第 24 卷第 6 期 无 机 化 学 学 报 Vol.24 No.6
2008 年 6 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 937~943

含大环[Ni([15]aneN$_5$)]$^{2+}$氰基桥联四核簇合物的合成、结构和磁性质

杨廷海 鲍松松 周 凯 李一志 郑丽敏*
(南京大学化学化工学院,配位化学研究所,南京 210093)

摘要:用 1,4,7,10,13-五氮十五烷(cpad)作为端基配体,合成了 2 个同构化合物[{Ni(cpad)}$_3$M(CN)$_6$]$_2$[M(CN)$_6$](ClO$_4$)$_3$·6H$_2$O (M=Cr^{3+}, **1**; Fe^{3+}, **2**),其中[M(CN)$_6$]$^{3-}$通过氰基桥联配位,4 个[Ni(cpad)]$^{2+}$阳离子形成四核簇[{Ni(cpad)}$_3$M(CN)$_6$]$^{3+}$,游离的[M(CN)$_6$]$^{3-}$和 ClO$_4^-$为平衡阴离子。晶体参数如下:**1**,三方晶系,$P\bar{3}c1$ 空间群,a=1.514 41(18) nm,c=3.080 7(6) nm,V=6.118 9(15) nm^3,Z=2;**2**,三方晶系,$P\bar{3}c1$ 空间群,a=1.497 62(17) nm,c=3.087 8(5) nm,V=5.997 6(14) nm^3,Z=2。变温磁化率显示在四核簇内氰基桥联的金属离子之间存在铁磁相互作用。

关键词:1,4,7,10,13-五氮十五烷;氰基桥联;四核簇;磁性质
中图分类号:O614.81$^+$3 **文献标识码**:A **文章编号**:1001-4861(2008)06-0937-07

Syntheses, Structures and Magnetic Properties of Cyanide-bridge Tetranuclear Clusters Containing [Ni([15]aneN$_5$-macrocycle)]$^{2+}$

YANG Ting-Hai BAO Song-Song ZHOU Kai LI Yi-Zhi ZHENG Li-Min*
(*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing* 210093)

Abstract: By using 1,4,7,10,13-pentaazacyclopentadecane (cpad) as terminal ligand, two isomorphous complexes [{Ni(cpad)}$_3$M(CN)$_6$]$_2$[M(CN)$_6$](ClO$_4$)$_3$·6H$_2$O (M=Cr^{3+}, **1**; Fe^{3+}, **2**) are obtained. Crystal data: **1**, trigonal, $P\bar{3}c1$, a=1.514 41(18) nm, c=3.080 7(6) nm, V=6.118 9(15) nm^3, Z=2; **2**, trigonal, $P\bar{3}c1$, a=1.497 62(17) nm, c=3.087 8(5) nm, V=5.997 6(14) nm^3, Z=2. Each compound contains a tetrahedron-shaped tetranuclear cluster [{Ni(cpad)}$_3$M(CN)$_6$]$^{3+}$, where [M(CN)$_6$]$^{3-}$ coordinates to three [Ni(cpad)]$^{2+}$ moieties through cyanide bridges. The positive charge of the cluster is balanced by both the discrete [M(CN)$_6$]$^{3-}$ and perchlorate anions. The temperature dependent magnetic susceptibility measurements reveal that dominant ferromagnetic interactions are mediated in both compounds, with very weak inter-molecular antiferromagnetic interactions. CCDC: 670129, **1**; 670130, **2**.

Key words: 1,4,7,10,13-pentaazacyclopentadecane; cyanide bridge; tetranuclear cluster; magnetic properties

0 Introduction

Polynuclear complexes with large spin ground states and high anisotropy have been of great interest in searching for new single molecule magnets (SMMs)[1~3]. Particular attention has been focused on discrete cyano-bridged clusters by using hexacyanometalate [M(CN)$_6$]$^{3-}$ (M=Cr, Fe) as precursors, combining with mononuclear complexes such as M^{II}(L)$^{m+}$ (M=Mn, Ni, Cu; L=diamine, polyamine or Schiff-base)[4~12]. Although the ground state of such clusters can be as high as 27/2 for CrMn$_6$ complex[5], most of them do not exhibit SMM behaviors due to the lack of sufficient anisotropy. Usually, the ground state anisotropy of a polynuclear cluster could originate

收稿日期:2008-02-26。收修改稿日期:2008-03-04。
国家自然科学资助项目(No.20325103,20631030),国家重点基础研究发展计划(No.2007CB925102)。
*通讯联系人。E-mail:lmzheng@nju.edu.cn;Fax:+86-25-83314502。
第一作者:杨廷海,男,29 岁,博士;研究方向:大环金属有机膦酸化学。

from the local anisotropy of single metallic ions, the exchange anisotropy and the overall structural anisotropy[6,13]. By introducing anisotropic $Mn^{Ⅲ}$ ion, Miyasaka et al reported tetranuclear $Mn^{Ⅲ}_3M^{Ⅲ}$ complexes [{Mn(salen)(EtOH)}$_3${M(CN)$_6$}] (M=Fe, Cr) which show strong frequency dependence and hysteresis on the field dependence of the magnetization[10]. Marvaud et al. found that the nuclearity and hence the structural anisotropy of these polynuclear compounds could be possibly controlled by changing either the stoichiometry, the nature of the terminal ligand, or the counterion[6].

1,4,7,10,13-pentaazacyclopentadecane (cpad) and its derivatives, as efficient macrocycle coordination ligands, have been widely studied in the fields of enzyme mimics[14], fluorescent probes[15], ion recognition[16,17], magnetic resonance imaging contrast agents and radiopharmaceuticals[18]. However, investigations on the structural chemistry of metal-cpad complexes are rather limited. Only a few reports, all represent mononuclear species, have been published including [Ni(cpad)ClO_4]ClO_4[19], [Ni(cpad)H_2O]$(ClO_4)(NO_3)$[20], [Mn(cpad)Cl_2][14a], [Mn(cpad)NO_3]NO_3[21], [Cu(cpad)]$(ClO_4)_2$[22], [Zn(cpad)]$(ClO_4)_2$[23], [Cd(cpad)]Cl_2, [Cd(L)NO_3]NO_3[24] and [Ln(cpad)NO_3]$\cdot CH_3CN$[25].

In this paper, we employ 1,4,7,10,13-pentaazacyclopentadecane (cpad) as the terminal ligand in order to affect the structural anisotropy of the cyanide-bridged clusters. Two new compounds [{Ni(cpad)}$_3$M(CN)$_6$]$_2$[Cr(CN)$_6$]$(ClO_4)_3\cdot 6H_2O$ (**1**) and [{Ni(cpad)}$_3$Fe(CN)$_6$]$_2$[Fe(CN)$_6$]$(ClO_4)_3\cdot 6H_2O$ (**2**) with tetranuclear structures are obtained. Their magnetic properties are studied.

1 Experimental

1.1 Material and physical measurements

The 1,4,7,10,13-pentaazacyclopentadecane was prepared according to the literature[26]. All the other starting materials were of reagent grade quality and purchased from commercial sources without further purification. Elemental analyses were performed on PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pallets. Thermal analyses were conducted in nitrogen with a heating rate of 20 ℃·min^{-1} on a Perkin Elmer Pyris 1 TGA instrument. The magnetic susceptibility measurements for **1** and **2** were carried out on polycrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer.

1.2 Syntheses

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared and handled with care.

1.2.1 Synthesis of [{Ni(cpad)}$_3$Cr(CN)$_6$]$_2$[Cr(CN)$_6$]$(ClO_4)_3\cdot 6H_2O$ (**1**)

To a solution of cpad (0.129 g, 0.6 mmol) in water (10 mL) was added nickel perchlorate (0.219 g, 0.6 mmol) dissolved in 5 mL of H_2O. The solution was heated and stirred for 10 min, then 0.065 g (0.2 mmol) of K_3[Cr(CN)$_6$] dissolved in 10 mL water was added dropwise, resulting in a change from purple to brown. After additional stirring of 20 min, the filtrate was evaporated for a week and brown block crystals were collected. Yield: 0.0257g (9.6% based on cpad). Anal. Found (calcd) for $C_{78}H_{162}Cl_3Cr_3N_{48}Ni_6O_{18}$ (%): C, 35.02(35.02); H, 6.14(6.10); N, 25.17(25.13). IR (KBr, cm^{-1}): 3 594w, 3 420m, 3 333w, 3 277s, 3 220s, 2 944m, 2 882m, 2 158 w, 2 126m, 1 619m, 1 476s, 1 455w, 1 341m, 12 84w, 1 209w, 1 091s, 1 023w, 966s, 914m, 884w, 848w, 825 w, 804 w, 785w, 623s, 534w, 456s.

1.2.2 Synthesis of [{Ni(cpad)}$_3$Cr(CN)$_6$]$_2$[Fe(CN)$_6$]$(ClO_4)_3\cdot 6H_2O$ (**2**)

This compound was prepared by a similar experimental procedure to that of **1**, except that K_3[Fe(CN)$_6$] instead of K_3[Cr(CN)$_6$] was used. Yield: 0.015 8 g (5.9% based on cpad). Anal. Found (calcd) for $C_{78}H_{162}Cl_3Cr_3N_{48}Ni_6O_{18}$ (%): C, 34.91 (34.87); H, 6.10 (6.07); N, 25.01 (25.02). IR (KBr, cm^{-1}): 3 416m, 3 330w, 3 275s, 3 210 s, 2 940m, 2 879m, 2 149w, 2 114m, 2 026w, 1 621m, 1 475 s, 1 456w, 1 341m, 1 285w, 1 209w, 1 092s, 1 023w, 963 s, 914m, 884w, 848w, 826w, 805w, 785w, 624s, 537w.

1.3 Crystal structure determination

Single crystals of dimensions 0.30 mm × 0.26 mm × 0.24 mm for **1** and 0.40 mm × 0.32 mm × 0.26 mm for **2** were selected for indexing and intensity data collection at 298 K on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized

Mo $K\alpha$ radiation (λ=0.071 073 nm). Numbers of measured and observed reflections [$I>2\sigma(I)$] are 22 509 and 4 035 (R_{int}=0.051 3) for **1** and 20 352 and 3 947 (R_{int}=0.054 2) for **2**, respectively. The data were integrated using the Siemens SAINT program[27]. The structures were solved by direct method and refined on F^2 by full matrix least-squares using SHELXTL[28]. All the non-hydrogen atoms were refined anisotropically. All H atoms were refined isotropically. Crystallographic and refinement details are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 670129, **1**; 670130, **2**.

Table 1　Crystallographic data for 1 and 2

Compound	**1**	**2**
Empirical fomula	$C_{78}H_{162}Cl_3Cr_3N_{48}Ni_6O_{18}$	$C_{78}H_{162}Cl_3Fe_3N_{48}Ni_6O_{18}$
M	2675.17	2686.72
Crystal system	Trigonal	Trigonal
Space group	$P\bar{3}c1$	$P\bar{3}c1$
a / nm	1.514 4(2)	1.497 6(2)
c / nm	3.080 7(6)	3.087 8(5)
V / nm^3	6.118 9(15)	5.997 6(14)
Z	2	2
D_c / (g·cm^{-3})	1.452	1.488
F(000)	2 802	2 814
μ / mm^{-1}	1.298	1.415
Goodness-of-fit on F^2	1.048	1.099
R_1, wR_2 [$I>2\sigma(I)$][a]	0.041 9, 0.081 9	0.048 1, 0.090 3
R_1, wR_2 (All data)[a]	0.065 9, 0.086 5	0.082 1, 0.094 0
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	338, –461	587, 906

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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

	1	**2**
M(1)-C(11)	0.206 3(3)	0.196 7(3)
C(11)-N(6)	0.115 2(4)	0.112 0(4)
M(1)-C(12)	0.207 0(3)	0.198 8(4)
C(12)-N(7)	0.114 0(4)	0.111 0(4)
Ni(1)-N(1)	0.210 9(2)	0.211 2(3)
Ni(1)-N(2)	0.216 1(2)	0.216 3(3)
Ni(1)-N(3)	0.213 3(3)	0.216 8(3)
Ni(1)-N(4)	0.207 9(3)	0.207 2(3)
Ni(1)-N(5)	0.207 9(2)	0.209 9(3)
Ni(1)-N(6)	0.205 6(2)	0.206 3(3)
C(11)-M(1)-C(12)	88.9(1)	88.0(1)
C(11)-M(1)-C(11A)	90.8(1)	90.5(1)
C(12)-M(1)-C(12B)	89.3(1)	92.0(1)
C(11)-M(1)-C(12A)	178.2(1)	178.6(1)
N(6)-Ni(1)-N(5)	95.4(1)	96.5(1)
N(6)-Ni(1)-N(4)	90.1(1)	88.9(1)
N(5)-Ni(1)-N(4)	82.9(1)	80.1(1)

Continued Table 2

N(6)-Ni(1)-N(1)	86.0(1)	87.4(1)
N(5)-Ni(1)-N(1)	82.6(1)	83.9(1)
N(4)-Ni(1)-N(1)	164.6(1)	163.1(1)
N(6)-Ni(1)-N(3)	90.8(1)	89.2(1)
N(5)-Ni(1)-N(3)	163.6(1)	161.0(1)
N(4)-Ni(1)-N(3)	81.9(1)	82.0(1)
N(1)-Ni(1)-N(3)	113.1(1)	114.5(1)
N(6)-Ni(1)-N(2)	161.5(1)	160.5(1)
N(5)-Ni(1)-N(2)	97.5(1)	99.5(1)
N(4)-Ni(1)-N(2)	104.6(1)	104.8(1)
N(1)-Ni(1)-N(2)	82.6(1)	83.2(1)
N(3)-Ni(1)-N(2)	80.4(1)	79.3(1)

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

2 Results and discussion

2.1 Syntheses and preliminary characterization

Complex **1** was initially formed in an aqueous solution containing a 1∶6 mixture of $[Cr(CN)_6]^{3-}$ and $[Ni(cpad)]^{2+}$, with the expect to yield a heptanuclear complex. However, crystallography analysis revealed that the Cr∶Ni molar ratio is 1∶2 in the product. The experiment was thus repeated by using the same starting materials with Cr∶Ni molar ratio of 1∶1~5. Same compound was obtained and a highest yield (12.4%) was achieved in the case of Cr∶Ni=1∶2. Compound **2** can be prepared by following a similar experimental procedure.

Fig.1 gives the IR spectra of compounds **1** and **2**. It is clear that both compounds show two sharp ν(CN) bands in the region of 2 110~2 160 cm^{-1}. The band appearing at the higher wavenumber (2 158 cm^{-1} for **1**, 2 149 cm^{-1} for **2**) is attributed to the stretching vibration of the bridging CN. While the band appearing at the lower wavenumber (2 126 cm^{-1} for **1**, 2 114 cm^{-1} for **2**) corresponds to the stretching vibration of the terminal CN ligands[29].

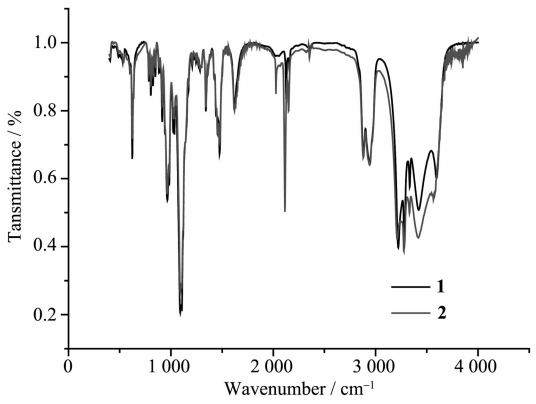
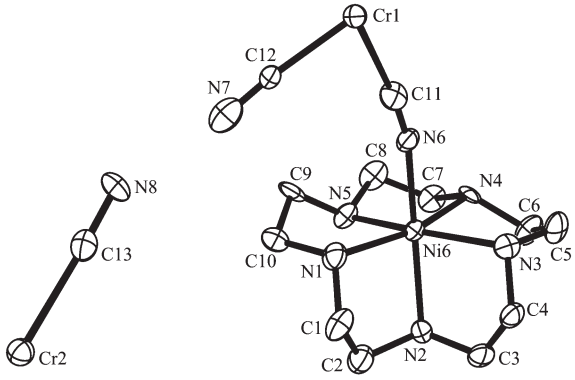


Fig.1 IR spectra of compounds **1** and **2**

2.2 Crystal structures

Compounds **1** and **2** are isomorphous. Both crystallize in trigonal space group $P\bar{3}c1$. Fig.2 shows the building unit of compound **1**. The asymmetric unit consists of one tetranuclear cation that has 1/3 occupancy, one free hexacyanochromate anion that has 1/6 occupancy, two perchlorates that have 1/3 occupancy and 1/6 occupancy respectively and two lattice water molecules that have 3/5 occupancy and 2/5 occupancy respectively. Hence the chemical formula of compound **1** is $\{[Ni(cpad)]_3Cr(CN)_6\}_2[Cr(CN)_6](ClO_4)_3\cdot 6H_2O$.

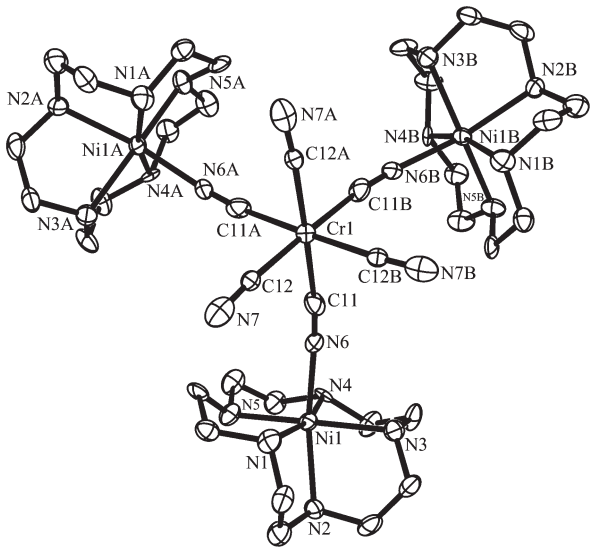


All H atoms, water molecules and perchlorate anions are omitted for clarity

Fig.2 Building unit of **1** (30% probability)

Within the tetranuclear cluster, the $[Cr(CN)_6]^{3-}$ serves as a meridional-tridentae building block to bind three $[Ni(capd)]^{2+}$ unit through three bridging CN lig-

ands (Fig.3). The cluster has a near C3 symmetry with the Cr atom residing on the three-fold rotation axis and three Ni atoms locating in general positions which are symmetrically related to each other. The presence of both bridging (C11N6) and terminal (C12N7) cyanide ligands within the cluster is reflected by their structural parameters with the Cr1-C11 bond length 0.206 3(3) nm shorter than that of Cr1-C12 0.207 0(3) nm while the C11N6 distance 0.115 2(4) nm longer than that of C12N7 0.114 0(4) nm. Each Ni atom has a distorted octahedral environment. Five of the six coordination sites are filled with nitrogen atoms (N1, N2, N3, N4, N5) from cpad macrocycle ligand. The remaining position is occupied by the N6 atom from the hexacyanochromate. The Ni-N bond lengths fall in the range 0.205 6(2)~0.216 1(2) nm, similar to those in compounds [Ni(L)(H_2O)](ClO_4)(NO_3) 0.206 9(4)~0.217 0(4) nm[20].



All H atoms are omitted for clarity

Fig.3　View of the tetranuclear cation in **1** (30% probability ellipsoids)

The structure of compound **2** is identical to that of **1** except that the $Cr^{Ⅲ}$ ion in **1** is substituted by $Fe^{Ⅲ}$ in **2**.

Marvaud et al. found that the reactions of $[Cr(CN)_6]^{3-}$ with $Ni(L)^{2+}$ (L=polyamine) under similar experimental conditions result in the formation of a $CrNi_6$ heptanuclear complex when L is tetren, a $CrNi_2$ trinuclear complexes when L is dienpy$_2$, and a $CrNi_3$ tetranuclear entities when L is dipropy$_2$[6,7]. The formation of tetranuclear clusters in compounds **1** and **2** could be related to the use of a particular terminal ligand, e.g. 1,4,7,10,13-pentaazacyclopentadecane.

It is worth noted that the other related tetranuclear compounds based on $[M(CN)_6]^{3-}$ is still limited in number. These include [{Mn(salen)(EtOH)}$_3${M(CN)$_6$}] (M=Fe, **1**; Cr, ***2***)[10] and [{$Fe^{Ⅲ}$(saldpt)}$_3${Cr(CN)$_6$}], {(saldpt)H_2=*N*,*N*′-bis(1-hydroxy-2-benzylidene)-1,7-diamino-4-azaheptane}[30] with T-hape structures, and [BztacnCr(CNNi(*i*-Prtacn)Cl)$_3$]$Cl_3\cdot 10H_2O$ (Bztacn=1,4,7-trisbenzyl-1,4,7-triazacyclononane, *i*-Prtacn=1,4,7-trisisopropyl-1,4,7-triazacyclononane)[31] and [{Cu(edma)}$_3$Cr(CN)$_6$], (edma =ethylenediaminemonoacetate)[32] with tetrahedron-shaped configuration.

2.3　Magnetic properties

The temperature dependent molar susceptibilities of compounds **1** and **2** have been measured in a magnetic field of 100 Oe in the temperature range 1.8~300 K. The effective magnetic moments at 300 K, calculated from $\mu_{eff}=2.828\ (\chi_M T)^{1/2}$, are 9.72 μ_B per Ni_6Cr_3 for **1** and 8.34 μ_B per Ni_6Fe_3 for **2**, agree well with the spin-only values of 9.64 μ_B for **1** [6(S_{Ni}=1), 3(S_{Cr}=3/2), g=2.0] and 7.55 μ_B for **2** [6(S_{Ni}=1), 3(S_{Fe}=1/2), g=2.0], respectively.

Fig.4 shows the $\chi_M T$ vs T plot of compound **1**. Clearly, the $\chi_M T$ value increases with decreasing temperature until reaching a maximum of 24.54 $cm^3\cdot K\cdot mol^{-1}$ at 14 K, corresponding to a ferromagnetic interaction between $Cr^{Ⅲ}$ and $Ni^{Ⅱ}$ as expected from the orbital orthogonal theory[33]. Thus the ground state of compound **1** is S=21/2. Below 14 K, the $\chi_M T$ value decline monotonously to 12.08 $cm^3\cdot K\cdot mol^{-1}$ at 1.8 K, attributed to inter-molecule interactions and/or zero-field splitting of the ground state. Assuming that the zero-field splitting

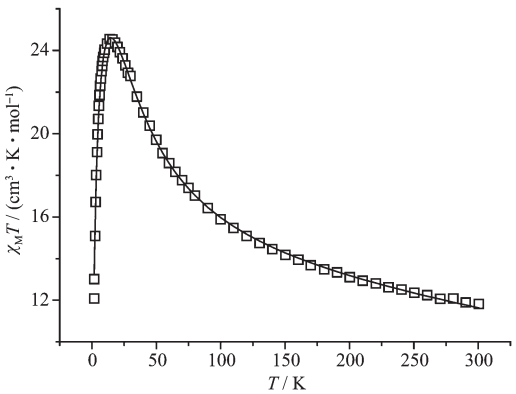


Fig.4　Plot of $\chi_M T$ (□) vs T for compound **1**

of the ground state is very small, the magnetic data were thus analyzed by an equation derived for a $CrNi_3$ tetranuclear cluster using the following Hamiltonian[34]:

$$\hat{H}=-J\hat{S}_{Cr}(\hat{S}_{Ni1}+\hat{S}_{Ni2}+\hat{S}_{Ni3})+\beta[g_{Cr}\hat{S}_{Cr}+g_{Ni}(\hat{S}_{Ni1}+\hat{S}_{Ni2}+\hat{S}_{Ni3})]\cdot\vec{H} \quad (1)$$

The equation become

$$\chi''=\frac{Ng^2\beta^2}{4kT}\frac{A}{B} \quad (2)$$

$$A=165+168e^{3x}+105e^{6x}+94e^{9x}+70e^{10x}+30e^{11x}+3e^{14x}+20e^{15x}+35e^{16x}+2e^{18x}+10e^{21x}$$

$$B=5+8e^{3x}+9e^{6x}+6e^{9x}+6e^{10x}+6e^{11x}+3e^{14x}+4e^{15x}+3e^{16x}+2e^{18x}+2e^{21x}$$

where N, g, k and β have their usual meanings, $x=-J/(2kT)$. By including the paramagnetic contribution of the discrete $[Cr(CN)_6]^{3-}$, the diamagnetic contribution (N_α) and the inter-molecular interaction (zJ'), the overall equation of χ_M can be obtained:

$$\chi'=2\chi''+\frac{5Ng^2\beta^2}{4kT}+N_\alpha \quad (3)$$

$$\chi_M=\frac{\chi'}{1-\frac{zJ'}{Ng^2\beta^2}\chi'} \quad (4)$$

A best fit, shown as the solid line in Fig.4, can be obtained in the temperature range 3~300 K with parameters g=2.13, J=15.46 cm^{-1}, N_α=−0.009 239 $cm^3\cdot mol^{-1}$ and zJ'=−0.068 cm^{-1}. The J value is comparable to that for compound $[BztacnCr(CNNi(i\text{-}Prtacn)Cl)_3]Cl_3\cdot 10H_2O$ (20 cm^{-1})[31]. Field dependent magnetization, measured at 1.8 K, confirms that the ground state of compound **1** is S=21/2 (supporting information).

Compound **2** shows a similar magnetic behavior (Fig.5). In this case, the $\chi_M T$ value increases upon cooling and approaches to a maximum of 11.45 $cm^3\cdot K\cdot mol^{-1}$ at 5.5 K, corresponding to a ferromagnetic interaction between low-spin Fe^{III} and Ni^{II}. Thus the ground state of compound **2** is S=7. The decrease of $\chi_M T$ value below 5.5 K is again attributed to inter-molecule interactions and/or zero-field splitting of the ground state. Assuming that the zero-field splitting of the ground state can be neglected, the theoretical equations can be derived as below:

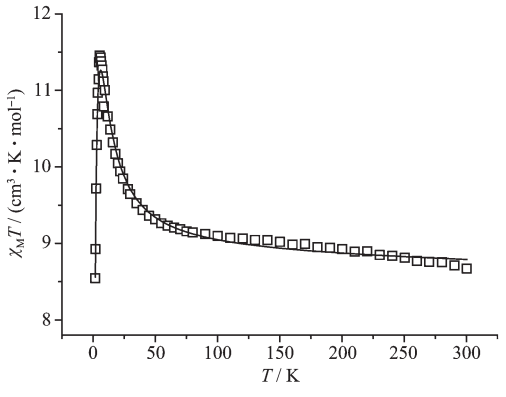


Fig.5 Plots of $\chi_M T$ (□) vs T for compound **2**

$$\hat{H}=-J\hat{S}_{Fe}(\hat{S}_{Ni1}+\hat{S}_{Ni2}+\hat{S}_{Ni3})+\beta[g_{Fe}\hat{S}_{Fe}+g_{Ni}(\hat{S}_{Ni1}+\hat{S}_{Ni2}+\hat{S}_{Ni3})]\cdot\vec{H} \quad (5)$$

$$\chi''=\frac{Ng^2\beta^2}{4kT}\frac{A'}{B'} \quad (6)$$

$$A'=84+70e^{x}+30e^{2x}+e^{3x}+3e^{5x}+20e^{6x}+35e^{7x}$$

$$B'=4+6e^{x}+6e^{2x}+e^{3x}+3e^{5x}+4e^{6x}+3e^{7x} \quad (x=-J/(2kT))$$

$$\chi'=2\chi''+\frac{Ng^2\beta^2}{4kT}+N_\alpha \quad (7)$$

The best fit of the magnetic data in the whole temperature range by using equations (**7**) and (**4**), which is shown as the solid line in Fig.5, results in parameters g=2.22, J=6.58 cm^{-1}, N_α=−0.0 003 914 $cm^3\cdot mol^{-1}$ and zJ'=−0.11 cm^{-1}. The J value is comparable to that for $[Ni(bpy)_2(H_2O)]\{[Ni(bpy)_2]_2[Fe(CN)_6]_2\}\cdot 12H_2O$, ($J$=6.6 cm^{-1})[35]. Preliminary investigation on the temperature dependent ac magnetic measurements of compound **2** reveals that no frequency dependent of the ac signals is observed (supporting information), excluding the possibility as a single molecule magnet.

3 Conclusions

Two new tetranuclear complexes $[\{Ni(cpad)\}_3M(CN)_6]_2[Cr(CN)_6](ClO_4)_3\cdot 6H_2O$ (**1**) and $[\{Ni(cpad)\}_3Fe(CN)_6]_2[M(CN)_6](ClO_4)_3\cdot 6H_2O$ (**2**) based on cpad are reported in this paper. Both show dominant ferromagnetic interactions with the coupling constants (J) being 15.46 and 6.58 cm^{-1} for compounds **1** and **2**, respectively.

References:

[1] Gatteschi D, Sessoli R. *Angew. Chem. Int. Ed.*, **2003**,**42**:268~297

[2] Aromí G, Brechin E K. *Struct. Bonding*, **2006**,**122**:1~4

[3] Beltran L C, Long J R. *Acc. Chem. Res.*, **2005**,**38**:325~334

[4] Langenberg K V, Batten S R, Berry K J, et al. *Inorg. Chem.*, **1997**,**36**:5006~5015

[5] Parker R J, Spiccia L, Berry K J, et al. *Chem. Commun.*, **2001**: 333~334

[6] Marvaud V, Decroix C, Scuiller A, et al. *Chem. Eur. J.*, **2003**, **9**:1692~1705

[7] Marvaud V, Decroix C, Scuiller A, et al. *Chem. Eur. J.*, **2003**, **9**:1677~1691

[8] Bonadio F, Senna M C, Ensling J, et al. *Inorg. Chem.*, **2005**, **44**:969~978

[9] Berlinguette C P, Dunbar K R. *Chem. Commun.*, **2005**:2451~2453

[10]Hitoshi M, Hitomi T, Tomokura M, et al. *Inorg. Chem.*, **2005**, **44**:5969~5971

[11]Rebilly J N, Catala L, Rivière E, et al. *Chem. Commun.*, **2006**:735~737

[12]Kou H Z, Zhou B C. *Eur. J. Inorg. Chem.*, **2004**:401~408

[13]Bencini A, Gatteschi D. *EPR of Exchange-Coupled Systems*, Springer, Berlin, **1990**.

[14](a)Riley D P, Weiss R H. *J. Am. Chem. Soc.*, **1994**,**116**:387~388

(b)Riley D P, Henke S L, Lennon P J, et al. *Inorg. Chem.*, **1996**,**35**:5213~5231

(c)Dees A, Zahl A, Puchta R, et al. *Inorg. Chem.*, **2007**,**46**: 2459~2470

[15]Akkaya E U, Huston M E, Czarnik A W. *J. Am. Chem. Soc.*, **1990**,**112**:3590~3593

[16]Kimura E, Kodama M, Yatsunami T. *J. Am. Chem. Soc.*, **1982**,**104**:3182~3187

[17]Agata R D, Grasso G, Iacono G, et al. *Org. Biomol. Chem.*, **2006**,**4**:610~612

[18]Kodama M, Koike T, Mahatma A B, et al. *Inorg. Chem.*, **1991**,**30**:1270~1273

[19]Lu T H, Lan W J, Chung C S. *Acta Crystallogr. Sect. C*, **1993**,**49**:961~963

[20]Osvath P, Weatherburn D C, Robinson W T. *Transition. Met. Chem.*, **1991**,**16**:344~346

[21]Riley D P, Lennon P J, Neuman W L, et al. *J. Am. Chem. Soc.*, **1997**,**119**:6522~6528

[22]Boeyens J C A, Oosthuizen E L. *J. Crystallogr. Spectrosc. Res.*, **1992**,**22**:3~7

[23]Notni J, Gorls H, Anders E. *Eur. J. Inorg. Chem.*, **2006**:1444~1455

[24]Franklin G W, Riley D P, Neumann W L. *Coord. Chem. Rev.*, **1998**,**174**:133~146

[25]Li D K, Gan X M, Tian M Y, et al. *Polyhedron.*, **1997**,**16**: 3991~3995

[26]Alessandro B, Luigi F, Antonio P. *Inorg. Chem.*, **1981**,**20**: 2544~2549

[27]*SANIT, Program for Data Extraction and Reduction, Siemens Analytical X-ray Instruments*, Madison, WI 53719, **1994**~**1996**.

[28]*SHELXTL* (*version* 5.0) *Reference Manual, Siemens Industrial Automation*, Analytical Instrumentation, Madison, WI, **1995**.

[29]Kou H Z, Zhou B C, Gao S, et al. *Inorg. Chem.*, **2003**,**42**: 5604~5611

[30]Radovan H, Roman B, Milan G, et al. *Inorg. Chem.*, **2004**,**43**: 4103~4105

[31]Rebilly J N, Catala L, Riviere E, et al. *Inorg. Chem.*, **2005**,**44**: 8194~8196

[32]Fu D G, Chen J, Tan X S, et al. *Inorg. Chem.*, **1997**,**36**:220~225

[33]Kahn O. *Molecular Magnetism*. New York: VCH Publishers, **1993**.

[34]Pei Y, Journaux Y, Kahn O. *Inorg. Chem.*, **1989**,**28**:100~103

[35]Berlinguette C P, Galan-Mascaros J R, Dunbar K R. *Inorg. Chem.*, **2003**,**42**:3416~3422