CHINESE JOURNAL OF CHEMISTRY

Account

Molecular and Crystal Magnetic Engineering of Polymetallic Coupling System: From Magnetic Molecules to Molecular Magnets

CHENG, Peng(程鹏)   LIAO, Dai-Zheng*(廖代正)

Department of Chemistry, Nankai University, Tianjin 300071, China

One of the main challenges in the field of molecular materials is the design of molecular ferromagnets. General design strategy includes two steps, that is molecular magnetic engineering and crystal magnetic engineering. The first step is the synthesis of ferromagnetically coupled polymetallic systems. The second step is the assembly of polymetallic systems with muti-dimensional structure and exhibiting a ferromagnetic transition. This paper summarized the strategies of molecular design and crystal engineering allowed to obtain such systems and our efforts in the fields of molecular magnetism and molecular-based magnets.

Introduction

The development, characterization, and exploitation of novel magnetic materials based on the assembly of molecular components are an exceptionally active and rapidly expanding field. Traditionally, magnets were limited to insoluble, metallurgically prepared inorganic network solids (metals, oxides, and rare earth intermetallics). The molecular-based magnets, defined as "useful substances prepared from molecules or molecular ions that maintain aspects of the parent molecular framework"[1] are of special significance because of the capacity for diversity in composition, structure and properties, both chemical and physical.

Although McConnell dominated the molecular-based magnets in theory and suggested a ferromagnetic coupling mechanism for organic system in 1963,[2] the success in laboratory was first reported in 1986. Ovchinnikov observed the magnetization curves of organic polymer 4,4'-butadiyne-1,4-diyl-bis(2,2',6,6'-tetramethyl-4-hydroxy-piperidin-1-oxyl.[3] Miller reported the first full characterized molecular-based magnets [Fe(C₅Me₅)₂](TCNE),[4] where C_5Me_5 and TCNE are pentamethylcyclopentadienyl and tetracyanoethylene, respectively. So far, three types of molecular-based systems exhibiting a ferromagnetic transition have been fully characterized from both structural and magnetic viewpoints. These systems are as follows: (i) organic radical system, such as N,N'-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane ($T_c = 1.46$ K);[5] (ii) metal-radical system, such as $[Mn(hfac)_2]_3(Rad)_2$ ($T_c = 46$ K),[6] where hfac and Rad are hexafluoroacetyacetonato and trinitroxide, respectively; (iii) metal complex system, such as $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ ($T_c = 69$ K).[7] Several molecular-based magnets with ferromagnetic transition above room temperature have been reported.[8-11] Their structures and mechanism, however, are unclear. The international conferences on molecular-based magnets have been hold every other year since 1989.[12]

The design of molecular-based ferromagnetic materials is one of the most stimulating challenges for chemists. General design strategy is shown below:

Spin carriers with unpaired electrons ⟶

Magnetic molecules with high spin ground state ⟶

Molecular-based magnets
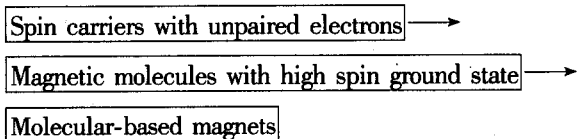
The first and second step are so called "molecular magnetic engineering" and "crystal magnetic engineering", respectively. In the field of molecular magnetism the most extensively used spin carriers are metal centres for constructing magnets. This review will focus on newly developed polymetallic coupling systems for both investigating the interaction between spin carriers and designing magnetic materials, mainly on our efforts in these areas.

Exchange interaction in polymetallic coupling system

Magnetic interaction between paramagnetic metal ions

The quantitative treatment of magnetic interactions between atoms as an exact science goes back almost seventy years to the early work of Heisenberg, Dirac and Van Vleck. Since 1950s,[13] the Heisenberg-Dirac-Van Vleck (HDVV) model have been applied widely to polymetallic coupling systems. For example, the susceptibility expression of different coupling system for binuclear complexes can be derived from the Hamiltonian:

$$H = - JS_1 \cdot S_2 \qquad (1)$$

The coupled binuclear copper(II) system (d^9-d^9), for example, is[13]

$$\chi_M = \frac{2Ng^2\beta^2}{kT}[\frac{1}{3 + exp(- J/kT)}]^{-1} \qquad (2)$$

where χ_M is the molar magnetic susceptibility and J is the exchange coupled parameter. Positive or negative J denoted ferromagnetic or antiferromagnetic interaction, respectively. The g is Lande factor, N being Avogadro's number and β the electronic Bohr magneton. k is the Boltzmann constant and equals to 0.695039 cm^{-1} · K^{-1}. In some cases, the corrections of zero field splitting (D), temperature-independent paramagnetism ($N\alpha$), molecular field (χ') and biquadratic terms (D_{ij}) are required. For more elaborate coupling systems, full matrix diagonalization (FMD) method and irreducible tensor operators (ITO) method can be applied to appraise the

magnetic exchange parameters.[14]

Binuclear copper(II) system

The magnetic interactions between metal ions are affected by many factors. Some magneto-structural correlations have been established,[15] such as the affection of bridging angle and dihedral angle, the extent of planarity of the binuclear bridged network, electron density on the bridging group, coordination mode of azide etc.

The μ-phenolato bridged binuclear copper(II) complexes with the di-Schiff base of 2,6-diformyl-4-substitutedphenol are interested in the past two decades. The reason for this is that the plethora of μ-phenolato complexes is their ready synthesis and subsequent utility for the study of magnetic interaction between Cu(II) ions. We synthesized a series of binuclear copper(II) complexes by using the ligand 2,6-diformyl-4-methylphenol di(benzoylhydrazone) (H_3L). This ligand could be formed keto-form (H_2L^-), keto-enol mixed form (HL^{2-}) and enol-form (L^{3-}) when reacted with a metal salt.[16] The tautomeric forms of the ligand are shown in Fig. 1. Three binuclear copper(II) complexes with exogenous azide bridge were obtained: [Cu$_2$(H$_2$L)(μ-N$_3$)]-(ClO$_4$)$_2$·1/2C$_2$H$_5$OH (1), [Cu$_2$(HL)(μ-N$_3$)(C$_2$H$_5$-OH)(H$_2$O)(ClO$_4$)] (2), and [Cu$_2$(L)(μ-N$_3$)]-(DMF) (3).[16,17] The crystal structure of 2 was determined by X-ray single crystal structural analysis and shown in Fig. 2. The structures of 1 and 3 were optimized by molecular mechanics method. The results showed that the copper(II) ions of 1 deviate too much from coordinate plane and the later chains are turned round against the binuclear bridging network. The magnetic orbitals cannot effectively overlap in this case and give smaller magnetic exchange integrals. The structure of 3 is similar to the crystal structure of 2 and the copper(II) ions basically site the coordinate plane. The charge of phenoxide atom were obtained as −0.205, −0.275, and −0.321 for 1, 2, and 3 by quantum chemical calculations. This suggested that the charge gathered around oxygen atoms when the hydrogen atoms in later chains lost and the carbon oxygen double bonds were broken into single bonds. The electron density of the bridging atoms (phenoxide) of the enol-form complex is larger than that of the keto-form complex in terms of electron transfer. The magnetic data were obtained from the experimental measurement and led to the sequence:

$|J|_{enol}(-176.7\ cm^{-1}) > |J|_{mixed\ enol-keto}(-132.4$ $cm^{-1}) > |J|_{keto}(-86.8\ cm^{-1})$

which is in agreement with the theoretical analysis based

on the structural factor and electronic effect. Compared with the other complexes of different exogenous bridging ligands, the magnetic interaction between copper (II) ions in enol-form is significantly stronger than that in keto-form.[18]
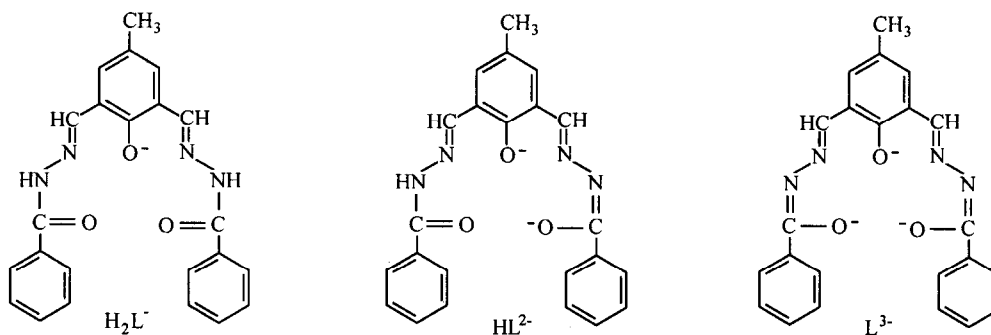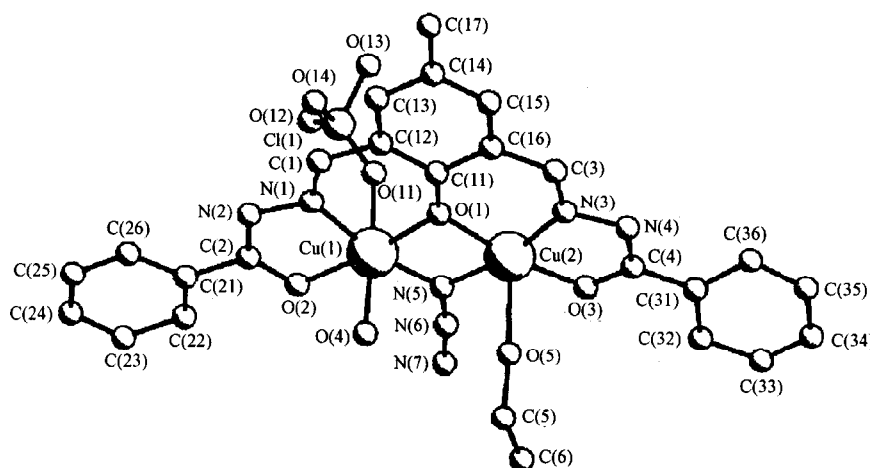

Fig. 1   Tautomer forms of the ligand.

Fig. 2   Crystal structure of 2.
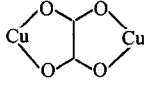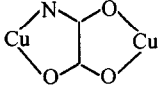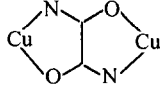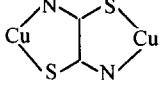
The exogenous bridging ligands, such as Br^-, Cl^-, OH^-, OR^- ($R = CH_3$ or C_2H_5), N_3^-, CNO^-, SCN^-, $C_3H_3N_2^-$ (pyrazole), are also important factors governing the magnetic interaction in this series of complexes. The magnetic studies indicate that the effect of exogenous bridging ligands on magnetic interaction is corresponding to that in spectrochemical series. This relationship has been observed in keto-form[19-21] and enol-form[18] complexes as well as other systems.[22] Detailed EPR studies on these complexes supported these results and gave the bond parameters by using the Kivelson-Neiman equation.[23]

When we consider the bridging network of the kind
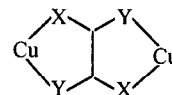
the interaction can be more important if the delocalization of the magnetic orbitals toward the X and Y atoms of the bridge is enhanced. This may be achieved by replacing oxygen atoms of $C_2O_4^{2-}$ by less electronegative atoms ($O > N > S$), so that to increase the metal-ligand interaction. The magnetic data of binuclear copper(II) complexes with different bridging ligands are summarized in Table 1.[24,25] In our study on nickel(II) and manganese(II) complexes with dithioxmato bridge, the antiferromagnetic interaction is much stronger than that in oxmato bridged complexes.[26]

Table 1 Magnetic data of binuclear copper(II) complexes with different bridging ligand

Bridging ligand	$C_2O_4{}^{2-}$	$C_2O_3NH^{2-}$	$C_2O_2(NR)_2{}^{2-}$	$C_2S_2(NR)_2{}^{2-}$
Binuclear copper(II) network				
J/cm^{-1}	-385.4	-425.5	-581	-730

Heterodinuclear coupled systems

The antiferromagnetic and ferromagnetic coupling looks like equal at first glance. However, less than 5% of well-characterized dinuclear complexes have been reported to be ferromagnetically coupled.[27] Quite a spectacular way of demonstrating the influence of the symmetry of the magnetic orbitals on the nature of the interaction is to compare the two complexes [CuVO(fsa)$_2$en·CH$_3$OH] (**4**) and [Cu$_2$(fsa)$_2$en·CH$_3$OH] (**5**), where (fsa)$_2$en^{4-} is the dinucleating ligand derived from N, N'-bis(4-carboxy-3-hydroxybenzyl)ethylenediamine.[28,29] In **4** and **5** (Fig. 3) the inner coordination site of the ligand is occupied by a Cu^{2+} ion. It is coordinated in a square pyramidal fashion by the nitrogen atoms and the phenolic oxygen atoms of the (fsa)$_2$en^{4-} ligand in the basal plane and by the CH$_3$OH ligand at the apex. The outer coordination site is occupied by a VO^{2+} ion in square pyramidal surroundings (**4**) or by a Cu^{2+} ion in planar surroundings (**5**). The plane containing the metal ions, perpendicular to the plane of the dinucleating ligand, is almost a mirror plane. In a 4 + 1 environment,
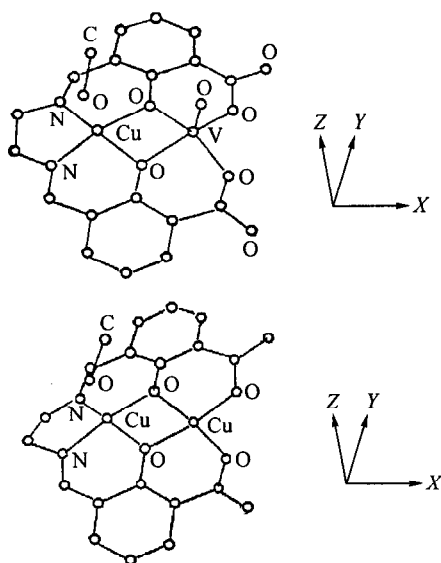
the most destabilized orbital occupied by the unpaired electron of Cu^{2+} is of the d_{xy}-type. The unpaired electron of the VO^{2+} ion occupies a $d_{x^2-y^2}$ type orbital. Consequently, the magnetic orbitals Φ_{Cu} in Cu^{2+} VO^{2+} and Cu^{2+} Cu^{2+} complexes are asymmetric with regard to the mirror-plane, while the magnetic orbital Φ_{VO} is symmetric with regard to the mirror-plane. Thus, the overlap integral $< \Phi_{Cu} | \Phi_{VO} >$ in Cu^{2+} VO^{2+} is equal to zero. The magnetic susceptibilities confirm that the interaction is actually ferromagnetic with a triplet ground state 118 cm^{-1} below the singlet state. In contrast, the overlap integral $< \Phi_{Cu} | \Phi_{Cu} >$ in Cu^{2+} Cu^{2+} is different from zero. The antiferromagnetic contribution is preponderant and the singlet state is now the lowest with a S-T gap of -650 cm^{-1}. This comparison between the Cu^{2+} VO^{2+} and Cu^{2+} Cu^{2+} pairs is shown schematically in Fig. 4.
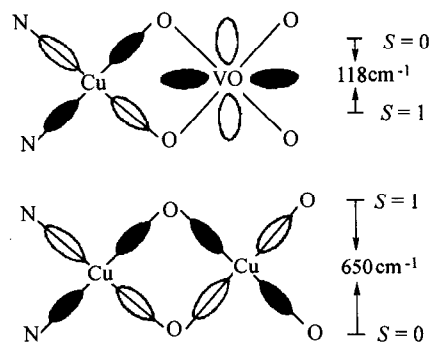
Fig. 4 Symmetry of magnetic orbitals.

Using a series of mononuclear complexes as versatile synthetic precursors (so called "complex ligand", Fig. 5), we synthesize heterodinuclear,[30-53] trinuclear[54,55] and tetranuclear[56,57] complexes. Furthermore, ferromagnetic coupled tetranuclear manganese (II)[58] and cobalt(II)[59] complexes bridged by o-phthalato ligand have also been obtained by our group.

Metal-radical systems

The radical is a kind of paramagnetic organic ligand

Fig. 3 Structure of **4** and **5**.

which can be coordinated to metal ions in both bridging and terminal positions. Nitronyl nitroxide mono-, bi-, tri- and polyradicals are stable and have been successful in designing the molecular-based magnetic materials.[60,61] Typical nitronyl nitroxide ligands are schematically shown in Fig. 6. Since the coordinated ability of the radicals is poor, co-ligands with strong electron-attracted group such as pfpr (pentafluoropropionate) and hfac (hexafluouoacetonate) are needed to participate in the coordination. The stronger the co-ligands attract electron, the larger the magnetic interaction between

radical and metal ion is. In the same co-ligand systems, the radicals have priority to coordinate to metal by less sterohindered oxygen atoms. The stronger the substitute of radicals attracts electron, the smaller the magnetic interaction between the radical and metal ion is. Our group undertook the synthesis and mechanistic study of the metal-radical complexes. Several series of metal-radical complexes with full structurally characterization have been obtained. The magnetic interaction and coupling mechanism of most characterized complexes have been interpreted.[62-70]
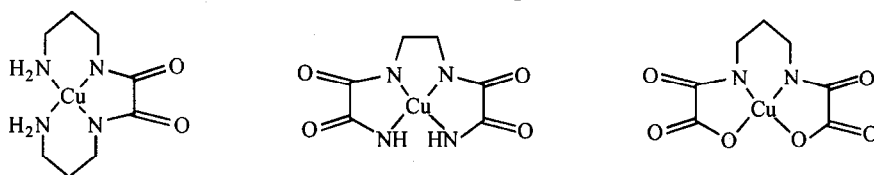

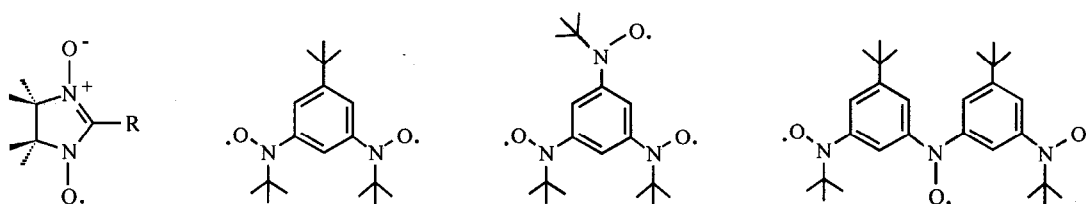Fig. 5   Selected synthetic precursors in our group.

Fig. 6   Selected redical ligands.

Molecular design of heterotrinuclear complexes with high spin ground state

In the field of design and synthesis of molecular-based ferromagnets, the first important step is synthesizing molecular entities with a large spin in the ground state. The linear ABA trinuclear species with local spins $2S_A > S_B + 1/2$ has been proven to stabilize a state of high spin multiplicity with no need of imposing ferromagneic interaction between the nearest neighbor magnetic centers.

Spin state structure and magnetic behavior of trinuclear species

For the linear and symmetrical trinuclear species ABA, the local spins are noted S_A and S_B. The interaction parameter in zero field may be written

$$H = - J(S_{A1}S_B + S_{A2}S_B) \qquad (3)$$

with $S_{A1} = S_{A2}$. In Eq. 3, it is assumed that the interaction between nearest neighbors is purely isotropic and that between terminal centers is negligible. The relative energies of the low-lying states are easily calculated as[71]

$$E_{S,S'} = - (J/2)[S(S + 1) - S'(S' + 1)] \qquad (4)$$

S denotes the spin of a given state, and S', the spin associate with the terminal ions ($S' = S_{A1} + S_{A2}$). In Eq. 4, S' varies by an integer value from 0 to $2S_A$ and for each S' value, S varies by an integer value from $|S' - S_B|$ to $S' + S_B$. Three situations may be distinguished concerning the distribution in energy of the spin state according to the relative values of S_A and S_B.[72] (i) If $2S_A \leq S_B$, the spin state structure is regular. In the case of antiferromagnetic interaction ($J < 0$), the ground state has the smallest spin $S_B - 2S_A$ and the most excited state has the highest spin $S_B + 2S_A$. $\chi_M T$ decreases in a continuous fashion when T decreases. (ii) If $2S_A = S_B + 1/2$ with S_A and $S_B \neq 1/2$, the spin state structure becomes irregular. For, $J < 0$, one may

have $E_1 < E_2$ with $S_1 > S_2$. However, the ground state is a doublet and remains the lowest spin multiplicity. The calculation shows that again $\chi_M T$ continuously decreases upon cooling. (iii) Finally, if $2S_A > S_B + 1/2$, the spin state structure is even more irregular, and for $J < 0$, the spin $2S_A - S_B$ of the ground state is not the

smallest spin anymore. On the other hand, the most excited state is again that with the largest spin $2S_A + S_B$. To illustrate the concept of spin state structure in a trinuclear species ABA, we schematized the spin state structure in Fig. 7. Each state is represented by an arrow of which the length is equal to the spin associated with the state.
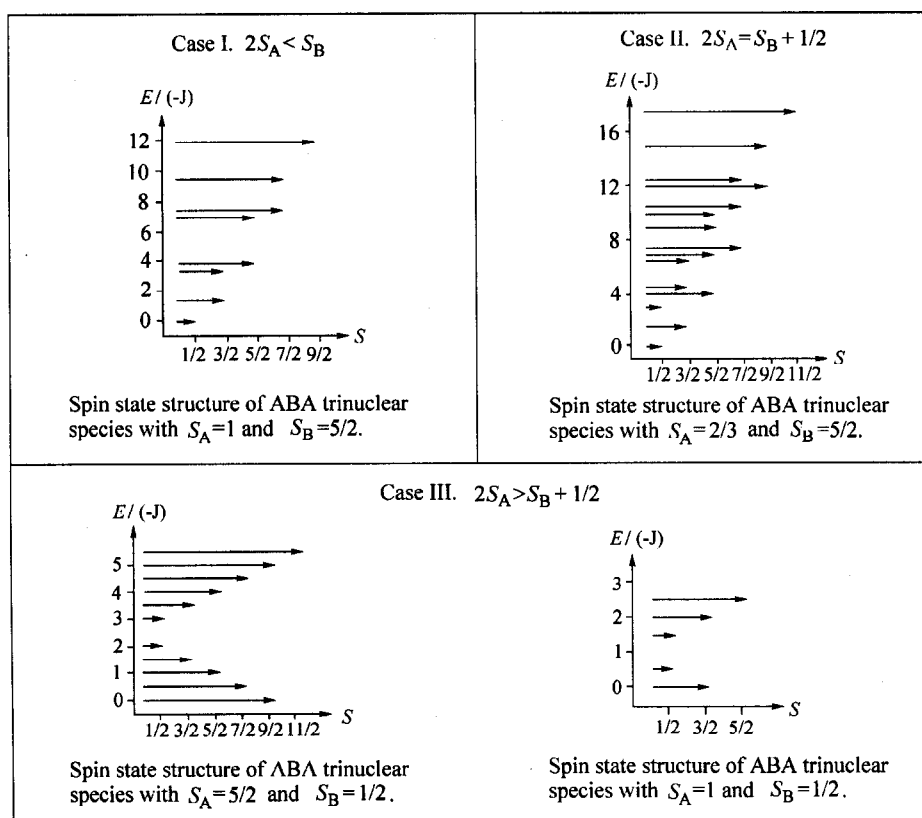

Fig. 7   Spin state structure of trinuclear specie ABA.

Design and synthesis of ABA *trinuclear complexes with irregular state*

The heterotrinuclear complexes with irregular state are very few because of the synthetic difficulty.[72-78] To overcome the limitation, a strategy is that a stable mononuclear compound such as propylene-1,3-bis-(oxamato)copper(II) [Cu(pba)$^{2-}$, see Fig. 5] and o-phenylene-bis(oxamato)-copper(II) [Cu(ebo)$^{2-}$], acts as a bridging block in designing heteronuclear compounds. Then the trinuclear complexes [MnCuMn] or [NiCuNi] were obtained by the reaction of mononuclear copper(II) precursors, Mn^{II} or Ni^{II} salts and terminal ligands (bipyridine or phenanthroline). The coordination environment of trinuclear complexes is shown in
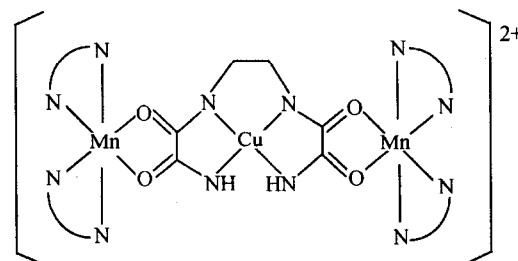
Fig. 8.

Fig. 8   Coordination environment of 6.

Among the limited examples, $\{[Mn(phen)_2]_2 [Cu-(ebo)]\}(ClO_4)_2 \cdot H_2O$ (6) showed ferromagnetic-like behavior at high temperature.[78] The $\chi_M T$ versus T plot of 6 is shown in Fig. 9. At room temperature, $\chi_M T$

is equal to 8.58 $cm^3 \cdot mol^{-1} \cdot K$ and gradually decreases with cooling temperature, reaching the expected minimum near 198 K with $\chi_M T = 8.49$ $cm^3 \cdot mol^{-1} \cdot K$; then $\chi_M T$ increases rapidly to a maximum at about 18 K with $\chi_M T = 11.85$ $cm^3 \cdot mol^{-1} \cdot K$, which is very close to the $\chi_M T$ value of the $S = 9/2$ ground state (12.3 $cm^3 \cdot mol^{-1} \cdot K$). The magnetic parameters were obtained by the expression of the magnetic susceptibility from the spin Hamiltonian ($S_{Cu} = 1/2$, $S_{Mn1} = S_{Mn2} = 5/2$) and given to be $J = -51.9$ cm^{-1}, $g_{Cu} = 2.00$ and $g_{Mn} = 2.04$. Compared with the other [MnCuMn] analogues, the value of $|J|$ of 6 was larger than that of bis(oxamido)-bridged system and led to the highest temperature ($T_{min} = 198$ K) showed ferromagnetic-like behavior to date.
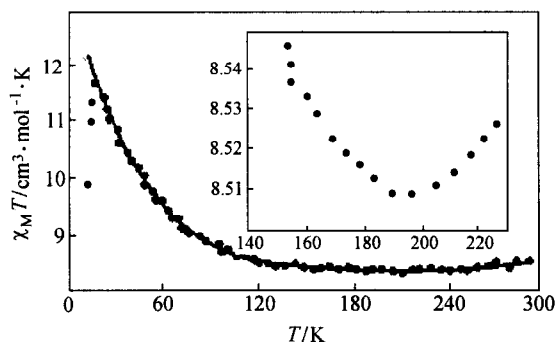

Fig. 9 $\chi_M T$ vs. T plot of **6**.

Other trinuclear complexes with ferromagnetic interaction

In the course of our study on heterotrinuclear complexes with irregular state, some of other trinuclear complexes were synthesized and showed ferromagnetic interaction. The chromium(III)-copper(II)-chromium(III) complexes, $\{[Cr(salen)]_2[Cu(pba)]\} \cdot 2H_2O$ (**7**) and $\{[Cr(salpn)]_2[Cu(pba)]\} \cdot 2H_2O$ (**8**), where pba = propylene-1,3-bis(oxamato), salen and salpn denote N,N-ethylenebis(salicylideneiminate) and N,N-1,3-propylene-bis(salicylideneiminate), showed ferromagnetic interaction with 16.6 cm^{-1}(**7**) and 18.5 cm^{-1}(**8**), respectively. The reason for this is due to the orthogonality of magnetic orbitals.[79] Other trinuclear complexes such as [CrNiCr] showed antiferromagnetic interaction.[80]

Another example is [GdCuGd] trinuclear species. In the coupling system containing gadolinium(III) and copper(II), the magnetic interaction has been proven to be ferromagnetic. The ferromagnetic coupled mechanism

could be interpreted in term of electron transfer ($3d_{Cu} \rightarrow 5d_{Gd}$).[81] Using the similar method, we synthesized a series of [GdCuGd] trinuclear complexes. The magnetic interaction in $\{[Gd(phen)_2(ClO_4)]_2[Cu(pba)]\}$-$(ClO_4)_2 \cdot 2H_2O$ (**9**) is expected to be ferromagnetic with $J = 3.56$ cm^{-1}.[82]

Assembly of high-dimensional metal complexes with unique magnetic properties

Molecules enable a substantially greater ability of control than atoms as building blocks for new materials. Assembling molecules into one-, two- or three-dimensional extended structure is of current interest. Combined with the magnetic studies, several typical systems were discussed.

Azido-bridged one-dimensional complexes

The structural and magnetic properties of azido-bridged polymetallic complexes have received considerable attention in the past two decades.[83] From the magnetic point of view, the most interesting characteristic of azido-bridged complexesis that the azido ligand is a very effective superexchange pathway for its two main coordination modes and very effectively forms one-, two-, and three-dimensional complexes, some of which show spontaneous magnetization at T_c between 16 and 40 K.[84] With the purpose of investigating further magnetic interaction and developing one-dimensional molecular-based materials, we succeeded in synthesizing a series of complexes $[M(4,4'-dimethylbipyridine)(N_3)_2]_n$ [M = Cu(II), Mn(II), Ni(II), Fe(II)].[85] The structure of copper(II) complex is shown in Fig. 10. Extended studies on manganese(II) complex[86] with different terminal ligand and heteronuclear nickel(II)-manganese(II) and copper(II)-manganese(II) complexes[85] have been done. All the studies on magnetic properties showed ferromagnetic-antiferromagnetic alternating interaction in the complexes.

When both azide ion and other bridging ligands were employed to assemble the complexes, some interesting three-dimensional Mn^{II}-azido systems have been obtained.[83,87] The crystal structure of [Mn(μ-4, 4'-bipyridine)(μ-1,3-azide)$_2$] showed helical chains of Mn^{II} ions of two different types. The chains of the first

type are connected by single EE (end to end) azido bridges (-Mn-N_3-Mn-N_3-), while the second type exhibit two consecutive EE azido bridges, followed by 4, 4'-bipyridine bridges (-Mn-N_3-Mn-N_3-Mn-4, 4'-bpy-). The whole structure has the form of a complex 3-D network as a result of the propagation of these different helicals.[87] The magnetic behavior of this complex is characteristic of a system with antiferromagnetic interactions in the high temperature region, up to 50 K, where a magnetic transition to a ferromagnetic state occurs.
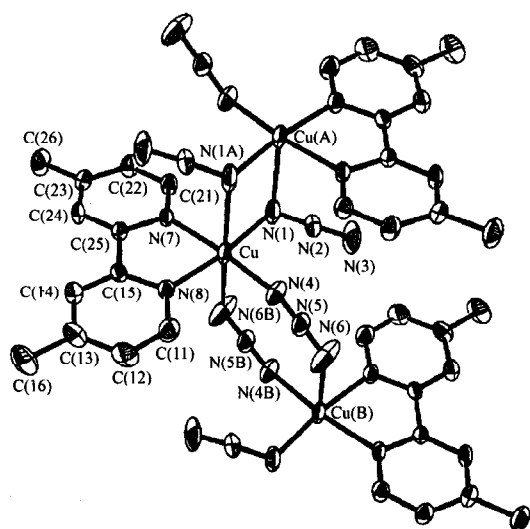
Cyanide-bridged one- and two-dimensional metal complexes *

Hexacyanometalate ions [M (CN)$_6$]$^{n-}$ are often used as building blocks for dimetallic magnetic materials.[88] Two types of dimetallic compounds have been derived from [M(CN)$_6$]$^{n-}$: 1) The Prussian-Blue family

Fig. 10   Crystal structure of [Cu(4,4'-dimethylbipyridine)(N_3)$_2$]$_n$.

constructed with a simple metal ion and 2) complex-based dimetallic assemblies constructed with a complex cation. Almost all members of the Prussian-Blue family show spontaneous magnetization, and high magnetic ordering temperature T_c are reported for some of them.[89] However, the magnetostructural correlation for Prussian-Blue compounds is still unclear due to the lack of structural information. Complex-based dimetallic assemblies with one-, two- and three-dimensional structure have been reported and exhibit ferromagnetic, antiferromagnetic or meta-magnetic behavior. Among them, the Cu^{II}-Fe^{III} and Ni^{II}-Fe^{III} bimetallic assemblies have been synthesized and characterized in much detail and exhibit a ferromagnetic interaction between adjacent copper(II) or nickel(II) and iron(III) ions through CN⁻ bridges.[90-95]
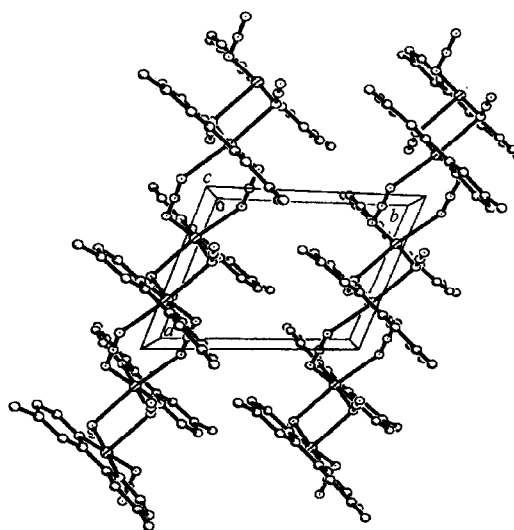
Molecular ferromagnet and metamagnet

The bimetallic assemblies of [Cu(en)]$_3$[Fe-(CN)$_6$]$_2$·$3H_2O$ [Cu$_3$Fe$_2$] and [NiL]$_3$[Fe(CN)$_6$]$_2$·$9H_2O$ [Ni$_3$Fe$_2$], where en and L represent ethylenedi-amine and 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane, have been synthesized. The magnetic measurements showed that [Cu$_3$Fe$_2$] and [Ni$_3$Fe$_2$] were molecular ferromagnet with T_c = 11 K and molecular metamagnet with T_c = 5 K, respectively. [Cu$_3$Fe$_2$] is obtained from the reaction of [Cu(en)(H$_2$O)$_2$] SO$_4$·H$_2$O and K$_3$[Fe(CN)$_6$] in water.[99] The complex is in quantitative yield and insoluble in ordinary organic solvents. On the basis of the spectra analytical data and nickel analogues, it seems reasonable to assume that [Cu$_3$Fe$_2$] consists of a polymer of [Cu(en)]$^{2+}$ and [Fe(CN)$_6$]$^{3-}$ ions linked together by cyanide bridges (Fig. 11). The magnetic measurements were performed with a SQUID magnetometer in the 4.2—300 K range and the magnetic behavior is shown in Fig. 12(a). At room temperature, $\chi_M T$ is equal to 2.69 cm^3·mol^{-1}·K (4.63 B.M.) per [Fe$_2$Cu$_3$], which increases gradually with decreasing temperature until 30 K, then abruptly below 30 K, up to the maximum value of 13.8 cm^3·mol^{-1}·K (10.51 B.M.) at 8.6 K; it then decreases below this
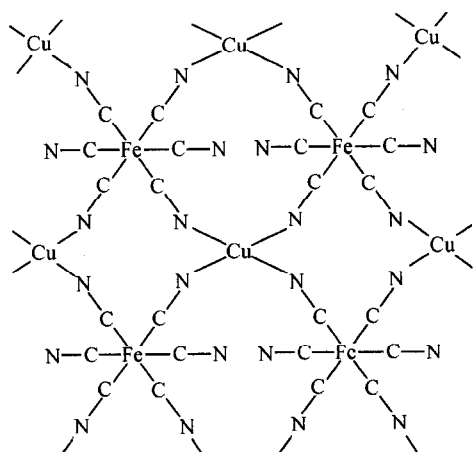
Fig. 11 Pssible structure of $[Cu_3Fe_2]$.

temperature. The maximum $\chi_M T$ is very large compared with the corresponding spin-only value (4.38 $cm^3 \cdot mol^{-1}$ $\cdot K$, 5.92 B.M.) expected for the highest total spin of a discrete Fe_2Cu_3 system. The magnetic behavior, as well as the Weiss constant ($+ 11$ K) suggested an intramolecular ferromagnetic interaction. The ferromagnetic interaction between the iron(III) and copper-(II) ions through the cyanide bridges can be rationalized by the strict orthogonality of magnetic orbitals of the low-spin iron(III) and copper(II) and illustrated in Fig. 13. In order to study the magnetic properties in detail and confirm the ferromagnetic phase transition, the field cooling magnetization (FCM), zero-field cooling magnetization (ZFCM) and hysteresis loop have been measured and shown in Fig. 12(b) and (c). As shown in Fig. 12(b), the FCM obtained cooling the sample under 1.0×10^{-5} T showed a rapid increase in magnetization when the temperature is lowered below 11 K. When the field was switched off, a remnant magnetization was observed which varnished at 11 K upon warming. The ZFCM showed a maximum at $T_c = 11$ K as expected for a polycrystalline ferromagnet. The magnetic hysteresis loop was measured at 5 K. The remnant magnetization and coercive field were obtained to be 0.17 $cm^3 \cdot mol^{-1} \cdot$ T and 2.5×10^{-5} T.

[Ni_3Fe_2] was prepared in a similar method used in [Cu_3Fe_2].[91] Its crystal structure was determined by X-ray diffraction. The asymmetric unit and 2D honeycomb-like structure are shown in Fig. 14. The structure consists of a neutral stair-shaped layer network with stoichiometry [NiL]$_3$[$Fe(CN)_6$]$_2$ and a hexagonal pattern. Each $Fe(CN)_6^{3-}$ unit used three C_3 rotational symmetry
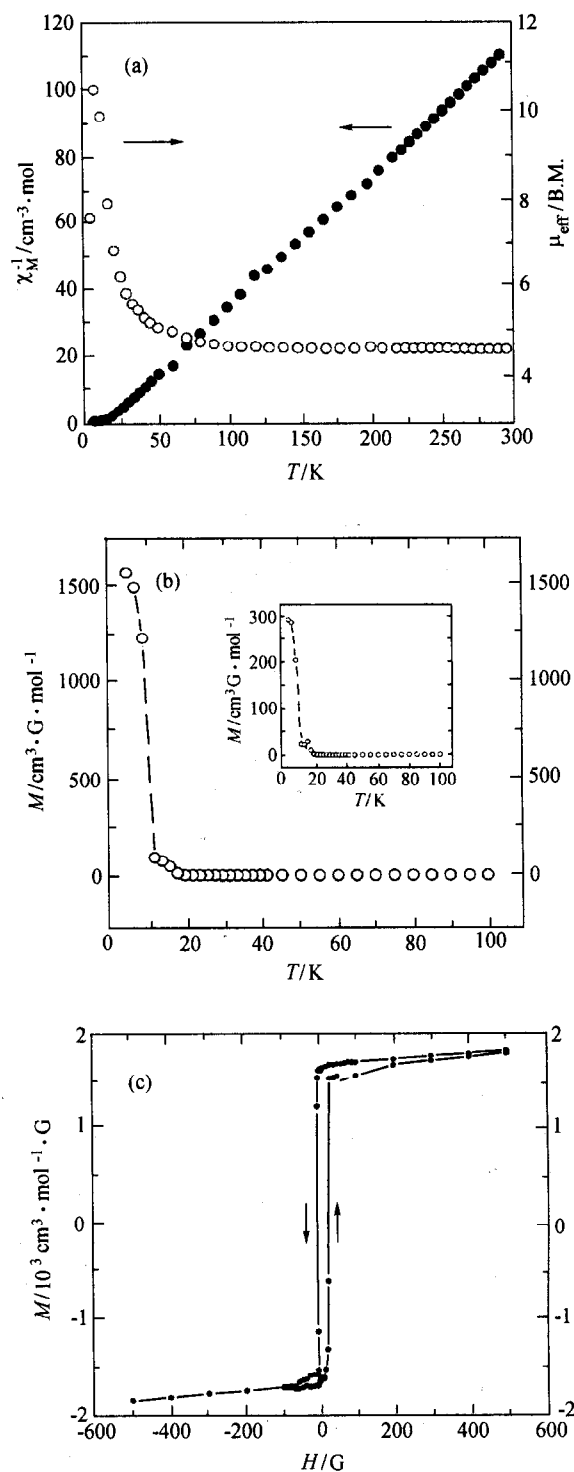

Fig. 12 Magnetic measurements of [Cu_3Fe_2]: (a) Plot of μ_{eff} and χ_M^{-1} vs. T; (b) FCM and ZFCM (insert); (c) hysteresis loop.

related cis C$\equiv$N groups to connect with three [NiL]$^{2+}$ giving rise to Fe—C $\equiv$ N—Ni linkages, whereas the three remaining symmetry related cis CN$^-$ groups are

monodentate. The adjacent Fe···Ni distance is 0.5102 nm. Each NiL unit is linked to two hexacyanoferrate-(III) ions in *trans* positions. The particular local molecular disposition leads to a honeycomb-like structure. The repeating hexagonal-like units adopt a chair conformation giving rise to an infinite waved layer.
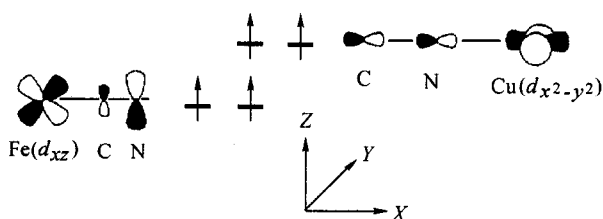

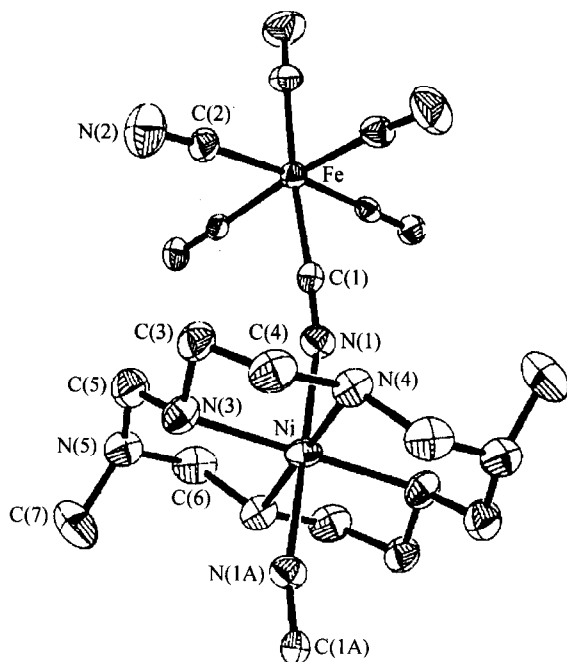**Fig. 13** Orthogonality of magnetic orbitals in [Cu_3Fe_2].

Fig. 14 ORTEO drawing and 2D honeycomb-like structure of [Ni_3Fe_2].

The magnetic susceptibilities of [Ni_3Fe_2] have been measured in the 1.7—300 K region and a plot of $\chi_M T$ vs. T is shown in Fig. 15. The $\chi_M T$ value at room temperature is 3.8 cm^3·mol^{-1}·K which increases smoothly down to 28.6 K and then sharply reaches a maximum value of 14.8 cm^3·mol^{-1}·K at 6.85 K, which is much larger than the spin-only value of 10.0 cm^3·mol^{-1}·K for $S_T = 4$ resulting from the ferromagnetic coupling of three nickel(II) ions and two low-spin iron(III) ions, strongly suggestive of the occurrence of magnetic ordering. The susceptibility above 6 K obeys the Curie-Weiss law with a positive Weiss constant $\theta = +9.0$ K. The ferromagnetic interaction between the iron(III) and nickel(II) ions is also due to the strict orthogonality of the magnetic orbitals of low-spin Fe^{III} (t_{2g}^5) and Ni^{II} (e_g^2). The onset of a long-range magnetic phase transition is further confirmed by the temperature dependence of the ac molecular susceptibility displayed in Fig. 16.
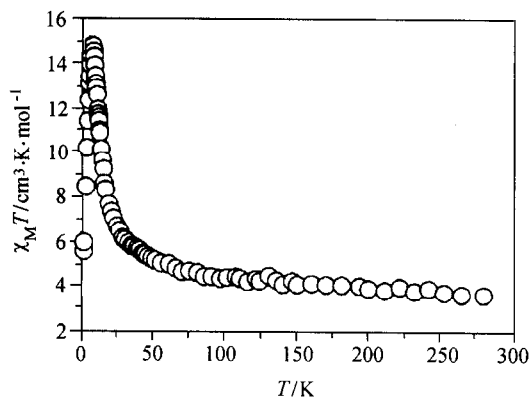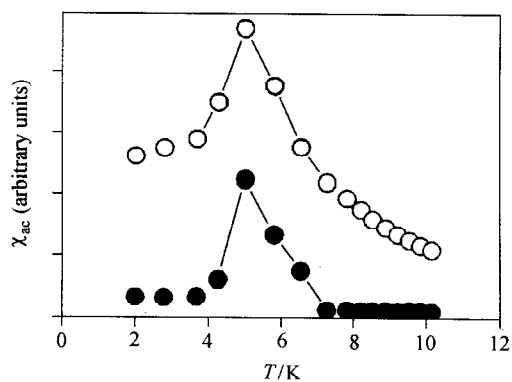

Fig. 15 Plot of $\chi_M T$ vs. T of [Ni_3Fe_2].

Fig. 16 Real, χ' (O), and imaginary, (χ''(●)), ac magnetic susceptibility as a function of temperature taken at 133 Hz for [Ni_3Fe_2].

The real part of the zero field ac magnetic susceptibility, $\chi'(T)$, has a maximum at $ca.$ 5 K for a frequency of 133 Hz, suggesting that T_c of $[Ni_3Fe_2]$ is about 5 K.

The field dependence of the magnetization (0—7 T) measured at 1.93 K is shown in Fig. 17(a) in the form of $M/N\mu_B$ (per Ni_3Fe_2 unit) vs. H, where M, N, μ_B and H are the magnetization, Avogadro's number, the electron Bohr magneton and applied magnetic field, respectively. The magnetization reaches a value of 7.5 $N\mu_B$ at 7 K which is close to the expected $S = 4$ value of 8 $N\mu_B$ for the $[Ni_3Fe_2]$ system. The magnetization was elaborately measured as a function of the external magnetic field (0—0.5 T) at 1.93 K (Fig. 17 (b)). A noticeable sigmoidal behavior is observed which suggests a metamagnet: the magnetization first increases slowly with the increased field and then sharply showing a spin-flipping from antiferromagnetic to ferromagnetic arrangement between the layers. In addition, the extremely small zero-field susceptibility value also suggests a metamagnet. Considering the small interlayer separation (0.919 nm), interlayer antiferromagnetic interaction could operate, which could be regarded as the origin of the metamagnetic behavior.
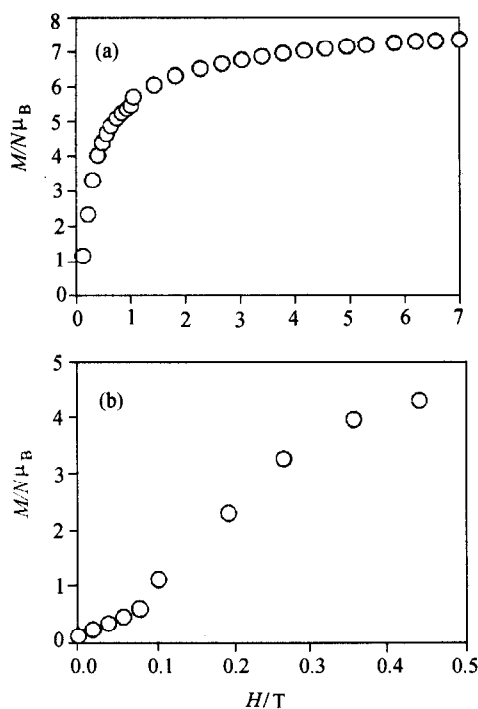

Fig. 17   Magnetization at 1.93 K as a function of the applied magnetic field: (a) up to 7 T and (b) at 0—0.5 T.

Conclusion and outlook

Since the space was limited, we only described a few of the results we recently obtained along the molecular and crystal magnetic engineering in polymetallic coupled system. The first success achieved has been the design of ferromagnetically coupled complexes. This result is important in the synthesis of molecular ferromagnets. Although more and more molecular-based magnets are reported, the ferromagnetic phase transition temperature is still very low (lower than liquid nitrogen temperature) for most molecular magnets. The assembly of polymetallic coupled system with multi-dimensional structure is one of the most active field at present.[100,101] The difficult problem to solve is to realize this orthogonality not only inside a molecular entity but at the scale of the crystal lattice. On the other hand, several molecular magnets with magnetic ordering temperature at liquid nitrogen temperature region[102-106] and even above room temperature were reported.[8-11] The structures of these complexes have not been determined and the ferromagnetic coupling mechanism is unclear. Moreover, they don't retain their molecular nature well.

The richness of coordination chemistry allowed us using basic but powerful concept to design new magnetic objects with original but predictable properties. Efforts are now directed to elaborate new systems with higher and higher blocking temperatures to provide clean nanoscale magnetic systems, both for checking models in fundamental quantum physics (magnetic tunneling effect...) and for applied materials science (magneto-optics, grant magneto-resistive effect, recording devices, contrast agents...).

Acknowledgment

## Reference

1   Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.;

Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1297.

2   McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

3   Yu Korshak, V.; Medvedeva, T. V.; Ovchinnikov, A. A. *Nature* **1987**, 326, 370.

4   Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

5   Chiarelli, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147.

6   Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803.

7   Ohba, M.; Usuki, N.; Fukita, N.; Okawa, O. *Angew. Chem. Int. Ed.* **1999**, *38*, 1795.

8   Manriquez, J.M.; Yee, G.T.; McLean, R.S.; Epstein, A.J.; Miller, J.S. *Science* **1991**, *252*, 1415.

9   Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701.

10 Holmes, S. M.; Girolami, G. *J. Am. Chem. Soc.* **1999**, *121*, 5593.

11 Hatlevik, O.; Bushmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914.

12 (a) *Proceedings for the VIIth International Conference on Molecule-based Magnets* (*ICMM VII*), Eds.: Dunbar, K. R.; Girolami, G. S., San Antonio, Texas, **2000**.
    (b) *Proceedings for the VIth International Conference on Molecule-based Magnets* (*ICMM VI*), Ed.: Kahn, O., Seignosse, France, **1998**.
    (c) *Proceedings for the Vth International Conference on Molecule-based Magnets* (*ICMM V*), Eds.: Itoh, K.; Takui, T., Osaka, Japan, **1996**.
    (d) *Proceedings for the IVth International Conference on Molecule-based Magnets* (*ICMM IV*), Eds.: Millar, J. S.; Epstein, A. J., Salt Lake City, Utah, **1994**.
    (e) *Proceedings for Chemistry and Physics of Molecule-based Magnetic Materials* (*ICMM III*), Ed.: Iwamura, H., Tokyo, Japan, **1992**.
    (f) *Proceedings for Magnetic Molecular Materials* (*ICMM II*), Eds.; Gatteschi, G.; Kahn, O.; Millar, J. S.; Palacio, F., Ciocco, Itlay, **1990**.
    (g) *Proceedings for Ferromagnetic and High Spin Molecular Based Materials* (*ICMM I*), Eds.; Millar, J. S.; Doughtery, D. A., Dallas, Texas, **1989**.

13 Bleaney, B.; Bowers, K. D. *Proc. R. Soc.* (*London*) *Ser. A* **1952**, *214*, 451.

14 Gatteschi, D.; Pardi, L. *Gazz. Chim. Acta* **1993**, *123*, 231.

15 Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *92*, 45.

16 Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.; Wang, G. L.; Yao, X. K.; Wang, H. G. *Inorg. Chim. Acta* **1996**, *248*, 135.

17 Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.; Wang, G. L.; Wang, L. G.; Lao, X. J.; Yao, X. K.; Wang, H. G.; Wang, G. X. *Acta Chim. Sin.*

1996, *54*, 554 (in Chinese).

18 Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.; Wang, G. L.; Wang, L. G.; Lao, X. J.; Yao, X. K.; Wang, H. G.; Wang, G. X. *Sin. in China*, Ser. B **1996**, *39*, 192.

19 Cheng, P.; Liao, D. Z.; Yan, S. P.; Cui, J. Z.; Jiang, Z. H.; Wang, G. L.; Yao, X. K.; Wang, H. G. *Helv. Chim. Acta* **1997**, *80*, 213.

20 Cheng, P.; Yan, S. P.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Chin. J. Chem.* **1994**, *12*, 314.

21 Yan, S. P.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L.; Wang, H. G.; Yao, X. K. *Polyhedron* **1992**, *11*, 879.

22 Yan, S. P.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1994**, *13*, 1801.

23 Cheng, P.; Bai, L. J.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1995**, *14*, 2519.

24 Verdaguer, M.; Julve, M.; Gleizes, A.; Kahn, O. *Nouv. J. Chim.* **1985**, *9*, 325.

25 Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y.; Murr, E. *Inorg. Chem.* **1984**, *23*, 4448.

26 Cui, J. Z.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1998**, *17*, 2517.

27 Chen, C. T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.

28 Kahn, O.; Galy, J.; Journaux, T.; Jaud, J.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165.

29 Galy, J.; Jaud, J,; Kahn, O.; Tola, P. *Inorg. Chim. Acta* **1979**, *36*, 229.

30 Liao, D. Z.; Okawa, H. *Inorg. Chim. Acta* **1986**, *118*, 21.

31 Zhang, Z. Y.; Liao, D. Z.; Jiang, Z. H.; Hao, S. Q.; Wang, G. L.; Yao, X. K.; Wang, H. G. *Inorg. Chim. Acta* **1990**, *173*, 201.

32 Yang, G. M.; Shi, J.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1998**, *17*, 1587.

33 Li, Y. T.; Yan, C. W.; Liao, D. Z. *Polyhedron* **1997**, *16*, 4379.

34 Sun, X. R.; Miao, M. M.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1996**, *15*, 2927.

35 Li, Y. T.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron* **1995**, *14*, 2209.

36 Ma, S. L.; Jiang, Z. H.; Liao, D. Z.; Yan, S. P.; Wang, G. L. *Polyhedron* **1995**, *14*, 373.

37 Li, Y. T.; Jiang, Z. H.; Ma, S. L.; Li, X. Y.; Liao, D. Z.; Yan, S. P.; Wang, G. L. *Polyhedron* **1994**, *13*, 475.

38 Ma, S. L.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Polyhedron* **1994**, *13*, 1647.

39 Ma, S. L.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Polyhedron* **1993**, *12*, 1523.

40 Liao, D. Z.; Shi, J.; Jiang, Z. H.; Yan, S. P.; Cheng, P.; Wang, G. L. *Polyhedron* **1992**, *11*, 2621.

41 Liao, D. Z.; Li, L. C.; Wang, G. L. *Polyhedron* **1991**, *10*, 1787.

42   Zhang, Z. Y.; Liao, D. Z.; Jiang, Z. H.; Hao, S.
     Q.; Wang, G. L.; Yao, X. K.; Wang, H. G. Sci. in
     China, Ser. B 1991, 34, 265.

43   Liao, D. Z.; Zhao, Q. H.; Wang, G. L. Sci. in Chi-
     na, Ser. B 1990, 33, 914.

44   Li, Y. T.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L.
     Acta Chim. Sin. 1996, 54, 679 (in Chinese).

45   Liao, D. Z.; Lin, B.; Wang, G. L. Acta Chim. Sin.
     1992, 50, 269 (in Chinese).

46   Liao, D. Z.; Jia, Z. Z.; Zhang, Z. Y.; Jiang, Z. H.;
     Wang, G. L. Acta Chim. Sin. 1991, 49, 483(in Chi-
     nese).

47   Liu, Z. M.; Jiang, Z. H.; Liao, D. Z.; Wang, G.
     L.; Yao, X. K.; Wang, H. G. Acta Chim. Sin. 1991,
     49, 981 (in Chinese).

48   Liao, D. Z.; Zhao, Q. H., Wang, G. L. Acta Chim.
     Sin. 1990, 48, 360 (in Chinese).

49   Liao, D. Z.; Zhao, Q. H., Wang, G. L. Acta Chim.
     Sin. 1990, 48, 797 (in Chinese).

50   Li, Y. T.; Yan, C. W.; Liao, D. Z. Chin. J. Chem.
     1999, 17, 24.

51   Li, Y. T.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L.
     Chin. J. Chem. 1995, 13, 216.

52   Li, Y. T.; Jiang, Z. H.; Liao, D. Z.; Yan, S. P.;
     Ma, S. L.; Wang, G. L. Chin. J. Chem. 1994, 12,
     414.

53   Liu, B.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.;
     Wang, G. L. Chem. Lett. 1999, 819.

54   Zhang, S. W.; Liao, D. Z.; Jiang, Z. H.; Wang, G.
     L. Polyhedron 1996, 15, 4289.

55   Liao, D. Z.; Li, L. C.; Wang, G. L. Chin. J. Chem
     1991, 9, 410.

56   Li, Y. T.; Jiang, Z. H.; Liao, D. Z.; Yan, S. P.;
     Ma, S. L.; Li, X. Y.; Wang, G. L. Polyhedron 1993,
     12, 2781.

57   Yang, G. M.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.;
     Wang, G. L.; Yao, X. K.; Wang, H. G. J. Cluster
     Sci. 1998, 9, 465.

58   Jiang, Z. H.; Ma, S. L.; Liao, D. Z.; Yan, S. P.;
     Wang, G. L.; Yao, X. K.; Wang, R. J. J. Chem.
     Soc., Chem. Commun. 1993, 745.

59   Jiang, Z. H.; Ma, S. L.; Liao, D. Z.; Yan, S. P.;
     Wang, G. L.; Yao, X. K.; Wang, R. J. Sci. in Chi-
     na, Ser. B 1994, 37, 923.

60   Caneschi, A.; Gatteschi, D.; Rey, P. Prog. Inorg.
     Chem. 1991, 39, 331.

61   Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.;
     Kahn, O. Science 1993, 261, 447.

62   Jiang, Z. H.; Sun, B. W.; Liao, D. Z.; Wang, G.
     L.; Dahan, F.; Tuchagues, J.-P. Inorg. Chim. Acta
     1998, 279, 69.

63   Jiang, Z. H.; Sun, B. W.; Liao, D. Z.; Wang, G.
     L.; Dahan, F.; Tuchagues, J.-P. Inorg. Chim. Acta
     1998, 279, 76.

64   Jiang, Z. H.; Yi, Q.; Liao, D. Z.; Huan, Z. W.;
     Bai, L. J.; Liu, A. J.; Yan, S. P.; Wang, G. L.;
     Yao, X. K.; Wang, R. J. Sin. in China, Ser. B
     1995, 25, 119 (in Chinese).

65   Sun, B. W.; Zhao, Q. H.; Liao, D. Z.; Jiang, Z.
     H.; Yan, S. P.; Wang, G. L. Sin. in China, Ser. B
     2000, 43, 105.

66   Sun, B. W.; Li, S. Q.; Liao, D. Z.; Jiang, Z. H.;
     Liu, A. J.; Yan, S. P.; Wang, G. L. Chin. J.
     Chem. 1998, 16, 436.

67   Zhang, L.; Li, S. Q.; Liao, D. Z.; Jiang, Z. H.;
     Yan, S. P.; Wang, G. L.; Wang, Z.; Shen, P. W.;
     Yao, X. K.; Wang, H. G. Chin. J. Chem. 1999,
     17, 342.

68   Zhang, L.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.;
     Wang, G. L. Helv Chim. Acta, in press.

69   Sun, B. W.; Zhao, Q. H.; Liao, D. Z.; Jiang, Z.
     H.; Yan, S. P.; Wang, G. L. Can. J. Chem. 2000,
     78, 1.

70   Jiang, Z. H.; Zhang, W.; Liao, D. Z.; Huan, Z. W.;
     Qi, Y. Q.; Wang, G. L. Polyhedron 1996, 15, 1429.

71   Kambe, K. J. Phys. Soc. Jpn 1950, 5, 48.

72   Pei, Y.; Journaux, Y.; Kahn, O. Inorg. Chem. 1988,
     27, 399.

73   Pei, Y.; Journaux, Y.; Kahn, O.; Dei, A.; gatteschi,
     D. J. Chem. Soc., Chem. Commun. 1986, 1300

74   Ribas, J.; Diaz, R.; Costa, R.; Journaux, Y.; Math-
     oniere, O.; Kahn, O.; Gleizes, A. Inorg. Chem. 1990,
     29, 2042.

75   Miao, M. M.; Liao, D. Z.; Jiang, Z. H.; Wang, G.
     L. Polyhedron 1995, 14, 1577.

76   Miao, M. M.; Liao, D. Z.; Jiang, Z. H.; Wang, G.
     L. Acta Chim. Sin. 1996, 54, 363 (in Chinese).

77   Miao, M. M.; Liao, D. Z.; Jiang, Z. H.; Cheng, P.;
     Wang, G. L. Chin. J. Chem. 1996, 14, 326.

78   Miao, M. M.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.;
     Wang, G. L. Chin. Sci. Bull. 1996, 41, 995.

79   Liao, D. Z.; Shi, J.; Jiang, Z. H.; Yan, S. P.;
     Wang, G. L. Acta Chim. Sin. 1994, 52, 171 (in Chi-
     nese).

80   Zhang, S. W.; Liao, D. Z.; Jiang, Z. H.; Wang, G.
     L. Polyhedron 1996, 15, 4289.

81   Andruh, M.; Ramade, I.; Codjovi, E.; Guillou, O.;
     Kahn, O.; Trombe, J. C. J. Am. Chem. Soc. 1993,
     115, 1822.

82   Miao, M. M.; Cheng, P.; Liao, D. Z.; Jiang, Z. H.;
     Wang, G. L. Acta Chim. Sin. 1997, 55, 285 (in Chi-
     nese).

83   Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.;
     Cortes, R.; Lezama, L.; Rojo, T. Coord. Chem. Rev.
     1999, 193-195, 1027.

84   Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner,
     F. A. Inorg. Chem. 1997, 36, 3440.

85   Shen, H. Y.; Bu, W. M.; Gao, E. Q.; Liao, D. Z.;
     Jiang, Z. H.; Yan, S. P.; Wang, G. L. Inorg. Chem.
     2000, 39, 396.

86   Tang, L. F.; Zhang, L.; Li, L. C.; Cheng, P.;
     Wang, Z. H.; Wang, J. T. Inorg. Chem. 1999, 38,
     6326.

87   Shen, H. Y.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.;
     Sun, B. W.; Wang, G. L.; Yao, X. K.; Wang, H.
     G. Chem. Lett. 1998, 469.

88 Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283.

89 Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaisser-mann, J.; Seuleiman, M.; Desplanche, C.; Scuiller, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190-192*, 1023.

90 Kou, H. Z.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Wang, G. L.; Yao, X. K.; Wang. H. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1503.

91 Kou, H. Z.; Bu, W. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Fan, Y. G. *J. Chem. Soc., Dalton Trans.* **1998**, 4161.

92 Kou, H. Z.; Gao, S.; Bu, W. M.; Liao, D. Z.; Ma, B. Q.; Jiang, Z. H.; Yan, S. P.; Fan, Y. G.; Wang, G. L. *J. Chem. Soc., Dalton Trans.* **1999**, 2477.

93 Kou, H. Z.; Bu, W. M.; Gao, S.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Fan, Y. G.; Wang, G. L. *J. Chem. Soc., Dalton Trans.* **2000**, 2996.

94 Kou, H. Z.; Gao, S.; Ma, B. Q.; Liao, D. Z. *Chem. Commun.* **2000**, 713.

95 Kou, H. Z.; Gao, S.; Ma, B. Q.; Liao, D. Z. *Chem. Commun.* **2000**, 1309.

96 Kou, H. Z.; Wang, H. M.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Huang, X. Y.; Wang, G.

L. *Aust. J. Chem.* **1998**, *51*, 661.

97 Kou, H. Z.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Wang, G. L.; Yao, X. K.; Wang, H. G.; Tuchagues, J.-P. *Acta Chem. Scand.* **1999**, *53*, 542.

98 Kou, H. Z.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Wang, G. L. *Acta Chim. Sin.* **1999**, *57*, 409 (in Chinese).

99 Kou, H. Z.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Wang, G. L. *Trans. Met. Chem.* **1996**, *21*, 349.

100 Shen, H. Y.; Bu, W. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Inorg. Chem.* **2000**, *39*, 2239.

101 Zhang, L.; Cheng, P.; Tang, L. F.; Weng, L. H.; Jiang, Z. H.; Liao, D. Z.; Yan, S. P.; Wang, G. L. *Chem. Commun.* **2000**, 717.

102 Gadet, V.; Mallah, T.; Castro, I.; Verdauger, M. *J. Am. Chem. Soc.* **1993**, *114*, 9213.

103 Mallah, T.; Thiebaut, S.; Verdauger, M.; Veillet, P. *Science* **1993**, *262*, 1554.

104 Entley, W. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 5165.

105 Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397.

106 Fitzgerald, J. P.; Kaul, B. B.; Yee, G. T. *Chem. Commun.* **2000**, 49.
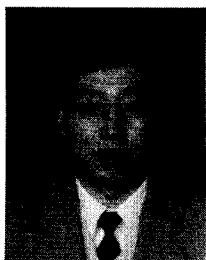
Prof. **Peng, Cheng** received his B.S., M.S. and Ph.D. degrees at Nankai University in 1985, 1991 and 1994, respectively. Subsequently he started his academic career at Nankai University and was appointed a full professor in 1996. After working at Laboratiore de Chimie de Coordination du CNRS, France as a visiting professor for three months, he moved to the United States and did postdoctoral research at Texas A&M University during 1997—1999. His main research interests include molecular material chemistry and bioinorganic chemistry.

(E-mail: pcheng@nankai.edu.cn)
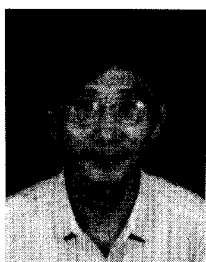
Prof. **Daizheng Liao** graduated from the Chemistry Department of Fudan University in 1962 and then he worked in the Chemistry Department of Nankai University as an assistant during 1962—1979. Later he promoted to Lecturer in 1979, associated professor in 1983, full professor in 1990. From 1985 to 1986 he was a visiting Professor at Kyushu University in Japan. His main research interests are the design of functional polynuclear complexes and molecular magnetism. So far he has published more than 400 research papers on domestic and international chemical journals.

(E-mail: coord@nankai.edu.cn)