含樟脑衍生物氰基桥联双金属配合物的合成、结构及磁性质

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摘要: 采用樟脑衍生物为配体,分别合成了氰基桥联 Cu(Ⅱ)-Fe(Ⅲ)-Cu(Ⅱ)三核配合物[{Cu(*D*,*L*-La)$_2$}$_2$Fe(CN)$_6$](ClO$_4$) (**1**)和 Mn(Ⅲ)-Fe(Ⅲ)双核配合物[Mn(*D*,*L*-Lb)(DMF)(Tp)Fe(CN)$_3$]·(H$_2$O)$_6$ (**2**)。晶体结构分析表明,化合物 **1** 中 Cu(Ⅱ)离子处于五配位的配位环境,分别和 1 个 *D*-La,1 个 *L*-La 及[Fe(CN)$_6$]$^{3-}$中的 1 个氰基配位,2 个 Cu(Ⅱ)离子通过[Fe(CN)$_6$]$^{3-}$桥联。通过分子间氢键作用,化合物 **1** 形成二维超分子网络结构。化合物 **2** 中,[(Tp)Fe(CN)$_3$]$^-$通过其中的 1 个氰基与[Mn(*D*,*L*-Lb)]$^+$桥联,其中 Mn(Ⅲ)离子为六配位,分别和四齿配体 Lb 的 2 个氧原子和 2 个氮原子、DMF 的 1 个氧原子及[(Tp)Fe(CN)$_3$]$^-$中的氰基氮原子配位。磁性研究表明,在化合物 **1** 中,Cu(Ⅱ)离子与 Fe(Ⅲ)离子之间表现出铁磁相互作用,用哈密顿函数$\hat{H}=-2J(\hat{S}_1\cdot\hat{S}_2+\hat{S}_2\cdot\hat{S}_3)$对其$\chi_M T$-*T* 曲线进行拟合,得到 **1** 的朗日因子 *g* 为 2.190,交换常数 *J* 为 0.55 cm^{-1}。

关键词: 樟脑衍生物; 氰基桥联; 异核配合物; 晶体结构; 磁性质
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Synthesis, Crystal Structures, and Magnetic Properties of Two Cyano-bridged Heterobimetallic Complexes with Camphor Derivative Ligands

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Abstract: A cyano-bridged trinuclear Cu$^{\text{Ⅱ}}_2$Fe$^{\text{Ⅲ}}$ complex [{Cu(*D*,*L*-La)$_2$}$_2$Fe(CN)$_6$](ClO$_4$) (**1**) (La=1,2,2-trimethylcyclopentane-1,3-diamine) and a cyano-bridged binuclear Mn$^{\text{Ⅲ}}$-Fe$^{\text{Ⅲ}}$ complex [Mn(*D*,*L*-Lb)(DMF)(Tp)Fe(CN)$_3$]·(H$_2$O)$_6$ (**2**) (Lb=*cis*-*N*,*N*′-(2-Hydroxybenzylidene)-1,2,2-trimethylcyclopenta-1,3-diamine) have been prepared and characterized. X-ray crystal structure analysis for complex **1** reveals that the copper ion is penta-coordinated by a *D*- and a *L*-diamine ligand, and two copper ions are bridge-connected by two cyanides from [Fe(CN)$_6$]$^{3-}$ in axial position. It shows a two-dimensional supramolecular network through hydrogen-bonding interaction. In complex **2**, the manganese ion is six-coordinated by two oxygen atoms and two nitrogen atoms from a quadridentate ligand Lb, as well as one oxygen atom from DMF and one cyanide nitrogen atom from [(Tp)Fe(CN)$_3$]$^-$ in axial positions. Magnetic study shows intramolecular ferromagnetic interactions in complex **1**. The best-fit for $\chi_M T$ vs *T* using the model, $\hat{H}=-2J(\hat{S}_1\cdot\hat{S}_2+\hat{S}_2\cdot\hat{S}_3)$, leads to the parameters *J*=0.551 cm^{-1} and *g*=2.190. CCDC: 626440, **1**; 626439, **2**.

Key words: camphor derivatives; cyanide bridging; heterobimetallic complexes; crystal structures; magnetic properties

Cyanide is a fascinating bridging ligand in the research for magnetic materials due to its convenience to design the structure and conformation of the molecules and the efficiency to tune the magnetic interaction[1]. To understand the magneto-structural correlation, intensive effort has been devoted to the

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synthesis of lower-dimensional heterobimetallic compounds. Recently, the approach of introduction of capping ligands as blocking groups into metal-cyanide systems to preclude the formation of multi-dimensional arrays has been developed[2]. If the transition metal ions toward hexacyanometallates are partially blocked with polydentate ligands, some interesting lower-dimensional heterobimetallic compounds with different topologies and structures have been obtained[1d,3,4]. An alternative synthetic strategy is to use the building blocks of modified cyanometallates $[M(L)_y(CN)_x]^{(x-m)-}$ where L is an organic polydentate ligand, such as phen, bipy[5], tacn and its derivatives[6], bpca[7], or Tp[8]. On the basis of those building blocks, many heterobimetallic complexes exhibiting interesting magnetic properties were synthesized, including single-molecule magnets[9] and single-chain magnets[10].

As part of an effort to develop new examples of lower-dimensional cyano-bridged heterobimetallic magnetic complexes, we chose camphor and its derivatives as starting materials. The introduction of these multidentate capping ligands will efficiently inhibit the growth of an extended solid. In this paper, a trinuclear complex $[\{Cu(D,L\text{-La})_2\}_2Fe(CN)_6](ClO_4)$ (**1**) and a binuclear complex $[Mn(D,L\text{-Lb})(DMF)(Tp)Fe(CN)_3]\cdot(H_2O)_6$ (**2**) with the racemic camphor derivative ligands, *D*,*L*-La (La=1,2,2-trimethylcyclopentane-1,3-diamine) and *D*,*L*-Lb (Lb=*cis*-*N*,*N*′-(2-Hydroxybenzylidene)-1,2,2-trimethylcyclopenta-1,3-diamine), were prepared and characterized.

1 Experimental

1.1 Materials and measurements

All solvents and chemicals were of analytical grade and used without further purification. Ligands *D*,*L*-1,2,2-trimethylcyclopentane-1,3-diamine and *D*,*L*-*cis*-*N*,*N*′ -(2-Hydroxybenzylidene)-1,2,2-trimethylcyclopenta-1,3-diamine were prepared according to the literature using camphor as the starting material via a multi-step synthesis method[11]. $[Mn(D,L\text{-Lb})\cdot H_2O]ClO_4$ was obtained according to the literature[12]. $[Bu_4N][(Tp)Fe(CN)_3]$ was prepared by modified literature methods[8a].

The solid infrared spectra (IR) were obtained from a Bruker IFS66V vacuum-type FTIP spectrophotometer using KBr pellets. Variable-temperature magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer. The magnetic field is 2 kOe.

1.2 Preparation of complex 1

D,*L*-1,2,2-trimethylcyclopentane-1,3-diamine(28.4 mg, 0.20 mmol), $Cu(ClO_4)_2$ (26.3 mg, 0.10 mmol) were dissolved in 10 mL of water/methanol (3∶1), and a blue solution was obtained. Then it was added dropwise a solution of $[Bu_4N]_3Fe(CN)_6$ (47.0 mg, 0.05 mmol) in 10 mL of H_2O. The color of the mixture changed from blue to green. Black-green plate-shape crystals of **1** suitable for X-ray diffraction measurement were obtained from the mixture solution by evaporation at room temperature for about a month. Yield: 75%. IR (KBr, cm^{-1}): 3 441(m), 3 300(s), 3 233 (s), 2 103(s), 2 026(s), 1 467(m), 1 398(s), 1 374(s), 1 086(m), 1 040(s), 682(s) and 623(s).

1.3 Preparation of complex 2

$[Bu_4N][(Tp)Fe(CN)_3]$ (59.1 mg, 0.10 mmol) was dissolved in 5 mL of acetonitrile, and it was added to a solution of $[Mn(D,L\text{-Lb})\cdot H_2O]ClO_4$ in 10 mL of acetonitrile. The reaction mixture was left overnight and black precipitate was collected. The precipitate was dissolved in 4 mL of DMF and a green solution was obtained. Ether vapor was diffused into this green solution and brown diamond-shape crystals suitable for X-ray diffraction measurement were collected after about one week. Yield: 82%. IR (KBr, cm^{-1}): 3 456 (m), 3 140(s), 3 104(s), 2 156(s), 2 118(s), 1 502(s), 1 408 (s), 1 315(s), 1 214(s), 1 117(s), 1 049(s), 763(s), 709(s), 659(s), 610(s).

1.4 Crystal structural analyses

The data of complexes **1** and **2** were collected on a Bruker SMART CCD area detector diffractometer at 298 K using graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). Intensity data were collected using the φ-ω scan mode in the range of $1.9° \leqslant \theta \leqslant 52.0°$ for complex **1** and $1.7° \leqslant \theta \leqslant 52.0°$ for complex **2**. Empirical absorption corrections for the intensity data were applied by SADABS program. The structures were solved by direct method, and refined by full-

matrix least-squares based on F^2. All non-hydrogen atoms in structure were refined with anisotropic displacement parameters. All hydrogen atoms were theoretically added. A summary of crystallographic data and refinement parameters is given in Table 1.

CCDC: 626440, **1**; 626439, **2**.

Table 1　Crystal data and structure refinement for complexes 1 and 2

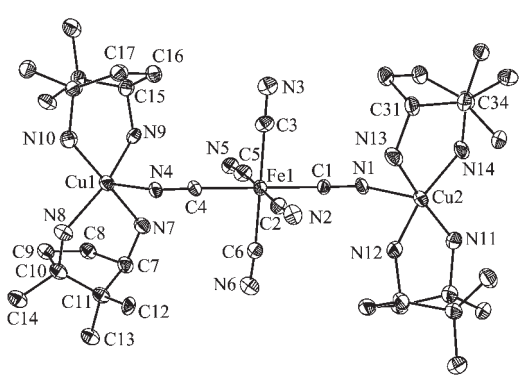
Complex	**1**	**2**
Empirical formula	$C_{38}H_{72}N_{14}O_4ClCu_2Fe$	$C_{74}H_{90}N_{24}O_{11}B_2Fe_2Mn_2$
M_r	1007.48	1734.90
T / K	293(2)	293(2)
λ (Mo $K\alpha$) / nm	0.0710 73	0.0710 73
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a / nm	1.556 1(4)	2.864 2(4)
b / nm	1.480 2(3)	1.306 4(2)
c / nm	2.219 8(5)	2.653 0(4)
β / (°)	109.152(4)	112.352(3)
V / nm	4.830 0(19)	9.181(2)
Z	4	4
D_c / (g·cm^{-3})	1.385	1.255
μ / mm^{-1}	1.277	0.643
F(000)	2 124	3 608
Crystal size / nm	0.24 × 0.26 × 0.32	0.24 × 0.26 × 0.32
θ range for data collection / (°)	1.9~26.0	1.7~26.0
Reflns. collected / unique	25 507 / 9 484 (R_{int}=0.041)	24 350 / 8 990 (R_{int}=0.039)
Observed reflns [$I>2\sigma(I)$]	5 960	6 395
Parameters refined	553	561
Goodness-of-fit on F^2	0.991	1.079
Final R indices [$I>2\sigma(I)$]	R_1=0.046 3, wR_2=0.095 3	R_1=0.056 7, wR_2=0.115 2
Maximum peak / (e·nm^{-3})	270	220
Minimum peak / (e·nm^{-3})	−650	−280

2　Results and discussion

2.1　Crystal structures

Selected bond lengths and angles for complexes **1** and **2** are complied in Tables 2 and 3.

The crystal structure indicates that compound **1** consists of discrete trinuclear $Cu^{Ⅱ}_2Fe^{Ⅲ}$ cations which are countered by perchlorate anions, as shown in Fig. 1. Both copper ions adopt a square pyramidal coordination geometry with four nitrogen atoms from a *D*- and a *L*-diamine ligand, as well as one cyanide nitrogen atom from $[Fe(CN)_6]^{3-}$ in the axial direction. The Cu-N_{CN} distances (0.232 3(2)~0.232 9(2) nm) are longer than the Cu-$N_{DL\text{-}1a}$ distances (0.198 8(3)~0.204 7(3) nm). However, these two copper centers are not in the exactly same coordination environment. In one copper center, the two diamine ligands are in "*cis*" form, but in the other copper centre, "*trans*" form is observed.



Probability of ellipsoid is 30%, hydrogen atoms and perchlorate anions are omitted for clarity

Fig.1　Molecular structure of the complex **1**

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

Cu1-N9	0.202 6(3)	Cu2-N11	0.199 7(3)	Fe1-C3	0.194 3(3)
Cu1-N10	0.198 8(3)	Cu2-N14	0.200 1(3)	Fe1-C4	0.195 0(3)
Cu1-N7	0.202 5(3)	Cu2-N12	0.202 3(3)	Fe1-C5	0.188 6(3)
Cu1-N8	0.202 0(3)	Cu2-N13	0.204 7(3)	Fe1-C6	0.193 0(3)
Cu1-N4	0.232 9(2)	Fe1-C1	0.193 0(3)		
Cu2-N1	0.232 3(2)	Fe1-C2	0.191 2(3)		
N9-Cu1-N10	93.87(11)	N1-Cu2-N13	96.11(10)	C1-Fe1-C5	93.10(13)
N7-Cu1-N8	91.12(11)	N1-Cu2-N11	93.57(10)	C2-Fe1-C4	93.25(13)
N13-Cu2-N14	94.91(11)	C5-Fe1-C6	86.53(13)	Cu2-N1-C1	126.0(2)
N11-Cu2-N12	96.35(11)	C3-Fe1-C5	93.47(13)	N1-C1-Fe1	174.1(3)
N4-Cu1-N7	93.19(10)	C2-Fe1-C3	88.57(13)	Cu1-N4-C4	123.5(2)
N4-Cu1-N9	105.53(10)	C2-Fe1-C6	91.43(13)	Fe1-C4-N4	174.9(3)

Table 3 Selected bond lengths (nm) and angles (°) for complex 2

Fe1-N2	0.196 7(2)	Mn2-O1	0.187 9(2)	B1-N1	0.155 4(5)
Fe1-N4	0.197 9(3)	Mn2-O2	0.188 7(2)	N1-N2	0.134 9(3)
Fe1-N6	0.197 1(2)	Mn2-O3	0.221 3(2)	O3-C37	0.123 1(4)
Fe1-C10	0.189 8(3)	Mn2-N7	0.227 1(3)	O1-C13	0.130 7(4)
Fe1-C11	0.191 5(3)	Mn2-N10	0.203 4(3)	O2-C20	0.130 3(4)
Fe1-C12	0.193 4(3)	Mn2-N11	0.200 6(3)		
N2-Fe1-N4	88.11(10)	O1-Mn2-N10	90.11(11)	Mn2-O1-C13	124.0(2)
N4-Fe1-N6	87.24(11)	O2-Mn2-N11	90.82(10)	Mn2-O2-C20	125.3(2)
N6-Fe1-N2	88.02(9)	N7-Mn2-N10	89.22(11)	Mn2-O3-C37	122.4(2)
C10-Fe1-C11	85.38(13)	N7-Mn2-N11	88.69(11)	N2-N1-B1	119.1(2)
C11-Fe1-C12	88.72(11)	N10-Mn2-N11	88.49(11)	C1-N1-B1	131.4(3)
C12-Fe1-C10	87.12(13)	O3-Mn2-O1	85.91(9)	Fe1-N2-N1	121.17(18)
N4-Fe1-C11	94.46(13)	O3-Mn2-O2	86.01(10)	Fe1-N2-C3	132.9(2)
N6-Fe1-C12	91.81(10)	O1-Mn2-O2	90.52(9)	Fe1-C10-N7	177.3(3)
N2-Fe1-C10	92.14(11)	O3-Mn2-N7	172.93(9)	Mn2-N7-C10	172.7(2)

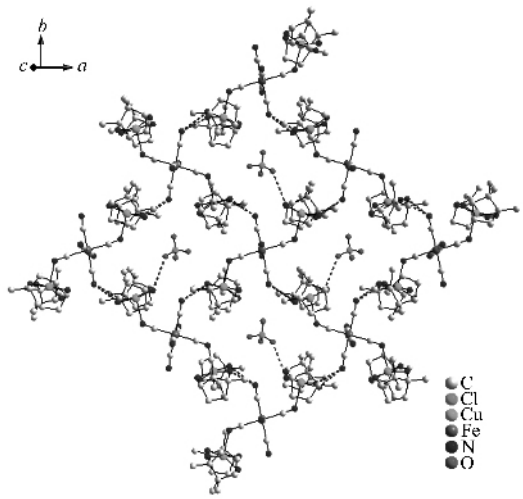
The cyanide bridge connecting copper and iron centers forms a "Z" shape, with Fe–C≡N angles falling in the range 174.1(3)°~174.9(3)° and Cu–N≡C angles falling in the range 123.5 (2)°~126.0 (2)°. The Fe-C bond distances range from 0.193 0(3) nm to 0.195 0(3) nm.

The crystal packing of complex **1** involves one kind of N–H···O hydrogen bonding interaction that connects $Cu^{II}_2Fe^{III}$ trinuclear units and perchlorate anions, as well as one N–H···N type which joins neighboring $Cu^{II}_2Fe^{III}$ trinuclear units, as illustrated in Fig.2 (Table 4). The perchlorate anions are included in the cavity formed by four $Cu^{II}_2Fe^{III}$ trinuclear units. As shown in Fig.2, a two-dimensional supramolecular network is formed through hydrogen-bonding interaction.

The crystal structure of complex **2** shows that the structure consists of a neutral dinuclear [Mn(*D*,*L*-Lb)(DMF)(Tp)Fe(CN)$_3$] cluster and six water molecules. As shown in Fig.3, in this dinuclear cluster, the [(Tp)Fe(CN)$_3$]$^-$ unit acts as a monodentate ligand through one of its three cyanide groups toward a

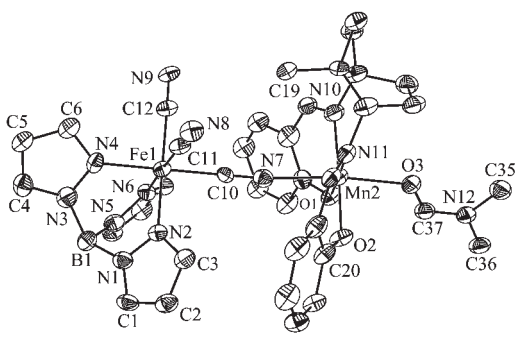
Table 4　Hydrogen bonding for complex 1

Doner–H···Accepter	D-H / nm	H···A / nm	D···A / nm	D–H···A / (°)
N8–H8D···N2	0.090 04	0.218 0(3)	0.305 8(4)	164.8(3)
N10–H10A···N2	0.090 02	0.217 5(7)	0.305 9(4)	166.8(4)
N1–H11B···N5	0.089 90	0.210 1(0)	0.298 9(4)	169.1(8)
N13–H13E···O2	0.089 92	0.243 8(7)	0.332 8(4)	169.8(2)
N14–H14D···N5	0.090 03	0.214 7(9)	0.302 9(4)	166.0(3)



Hydrogen atoms are omitted

Fig.2　Intermolecular hydrogen bonding in complex **1**



Probability of ellipsoid is 30%, hydrogen atoms are omitted for clarity

Fig.3　Molecular structure of the [Mn(*D*,*L*-Lb)(DMF)(Tp)Fe(CN)$_3$] unit of complex **2**

{[Mn(*D*,*L*-Lb)][DMF]}$^+$ core. The iron atom is six-coordinated with three Tp nitrogen atoms and three cyanide carbon atoms. The bonds and angles of the [(Tp)Fe(CN)$_3$]$^-$ unit are in consistence with those observed previously in structures containing [(Tp)Fe(CN)$_3$]$^-$ [8,9b~e,10c]. The manganese atom is six-coordinated in an elongated octahed-ral geometry. Two oxygen atoms and two nitrogen atoms from the quadridentate ligand *D*,*L*-Lb form the equatorial plane while one nitrogen atom from the cyanide bridge and one oxygen atom from DMF mole-cule occupy the axial positions. The Mn-N_{CN} distance (0.227 1(3) nm) is longer than the Mn-$N_{D,L\text{-Lb}}$ distances (0.200 6 (3)~0.203 4 (3) nm), which is similar to that ob-served for complex **1**. Also, The Mn-O_{DMF} distance (0.221 3(2) nm) is longer than the Mn-$O_{D,L\text{-Lb}}$ distances (0.178 9 (2)~0.188 7 (2) nm). The cyanide bridge conn-ecting metal centers is quite close to linearity, with Fe–C≡N and Mn–N≡C angles being 177.3 (3)° and 172.7 (2)°, respectively. Non-coordinated water mole-cules are inserted into crystal spacing and no classical hydrogen-bonding interaction between solvated water molecules and ligands is observed.

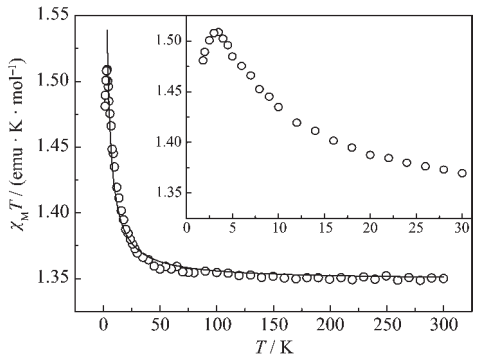
2.2　Spectroscopic studies

In the IR spectrum of complex **1**, two sharp N-H stretching vibration bands at 3 300 and 3 233 cm^{-1} are assigned to coordinated amino groups, which are shifted to lower frequencies compared to the free amino groups of ligand *D*,*L*-La (3 432 and 3 378 cm^{-1}). However, in the IR spectrum of complex **2**, the absence of $\delta_{N\text{-}H}$(1 581 cm^{-1}) confirms that the ligand *D*,*L*-Lb is coordinated to Mn(Ⅲ) ions in the deprotonated form. Moreover, in the IR spectrum of **1**, there are two kinds of $\nu_{C\equiv N}$(2 103 and 2 106 cm^{-1}), in corresponding to the coordinated C≡N bonds and free C≡N bonds, respectively. Similarly, for complex **2**, two stretching vibrations at 2 156 and 2 118 cm^{-1} are also assigned to two different coordination modes of C≡N in [(Tp)Fe(CN)$_3$]$^-$.

2.3　Magnetic properties

The temperature dependence of $\chi_M T$ for complex **1** measured at a field of 2 kOe is shown in Fig.4. On decreasing temperature, $\chi_M T$ increases gradually from the room temperature value of 1.350 emu·K·mol^{-1}, which is higher than the spin-only value of 1.125

emu·K·mol^{-1} per $Cu^{II}_2Fe^{III}$ unit. It reaches 1.509 emu·K·mol^{-1} at 3.5 K, and then decreases abruptly till 2 K. This behavior indicates the dominant ferromagnetic interaction. Based on the structure, the Hamiltonian can be described as: $\hat{H}=-2J\ (\hat{S}_1\cdot\hat{S}_2+\hat{S}_2\cdot\hat{S}_3)$, where $\hat{S}_1$, $\hat{S}_2$ and $\hat{S}_3$ are the spin operators of copper(Ⅱ), iron(Ⅲ) and copper(Ⅱ) ions, respectively. The best fit between 3.5 and 300 K gives: g=2.19, J=+0.55 cm^{-1} ($R=6\times10^{-5}$).



Solid line is the fitting from 300 to 3.5 K

Fig.4 Temperature dependence of $\chi_M T$ for complex **1** at a field of 2 kOe

As we know, chiral magnetic materials combining magnetism and optical activity have become a quite challenging topic for its important potential application as multifunctional materials after the discovery of magneto-chiral dichroism (MChD)[13]. Our further work is to prepare chiral *D*-La and *D*-Lb from the starting material *D*-camphor and to construct chiral magnetic complexes with them as the auxiliary ligands.

References:

[1] (a)Dunbar K R, Heintz R A. *Prog. Inorg. Chem.*, **1997**,**45**:283~391
(b)Weihe H, Güdel H U. *Comments. Inorg. Chem.*, **2000**,**22**:75~103
(c)Miller J S. *MRS. Bull.*, **2000**,**25**:60~64
(d)Marvaud V, Decroix C, Scuiller A, et al. *Chem. Eur. J.*, **2003**,**9**:1677~1691

[2] (a)Marvaud V, Decroix C, Scuiller A, et al. *Chem. Eur. J.*, **2003**, **9**:1692~1705
(b)Lescouëzec R L, Toma L M, Vaissermann J, et al. *Coord. Chem. Rev.*, **2005**,**249**:2691~2729 and references therein
(c)Beltran L M C, Long J R. *Acc. Chem. Res.*, **2005**,**38**:325~334

[3] (a)Ohba M, Ōkawa H. *Coord. Chem. Rev.*, **2000**,**198**:313~328
(b)Černák J, Orendáč M, Potočňák I, et al. *Coord. Chem. Rev.*, **2002**,**224**:51~66

[4] (a)Berlinguette C P, Vaughn D, Cañada-Vilalta C, et al. *Angew. Chem., Int. Ed.*, **2003**,**42**:1523~1526
(b)Mironov V S, Chibotaru L F, Ceulemans A. *J. Am. Chem. Soc.*, **2003**,**125**:9750~9760

[5] (a)Toma L, Lescouëzec R, Vaissermann J, et al. *Chem. Eur. J.*, **2004**,**10**:6130~6145
(b)Zhang Y Z, Gao S, Wang Z M, et al. *Inorg. Chem.*, **2005**,**44**: 4534~4545
(c)Toma L, Toma L M, Lescouëzec R, et al. *J. Chem. Soc. Dalton Trans.*, **2005**:1357~1364

[6] (a)Berseth P A, Sokol J J, Shores M P, et al. *J. Am. Chem. Soc.*, **2000**,**122**:9655~9662
(b)Shores M P, Sokol J J, Long J R. *J. Am. Chem. Soc.*, **2002**,**124**:2279~2292
(c)Yang J Y, Shores M P, Sokol J J, et al. *Inorg. Chem.*, **2003**,**42**:1403~1419

[7] (a)Lescouëzec R, Vaissermann J, Toma L M, et al. *Inorg. Chem.*, **2004**,**43**:2234~2236
(b)Wen H R, Wang C F, Zuo J L, et al. *Inorg. Chem.*, **2006**,**45**: 582~590

[8] (a)Lescouëzec R, Vaissermann J, Lloret F, et al. *Inorg. Chem.*, **2002**,**41**:5943~5945
(b)Wang S, Zuo J L, Zhou H C, et al. *Eur. J. Inorg. Chem.*, **2004**,**43**:3681~3687
(c)Wen H R, Wang C F, Song Y, et al. *Inorg. Chem.*, **2006**,**45**: 8942~8949
(d)Gu Z G, Yang Q F, Liu W, et al. *Inorg. Chem.*, **2006**,**45**: 8895~8901

[9] (a)Sokol J J, Hee A G, Long J R. *J. Am. Chem. Soc.*, **2002**, **124**:7656~7657
(b)Wang S, Zuo J L, Zhou H C, et al. *Angew. Chem., Int. Ed.*, **2004**,**43**:5940~5943
(c)Ni Z H, Kou H Z, Zhang L F, et al. *Angew. Chem. Int. Ed.*, **2005**,**44**:7742~7745
(d)Li D, Parkin S, Wang G, et al. *J. Am. Chem. Soc.*, **2006**, **128**:4214~4215
(e)Wang C F, Zuo J L, Bartlett B M, et al. *J. Am. Chem. Soc.*, **2006**,**128**:7162~7163

[10](a)Lescouëzec R, Vaissermann J, Ruiz-Pérez C, et al. *Angew. Chem., Int. Ed.*, **2003**,**42**:1483~1486
(b)Toma L M, Lescouëzec R, Lloret F, et al. *Chem. Commun.*, **2003**,**15**:1850~1851
(c)Wang S, Zuo J L, Gao S, et al. *J. Am. Chem. Soc.*, **2004**, **126**:8900~8901
(d)Toma L M, Lescouëzec R, Pasún J, et al. *J. Am. Chem. Soc.*, **2006**,**128**:4842~4853

[11]Yang Z H, Wang L X, Zhou Z H, et al. *Tetrahedron: Asymmetry.*, **2001**,**11**:1579~1582

[12]Ashmawy M M, McAuliffe C A, Parish R V. *J. Chem. Soc. Dalton. Trans.*, **1985**:1391~1397

[13]Rikken G L J A, Raupach E. *Nature*, **1997**,**390**:493~494