nitrogen atoms of two cyano-bridges situated at the axial sites [Ni-N$_{ax}$=0.211 6(3) nm]. The bridging cyanides coordin-



Symmetry code: A: $-x+2$, $-y+1$, $-z+1$

Fig.1　Coordination structure of complex **1**; Thermal ellipsoids are drawn at the 30% level (H atoms and H_2O molecules were omitted for clarity)

ate to Ni atom in a linear fashion [Ni-N-C=173.8(3)°]. The C-N (cyano) distances vary from 0.114 3(5) to 0.114 8(6) nm, the Ni-Fe intramolecular distances through the cyano-bridges are 0.517 6(5) nm.

2.2 Magnetic properties

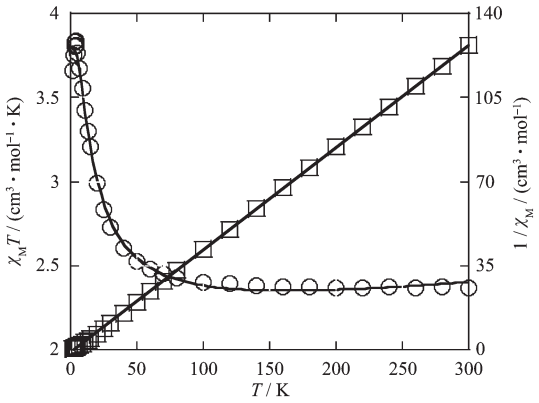
The magnetic behaviors of **1** are shown in Fig.2. The $\chi_M T$ value of 2.37 $cm^3 \cdot K \cdot mol^{-1}$ (4.35 μ_B) at room temperature is higher than the expected value of 1.75 $cm^3 \cdot K \cdot mol^{-1}$ (3.74μ_B) for two low-spin Fe(Ⅲ) atoms (S_{Fe}=1/2, g=2.0) and one Ni(Ⅱ) atom (S_{Ni}=1, g=2.0), which can be ascribed to the orbital contributions from the low-spin Fe(Ⅲ) centers [7]. When the temperature is lowered, it increases slowly up to a maximum value of 3.48 $cm^3 \cdot K \cdot mol^{-1}$ around 4 K. This behavior indicates the existence of ferromagnetic interactions between magnetic centers. Then a sharp drop below 4 K is observed. The plot of $1/\chi_M$ vs T in the range 15~300 K obeys the Curie-Weiss law with a small positive Weiss constant of Θ=2.65 K. The positive Weiss constant also suggests ferromagnetic interactions between Fe(Ⅲ) and Ni(Ⅱ) ions through the linear cyano-bridges. The ferromagnetic interaction is due to the orthogonality of the magnetic orbitals of Fe(Ⅲ) and Ni(Ⅱ) ions. The data were modeled with the following expression of χ_M:

$$\chi_M=\frac{2Ng^2\beta^2}{kT}\frac{A}{B}+\frac{\rho}{T}$$

$$A=1+5\exp(\frac{2J}{kT})+\exp(\frac{-2J}{kT})$$

$$B=3+5\exp(\frac{2J}{kT})+3\exp(\frac{-2J}{kT})+\exp(\frac{-4J}{kT})$$

The best fit to the experiment data above 4 K gives g=2.35, J=8.13 cm^{-1}, ρ=0.043 1 with a correlation coefficient of 0.998 0, where J is the exchange coupling parameter between Fe(Ⅲ) and Ni(Ⅱ) through the cyano-bridges and ρ is the percentage of impurity in sample.



Solid line corresponds to the best-fit curve

Fig.2 Temperature dependence of $\chi_M T$ (○) and $1/\chi_M$(□) vs T for **1**

Previous studies have shown that the J values are related to the bond angles of Ni–N≡C[8~10]. In order to discuss the correlations between the structures and the J values reported for related systems, the related bond angles and J values are collected in Table 3. From Table 3 it can be found that the larger Ni–N≡C angles lead to the stronger ferromagnetic coupling between Ni and Fe(Ⅲ) through the cyano-bridge. This can be attributed to the relationship between the overlap of the magnetic orbits of $Fe^{Ⅲ}$ and $Ni^{Ⅱ}$ ions and the Ni–N≡C bond angles. The degree of the overlap of the magnetic orbitals of $Fe^{Ⅲ}$ and $Ni^{Ⅱ}$ ions is proportional to Ni–N≡C bond angles. The larger magnetic orbitals overlap will lead to the stronger $Fe^{Ⅲ}$-CN-$Ni^{Ⅱ}$ ferromagnetic interactions

Table 3 Related bond angles and the J values in cyano-bridged compounds based on $[(Tp)Fe(CN)_3]^-$

Complex	Metal	M-NC / (°)	g	J / cm^{-1}	Ref
$\{[Tp^*Fe^{Ⅲ}(CN)_3Ni^{Ⅱ}(DMF)_4]_2[OTf]_2\}\cdot 2DMF$	Ni-Fe	176.4(3)	2.20	5.3	[8]
$[NiL][(Tp)Fe(CN)_3]_2\cdot 4H_2O$	Ni-Fe	173.8(3)	2.35	8.13	This work
$[(Tp)_3(Tpm^{Me})_2Fe^{Ⅲ}_3Ni^{Ⅱ}_2(CN)_9]ClO_4\cdot 15H_2O$	Ni-Fe	168.4(2)	2.27	4.84	[9]
$[(Tp)_2Fe^{Ⅲ}(CN)_6Ni(en)_2]$	Ni-Fe	153.8(3)	2.25	1.20	[10]

Tp*=hydridotris(3,5-dimethylpyrazol-1-yl)borate, Tpm^{Me}=tris(3,5-dimethyl-1-pyrazoyl)-methane.

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