

基于 $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ 氰基桥联双核配合物的合成、结构和磁性研究

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摘要: 采用 $[\text{TpFe}^{\text{III}}(\text{CN})_3]^-$ 作为构筑基块, 合成并表征了一个氰基桥联双核配合物 $[(\text{Tp})\text{Fe}^{\text{III}}(\text{CN})_3\text{Cu}^{\text{II}}(\text{bpy})_2]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**1**)。对化合物 **1** 进行了晶体结构分析, 其晶胞参数为 $a=0.904\,26(5)$ nm, $b=1.352\,56(7)$ nm, $c=1.556\,02(8)$ nm, $\alpha=106.08(1)^\circ$, $\beta=95.79(1)^\circ$, $\gamma=91.01(1)^\circ$, $P\bar{1}$ 空间群。在这个化合物中, $[\text{TpFe}^{\text{III}}(\text{CN})_3]$ 通过其中 1 个氰基与 $[\text{Cu}(\text{bpy})_2]^{2+}$ 桥联, 而另外 2 个氰基未参与配位。磁性研究表明, 在化合物 **1** 中, $\text{Cu}(\text{II})$ 与 $\text{Fe}(\text{III})$ 离子之间表现为铁磁相互作用。用哈密顿函数 $H=-2J S_{\text{Fe}} S_{\text{Cu}}$ 对其 $\chi_{\text{M}} T-T$ 曲线进行了拟合, 得到 **1** 的朗德因子 $g=2.34$ 和交换常数 $J=5.52\text{ cm}^{-1}$ 。

关键词: 晶体结构; 双核配合物; 磁化率; 氰基桥联

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Synthesis, Structure and Magnetic Properties of Cyano-bridged Dinuclear Complex Based on $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$

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Abstract: By using a tricyanometalate precursor $[\text{TpFe}^{\text{III}}(\text{CN})_3]^-$ ($\text{Tp}=\text{hydrotris (pyrazolyl)borate}$) as a structural building block, a new cyanide-bridged dinuclear complex, $[(\text{Tp})\text{Fe}^{\text{III}}(\text{CN})_3\text{Cu}^{\text{II}}(\text{bpy})_2]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**1**) ($\text{bpy}=2, 2'$ -bipyridine), has been prepared and characterized. It crystallizes in triclinic space group $P\bar{1}$, with $a=0.904\,26(5)$ nm, $b=1.352\,56(7)$ nm, $c=1.556\,02(8)$ nm, $\alpha=106.08(1)^\circ$, $\beta=95.79(1)^\circ$, $\gamma=91.01(1)^\circ$. In the complex, $[\text{TpFe}(\text{CN})_3]^-$ acts as a monodentate ligand toward a central $[\text{Cu}(\text{bpy})_2]^{2+}$ core through one of its three cyanide groups, the other two cyanides remaining terminal. Magnetic studies for complex **1** show ferromagnetic coupling between the $\text{Cu}(\text{II})$ and $\text{Fe}(\text{III})$ ions, giving an $S=1$ ground state. The best-fit for $\chi_{\text{M}} T$ vs T with an Hamiltonian $H=-2J S_{\text{Fe}} S_{\text{Cu}}$ leads to the parameters $g=2.34$, $J=5.52\text{ cm}^{-1}$ for **1**. CCDC: 622244.

Key words: crystal structure; dinuclear complex; magnetic properties; cyano-bridged

The research on cyanide-bridged coordination assemblies of Prussian Blue type have undergone remarkable growth in the past two decades due to their

unique magnetic behavior^[1]. However, the application of three-dimensional Prussian Blue analogues obtained by using a stable hexacyanometallic anion $[\text{M}(\text{CN})_6]^{n-}$ as

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building block toward fully solvated transition metal ions was limited because of their insolubility and difficulty to give single crystals. In the last few years, assembly based on pre-designed building blocks, in which metal coordination sites are partially blocked, was used to construct molecular clusters and low dimensional coordination polymers^[2].

Recently, a new synthetic strategy for achieving cyanide-bridged bimetallic systems by using modified cyanometallates, $[\text{M}(\text{L})_x(\text{CN})_y]^{(x-m)-}$ (M =first row transition metallic ions and L =organic polydentate ligands), as multidentate ligands and linkers were developed, such as $[\text{M}(\text{L})(\text{CN})_4]^-$ ($\text{M}=\text{Cr}^{3+}$, Fe^{3+} , $\text{L}=1, 10$ -phenanthroline; 2,2'-bipyridine)^[3], $[(\text{tacn})\text{M}(\text{CN})_3]$ ($\text{M}=\text{Co}^{3+}$, Cr^{3+} ; $\text{tacn}=1,4,7$ -triazacyclononane)^[4], $[(\text{tach})\text{M}(\text{CN})_3]$ ($\text{M}=\text{Cr}^{3+}$, Fe^{3+} , Co^{3+} ; $\text{tach}=1,3,5$ -triaminocyclohexane)^[5], $[(\text{Me}_3\text{tacn})\text{M}(\text{CN})_3]$ ($\text{M}=\text{Cr}^{3+}$, Mo^{3+} ; $\text{Me}_3\text{tacn}=\text{N}, \text{N}', \text{N}''$ -trimethyl-1,4,7-triazacyclononane)^[6], $[\text{Et}_4\text{N}][\text{Re}(\text{triphos})(\text{CN})_3]$ ($\text{triphos}=1,1,1$ -tris(diphenylphosphino-methyl)ethane)^[7], $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ ($\text{Tp}=\text{hydrotris}(\text{pyrazolyl})\text{borate}$)^[8] and $[(\text{Tp}^*)\text{Fe}(\text{CN})_3]^-$ ($\text{Tp}^*=\text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$)^[9]. On the basis of these building blocks, some heterobimetallic complexes exhibiting interesting structure and magnetic properties were synthesized, including several single-molecule magnets and single-chain magnets that are possibly useful for information storage and computer science.

As part of an effort to develop new examples of cyanide-bridged heterobimetallic magnetic complexes using $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ as building block, herein, we report the synthesis, crystal structure and magnetic properties of a new dinuclear cluster $[(\text{Tp})\text{Fe}^{\text{III}}(\text{CN})_3\text{Cu}^{\text{II}}(\text{bpy})_2]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**1**).

1 Experimental

1.1 General

All reagents used in the synthesis were of analytical grade. $(\text{Bu}_4\text{N})[(\text{Tp})\text{Fe}(\text{CN})_3]$ was synthesized as described previously^[8]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. Infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region. Magnetic susceptibility

measurements of polycrystalline samples were measured over the temperature range 1.8~300 K with a Quantum Design MPMS-XL7 SQUID magnetometer and using an applied magnetic field from 100 to 2 000 Oe. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

1.2 Synthesis of $[(\text{Tp})\text{Fe}(\text{CN})_3\text{Cu}(\text{bpy})_2]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**1**)

Solid $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.5 mg, 0.05 mmol) and bpy (15.6 mg, 0.1 mmol) were mixed in 10 mL of CH_3OH . Then a methanol solution (5 mL) of $(\text{Bu}_4\text{N})[(\text{Tp})\text{Fe}(\text{CN})_3] \cdot \text{H}_2\text{O}$ (30 mg, 0.05 mmol) was added to the solution. Slow evaporation of the resulting brown solution at room temperature, dark brown crystals of **1** suitable for X-ray diffraction were obtained. Yield: 52%. Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{BClCuFeN}_{13}\text{O}_5$ (%): C, 46.45; H, 3.43; N, 21.34; Found (%): C, 46.49; H, 3.40; N, 21.31. IR (KBr, cm^{-1}): 2 119 and 2 151 (ν_{CN}).

1.3 X-ray structure determination

The crystal structure was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromatized $\text{Mo } K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) at 298 K. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. Structure was solved by direct methods using the program SHELXS-97. The positions of metal atoms and their first coordination spheres were located from direct-methods E -maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso} . Final crystallographic data and values of R_1 and wR are listed in Table 1.

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Table 1 Crystallographic data for 1

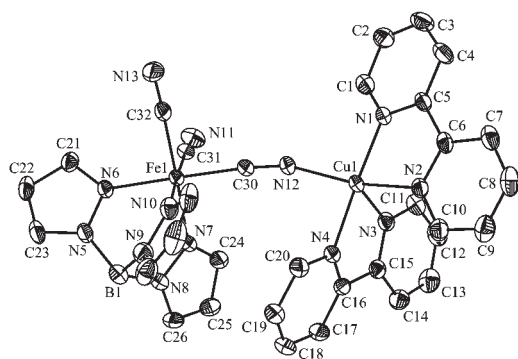
Formula	C ₃₃ H ₂₉ BClCuFeN ₁₃ O ₅	<i>T</i> / K	298(2)
Formula weight	853.34	λ / nm	0.071 073
Crystal system	Triclinic	μ / mm ⁻¹	1.119
Space group	$P\bar{1}$	<i>F</i> (000)	870
<i>a</i> / nm	0.904 26(5)	θ range / (°)	1.57~25.00
<i>b</i> / nm	1.352 56(7)	<i>hkl</i> range	-10 ≤ <i>h</i> ≤ 9, -16 ≤ <i>k</i> ≤ 14, -18 ≤ <i>l</i> ≤ 18
<i>c</i> / nm	1.556 02(8)	Collected	6 335
α / (°)	106.08(1)	Unique	5 502
β / (°)	95.79(1)	Parameters	496
γ / (°)	91.01(1)	Goodness of fit	1.088
<i>Z</i>	2	<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.039 8
<i>V</i> / nm ³	1.817 3(2)	<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.118 1
<i>D</i> _{calc} / (g·cm ⁻³)	1.559		

2 Results and discussion

2.1 Crystal structure

The crystal structure of complex **1** is shown in Fig.1. Complex **1** consists of dinuclear cations of the formula [(Tp)Fe^{III}(CN)₃Cu^{II}(bpy)₂]²⁺, uncoordinated perchlorates and crystallized methanol molecules. In the dinuclear cluster, [(Tp)Fe(CN)₃]⁻ acts as a monodentate ligand through one of its three cyanide groups toward a central [Cu(bpy)₂]²⁺ core. Each iron(III) ion is coordinated by three Tp nitrogen atoms and three cyanide carbon atoms, taking a similar *C*_{3v} symmetry. Good agreement is observed between the Fe^{III}-C (cyano) bond lengths in **1** (0.191 4(3)~0.193 4(3) nm) and those in low-spin tricyano iron(III) complexes [Ph₄P][Fe(CN)₃] (0.191 0(6)~0.192 9(7) nm) and [Et₄N][Fe(CN)₃] (0.189 9 (2)~0.190 8(2) nm)^[8,9]. The Fe-CN angles for

both terminal (176.6(3)° and 177.8(3)°) and bridging (174.8(3)°) cyanide groups depart somewhat from strict linearity. The Cu(II) ions are coordinated to two bpy ligands as well as to one nitrogen atoms of cyanide bridge, forming a square-pyramidal coordination conformation. The base positions of the square-pyramid are occupied by one cyanide nitrogen atom and three bpy nitrogen atoms with bond lengths distributed within the range 0.199 6(2)~0.203 3(2) nm. And the apical position is occupied by the remaining nitrogen atoms of the bpy ligand with much longer bond length 0.219 2(2) nm. The dinuclear [(Tp)Fe^{III}(CN)₃Cu^{II}(bpy)₂]²⁺ clusters are further linked through weak bonding (Cu(1)···N(13)', 0.306 7(4) nm; symmetry operator: 2-*x*, 1-*y*, 1-*z*) to form the tetranuclear clusters of [(Tp)Fe^{III}(CN)₃Cu^{II}(bpy)₂]⁴⁺, as shown in Fig.2. The intramolecular



Thermal ellipsoids are drawn at the 30% probability levels

Fig.1 Perspective drawing of the dinuclear cluster of [(Tp)Fe^{III}(CN)₃Cu^{II}(bpy)₂]²⁺ in **1** showing the atom numbering

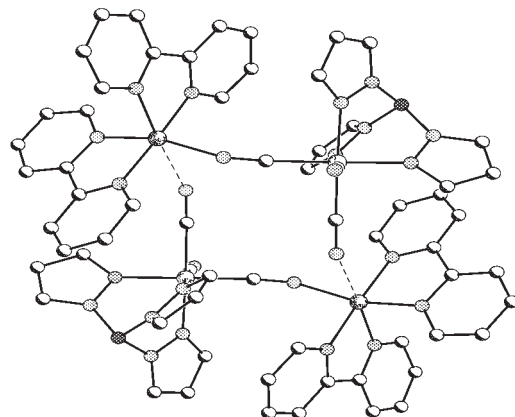


Fig.2 View of the tetranuclear cluster of [(Tp)Fe^{III}(CN)₃Cu^{II}(bpy)₂]⁴⁺ of complex **1** formed by weak bonding linkage

Fe...Cu separations through bridging cyanides are 0.495 1 (4) nm. Whereas, the shortest intermolecular

Fe...Cu distances are 0.555 1 nm. Selected bond lengths and angles are compiled in Table 2.

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

Fe(1)-C(30)	0.191 4(3)	Fe(1)-C(31)	0.193 0(4)	Fe(1)-C(32)	0.193 4(3)
Fe(1)-N(6)	0.198 7(2)	Fe(1)-N(7)	0.198 7(2)	Fe(1)-N(10)	0.198 7(3)
Cu(1)-N(1)	0.198 6(2)	Cu(1)-N(2)	0.203 3(2)	Cu(1)-N(3)	0.219 2(2)
Cu(1)-N(4)	0.200 8(2)	Cu(1)-N(12)	0.197 7(2)	C(30)-N(12)	0.114 6(4)
C(31)-N(11)	0.115 3(5)	C(32)-N(13)	0.113 9(4)		
N(11)-C(31)-Fe(1)	176.6(3)	N(12)-C(30)-Fe(1)	174.8(3)	N(13)-C(32)-Fe(1)	177.8(3)
C(30)-Fe(1)-N(6)	178.67(1)	C(30)-Fe(1)-N(7)	91.18(1)	C(30)-Fe(1)-N(10)	91.12(1)
C(31)-Fe(1)-N(6)	94.26(1)	C(31)-Fe(1)-N(7)	89.91(1)	C(31)-Fe(1)-N(10)	177.34(1)
C(32)-Fe(1)-N(6)	90.20(1)	C(32)-Fe(1)-N(7)	177.86(1)	C(32)-Fe(1)-N(10)	93.24(1)
C(30)-N(12)-Cu(1)	159.2(2)	N(12)-Cu(1)-N(1)	94.31(1)	N(12)-Cu(1)-N(2)	157.40(1)
N(12)-Cu(1)-N(3)	105.12(1)	N(12)-Cu(1)-N(4)	88.52(1)		

2.2 Magnetic properties

The susceptibility variations in different temperatures were measured in 1.8~300 K. For complex **1**, at room temperature, the $\chi_M T$ value is 1.04 emu·K·mol⁻¹ (Fig.3), which is much higher than the spin-only value of 0.75 emu·K·mol⁻¹ ($g=2.0$) expected for one low-spin Fe^{III} ($S=1/2$) and one Cu^{II} ($S=1/2$) ions in the absence of any exchange coupling. This indicates that there exists significant spin-orbit coupling of the $^2T_{2g}$ ground term for Fe^{III} ions in **1**. Between 300 and 20 K, the $\chi_M T$ values exhibit a quasi linear dependence with T from 1.04 to 1.06 emu·K·mol⁻¹, and then it abruptly increases reaching a maximum of 1.52 emu·K·mol⁻¹ at 1.8 K, suggesting ferromagnetic coupling resulted from the orthogonal spin orbitals of the Fe^{III} (t_{2g}) and square pyramidal Cu^{II} (b_{1g}) centers. This magnetic nature could be further supported by the

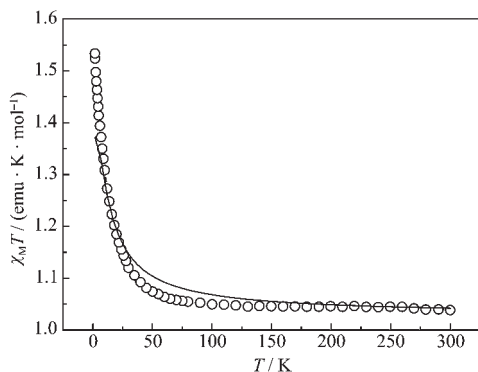


Fig.3 Temperature dependence of $\chi_M T$ product for **1** at 2000 Oe

apparently unsaturated magnetization value of $2.04N\beta$ mol⁻¹ under a 7 T magnetic field at 1.8 K, confirming an $S=1$ ground state for the cluster (Fig.4).

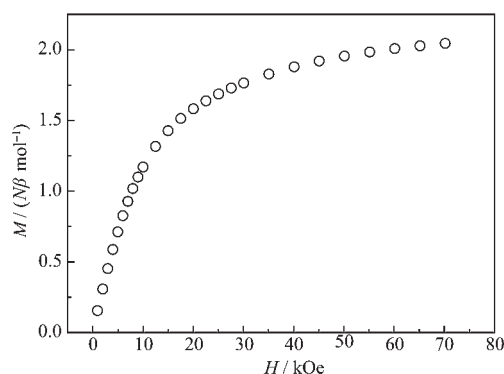


Fig.4 Field dependence of magnetization at 1.8 K for complex **1**

According to the structures, the exchange Hamiltonians of **1** can be described as: $H = -2JS_{Fe}S_{Cu}$. The best fitting results were obtained from 300 to 5 K: $g=2.34$, $J_1=5.52$ cm⁻¹, $R = \sum [(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2 / \sum (\chi_M T)_{obs}^2 = 7.4 \times 10^{-4}$.

The large Landé splitting can be ascribed to a combination of the orbital contributions from the low-spin Fe^{III} centers and individual factors of greater than 2 associated with the Cu^{II} centers. The magnitude of the exchange coupling is somewhat lower than the 15 cm⁻¹ estimated for face-centered cubic cluster $[Tp_8(H_2O)_6 Cu_6 Fe_8(CN)_{24}]^{4+}$ [8d] and the 8.5 cm⁻¹ observed for other single-molecule magnet $[Tp_2(Me_3tacn)_3 Cu_3 Fe_2(CN)_6]^{4+}$ [8g], but comparable to the 5 cm⁻¹ observed for other

molecules with Fe^{III}-CN-Cu^{II} linkages^[10].

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