

氰根桥联三核异金属配合物的合成、晶体结构及磁性研究

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摘要: 采用 $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ ($\text{Tp}=\text{hydrotris}(\text{pyrazolyl})\text{borate}$)与 $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ 反应, 合成了氰根桥联的异金属三核配合物 $[\text{Mn}(\text{phen})_2][(\text{Tp})\text{Fe}(\text{CN})_3]_2 \cdot 5\text{H}_2\text{O}$ (**1**) ($\text{phen}=1, 10\text{-phenanthroline}$), 并对其结构和磁性进行了研究。晶体结构分析结果表明该化合物晶体属于三斜晶系, $P\bar{1}$ 空间群。在该配合物中, $\text{Mn}(\text{II})$ 与 2 个 phen 分子及 2 个 $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ 配位, 形成一种弯曲的三核结构。磁性测量结果表明, $\text{Mn}(\text{II})$ 和 $\text{Fe}(\text{III})$ 之间通过氰根桥联产生弱的反铁磁相互作用。

关键词: 氰根桥联异核金属配合物; 结构; 磁性

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Crystal Structure and Magnetic Properties of Trinuclear Heterometallic Complex $[\text{Mn}(\text{phen})_2][(\text{Tp})\text{Fe}(\text{CN})_3]_2$

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Abstract: Using $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ ($\text{Tp}=\text{hydrotris}(\text{pyrazolyl})\text{borate}$) as a building block, one trinuclear complex $[\text{Mn}(\text{phen})_2][(\text{Tp})\text{Fe}(\text{CN})_3]_2 \cdot 5\text{H}_2\text{O}$ (**1**) ($\text{phen}=1, 10\text{-phenanthroline}$) was prepared and its structure and magnetic property were studied. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, which consists of a neutral $\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}$ unit and five H_2O molecules. In compound **1**, the Mn^{II} ion is coordinated by two $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ moieties through cyano-bridges in *cis* positions, resulting in a bended trinuclear structure. The magnetic properties have been investigated in the range of temperature 2~300 K. Antiferromagnetic coupling occurs in cyano-bridged $\text{Mn}^{\text{II}}\text{-NC-Fe}^{\text{III}}$. CCDC: 611689.

Key words: cyano-bridged heterometallic complexes; structure; magnetic properties

0 Introduction

The magnetism based on coordination compounds is one of the most active fields in coordination chemistry. The main active research areas in this field include the synthesis of single-molecule magnets^[1] and single-chain magnets^[2], high- T_c magnetic materials^[3]

and magneto-optical or magneto-conductor multifunctional materials^[4]. 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^[5]. To understand the correlation between the crystal structures and magnetic properties, various heterobimetallic

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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^[6]. In order to extend investigation of the relationship between structure and magnetic properties of the cyano-bridged compounds, we choose $(Bu_4N)[(Tp)Fe(CN)_3]$ (Tp =hydrotris(pyrazolyl)borate) as building block to synthesize heterobimetallic complex. Due to bearing a negative charge, $[(Tp)Fe(CN)_3]^-$ is easy to coordinate with metal core with positive charge, which is beneficial in preparation of cyanide bridged compounds^[7]. Herein, we report on the preparation, crystal structure and magnetic property of a trinuclear complex $[Mn(phen)_2][(Tp)Fe(CN)_3]_2 \cdot 5H_2O$ (**1**) ($phen=1,10$ -phenanthroline).

1 Experimental

1.1 General

$(Bu_4N)[(Tp)Fe(CN)_3]_2$ was prepared according to the literature method^[7]. 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 $[Mn(phen)_2][(Tp)Fe(CN)_3]_2 \cdot 5H_2O$ (**1**)

To a solution of $(Bu_4N)[(Tp)Fe(CN)_3]$ (30 mg, 0.05

mmol) in 7 mL of methanol was added a solution of $Mn(Ac)_2 \cdot 4H_2O$ (6 mg, 0.025 mmol) in 8 mL of methanol. The resulting mixture was stirred at room temperature for 5 min and filtrated. The filtrate was layered with a methanol solution (5 mL) of $phen$ (9 mg, 0.045 mmol). After three days, needle-shaped red crystals of **1** formed from the solution. The crystals were collected, washed with methanol, and dried in the air. Yield: 78%. Anal. Calcd. for $C_{48}H_{46}B_2Fe_2MnN_{22}O_5$ (%): C, 48.07; H, 3.87; N, 25.69; Found (%): C, 48.01; H, 4.09; N, 25.58. IR (KBr pellet): ν_{CN} 2 140, 2 128 cm^{-1} .

1.3 Crystal structure determination

Single-crystal diffraction data of **1** was collected at 173(2) K on a Bruker Smart 1000 CCD diffractometer with $Mo K\alpha$ radiation ($\lambda=0.071\ 073$ nm). 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 and included in structure factor calculations in the final stage of full-matrix least-squares refinement with fixed isotropic thermal parameters. The hydrogen atoms of water molecules were located from the difference Fourier map and refined isotropically; the H-O 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 programs^[8]. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

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Table 1 Crystal data for complex **1**

Complex	1	$F(000)$	1 220
Chemical formula	$C_{48}H_{46}B_2Fe_2MnN_{22}O_5$	Crystal size / mm	$0.41 \times 0.31 \times 0.12$
Molecular weight	1 194.29	θ range for data collection / (°)	1.99 to 26.00
Crystal system	Triclinic	Limiting indices	$-14 \leq h \leq 17, -17 \leq k \leq 10, -17 \leq l \leq 17$
Space group	$P\bar{1}$	Reflections collected / unique (R_{int})	14 878 / 10 491 (0.061 4)
a / nm	1.386 6(4)	D_c / ($Mg \cdot m^{-3}$)	1.45
b / nm	1.420 6(4)	μ / mm^{-1}	0.818
c / nm	1.450 5(4)	Data / restraints / parameters	10 491 / 36 / 751
α / (°)	92.406(5)	Goodness-of-fit on F^2	0.97

Continued Table 1

$\beta / (^{\circ})$	94.166(5)	Final R indices [$I \geq 2\sigma(I)$] R_1, wR_2	0.067 0, 0.136 0
$\gamma / (^{\circ})$	105.911(5)	R indices (all data) R_1, wR_2	0.161 8, 0.171 3
V / nm^3	2.734 8(13)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	678 and -521
Z	2		

Table 2 Selected bond distances (nm) and bond angles ($^{\circ}$) for compound 1

Fe(1)-C(19)	0.192 2(7)	Fe(1)-C(20)	0.192 2(6)	Fe(1)-C(21)	0.192 1(7)
Fe(2)-C(22)	0.191 2(6)	Fe(2)-C(23)	0.191 4(7)	Fe(2)-C(24)	0.192 7(8)
Fe(1)-N(2)	0.197 0(5)	Fe(1)-N(4)	0.197 4(5)	Fe(1)-N(6)	0.196 8(5)
Fe(2)-N(8)	0.197 6(5)	Fe(2)-N(10)	0.195 9(5)	Fe(2)-N(12)	0.196 7(5)
Mn(1)-N(13)	0.217 0(6)	Mn(1)-N(16)	0.217 2(5)	Mn(1)-N(19)	0.224 5(5)
Mn(1)-N(20)	0.224 6(4)	Mn(1)-N(21)	0.231 8(5)	Mn(1)-N(22)	0.226 1(5)
N(13)-C(19)	0.114 5(7)	N(14)-C(20)	0.114 7(7)	N(15)-C(21)	0.115 0(7)
N(16)-C(22)	0.114 8(7)	N(17)-C(23)	0.115 1(7)	N(18)-C(24)	0.115 5(9)
C(21)-Fe(1)-C(20)	88.4(2)	C(21)-Fe(1)-C(19)	90.3(3)	C(20)-Fe(1)-C(19)	89.4(3)
C(21)-Fe(1)-N(6)	178.4(2)	C(20)-Fe(1)-N(6)	90.4(2)	C(19)-Fe(1)-N(6)	90.7(2)
C(21)-Fe(1)-N(2)	90.8(2)	C(20)-Fe(1)-N(2)	92.0(2)	C(19)-Fe(1)-N(2)	178.3(2)
N(6)-Fe(1)-N(2)	88.3(2)	C(21)-Fe(1)-N(4)	91.2(2)	C(20)-Fe(1)-N(4)	179.4(2)
C(19)-Fe(1)-N(4)	91.1(2)	N(6)-Fe(1)-N(4)	90.0(2)	N(2)-Fe(1)-N(4)	87.6(2)
C(22)-Fe(2)-C(23)	86.6(2)	C(22)-Fe(2)-C(24)	88.2(3)	C(23)-Fe(2)-C(24)	86.5(3)
C(22)-Fe(2)-N(10)	91.4(2)	C(23)-Fe(2)-N(10)	177.8(2)	C(24)-Fe(2)-N(10)	92.4(2)
C(22)-Fe(2)-N(12)	90.2(2)	C(23)-Fe(2)-N(12)	91.6(2)	C(24)-Fe(2)-N(12)	177.6(2)
N(10)-Fe(2)-N(12)	89.4(2)	C(22)-Fe(2)-N(8)	177.5(3)	C(23)-Fe(2)-N(8)	93.6(2)
C(24)-Fe(2)-N(8)	94.3(2)	N(10)-Fe(2)-N(8)	88.5(2)	N(12)-Fe(2)-N(8)	87.3(2)
N(13)-Mn(1)-N(16)	90.0(2)	N(13)-Mn(1)-N(19)	91.01(18)	N(16)-Mn(1)-N(19)	164.66(17)
N(13)-Mn(1)-N(20)	107.14(18)	N(16)-Mn(1)-N(20)	91.39(17)	N(19)-Mn(1)-N(20)	73.70(16)
N(13)-Mn(1)-N(22)	93.97(18)	N(16)-Mn(1)-N(22)	103.11(17)	N(19)-Mn(1)-N(22)	92.09(17)
N(20)-Mn(1)-N(22)	154.44(18)	N(13)-Mn(1)-N(21)	166.36(17)	N(16)-Mn(1)-N(21)	89.21(18)
N(19)-Mn(1)-N(21)	93.34(18)	N(20)-Mn(1)-N(21)	86.49(17)	N(22)-Mn(1)-N(21)	72.98(18)
N(13)-C(19)-Fe(1)	176.5(5)	N(15)-C(21)-Fe(1)	177.2(6)	N(16)-C(22)-Fe(2)	175.1(6)
N(17)-C(23)-Fe(2)	177.3(6)	C(19)-N(13)-Mn(1)	172.9(5)	C(22)-N(16)-Mn(1)	169.4(5)

2 Results and discussion

2.1 Structure description

The crystal structure of complex **1** is shown in Fig.1. The $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ unit acts as a monodentate ligand through one of its three cyanide groups toward a central $[\text{Mn}(\text{phen})_2]^{2+}$ core. Each Fe(III) ion is six-coordinated with three Tp nitrogen atoms and three cyanide carbon atoms with a C_{3v} symmetry^[9]. The Fe-C(cyano) bond lengths range from 0.191 2(6) to 0.192 7(8) nm, which is in good agreement with those observed in

other low-spin iron(III) complexes^[9,10]. The Fe-C $\equiv$ N angles for terminal range from 176.2(3) $^{\circ}$ to 179.0(3) $^{\circ}$ and the angles for bridging range from 177.2(6) $^{\circ}$ to 177.3(6) $^{\circ}$, which departs slightly from strict linearity.

The Mn atom is six-coordinated with four nitrogen atoms from phen molecules and two cyanide nitrogen atoms. The Mn-N(phen) distances range from 0.224 5(5) to 0.231 8(5) nm. The Mn-N(CN) distances are 0.217 0(6) and 0.217 2(5) nm, respectively. The Mn-N $\equiv$ C angles are 172.9(5) $^{\circ}$ and 169.4 (5) $^{\circ}$. The Mn-Fe intramolecular distances are 0.522 1(5) and

0.519 6(3) nm, respectively.

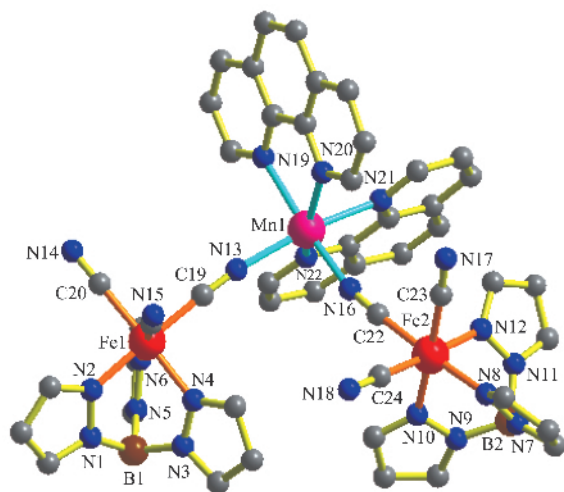
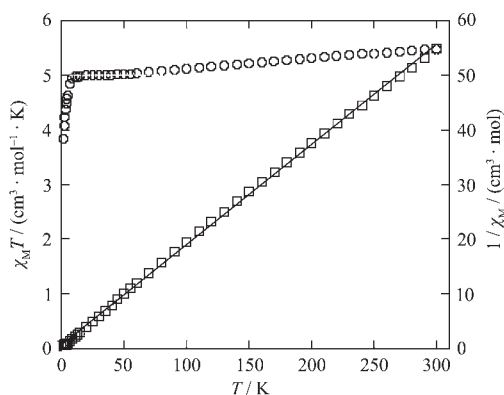


Fig.1 Coordination structure of complex **1** (H atoms and H₂O molecules were omitted for clarity)

2.2 Magnetic properties

The magnetic properties of **1** are shown in Fig.2. The $\chi_M T$ value at 300 K is $5.47 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ($6.61\mu_B$), which is slightly larger than the spin-only value ($4.61 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, $6.07\mu_B$) for two uncoupled low-spin Fe(III) atoms ($S_{\text{Fe}}=1/2$, $g=2.0$) and one high-spin Mn(II) atom ($S_{\text{Mn}}=5/2$, $g=2.0$). When the temperature decreased, the $\chi_M T$ values were gradually down to $4.93 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 9 K, and then decreased steeply to $3.83 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K, indicating an antiferromagnetic interactions between the Mn(II) and Fe(III) ions. In the temperature range 2~300 K, the magnetic susceptibility data were fitted with the Curie-Weiss law with $C=6.01 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta=-3.00 \text{ K}$, also indicating the anti-



The solid line shows the Curie-Weiss fitting

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

ferromagnetic interactions between the Mn(II) and Fe(III) ions.

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