REVIEW ARTICLES

Crystal structures and magnetic properties of cyano-bridged 4f-3d complexes[*]

YAN Bing (曰　冰) and CHEN Zhida (陈志达)[**]

State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China; Peking University-Hong Kong University Joint Laboratory of Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China

Abstract　　The most recent research progress in the fields of the crystal structure and magnetochemistry for rare earth-transition metal cyano-bridged complexes is reviewed in detail. The emphasis is put on the introduction to the research achievements of our group in this field, including all the types of complexes with different crystal structures in these systems such as dinuclear, trinuclear, one-dimensional chain and hydrogen-bonded network ion-pairs. At the same time a few examples of rare earth-transition metal molecular-based magnets have been found to exhibit excellent magneto-chemical properties, such as the long-range magnetic ordering, the higher critical temperature T_c and the stronger coercive force. These results will be expected to promote the research development in this field.

Keywords: molecular-based magnets, cyano-bridged complexes, 4f-3d, crystal structures, magnetic properties.

Molecular-based magnetic material is a new hot research subject[1~5], and the cyano-bridged Prussian blue analogues are a kind of important molecular-based magnets[6~10]. Extensive researches have been carried out on the structures and magnetic properties of cyano-bridged complexes, which are mainly focused on the transition metal cyano-bridged complexes[11~15]. Little was reported on the rare earth-transition metal cyano-bridged complexes and studies were mainly on the polynuclear Gd-Cu complexes[16~20], most of which do not show special magnetochemical properties. These complexes are either lacking in crystal structures to display the intrinsic coupling mechanism of the excellent properties, or having low coercive force despite the higher critical temperature. Recently Gao's research group in Peking University synthesized a series of zero-dimensional (dinuclear, trinuclear), one-dimensional chain, two-dimensional layer and hydrogen-bonded ion pair 4f-3d complexes using 2,2'-bipyridine, 1,10-phenanthroline, 2,2'-bipyridyl-N, N'-dioxide, N, N'-dimethylformide and bipymidine as hybrid ligands. The corresponding structures and magnetic properties were studied[1), 2), [21,22]]. Our group synthesized some cyano-bridged rare earth-Fe (Cr) complexes using

---

1) Ma, B. Q. Structures and magnetic properties of 4f-3d complexes. Ph. D dissertation of Peking University, 2000.

2) Yi, T. Structure, magnetic properties of heteronuclear 4f-3d complexes and their applications in the synthesis of nano-structured material. Ph. D dissertation of Peking University, 1997.

$[M(CN)_6]^{3-}$ (M = transition metal) fragment as building blocks and N,N′-dimethylformide, N-N′-dimethylacetamide as hybrid ligands[3]. Table 1 lists the main kinds of cyano-bridged rare earth-transition complexes.

Table 1   Structures of cyano-bridged rare earth-transition metal complexes

Structure	Complex	Reference
Three-dimensional	$LnFe(CN)_6 \cdot nH_2O$ (Ln = La—Nd, $n = 5$; Ln = Sm—Nd, $n = 4$)	[21]
	$LnCr(CN)_6 \cdot 5H_2O$ (Ln = La—Lu)	[21]
Two-dimensional	$Ln(bipm)(H_2O)_4Fe(CN)_6 \cdot 3H_2O$ (Ln = La, Nd)	1)
One-dimensional	$[Ln(napy)_2(H_2O)_3Fe(CN)_6]_n \cdot 4H_2O$ (Ln = La, Ce, Eu, Gd)	[22]
	$[Ln(bipy)_2(H_2O)_4Fe(CN)_6]_n \cdot 4H_2O \cdot 1.5bipy$ (Ln = Eu, Gd, Y, Er, Yb)	2)
	$[Eu(phen)_2(H_2O)_2Fe(CN)_6 \cdot 2phen]_n$	2)
	$[Eu(terpy)_2(H_2O)_4Fe(CN)_6]_n$	[23]
	$[Ln_2(DMF)_{10}M(CN)_4]_n$ (Ln = Sm, Eu, Er, Yb and M = Ni, Pt, Pd)	[24]
	$[Eu(DMF)_4M(CN)_4]_n$ (M = Ni, Pt)	[25]
	$[Ln_6(DMF)_{16}(\mu_6\text{-}O)(\mu3\text{-}O)_8Pd(CN)_5]_n$	[26]
	$[Ce(gly)_3(H_2O)Fe(CN)_6]_n$	[27]
	$[Ln(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$ (Ln = Sm, Eu, Gd)	This work
	$[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$	This work
	$[Ln(bet)_2(H_2O)_3Fe(CN)_6]_n$ (Ln = Pr—Dy)	This work
Trinulear	$\{[Nd(bipy)_2(H_2O)_4]_2[Fe(CN)_6]\}[Fe(CN)_6] \cdot 8H_2O$	[28]
	$\{[Gd(DMA)_3(H_2O)_4]_2[Fe(CN)_6]\}[Fe(CN)_6] \cdot 3H_2O$	This work
Dinuclear	$Ln(DMF)_4(H_2O)_4Fe(CN)_6 \cdot H_2O$ (Ln = Sm, Gd, Er)	[29]
	$Ln(pyo)_4(H_2O)_3Fe(CN)_6 \cdot 2H_2O$ (Ln = Ce—Er)	3)
	$Ln(pyo)_5(H_2O)_2Cr(CN)_6 \cdot 2pyo \cdot 2H_2O$ (Ln = Ce—Nd)	3)
	$Ln(pyo)_5(H_2O)_3Fe(CN)_6 \cdot 2H_2O$ (Ln = Sm—Er)	3)
	$Ln(dpdo)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$ (Ln = Eu, Gd, Y)	1), [30]
	$Ln(dpdo)_2(H_2O)_3Cr(CN)_6 \cdot 4H_2O$ (Ln = Nd, Gd, Y)	1)
	$Ho(DMA)_3(H_2O)_3Fe(CN)_6 \cdot 3H_2O$	This work
Ion pair	$[Yb(H_2O)_8][Fe(CN)_6] \cdot 5napy \cdot 6H_2O$	[22]
	$[Er(DMA)_3(H_2O)_4][Fe(CN)_6]$	4)
	$Ln(MPL)_3(H_2O)_5Fe(CN)_6$ (Ln = La—Dy)	3)
	$La(dpdo)_2(H_2O)_5Fe(CN)_6 \cdot 2H_2O$	1)
	$[Ln(DMA)_4(H_2O)_3][Cr(CN)_6] \cdot 2H_2O$ (Ln = Sm, Gd)	This work
	$[Er(DMA)_3(H_2O)_4][Cr(CN)_6]$	This work
	$[Er(MPL)_4(H_2O)_3][Cr(CN)_6] \cdot 2H_2O$	This work

bipm = bipymidine; napy = 1,8-naphanthroline; phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine; terpy = 2,2′: 6′,2′-tetrapyridine; pyo = 2-pyrrolidinone; DMF = N, N′-dimethylformide; DMA = N, N′-dimethylacetamide; bet = betaine; MPL = N-methyl-pyrrolidinone; dpdo = 2,2′-bipyridyl-N,N′-dioxide.

---

1) and 2) See footnetes on Page 401.

3) Sun X. R. Synthesis, structures and magnetism of cyano-bridged heterometallic complexes. Ph. D dissertation of Peking university, 1999.

4) Kou H. Z. Structures and magnetism of cyano-bridged hybrid-type prussian blue complexes. Ph. D. Dissertation of Nankai University, 1999.

Table 1 shows that the hybrid ligands, rare earth ions and transition metal ions will influence the composition, the coordination environment of rare earth ions and the crystal structure. The steric effect of hybrid ligands has great influences on the coordination environment of rare earth ions and the crystal structures of complexes. For example, using 2-pyrrolidinone ligand, dinuclear cyano-bridged complexes will form: $Ln(pyo)_4(H_2O)_3Fe(CN)_6 \cdot 2H_2O$ (Ln = Ce—Er), $Ln(pyo)_5(H_2O)_2Cr(CN)_6 \cdot 2pyo \cdot 2H_2O$ (Ln = Ce—Nd) and $Ln(pyo)_5(H_2O)_3Fe(CN)_6 \cdot 2H_2O$ (Ln = Sm—Er)[3]; using N-methyl-pyrrolidinone ligand, ion-pair complexes will form: $Ln(MPL)_3(H_2O)_5Fe(CN)_6$(Ln = La—Dy)[1] because the methyl group in the MPL molecule enhances the steric hindrance; using 1, 8-naphanthroline, 1, 10-phenanthroline, 2, 2'-bipyridine, 2, 2': 6', 2'-tetrapyridine and betaine as hybrid ligands, one-dimensional chain complexes are obtained[2], [22, 23]; and using bipymidine ligand, two-dimensional layer-like compounds are formed[3]. Another example is that we have prepared ion-pair complexes with different terminal ligands using $Er(NO_3)_5$ and $Fe(CN)_6$ as reactant. The coordination environment for Er ion can be different: for N-pyrrolidinone, four MPL ligands surround Er ion; for N, N'-dimethylacetamide, only three DMA ligands do. Using different $[M(CN)_6]^{3-}$ (M = transition metal ions) molecular fragment as the building block, one can also obtain a different coordination surrounding of rare earth ions and the crystal structures of complexes. For instance, using DMF as hybrid ligands, here we give a detailed introduction to the crystal structure of cyano-bridged 4f-3d complexes (Figure 1).

The first type is one-dimensional chain complex $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$, (Fig. 1 (a)). Sm atom is of an eight coordination consisting of six oxygen atoms from two DMA molecules and four water molecules as well as two nitrogen atoms from the two bridging CN. It is worthwhile to note that one-dimensional chain -Fe-C(1)N(1)-Sm-N(6)C(6)-Fe-C(1)N(1)-Sm- is formed with the two trans-bridged cyanides, like the β-folding chain of a protein molecule. We also synthesized similar one-dimensional chain structural complexes $[Ln(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$, Ln = Sm, Eu, Gd; $[Ln(bet)_2(H_2O)_3Fe(CN)_6]_n$(Ln = Pr, Nd, Eu, Gd, Tb, Dy), which form the β-folding of protein molecule through two cis (Ln and Mn) or trans (Ln and Fe) cyanides between rare earth ions and transition metal ions. There are many other reports on these kinds of complexes[2], [22~27]. One-dimensional chain structural cyano-bridged complexes are composed of four types: (i) two cis-cyanides and two nitrogen atoms bonded with the opposite position of the rare earth ion; (ii) two trans-cyanides and two nitrogen atoms bonded with the opposite position of the rare earth ion; (iii) two cis-cyanides and two nitrogen atoms bonded with the adjacent position of the rare earth ion; (iv) two trans-cyanides and two nitrogen atoms bonded with the adjacent position of the rare earth ion. structure (i) is the most common, such as Ln-Mn complexes; and Ln-Fe complexes belong to structure (ii); structures (iii) and (iv) are described in References [23] and [27].

The second type is trinuclear $\{[Gd(DMA)_3(H_2O)_4]_2Fe(CN)_6\}[Fe(CN)_6] \cdot 3H_2O$ (Fig. 1 (b)). Each Fe atom is bridged with two Gd atoms through two cyano groups (C(5)N(5) and C(6)N(6)). Each Gd atom is of eight-coordination, in which seven coordinated oxygen atoms come from the three DMA molecules, and the four water molecules and each has one coordinated nitrogen

---

1) ~ 3) See footnotes on page 402.
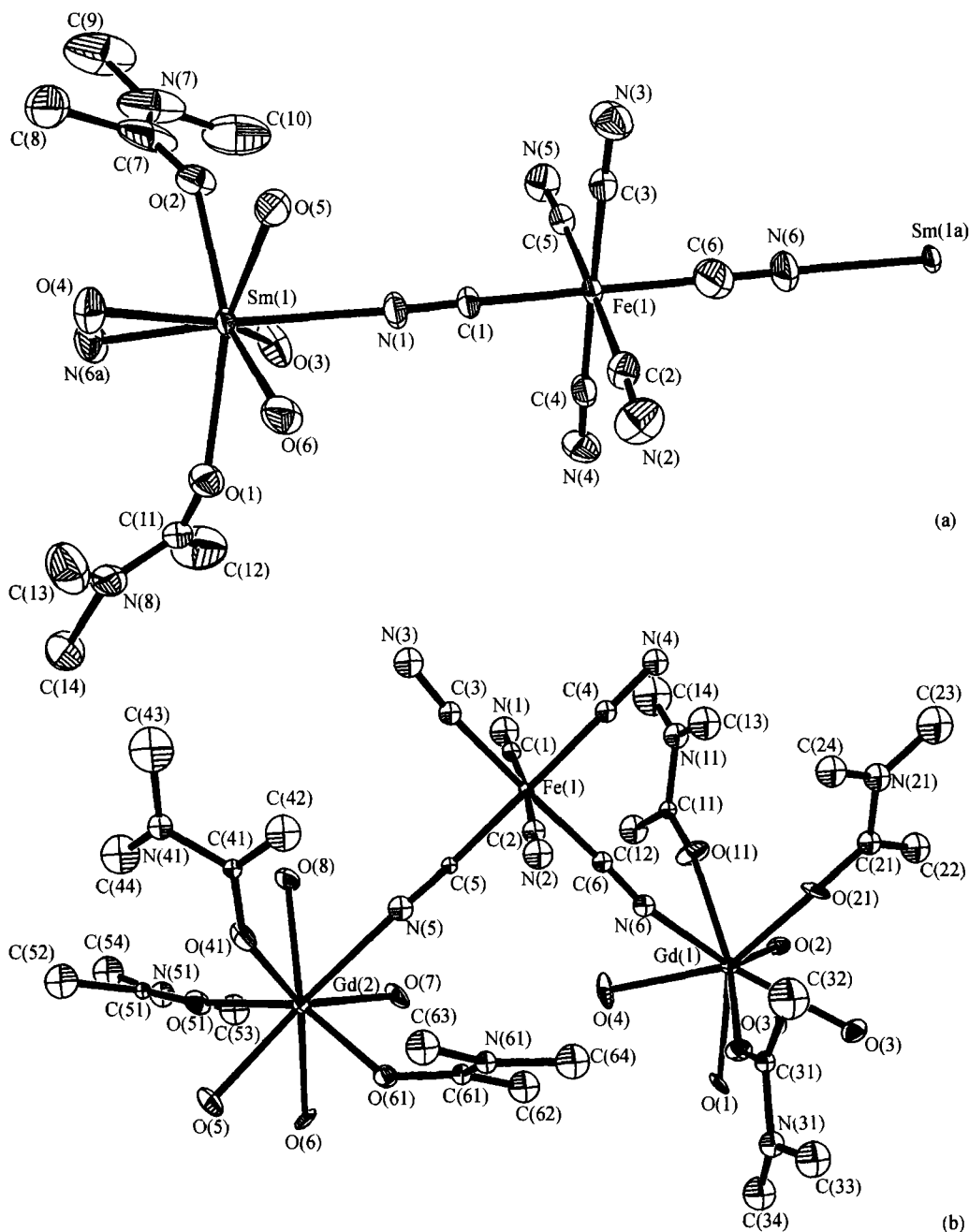
Fig. 1   Crystal structures of [SmFe]$_n$ complex (a) and Gd$_2$Fe complex (b).

atom from the bridging cyanide ligands. Fe atom is bridged with the two Gd atoms through two cyanides (C5N5 and C6N6). It is interesting to note that one DMA molecule coordinated to Gd atom has two kinds of stereo configuration, in which the only difference is that, besides the coordinated oxygen atoms of acetamide group of DMA, the other atoms rotate 180° around the O-Gd axis. The crystal structure of Gd$_2$Fe complex indicates that there is a central cyano-bridged framework. In the

trinuclear structure of Gd(1)-N(6)C(6)-Fe-C(5)N(5)-Gd(2), the two *cis*-cyano group bridges, one Fe atom and two Gd atoms form an isolated molecule. Ref. [28] reported a similar type of complexes.

The third type is an isolated dinuclear $Ho(DMA)_3(H_2O)_3Fe(CN)_6 \cdot 3H_2O$ (Fig. 2(a)). The Ho atom is of seven coordination and the coordination polyhedron can be described as a slightly distorted pentagonal bipyramid. Six oxygen atoms of three H_2O molecules and three DMA molecules and one N atom of the bridging CN ligand coordinated to Ho. In addition, the terminal cyanide is also hydrogen-bonded to some H_2O molecules of the adjacent Ho-Fe fragment. Ma[1], Yi[2], Sun[3], Kou[29] and Gao et al.[30]. reported similar dinuclear complexes, who used DMF, pyro and dpdo as hybrid ligands, $K_3Fe(CN)_6$ and $K_3Cr(CN)_6$ as building blocks.

The fourth type is $[Er(DMA)_3(H_2O)_4][Cr(CN)_6]$ (Fig. 2(b)), which consists of $[Er(DMA)_3(H_2O)_4]^{3+}$ and $[Cr(CN)_6]^{3-}$. In the cation $[Er(DMA)_3(H_2O)_4]^{3+}$, Er atom has seven coordinated oxygen atoms from three DMA molecules (O(11), O(21) and O(31)) and three H_2O molecules (O(1), O(2) and O(3)). The coordination polyhedron can also be described as a slightly distorted pentagonal bipyramid (Fig. 2(b)), among which the two apexes are two coordinated oxygen atoms of DMA molecules, O(21) and O(31). The symmetry mirror plane is a pentagon composed of O(11), O(4), O(2), O(1) and O(3). Er atom, four H_2O and one DMA group lie in the mirror plane, the other two symmetrical DMA groups show some distortion, the bond lengths between the two apex oxygen atoms and central Er atom are approximately equal. Besides the static electricity interaction between the ion pairs, there exists the hydrogen bond between the coordinated H_2O molecules in $[Er(DMA)_3(H_2O)_4]^{3+}$ and the CN groups of $[Cr(CN)_6]^{3-}$. Similar ion pair complexes can be seen in the papers of Ma[1], Sun[3], Adachi[22] and Kou[29].

Besides, Ma et al.[1] prepared the first example of two-dimensional layer-like structural cyano-bridged 4f-3d complexes using bipymidine $Ln(bipm)(H_2O)_4Fe(CN)_6 \cdot 3H_2O$ (Ln = La, Nd). Each Nd ion coordination is of two N atoms from chelated bipymidine ligand, four H_2O molecules and three N atoms of bridged cyanides. Two Fe ions are located in the symmetry center: one links up the adjacent Nd ion with two para-cyano groups, and the other links up the adjacent Nd ion with four cyano groups.

From the reaction between Ln^{3+} and $[Fe(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, respectively, three-dimensional cyano-bridged complexes are obtained[23]. Among $LnFe(CN)_6 \cdot nH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), the complexes containing Sm, Gd, Dy, Ho, Er and Tm exhibit ferromagnetic behavior, Tb complex shows higher magnetic phase-transfer temperature T_c (11.7 K). All the other rare earth hexacyanometallates show antiferromagnetic behavior. Some researches have been carried out on the magnetic properties of dinuclear 4f-3d cyano-bridged complexes, and the magnetic susceptibilities for Gd-Fe and Gd-Cr complexes have been analyzed. It is found that the ferromagnetic coupling is dominant between Gd ion and Fe or Cr ions[1,3], a few complexes show antiferromagnetic coupling[1]. Besides this, it has been found that there exists ferr-
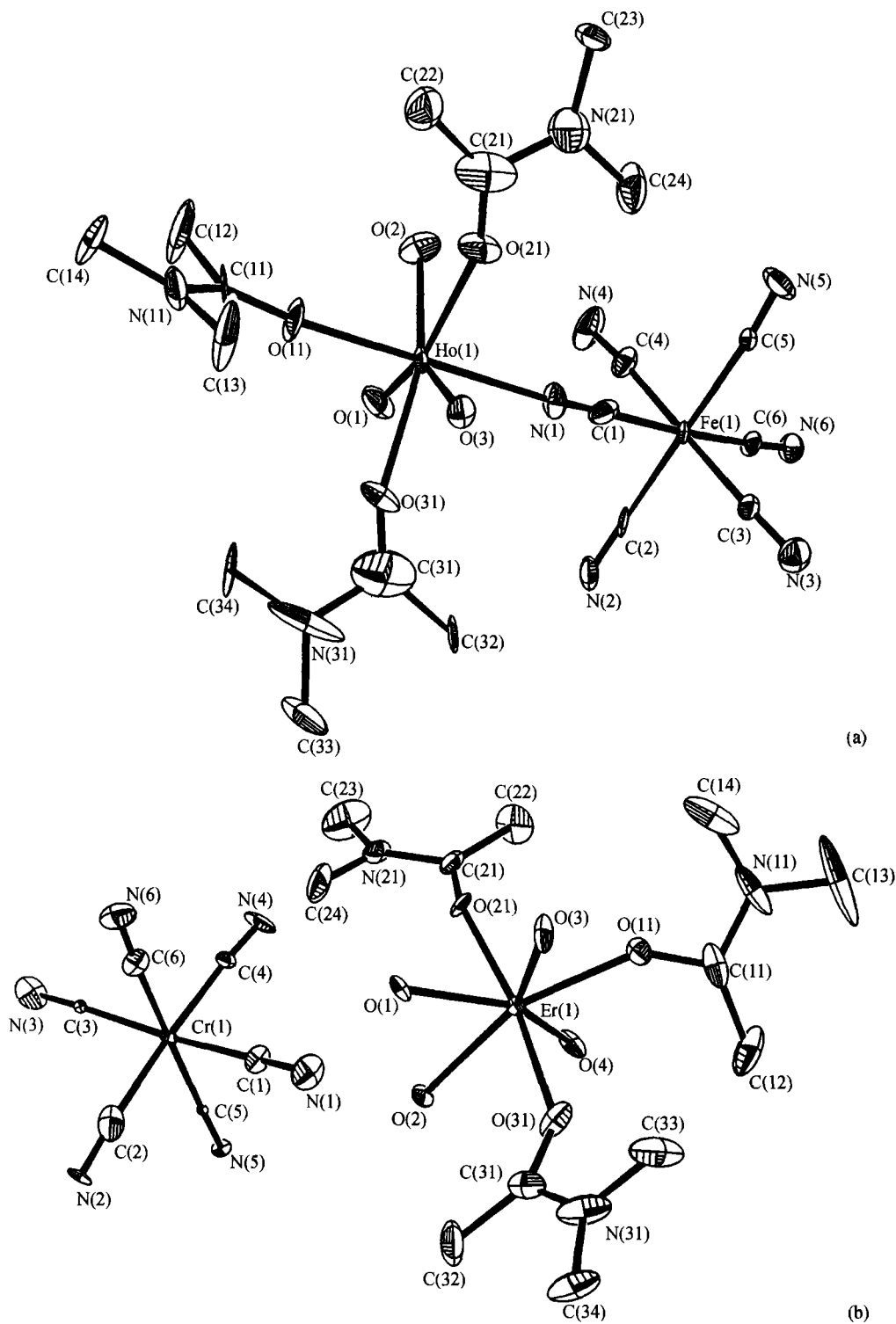
Fig. 2 Crystal structures of HoFe (a) and ErCr complex (b).

imagnetic phase-transfer behavior in some compounds at low temperature range[1),2)] .

We measured the variable temperature susceptibilities of several series of cyano-bridged rare earth-transition metal complexes and found a weak antiferromagnetic interaction between rare earth ions and transition metal ions in most of these complexes. Among them, some complexes show interesting magnetochemical properties, especially one-dimensional chain structural complexes [Sm $(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$ and $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$ exhibit macroscopic magnetic ordering. The alternating magnetic susceptibility of $[Sm(DMF)_4(H_2O)_2Mn(CN)_6 \cdot H_2O]_n$ at 111 Hz appears both in-phase χ'_m and out-of-phase χ''_m (Fig. 3(a)). The imaginary part of the alternating susceptibility indicates the existence of long-range magnetic ordering, and the larger coercive force. According to the peak of $\chi'_m(T)$ curve, the critical temperature T_c is determined at 18 K, which is the highest temperature in the reported 4f-3d complexes. The hysteresis loop of the complex is determined at 5.7 K (Fig. 3(b)), which reveals the stronger coercive force $H_c = 600$ Oe and remnant magnetization $M_R = 0.69$ $N\beta mol^{-1}$.
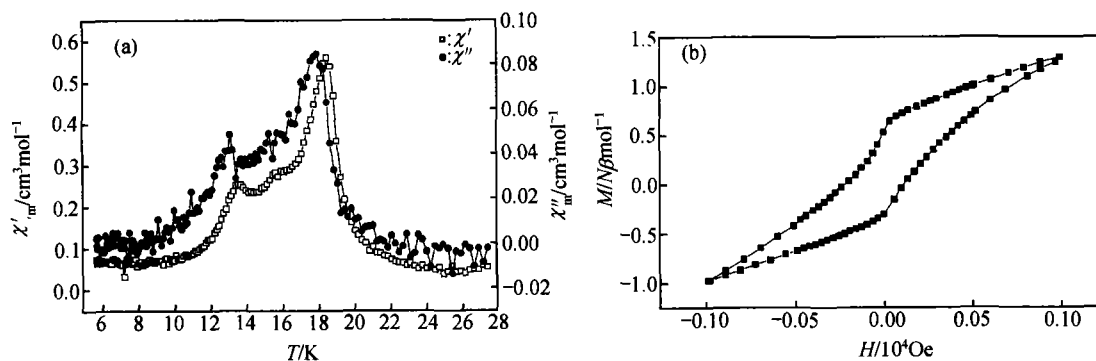

Fig. 3   Plot of in-phase χ'_m and out-of-phase χ''_m of magnetic susceptibility for $[SmMn]_n$ complex at 111 Hz (a) and hysteresis loop 5.7 K (b).

Figure 4 (a) shows the alternating magnetic susceptibilities of $[Sm(DMA)_2(H_2O)_4Fe(CN)_6 \cdot 5H_2O]_n$ at 199 Hz, with both in-phase χ'_m and out-of-phase χ''_m. The critical temperature T_c is determined at 3.5 K from $\chi'_m(T)$ curve. The hysteresis loop for the complex is determined at 1.8 K (Fig. 4(b)), which is similar to the above SmMn complex. The stronger coercive force $H_c = 1400$ Oe and remnant magnetization $M_R = 0.11$ $N\beta mol^{-1}$ are obtained. The magnetic properties of the above two complexes are not commonly found in cyano-bridged rare earth-transition metal complexes.

Using the broken symmetry approach proposed by Noodleman[32], $E_{HS} - E_{BS} = [- S_{max}(S_{max} + 1) + \sum_{S}^{S_{max}} A_1(S) \cdot S(S+1)]$, the energy difference between the highest spin state (HS) and broken symmetry state (BS) of a molecule can be calculated, where E is the energy, S the spin state of the molecule and $A_1(S)$ the square of Clebsch-Gordan coefficient. Combining the density functional theoretical method in quantum chemistry, the Heisenberg magnetic coupling constant J between magnetic carriers can be calculated, which further determines the nature of ferromagnetic, ferrimag-
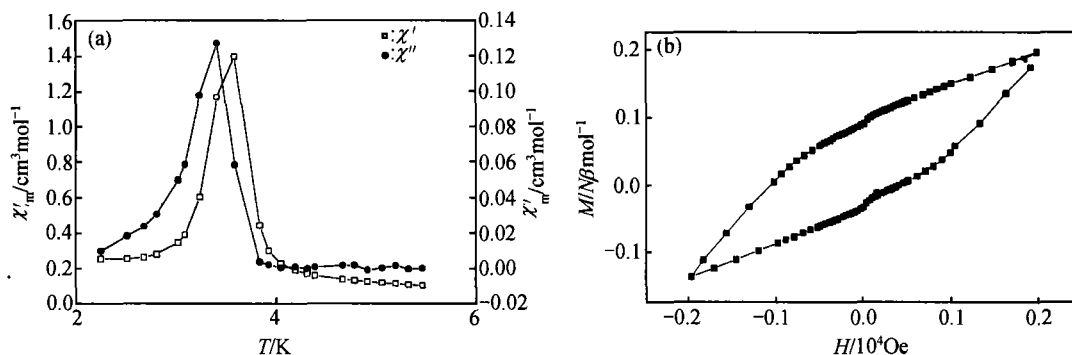
1) and 2) See footnotes on page 401.

Fig. 4   Plot of in-phase χ'_m and out-of-phase χ''_m of magnetic susceptibility for $[SmFe]_n$ complex at 199 Hz (a) and hysteresis loop at 1.8 K (b).

netic and antiferromagnetic interaction between these magnetic carriers and the degree of these interactions[1], [31, 32]. The calculation for J is carried out using Amsterdam density functional (ADF) package version 2.3[33]. And the calculation of local density approximation (LDA) with exchange and correlation potentials makes use of Vosko, Wilk and Nusair correlation functional[34]. During the calculation, Becke's nonlocal (NL) exchange correlation and Perdew's NL correlation correction are added \ + [35]. Convergence criterion is judged by the commutator of density matrix and Fock matrix. Once the maximum element of the commutator is smaller than 10^{-5}, and the norm of the commutator is less than 10^{-4}, the convergence is considered to be achieved. The numerical integration procedure adopts the polyhedron method developed by Velde et al.[33]. and the integration precision parameter is set to be 3.5. The molecular magnetic interaction is sensitive to the molecular structure, so E_{HS} and E_{BS} can be obtained by means of a calculation over the whole molecule using the direct experimental geometrical configuration. For $[Gd(pyo)_4(H_2O)_3][Fe(CN)_6] \cdot 2H_2O$ complex, from the above formula, $E_{HS} - E_{BS} = -7 J$, and J value calculated is 8.1 cm^{-1}; the experimental value is 0.74 cm^{-1}. In spite of the difference between the calculated value and experimental value, the calculated result is acceptable in view of the present calculated level with a very small absolute value of J. The calculated value and experimental value of J are both positive, indicating that the magnetic coupling between Gd-Fe belongs to ferromagnetic interaction. Simultaneously one can also obtain the spin electronic density map of $[Gd(L)_4(H_2O)_3][Fe(CN)_6] \cdot 2H_2O$ molecule (Fig. 5). In the high spin state (HS), the spin electrons of Gd(III) and Fe(III) induce the spin polarization of surrounding ligands, which leads to the spin density of surrounding ligands taking an opposite sign to that of Gd(III)Fe(III). The spin polarization effect propagates with the alternate spin sign away from the paramagnetic center. Then is the spin polarization between Gd(III) and Fe(III) complementary or counter-active on C1N1? From Fig. 5, the opposite polarization effect of the two magnetic centers on C1N1 is counteractive, resulting in the spin polarization of Fe(III) on C1 larger than Gd(III), and a negative spin density; while for N1, the polarization of Gd(III) is larger than Fe(III) and the spin density of N1 is negative.

     In conclusion, in order to enhance the magnetic anisotropy and molecular magnetic moment, we

---

1) Yan, F. The density functional theoretical method and its application in molecular magnetism. Master thesis of Peking University, 2000.
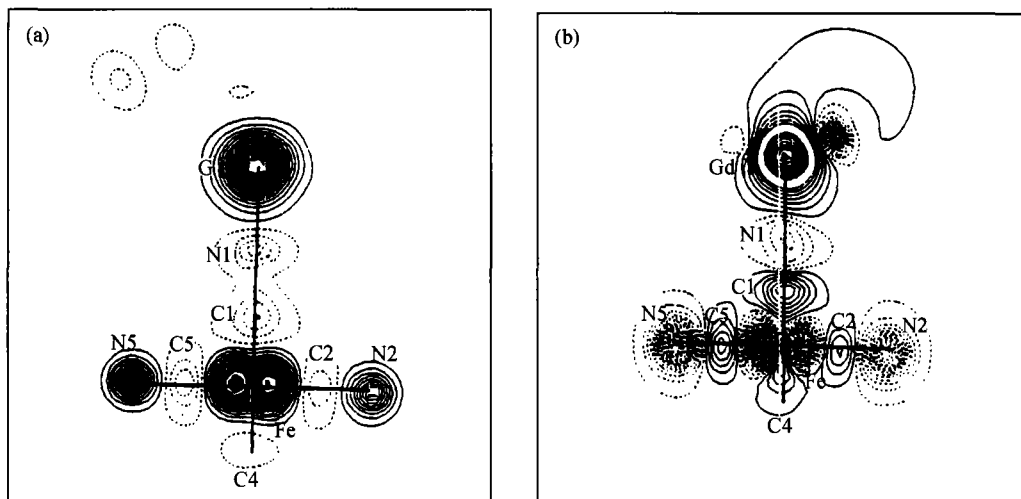
Fig. 5   Spin density maps of $[Gd(L)_4(H_2O)_3][Fe(CN)_6] \cdot 2H_2O$. (a) High spin state; (b) broken symmetry state.

designed and synthesized cyano-bridged rare earth-transition metal complexes with different hybrid ligands, among which SmMn and SmFe exhibit some novel magnetic properties. Using the broken symmetry approach combined with density functional theoretical method, the spin density distributions of typical complexes have been calculated, indicating that the magnetic coupling interaction between rare earth and transition metal ions is through a spin polarization mechanism. The research on the cyano-bridged 4f-3d complexes molecular-based magnets needs to be extended and developed in the following aspects: (i) selecting new building blocks and adopting new synthetic methods, to prepare some new complexes and to study their crystal structure and magnetic properties in order to discover novel excellent molecular-based magnets; (ii) to study the relationship between the crystal structures and corresponding magnetic properties for the complexes whose structures and magnetic properties have been known; (iii) from the quantum chemistry, to study the magnetic model of all kinds of structural cyano-bridged 4f-3d complexes in order to elucidate the magnetic coupling mechanism between metal ions; (iv) using the broken symmetry approach combined with the density functional theoretical method, to calculate and approximately calculate the spin density maps in order to elucidate the magnetic coupling mechanism between metal ions; (v) according to the correlation among structures, theory and magnetic properties, to design novel molecules and discover cyano-bridged 4f-3d complexes with excellent magnetic properties; (vi) on the basis of the above research, to achieve the excellent molecular-based magnets by assembly and develop new applied research field.

References

1   Cheng, P. et al. Molecular magnetic engineering of polymetallic coupling systems. Chin. Chem. Bull., 1994, 2: 9.
2   Miller, J. S. et al. Organic and organometallic molecular magnetic materials-designer magnets. Angew. Chem. Int. Ed. Engl., 1994, 33: 385.
3   Ferlay, S. et al. A room-temperature organometallic magnet based on Prussian blue. Nature, 1995, 378: 701.
4   Kahn, O. et al. Magnetism of heterobimetallics: toward molecular-based magnets. Adv. Inorg. Chem., 1995, 43: 179.
5   Zhuang, J. Z. et al. Molecular-based magetic complexes. Prog. Nat. Sci., 1996, 6: 21.
6   Bignozzi, C. A. et al. Intramolecular electron transfer in cyano-bridged polynuclear complexes. New. J. Chem., 1996, 20: 731.

7   Buschmann, W. E. et al. Electron transfer, linkage isomerization, bulk magnetic order, and spin-glass behavior in the iron hexacyanomanganate Prussian blue analogue. Chem. Eur. J., 1999, 5: 3019.

8   Re, N. et al. The synthesis and characterization of two-dimensional ferromagnetic extended structures containing high-spin ($S = 5/2$) and low-spin ($S = 1/2$) iron (III) bridged by cyanide groups. Inorg. Chem., 1998, 37: 2717.

9   Kahn, O. Blueprint for success. Nature, 1995, 378: 667.

10   Miyasaka, H. et al. The two-dimensional network structure and metamagnetic properties of the 2:1 complex of [Mn(3-metosalen)(H_2O)]ClO_4 and K_3[Fe($CN)_6$]. Angew. Chem. Int. Ed. Engl., 1995, 34: 1446.

11   Ohba, M. et al. [Mn(en)]$_3$[Cr($CN)_6$]$_2\cdot4H_2O$: a three-dimensional dimetallic ferrimagnet (T_c = 69 K) with a defective cubane unit. Angew. Chem. Int. Ed. Engl., 1999, 38: 1795.

12   Sun, X. R. et al. Synthesis, structure and properties of cyano-bridged heterometallic complex $\{[Cu(amet)_2][Fe(CN)_6]\}_\infty$. Prog. Nat. Sci., 1999, 9(6): 425.

13   Otsuka, T. et al. Crystal structure and energy transfer in double-complex salts composed of tris (2,2'-bipyridine) ruthenium (II) or tris (2,2'-bipyridine) osmium (II) and hexacyanochromate (III). Inorg. Chem., 1999, 38: 1340.

14   Buschmann, P. S. C. et al. Magnetic field induced reversed (negative) magnetization for electrochemically deposited T_c = 260 K oxidized films of chromium cyanide magnets. Adv. Mater., 1996, 9: 645.

15   Sun, X. R. et al. Synthesis, characterization and magnetic properties of cyano-bridged $Cu_2^{II}Fe^{II}$ and $Ni_6^{II}Fe^{II}$ compounds. Acta. Sci. Nat. Univ. Pek., 2000, 36: 253.

16   Blake, A. J. et al. Heterometallic compounds involving d- and f-block elements: synthesis, structure, and magnetic properties of two new Ln_xCu_4 complexes. Angew. Chem. Int. Ed. Engl., 1991, 30: 1139.

17   Andruh, M. et al. Crystal structure and magnetic properties of [Ln_2Cu_4] hexanuclear clusters (where Ln = trivalent lanthanide). Mechanism of the Gd(III)-Cu(II) magnetic interaction. J. Am. Chem. Soc., 1993, 115: 1822.

18   Costes, J. P. et al. A genuine example of a discrete bimetallic (Cu, Gd) complex: structural determination and magnetic properties. Inorg. Chem., 1996, 35: 2400.

19   Costes, J. P. et al. A general route to strictly dinuclear Cu(II)/Ln(III) complexes. Structural determination and magnetic behavior of two Cu(II)/Gd(III) complexes. Inorg. Chem., 1997, 36: 3429.

20   Costes, J. P. et al. Is ferromagnetism an intrinsic property of the Cu^{II}/Gd^{III} couple? 1. structures and magnetic properties of two novel dinuclear complexes with a μ-phenolato-μ-oximato (Cu, Gd) core. Inorg. Chem., 2000, 39: 169.

21   Hulliger, F. et al. Rare earth ferricyanides and chromicyanides LnM($CN)_6\cdot nH_2O$. J. Solid. State. Chem., 1976, 18: 283.

22   Adachi, G. et al. New development of studies on rare earth complexes. The Rare Earth Society of Japan, Tokyo: Academic Publishers, 1997.

23   Knoeppel, D. W. et al. Hetermetallic one-dimensional complexes containing cyaoide-bridged lanthanides (III) and transition metals. Inorg. Chem., 1998, 37: 4828.

24   Knoeppel, D. W. et al. Unusual one-dimensional ladder structure containing divalent europium and the tertracyanometallates Ni $(CN)_4^{2-}$ and Pt($CN)_4^{2-}$. Inorg. Chem., 1996, 35: 5328.

25   Knoeppel, D. W. et al. Cyanide-bridged lanthanide-transition metal one-dimensional arrays $\{(DMF)_{10}Yb_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Yb_2[Pt(CN)_4]_3\}_\infty$. Inorg. Chem., 1996, 35, 1747.

26   Liu, J. P. et al. An unusual cyanide bridging lanthanide-transition metal complex that containing the one-dimensional cationic array $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_6]^{8+}\}_\infty$. Inorg. Chem., 1998, 37: 5410.

27   Granda, S. G. et al. Aqua (hexacyanoferrato-N) bis (μ-glycine)-glycinecerium (III) monohydrate. Acta. Cryst., 1996, C52: 1679.

28   Yi, T. et al. A cyano ionic pair complex: [FeNd$_2$($CN)_6$($C_{10}H_8N_2$)$_4$($H_2O)_8$][Fe($CN)_6$]$\cdot 8H_2O$. Acta, Cryst., 1998, C54, 41.

29   Kou, H. Z. et al. A dinuclear cyano-bridged complex based on hexacyanoferrate(III) and samarium(III) nitrate: synthesis and crystal structure. J. Chem. Cryst., 1998, 28: 303.

30   Gao, S. et al. Crystal structure and magnetism of hetero-binuclear complexes RE(dpto)$_2$($H_2O)_3$Fe($CN)_6\cdot 4H_2O$ (RE = Gd, Y). Mol. Crtst. Liq. Cryst., 1999, 335: 201.

31   Yan, F. et al. Magnetic coupling constants and spin density maps for heteronuclear complexes GdCu(OTF)$_3$(bdmap)$_2$(H_2O) (THF, [Gd($C_4H_7ON)_4$($H_2O)_3$][Fe($CN)_6$]$\cdot 2H_2O$ and [Gd($C_4O_7ON)_4$($H_2O)_3$][Cr($CN)_6$]$\cdot 2H_2O$. A density functional study. J. Phys. Chem., 2000, A104: 6295.

32   Noodleman, L. Valence bond description of antiferromagnetic coupling in transition metal dimmers. J. Chem. Phys., 1981, 74: 5737.

33   Amsterdam Density Functional (ADF) version 2.3, Scientific Computing and Modeling, Theoretical Chemistry, Amsterdam: Virje Universiteit, 1997.

34   Vosko, S. J. et al. Accurate spin-dependent electron liquid correlation energies for local spin density calculation: a critical analysis. Can. J. Phys., 1980, 58: 1200.

35   Becke, A. D. et al. Density functional exchange energy approximation with local density approximation. Int. J. Quant. Chem., 1989, S23: 599.