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3d−4f Combined Chemistry: Synthetic Strategies and Magnetic Properties

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Heterometallic 3d−4f complexes are of high interest in molecular magnetism: the lanthanide ions bring large and, in most cases, anisotropic magnetic moments. The combination of 3d and 4f metal ions, which differ through their chemistries and stereochemical preferences, leads to a rich variety of heterometal complexes, ranging from discrete entities to 3-D coordination polymers. This paper reviews recent achievements in this field: (i) oligonuclear complexes for studying the nature of the 3d−4f exchange interaction; (ii) construction of single-molecule magnets; (iii) magnetic properties of 3d−4f coordination polymers.

Introduction

The combination of different spin carriers within the same molecular entity leads to a wide variety of magnetic properties of polynuclear complexes.[1] Important concepts in molecular magnetism, such as irregular spin-state structure and one-dimensional (1-D) systems with a ferrimagnetic spin arrangement, with ferromagnetic coupling arising from the orthogonality of the magnetic orbitals, have been illustrated by heterospin systems.[2] Molecular magnetism definitely stimulated the inorganic synthesis. Chemists are now able to design heterometallic complexes exhibiting various nuclearities, dimensionalities, and peculiar topologies of the spin carriers. Such compounds are of interest not only in materials science but also in physics and theoretical chemistry, providing interesting cases of investigation.

The chemistry of 3d−4f heterometal complexes has also been boosted by the tremendous development of molecular magnetism.[3] Lanthanide ions bring large and, in some cases, high anisotropic magnetic moments. The first investigation of the magnetic properties of a 3d−4f heterometallic complex is due to Gatteschi et al., who observed and characterized the ferromagnetic interaction between Cu^{II} and Gd^{III}.[4] Subsequent works have shown that, in most cases, this interaction is ferromagnetic.[5] In a first stage, in the early

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1990s, the big spin of the $\mathrm{Gd^{III}}$ ion ($S = {}^{7}/_{2}$, $^{8}\mathrm{S}_{7/2}$) and the occurrence of ferromagnetic interactions between $\mathrm{Cu^{II}}$ and $\mathrm{Gd^{III}}$ in a large majority of complexes were very appealing in the design of molecule-based magnets. Moreover, the absence of the orbital contribution to the magnetic moment of the $\mathrm{Gd^{III}}$ ion allowed the straightforward determination of the exchange coupling constants by using the isotropic HDVV spin Hamiltonian, highlighting the factors that affect the nature and magnitude of the $\mathrm{Cu^{II}}$−$\mathrm{Gd^{III}}$ exchange interaction. On the other hand, lanthanide ions with anisotropic magnetic moments are good candidates as building blocks in the construction of magnetic materials with large hysteresis loops.[6] However, the rather weak $\mathrm{Cu^{II}}$−$\mathrm{Ln^{III}}$ exchange interactions lead to low critical temperatures of the molecule-based magnets ($T_c < 2$ K),[7] and the interest in such systems decreased somehow.

More recently, the interest of chemists moved toward lanthanides exhibiting a high anisotropy, as a prerequisite for the design of single-molecule magnets (SMMs) and single-chain magnets (SCMs). The best candidates are $\mathrm{Tb^{III}}$ (ground term:$^{7}\mathrm{F}_6$) $\mathrm{Dy^{III}}$ ($^{6}\mathrm{H}_{15/2}$), and $\mathrm{Ho^{III}}$ ($^{5}\mathrm{H}_8$). Indeed, several SMMs based upon 3d and 4f ($\mathrm{Tb^{III}}$, $\mathrm{Dy^{III}}$, and $\mathrm{Ho^{III}}$) ions were reported recently.[8] Moreover, it has been shown that even mononuclear $\mathrm{Tb^{III}}$ and $\mathrm{Dy^{III}}$ complexes fulfill the conditions to exhibit a slow relaxation of the magnetization.[9] SCMs constructed from anisotropic lanthanide ions are known as well.[10]

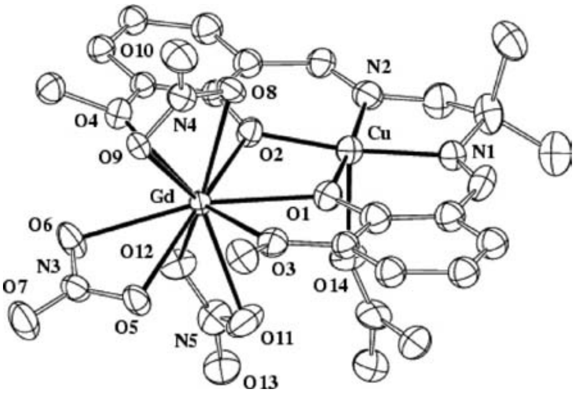

Figure 1. ORTEP plot for the dinuclear Cu−Gd complex with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted.

The peculiarity of the $\mathrm{Cu^{II}}$−$\mathrm{Gd^{III}}$ coupling raised further questions concerning the nature of the exchange interactions between (i) $\mathrm{Cu^{II}}$ and the other trivalent lanthanide cations, (ii) $\mathrm{Gd^{III}}$ and other 3d metal ions, and (iii) 3d metal ions, other than copper, and all of the lanthanides. In order to address these questions, numerous 3d−4f complexes, mainly binuclear, have been synthesized and investigated. They provide useful information for understanding the magnetic behavior of more complicated systems, such as 3d−4f coordination polymers with various dimensionalities.

Dinuclear 3d−4f Complexes Derived from Schiff Bases

The main interest of the first trinuclear Cu−Gd−Cu complex described in 1985 by the "Gatteschi team"[4] was to evidence the ferromagnetic nature of the Cu−Gd interaction. In order to check the magnetic behavior of molecular complexes comprising simultaneously 3d and 4f complexes, it seemed desirable to develop a general route allowing the synthesis of strictly dinuclear complexes. This aim was realized by use of Schiff base ligands having an inner $\mathrm{N_2O_2}$ coordination site capable of linking the 3d ion and an outer and larger $\mathrm{O_2O_2}$ coordination site that can coordinate a 4f ion, according to a stepwise process where the 3d ion is first introduced before the resulting complex is used as a ligand to coordinate the 4f ion and to give the expected final dinuclear species. The first example, published in 1996, involved the Schiff base compartmental ligand resulting from the reaction of *o*-vanillin with 1,2-diamino-2-methylpropane, complexation of the copper into the inner site followed by reaction of the neutral copper complex with gadolinium nitrate.[11] The copper ion is pentacoordinate to the four $\mathrm{N_2O_2}$ atoms of the ligand and to the oxygen atom of an acetone molecule in an apical position, while the gadolinium ion is decacoordinate to the two phenoxo and two methoxy oxygen atoms of the ligand and to the six oxygen atoms coming from the three chelating nitrato anions (Figure 1). The copper and gadolinium ions are linked by two phenoxo oxygen atoms responsible for the transmission of a ferromagnetic interaction between the copper and gadolinium ions. According to the isotropic Hamiltonian $H = -J(S_{\mathrm{Cu}}S_{\mathrm{Gd}})$, the

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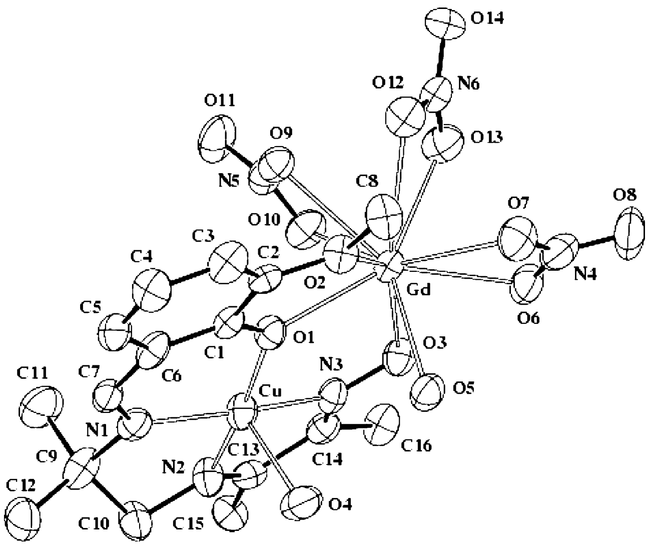

Figure 2. Molecular plot for the dinuclear Cu−Gd complex with a dissymmetric (O, N−O) bridge, ellipsoids drawn at the 50% probability level, and hydrogen atoms omitted.

magnitude of the interaction parameter J is equal to 7.2(1) cm^{-1}. Several other dinuclear complexes have been prepared by changing the gadolinium coordination sphere by the introduction of diverse anions,[5c,12,13] by modifying the length of the diamino chain, or by suppressing it and keeping only the imine functions.[14] From the structural determinations and magnetic studies, a correlation is found between the value of the ferromagnetic interaction J and the dihedral angle, α, between the two planes (OCuO and OGdO) involving the bridging oxygen atoms and each metal ion. The largest J value corresponds to a practically planar CuO_2Gd core [J = 10.1 cm^{-1} for $\alpha = 1.7(2)°$]. It decreases to 4.2 and 1.4 cm^{-1} for an α increase of 19.1(2)° and 39.6°, respectively.

A similar observation has been reported for two dinuclear Cu−Gd complexes with dissymmetric double bridges implying phenoxo and oximato functions.[15] Replacement of a phenoxo bridge by an oximato bridging function yields pentaatomic Cu(O,N−O)Gd cores with the nitrogen atom of the oxime function linked to the copper ion while the oxygen atom is coordinated to the gadolinium ion (Figure 2). These two complexes only differ by the length of the diamino chain, with two or three carbon atoms. In the latter case, the most important distortion [$\alpha = 39.1(1)°$] is associated with an antiferromagnetic interaction ($J = -0.5$ cm^{-1}), while the other complex with $\alpha = 6.1(3)°$ presents a ferromagnetic interaction ($J = 3.5$ cm^{-1}). The conjugated effects of the α angle and the dissymmetry of the bridge have been able to give two antiferromagnetic exceptions to the widespread occurrence of the ferromagnetic coupling in Cu−Gd complexes. A theoretical work directed toward the mechanism of ferromagnetic coupling in Cu−Gd complexes has evidenced the active role played by the ligand and by the empty 5d Gd orbitals slightly hybridized with the 4f orbitals via a spin-polarization effect transmitted by the ligand.[16] More recently, a new Cu−Gd complex with a dissymmetric phenoxo−hydroxo bridge has been reported (Figure 3), along with the corresponding trinuclear complex.[17] In spite of these nonsymmetric bridges, ferromagnetic interactions operate in these complexes [$J = 8.4(1)$ cm^{-1} with $\alpha = 0.3(1)°$ for the dinuclear complex]. These results corroborate preponderance of the planarity of the $\text{Cu−O}_2\text{−Gd}$ core over the dissymmetry of the bridges. However, the dominating role of a structural factor is a strong experimental argument in favor of a decisive contribution of the 5d Gd orbitals in the magnetism of the Cu−Gd complexes.

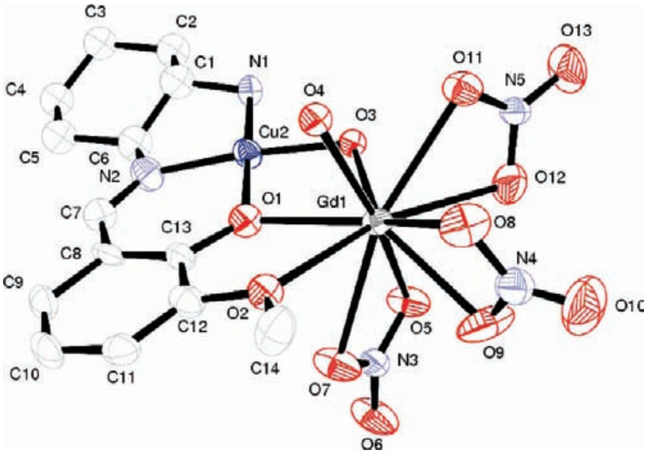

Figure 3. ORTEP plot of the Cu−Gd complex with a dissymmetric phenoxo−hydroxo bridge at the 30% probability level and hydrogen atoms omitted for clarity.

Another advantage of Schiff base ligands, which makes the process even more general, comes from the fact that they are able to make complexes with the entire set of 3d complexes, so that they allow the nature of the 3d and 4f ions to be varied without destroying the nuclearity of the resulting complexes. So, these compartmental ligands have allowed the preparation of heterodinuclear $\text{Ni}^{\text{II}}\text{−Gd}^{\text{III}}$, $\text{Co}^{\text{II}}\text{−Gd}^{\text{III}}$, and $\text{Fe}^{\text{II}}\text{−Gd}^{\text{III}}$ complexes in which ferromagnetic interactions are again observed. Although there is no general solution for the exchange phenomenon in the presence of orbital degeneracy, it has been shown that the orbital contribution is significantly quenched when the Fe^{II} or Co^{II} environment deviates from ideal octahedral geometry.[18] Diagonalization of the full matrix was carried out with Magpack,[19] taking into account an interaction parameter J and a D term for axial single-ion zero-field splitting. As expected the J values decrease in going from nickel (3.6

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cm^{-1})[20] to cobalt (0.9 cm^{-1}, $D = 4.23\ \mathrm{cm}^{-1}$)[21] and iron (0.5 cm^{-1}, $D = 2.06\ \mathrm{cm}^{-1}$).[22] $\mathrm{V^{IV}}$, such as the vanadyl ion $\mathrm{VO^{2+}}$, yields also dinuclear complexes that are versatile for ferro- and antiferromagnetic interactions.[23,24] On the contrary, these ligands are capable of chelating the 3d ions in their oxidation state III, but these complexes do not yield the expected $\mathrm{3d^{III}}$ Gd entities. Indeed, with $\mathrm{Mn^{III}}$ ions, two cationic $\mathrm{L^1Mn(H_2O)_2^+}$ species coexist with dianionic $\mathrm{[Gd(NO_3)_5(MeOH)]^{2-}}$ species, without any magnetic Mn−Gd interaction,[25] as a consequence of the repulsion between the positively charged $\mathrm{L^1Mn(H_2O)_2^+}$ species and $\mathrm{Gd^{3+}}$ ions, ($\mathrm{H_2L^1}$ = *N*,*N*′-2,2-dimethylpropylenedi(3-methoxysalicylideneimine). This hypothesis is confirmed in iron chemistry, where the μ-oxodiiron(III) complexes react with gadolinium to give tetranuclear Gd−Fe−O−Fe−Gd entities with large antiferromagnetic Fe−Fe interactions. Modeling of the experimental data leads to the conclusion that the Fe−Gd interaction is small and, unexpectedly, antiferromagnetic (−0.7 cm^{-1}).[26] Furthermore, a neutral $\mathrm{Fe^{III}}$ complex made with a tripodal and trianionic Schiff base ligand furnishes an example of the $\mathrm{Fe^{III}}$−$\mathrm{Gd^{III}}$ complex in which a ferromagnetic interaction (0.66 cm^{-1}) is active.[27] It has to be noted that, because of scrambling of the $\mathrm{Mn^{III}}$ and $\mathrm{Gd^{III}}$ ions, the equivalent $\mathrm{Mn^{III}}$−$\mathrm{Gd^{III}}$ complex does not exist.

Replacement of gadolinium ions by other lanthanide ions does not bring any difficulty from the synthetic point of view. On the contrary, difficulties in analyzing the magnetic properties of the Cu−Ln couples arise from the fact that the ground states of the $\mathrm{Ln^{3+}}$ ions, except for Ln = La, Eu, Gd, and Lu, have a first-order angular momentum, which prevents the use of a spin Hamiltonian for isotropic exchange. This anisotropy problem prompted us to investigate a more empirical approach based on a comparison of the magnetic properties of homologous and isomorphous Cu−Ln and Ni−Ln complexes, which crystallize in the same monoclinic space group $P2_1/c$ all along the series.[28] This relationship in conjunction with the diamagnetism of the $\mathrm{Ni^{2+}}$ ion allows an empirical evaluation of the crystal-field effect on the magnetic properties as well as an approach toward the nature of the coupling between the $\mathrm{Cu^{II}}$ and $\mathrm{Ln^{III}}$ ions in the series. The Cu−Ln interaction is antiferromagnetic for Ln = Ce, Nd, Sm, Tm, and Yb and ferromagnetic for Ln = Gd, Tb, Dy, Ho, and Er. The Cu−Pr and the Cu−Eu pairs are devoid of any significant interaction along with the Cu−La and Cu−Lu pairs, in accordance with the nonmagnetic nature of the ground state for these lanthanide ions. A similar study has been realized with 1-D Cu−Ln and Zn−Ln chains.[29]

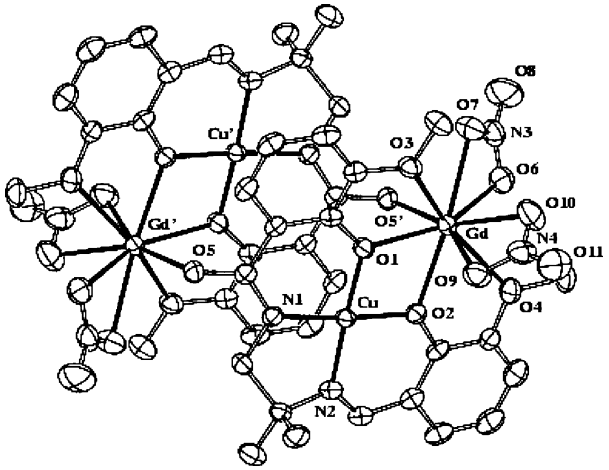

Figure 4. Perspective view of a tetranuclear complex $\mathrm{[L^2CuGd(NO_3)_2 \cdot CH_3OH]_2}$ at the 50% probability level and with hydrogen atoms omitted for clarity ($\mathrm{H_3L^2}$ = 2-hydroxy-*N*-({2-[(2-hydroxy-3-methoxyphenyl)methylene]amino}-2-methylpropyl)-3-methoxybenzamide).

Complexes of Higher Nuclearity: SMMs

In order to increase the nuclearity of the 3d−4f complexes, several attempts have been experienced with more or less success. The simplest one consists of substituting the anions chelated to the lanthanide ions by bridging ligands. So, with the use of trifluoroacetate[30] or thiocyanate[31] anions, trinuclear Cu−Ln−Cu or 1-D Cu−Ln chains have been characterized, respectively. Unfortunately, the absence of magnetic interaction through the thiocyanate bridges makes the chains behave as dinuclear units. Because the Cu−Gd interactions are mainly ferromagnetic, a bottom-up strategy starting with dinuclear Cu−Gd entities will give high-spin species if the arrangement of the copper and gadolinium ions is controlled in such a way that each copper ion interacts with a lanthanide ion only and vice versa. The assembling process is expected to be achieved by introducing a supplementary function without affecting the preexistent $\mathrm{N_2O_2}$ and $\mathrm{O_4}$ sites. Keeping this in mind, an original family of dissymmetric ligands with an amide function replacing an imine function has been synthesized. Introduction of an amide function has several advantages: the ligand becomes trianionic so that only two anions are needed to bring the electroneutrality of the resulting complex. In the case of chelating nitrato anions, two positions of the gadolinium coordination sphere are released, so that it is expected that the oxygen atom of the amide function, not involved in the inner $\mathrm{N_2O_2}$ copper coordination site, can enter into coordination with the gadolinium ion of a neighboring unit. This is what happens, but the head-to-tail arrangement of the Cu−Gd units impedes the formation of chains and yields only tetranuclear units,

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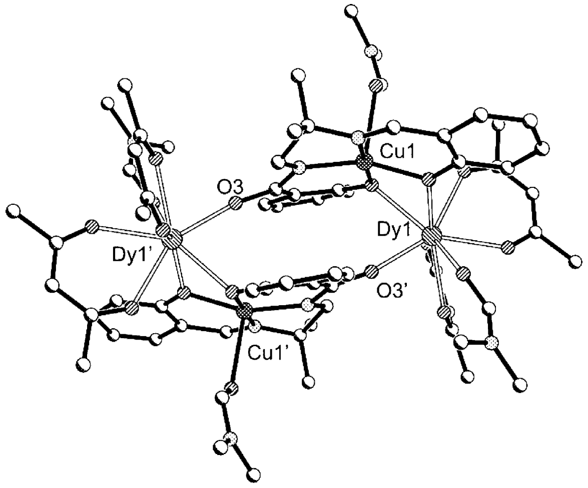

Figure 5. Molecular structure of the tetranuclear complex $[L^3CuDy(hfa)_2(DMF)_2]_2$ with thermal ellipsoids drawn at the 50% probability level and hydrogen and fluorine (hfa) atoms omitted (H_3L^3 = 2-hydroxy-*N*-({2-[(2-hydroxyphenyl)methylene]amino}-2-methylpropyl)-benzamide).

as shown in Figure 4.[32] The magnetic study confirms that two ferromagnetic interactions are active, the stronger one through the double phenoxo bridge (6.9 cm^{-1}) and the weaker one (0.6 cm^{-1}) through the single amido bridge Cu−N−C−O−Gd. The magnetization data confirm the $S = 8$ ground state generated by a small number of metal ions, four in the present complex. Several attempts have been directed toward ligand modifications in order to check if it was possible to increase the interaction parameters or to synthesize complexes of different nuclearities.[8j,33,34] Unfortunately, changes of the outer coordination site or replacement of the anionic species by auxiliary diketonato ligands always yield again tetranuclear complexes.

Introduction of anisotropic ions such as terbium or dysprosium into these $[Cu-Ln]_2$ complexes furnishes the first example of Cu−Ln SMMs, characterized by an effective anisotropy barrier of 21 K and a preexponential factor $\tau_0 = 2.7 \times 10^{-8}$ s.[8a] In that case, the lanthanide coordination site is made of three oxygen atoms from the ligand, while two auxiliary hexafluoroacetylacetonato (hfac) ligands complete the lanthanide coordination sphere, along with the oxygen atom of the amide function and a solvent molecule [*N*,*N*′-dimethylformamide (DMF) or methanol]. With chelating nitrato anions, these molecules behave again as SMMs but the double-S-like curves of the hysteresis loops are characteristic for small antiferromagnetic interactions between molecules, which confirms the insulation role played by the auxiliary hfa ligands.[8j] Furthermore, it has been shown that, with auxiliary hfa ligands, the outer coordination site can be reduced to the two bridging phenoxo oxygen atoms, which are sufficient to yield tetranuclear complexes with an alternate Cu−Ln arrangement (Figure 5).[8l] Depending on the solvent of crystallization, methanol or DMF, the copper coordination sphere is square planar (methanol) or five-coordinate with a DMF molecule in the apical position. The net result is an increase of the Cu···Cu intermolecular interactions, from 6.8 to 10.4 Å. These slight structural differences are passed on the features of the hysteresis loops of the $[Cu-Dy]_2$ molecules. The hysteresis loops are larger in the case of the best isolated tetranuclear species (Figure 6), and it seems possible to attribute the changes to intermolecular magnetic dipolar interactions.

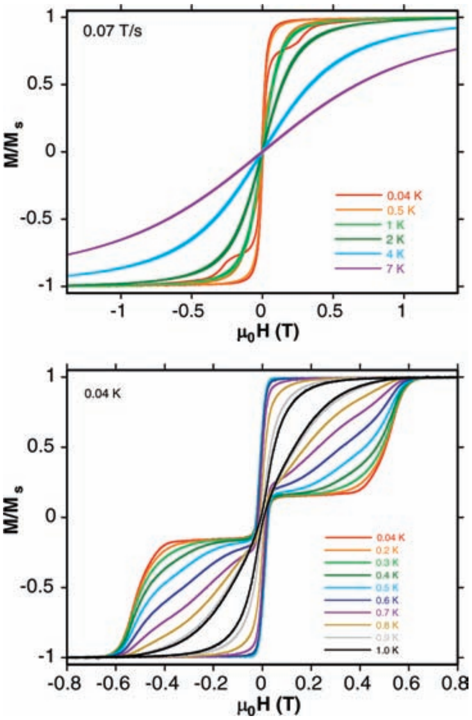

Figure 6. Magnetization (*M*) vs magnetic field (*H*) hysteresis loops for single crystals of $[L^3CuDy(hfa)_2(MeOH)]_2$ (up) and $[L^3CuDy(hfa)_2(DMF)_2]_2$ (down) at indicated temperatures and field sweep rates. *M* is normalized to its saturation value at 1.4 T.

The strategy of the amide−imine ligands toward high-spin complexes is limited by the presence of a unique amide function per ligand. A way to circumvent the problem consists of using building blocks containing two amide functions. These two functions can be brought by the same ligand or introduced in a starting unit made of two metal−ligand entities self-assembled by a second metal ion. If the first solution gives complexes of very low solubility, the anionic copper complex of the 2-hydroxy-*N*-{2-[(2-hydroxyethyl)amino]ethyl}benzamide ligand[10a] (H_3L^4) reacts with lanthanide ions to give entities formulated as $[(L^4Cu)_2Ln(NO_3)]_n$, quite reminiscent of the structurally determined complex in which $Ln(NO_3)$ replaces $[Mg(H_2O)_6]$ (Figure 7). The magnetic study confirms the presence of ferromagnetic Cu−Gd interactions into the trinuclear unit and also in between these trinuclear units. The gadolinium ion must be doubly bridged to each copper ion through the phenoxo and alkoxo oxygen atoms within the trinuclear unit, while the free oxygen atoms of the external amido groups may coordinate to Gd^{3+} ions of different units. Such an assembling leads to a chain of tetranuclear Gd_2Cu_2 motifs, which are linked through the gadolinium ions located at the opposite vertexes. Using the exact diagonalization of a closed

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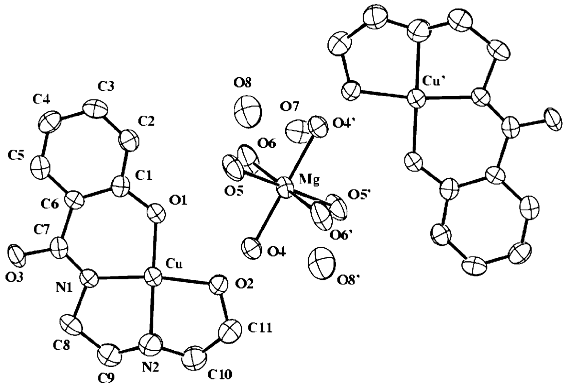

Figure 7. Perspective view of $[(L^4Cu)_2Mg(H_2O)_6]$ with thermal ellipsoids at the 50% probability level (H_3L^4 = 2-hydroxy-*N*-{2-[(2-hydroxyethyl)amino]ethyl}benzamide). Hydrogen atoms are omitted.

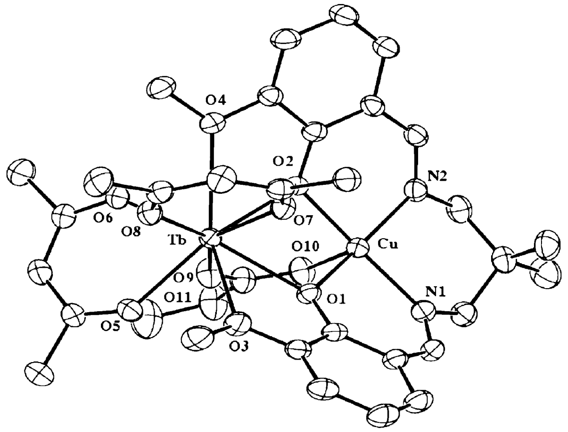

Figure 8. Molecular structure of $[L^1Cu(O_2COMe)Tb(thd)_2]$. Hydrogen atoms and CH_3 from thd are omitted for clarity.

chain of four trinuclear units, a very good agreement ($R = 1 \times 10^{-5}$) between the experimental and calculated values is obtained by taking two ferromagnetic parameters, $J = 2.5$ cm^{-1} (through CuO_2Gd) and $J' = 1.75$ cm^{-1} (through CuNCOGd). The magnetic study of the equivalent $[(L^4Cu)_2Tb(NO_3)]_n$ indicates that ferromagnetic Cu−Tb interactions are active and that it behaves as a SCM with an energy barrier for the reversal of magnetization equal to 28.5 K and a τ_0 of 3.8×10^{-8} s.

Dinuclear Cu−Tb molecules can also behave as SMMs. The first example $[L^1Cu(O_2COMe)Tb(thd)_2]$ was obtained with the Schiff base H_2L^1, thd (thd = tetramethylheptanedionato), and a monomethylcarbonate ligand (O_2COMe), which appears during the reaction pathway, coming from the reaction of methanol with atmospheric carbon dioxide (Figure 8).[8k] The monomethylcarbonate ligand bridges the copper and terbium ions, giving again well-separated dinuclear units. An Arrhenius plot of $\ln(\tau)$ vs $1/T$ allowed the determination of the effective anisotropy barrier $U_{\mathrm{eff}} = 13.8$ K and the preexponential factor $\tau_0 = 3 \times 10^{-7}$ s. The absence of such a behavior in the Zn−Tb equivalent complex confirms that the out-of-phase alternating (ac) magnetic component observed in the Cu−Tb complex is a property characteristic of the Cu−Tb pair and cannot be attributed to the terbium ion alone.

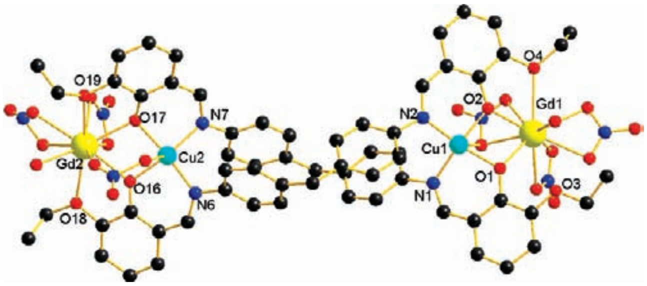

Figure 9. Molecular structure of the helicate, with a partial atom labeling scheme and hydrogen atoms omitted.

The structural determination of a double-stranded helicate containing two isolated Cu−Gd pairs (Figure 9) with reduced Cu$\cdots$Gd distances [3.339(2) and 3.425(2) Å] was reported recently.[35] The magnetic investigation shows ferromagnetic Cu−Gd interactions ($J = 4.5$ cm^{-1}) through two phenoxo oxygen atoms. Replacement of gadolinium with anisotropic terbium ions yields helicates showing slow relaxation of the magnetization and magnetization hysteresis loops. Studies of the relaxation and hysteresis loops establish SMM behavior, which is influenced by weak intramolecular interactions. A nonanuclear $[Dy_3Cu_6]$ complex,[8h] in which six alkoxo oxygen atoms of the deprotonated tridentate Schiff base ligands and six OH groups bridge the different metal ions in a μ_3 fashion, exhibits features typical of SMMs, with an anisotropy barrier of 25 K associated with a very slow zero-field relaxation, and a large coercive field demonstrates the ability of the 3d−4f strategy to increase the spin ground state, the negative axial anisotropy, and, as a consequence, the relaxation time.

Until now, the reported SMMs have anisotropy brought by 4f ions. Because Schiff base ligands allow the synthesis of 3d−4f complexes with anisotropic 3d ions, SMM complexes in which anisotropy is introduced by the 3d ion or the 3d and 4f ions are expected. An example of a trinuclear Co−Gd−Co was recently described. Each cobalt ion is surrounded by a tripodal hexadentate ligand, and two of these mononuclear complexes are assembled by a gadolinium ion to give the final trinuclear complex that presents ferromagnetic Co−Gd interactions and behaves as a SMM characterized by an energy gap of 27.2 K and a preexponential factor of 1.7×10^{-7} s.[36]

Extended Structures

The interest in the chemistry of heterometallic coordination polymers containing lanthanides was stimulated, back in the early 1990s, by the search for "classical" molecule-based magnets [compounds exhibiting three-dimensional (3-D) magnetic ordering with spontaneous magnetization below a critical temperature]. The very first Cu^{II}−Ln^{III} coordination polymers with relevance in molecular magnetism were

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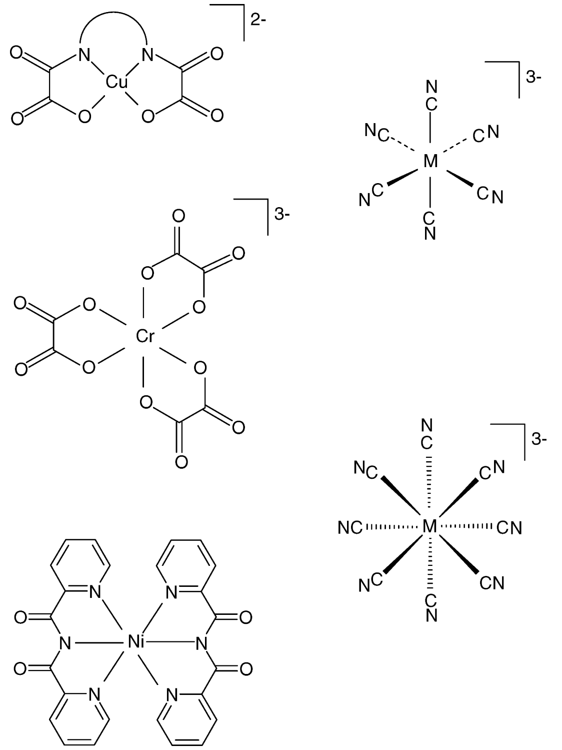
described in 1992.[37] These compounds were obtained following Kahn's general strategy, leading to heterobimetallics, which consists of self-assembly processes involving bis(oxamato)copper(II) complexes and various assembling cations (either naked or carrying blocking ligands). Indeed, these bianionic copper(II) complexes can efficiently act as ligands toward a second metal ion and generate a quite rich coordination chemistry.[38] The spin topology of the resulting coordination polymers is influenced by (i) the charge of the assembling cation, (ii) the nature (3d or 4f) of the second metal ion, and (iii) the molar ratio between the assembling cation and the anionic building block. While in the case of the 3d assembling cations the network topologies can be easily controlled, the peculiarities of the lanthanide ions (high coordination numbers, low stereochemical preferences, and rather weak metal−ligand bonds) make the prediction of the final solid-state architectures difficult.

In principle, heterometallic coordination polymers can be obtained following one of these synthetic routes: (1) the building-block approach mentioned above (complexes as ligands); (2) the building-block approach, by employing oligonuclear 3d−4f complexes as nodes; (3) one-pot reactions, by mixing together the two metal ions as well as the bridging ligand. Rather a technique than a strategy, solvothermal/hydrothermal syntheses serendipitously combine elements from these approaches. Solvothermal techniques can lead to unique structural features, although unpredictable in most cases, accompanied by interesting magnetic properties.

The most representative building blocks in the design of heterometallic coordination polymers, including the 3d−4f ones, are as follows: (a) bis(oxamato)metal(II) complexes [metal(II) = copper, nickel, zinc];[37,39] (b) tris(oxalato) complexes;[40] (c) polycyano complexes (both homo- and heteroleptic);[41] (d) $[M(bpca)_2]$ [Hbpca = bis(2-pyridylcarbonyl)amine; Scheme 1].[42,43]

Scheme 1



Let us first illustrate the building-block approach with systems obtained by using $[M(bpca)_2]$ tectons. When the lanthanide ions carry blocking ligands, then oligonuclear $M^{II}-Ln^{III}$ complexes can be obtained. For example, the assembling process between $[M(bpca)_2]$ and $Dy(hfac)_3$ leads to linear trinuclear complexes, $\{Dy(hfac)_3\}_2[\{M(bpca)_2\}](CHCl_3)$ (M = Ni, Fe), which are isostructural (Hhfac = hexafluoroacetylacetone).[42] The dysprosium ion is particularly attractive for constructing SMMs, because of its high anisotropy. Indeed, the dynamic magnetic measurements indicate for both compounds a slow relaxation of the magnetization, with the energy barrier of 4.9 and 9.7 K for the nickel derivative and, respectively, for the iron one. A weak ferromagnetic interaction occurs between the Dy^{III} and Ni^{II} ions, whereas with the second compound there is no coupling between the dysprosium ions across the diamagnetic Fe^{II} ion. The most interesting outcome of this study is that the intramolecular ferromagnetic interaction in the $[Dy_2Ni]$ derivative has a negative effect on the energy barrier for the reversal of the magnetization, that is, a lower value for $[Dy_2Ni]$ than for $[Dy_2Fe]$. The explanation for this behavior is the orthogonal arrangement of the dysprosium coordination polyhedra, due to the rigidity of the two bpca ligands, which are almost perpendicular to each other. Assuming that the Ising axis of each Dy^{III} ion is not oriented along the Dy−Ni−Dy direction, this structural conformation leads to a strong reduction of the magnetic anisotropy.

On the other hand, the reaction between $[Ni(bpca)_2]$ and lanthanide(III) nitrates affords isotructural complexes with the formula $[\{Ln(O_2NO)(H_2O)_3\}\{Ni(bpca)_2\}](NO_3)_2\cdot 3H_2O$ (Ln = Gd, Tb, Dy).[43] Their structure consists of linear infinite cationic chains with Ln^{III} ions connected by $[Ni(bpca)_2]$ complexes acting as bridging bis-bidentate ligands (Figure 10). The charge of the chains is counterbalanced by uncoordinated nitrate ions. Very weak ferromagnetic interactions occur between the Ni^{II} and Gd^{III} ions within the chain ($\theta = +0.15$ K). Although Tb^{III} and Dy^{III} are strongly anisotropic, the corresponding chains show only a small frequency dependence of the in-phase and out-of-phase

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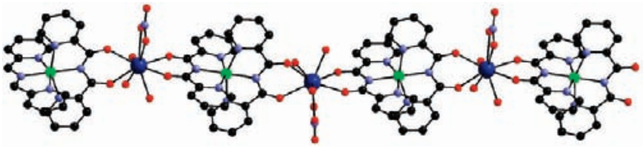
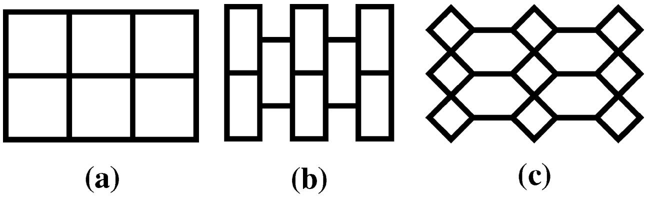


Figure 10. View of a cationic chain $[\{Ln(O_2NO)(H_2O)_3\}\{Ni(bpca)_2\}]_n^{2n+}$ (green, nickel; dark blue, lanthanide; light blue, nitrogen; red, oxygen).

signals (χ' and χ'', respectively). Moreover, no field dependence of the out-of-phase susceptibility was observed with the two compounds. The main reason for the absence of the SCM behavior for these compounds is probably the poor isolation of the magnetic chains in the crystal (extended network of hydrogen bonds along with $\pi-\pi$ stacking interactions established between aromatic rings arising for neighboring chains). The symmetry of the lanthanide polyhedron plays also an important role.[44] Interestingly, the slight modification of the crystallization procedure, by changing the solvents, leads to other types of chains (wavelike instead of linear), with all of the nitrato groups coordinated to the lanthanide cations: $[\{Ln(O_2NO)_3\}\{Ni(bpca)_2\}]\cdot nH_2O$ (Ln = Gd, Tb, $n = 6.5$; Ln = Dy, Ho, $n = 5.5$).[45] The magnetic measurements revealed negligible interactions for the gadolinium derivative, weak ferromagnetic interactions for [NiTb] and [NiDy], and weak antiferromagnetic interactions for [NiHo]. The dynamic magnetic studies showed that the Tb^{III}, Dy^{III}, and Ho^{III} derivatives exhibit field-dependent slow relaxation of the magnetization, suggesting potential SCM properties.

Cyano-Bridged Coordination Polymers. A large family of heterometallic d−f coordination polymers is constructed by using anionic polycyano complexes as building blocks. The rich structural variety of these complexes arises from two sources: (1) the availability of numerous homoleptic polycyanometallates; (2) the nature of the ancillary ligands attached to the assembling cations. The following anionic cyano complexes are currently used as templates: $[M^I(CN)_2]^-$ (M = Ag, Au); $[M^{II}(CN)_4]^{2-}$ (M = Ni, Pd, Pt); $[M^{III}(CN)_6]^{3-}$ (M = Cr, Fe, Co, Ru); $[M(CN)_8]^{q-}$ (M = Nb^{IV}, Mo^{IV}, W^{IV}, Mo^V, W^V). Of course, the most interesting from the magnetic point of view are those systems constructed by using paramagnetic tectons, e.g., $[M(CN)_6]^{3-}$ (M = Fe, Cr)[41] and $[M(CN)_8]^{3-}$ (M = Mo, W).[46] The number of organic molecules that can be used to block several coordination sites at the assembling cations is unlimited. They can have various denticities, ranging from monodentate to polydentate, and can be linear, tripodal, or macrocyclic. Their main role is to control the number of available coordination sites of the assembling cation and their relative position.

Scheme 2



The synthetic potential of the anionic polycyanometallates in the design of the heterometal complexes has been increased by attaching blocking ligands not only to the assembling cations but also to the anionic units, by replacing two or three cyano groups by bi- or tridentate ligands, for example, $[M(AA)(CN)_4]^-$ [M = Cr^{III}, Fe^{III}; AA = 2,2′-bpy, 1,10-phen, ethylenediamine, 2-(aminomethyl)pyridine], $[M(BBB)(CN)_3]^-$ [BBB = tridentate monoanionic ligands: bpca− = bis(2-pyridylcarbonyl)amidate; $HB(pz)_3^-$ = hydrotris(1-pyrazolyl)borate],[47] and *trans*-$[Ru^{III}(acac)_2(CN)_2]^-$ (acac = acetylacetonate).[48] Numerous 3d−3d′ complexes with interesting magnetic properties have been obtained,[47,48] but the utilization of these heteroleptic complexes as ligands toward lanthanide ions remains largely unexploited.

In the experimental point, hexacyanometallates ($[M(CN)_6]^{3-}$, M = Fe, Co, Cr, etc.) are the simple and direct building blocks for construction of cyano-bridged heterometal coordination polymers, because the nitrogen ends of cyanide of hexacyanometallates are strong donor atoms that could link two metal ions. A rational strategy for the synthesis of the network is the suitable combinations of cyanide-contained precursors and other coligands as well as the adjustment of their stoichiometries, and consequently many kinds of two-dimensional (2-D) 3d−4f arrays (Scheme 2) based on hexacyanometallates(III) have been obtained.

The assembling process between $K_3[M(CN)_6]$ (M = Fe, Co) and bpym (2,2′-bipyrimidine) with $Nd(NO_3)_3$ in a 1:1:1 molar ratio affords isostructural complexes $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ (M = Fe, Co).[49] These two compounds are the first 2-D cyanide-bridged compounds containing both lanthanide and transition-metal ions. Their crystal structures (Figure 11a) have a unique topological architecture type that is very different from the known 2-D cyanide-bridged structures (square,[50] honeycomb,[51] brick wall,[52] and partial cubane structures)[53] and also of other 2-D coordination

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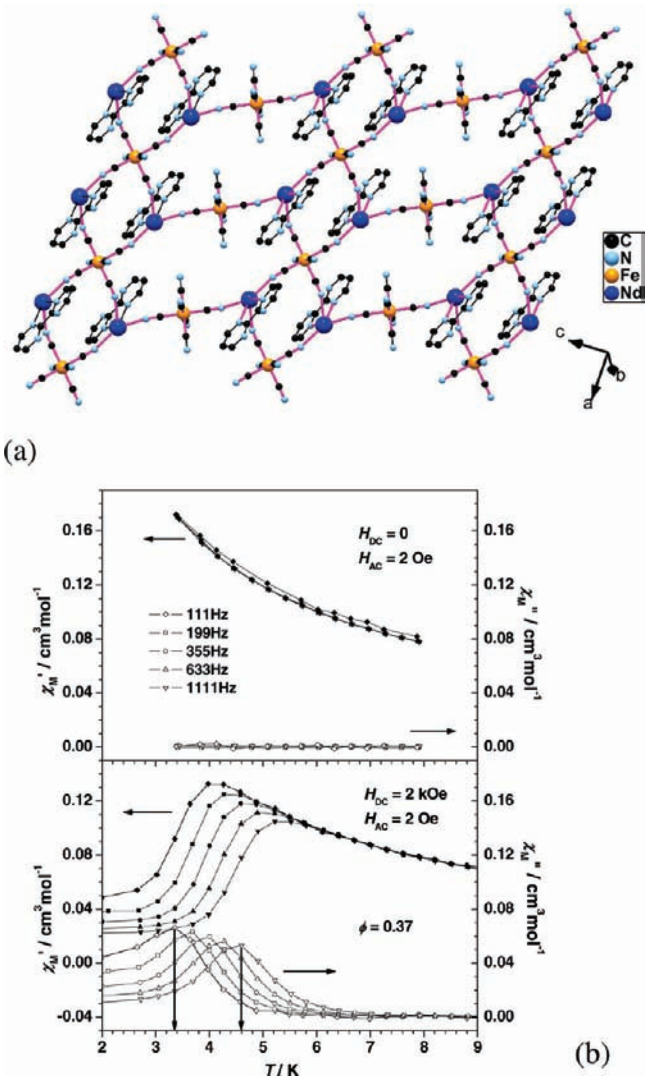

Figure 11. (a) Layer structure of $[NdFe(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ with alternating fused rows of rhombuslike $Fe_2Nd_2(CN)_4$ rings and six-sided $Fe_4Nd_4(CN)_8$ rings. The water molecules are omitted for clarity. (b) Frequency dependence of ac susceptibility at 0 and 2 kOe dc bias field for compound $[NdCo(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$. The filled symbols are for the in-phase component χ_M'; the open symbols are for the out-of-phase component χ_M''.

polymers (grid, kagome, herringbone, and triangular),[54] which consist of a 2-D network with alternating fused rows of rhombuslike $M_2Nd_2(CN)_4$ rings and six-sided $M_4Nd_4(CN)_8$ rings. Each Nd^{3+} ion is nine-coordinated, and the bpym ligand coordinates to Nd^{3+} ions in a bichelating fashion. One of the two crystallographically independent M^{3+} centers employs four CN^- groups in the same plane to connect the Nd^{3+} ions, giving rise to a double-stranded chain. The double-stranded chains are connected by $M(CN)_6{}^{3+}$ units along the *c* direction, forming the 2-D network. The lattice water molecules reside between layers and link the 2-D sheets into a 3-D network through extensive hydrogen bonds. For $[NdFe(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$, the depopulation of Stark levels of Nd^{3+} ions results in a decrease of $\chi_M T$ with decreasing temperature. Ferromagnetic interactions exist between the Nd^{3+} and Fe^{3+} ions. No long-range ordering was observed down to 2 K based on measurements of the field-dependent magnetization and the zero-field ac susceptibility. Compound $[NdCo(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ contains only one type of paramagnetic Nd^{3+} ion. No long-range ordering or any spin-glass-like behavior is observed at zero static field. However, under an intermediate direct current (dc) bias field (2 kOe), the unusual field-dependent magnetic relaxation is observed (Figure 11b), with a considerably larger φ value of 0.37 [$\varphi = \Delta T_P/T_P\Delta(\log f)$] than that for normal spin glass (<0.1),[55] suggesting a SMM-like relaxation behavior, which was previously tentatively attributed to the geometrical frustration of Nd^{3+} ions, but because the coupling between of Nd^{3+} ions should be very weak, it is essentially an "isolated ion" or "isolated ionlike" system. In this respect, an explanation for the origin of dc-field-induced relaxation might be the lifting of the Kramer's degeneracy by the magnetic field. Anyway, this seems to be a rather general phenomenon in many weak-coupled or isolated magnetic molecular systems,[56,58] and the question is still open and more efforts are expected.

By the addition of DMF to the reaction between $Ln(NO_3)_3\cdot H_2O$ and $K_3[Cr(CN)_6]$, two 2-D isostructural bimetallic complexes $[Ln(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ (M = Gd, Sm) are obtained,[57] which consist of novel brick-wall-like neutral layers with slightly distorted Cr_3Ln_3 rectangles. In $[Gd(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$, for instance, each $[Cr(CN)_6]^{3-}$ unit uses three cyanide groups in the meridional arrangement to connect with three $[Gd(DMF)_2(H_2O)_3]^{2+}$ units (Figure 12a). Each $[Gd(DMF)_2(H_2O)_3]^{2+}$ unit links three $[Cr(CN)_6]^{3-}$ ions, with the bridging cyanides and the bridged metal ions lying in a plane. This local molecular disposition extends to generate a flat brick-wall-like structure, which is the first cyano-bridged 3d−4f complex with such a topology. For the two compounds, the adjacent Ln^{III} and Cr^{III} ions are antiferromagnetically coupled. In general, the compounds behave as metamagnets (for Gd−Cr, see Figure 12b) and switch from an antiferromagnetic ground state to a ferrimagnetic-like state upon application of large enough fields, which is the first observation for two-dimensional (2-D) cyano-bridged 3d−4f complexes. Because of the antiferromagnetic interaction between the

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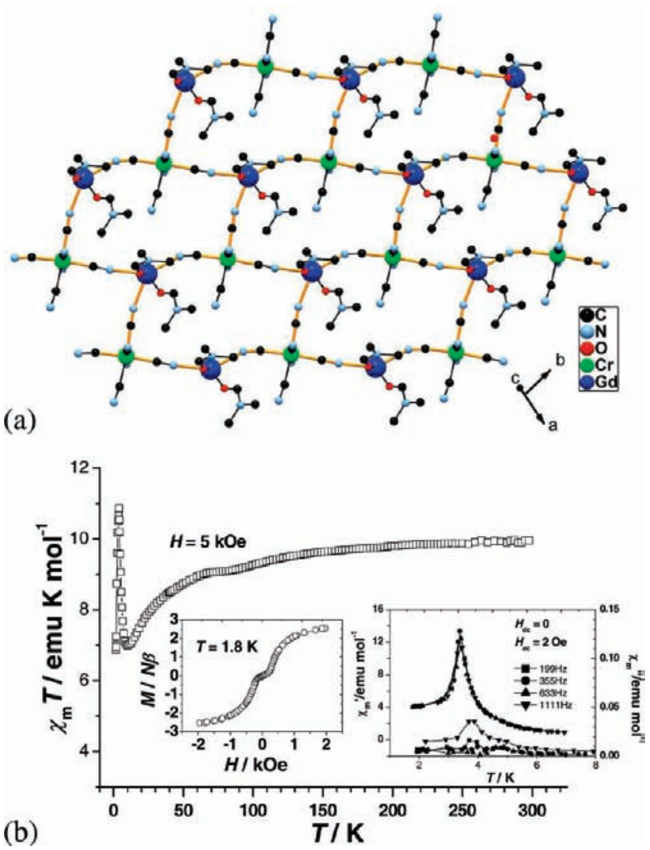

Figure 12. (a) Brick-wall-like structure of $[Gd(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$. (b) Temperature dependence of $\chi_M T$ for $[Gd(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$. Inset: left, isothermal magnetization at 1.8 K; right, real and imaginary ac magnetic susceptibilities in zero applied dc field and an ac field of 2 Oe at different frequencies for $[Gd(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$.

ferrimagnetic layers, they reach a long-range antiferromagnetic ordering at 3.5 and 4.2 K, respectively.

Using a bridging ligand as the coligand, with polycyanometallate, can also build up 2-D 3d−4f compounds. Six novel cyano/bpdo mixed-bridged heterometallic compounds $[Ln^{III}(bpdo)(H_2O)_2M^{III}(CN)_6]\cdot 2H_2O$ (Ln = Nd, Sm, Gd, Tb with M = Fe; Ln = Nd, Sm with M = Co) have been obtained by employing 4,4′-bipyridine-*N*,*N*′-dioxide (bpdo) ligands as cobridges.[58] They have the same 2-D corrugated gridlike layer structures (Figure 13), where each $[M(CN)_6]^{3-}$ unit uses four coplanar cyanide groups to connect with four square-antiprism Ln^{3+} ions, and accordingly each Ln^{3+} ion links four $[M(CN)_6]^{3+}$ units. Simultaneously, the next-nearest Ln^{3+} ions are bridged by bpdo in the diagonal direction from the same layer but not from two different layers, which play a special role in stabilizing the gridlike layer. Magnetic studies showed that the $Ln^{3+}-Fe^{3+}$ interaction is ferromagnetic for Nd−Fe, antiferromagnetic for Sm−Fe and Gd−Fe, and negligible for Tb−Fe. Especially, Sm−Fe and Gd−Fe compounds exhibit ferrimagnetic orderings below 2.9 and 1.9 K, respectively. Additionally, the Nd−Co compound shows an unusual field-induced magnetization relaxation.

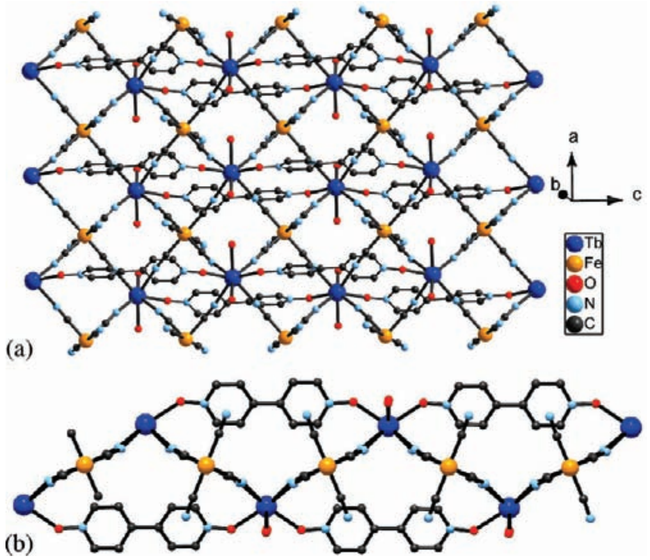

Figure 13. (a) View of a 2-D gridlike $Tb^{3+}-Fe^{3+}$ layer mixed-bridged by cyanide and bpdo in the *ac* plane. (b) Projection of the corrugated layer.

“Complex ligands” are good building blocks in the successful construction of 3d−3d′−4f complexes. The treatment of [CuL] (L = 1,4,8,11-tetraazacyclotradecane-2,3-dione)[59] and $GdCl_3\cdot 6H_2O$ with $K_3[Cr(CN)_6]$ in an H_2O/EtOH mixture gives rise to a unique 2-D mixed bridging-ligand complex $Gd(CuL)_4Cr(CN)_6\cdot 5H_2O$.[60] It is the first structurally characterized 2-D heterotrimetallic complex containing a rare-earth cation and two different 3d metal ions (Figure 14), which comprises a bridging $[Cr(CN)_6]^{3-}$ ion, four macrocyclic Cu^{II} units, and one Gd^{III} ion with a nonplanar layer structure. The Gd^{III} ion is surrounded by eight oxygen atoms from four {Cu−L} groups, thus yielding a local $[Gd(CuL)_4]$ moiety. Each $[Cr(CN)_6]^{3-}$ ion connects to four different Cu−L units through four equatorial CN^- bridges with two *trans*-CN^- ligands intact. The layer topology can be described as a distorted gridlike structure with two Cr^{III} and two Gd^{III} ions at the vertices and four {Cu−L} groups at the four sides of each “propeller”. Global ferromagnetic interactions are present between adjacent metal ions, but no spontaneous magnetization exists down to 1.8 K.

Using the same reaction conditions, structural changes were induced by varying three parameters: the building blocks $[M(CN)_6]^{3-}$ (M^{3+} = Fe, Cr, Co), the specific lanthanide ion (Ln^{3+}), and the blocking ligands [2,2′-bipyridine (bpy), DMF, and 2,2′:6′,2″-terpyridine

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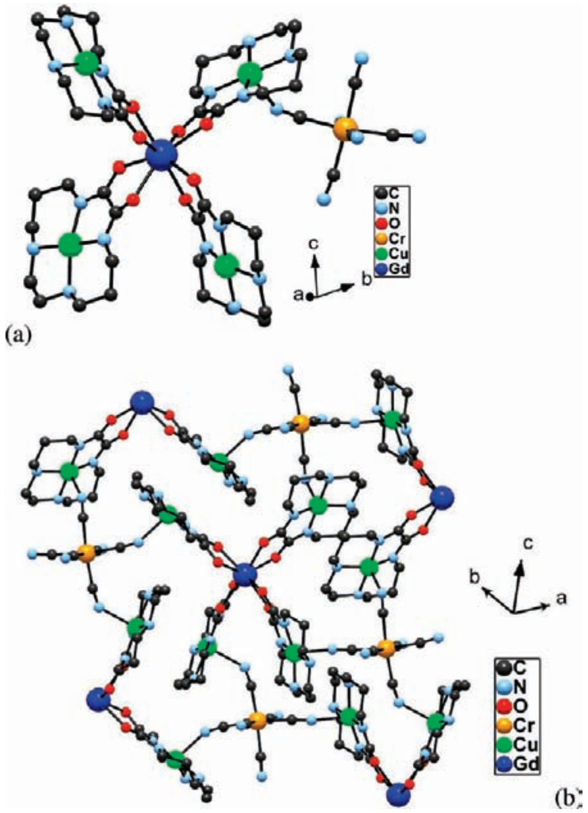


Figure 14. (a) $GdCrCu_4$ unit of the heterotrimetallic compound $Gd(CuL)_4Cr(CN)_6 \cdot 5H_2O$. (b) Layer structure of $Gd(CuL)_4Cr(CN)_6 \cdot 5H_2O$. Water molecules are omitted for clarity.

(terpy)].[61−66] The [$Ln^{3+}-Co^{3+}$] and [$La^{3+}-M^{3+}$] or [$Lu^{3+}-M^{3+}$] (M^{3+} = Fe, Cr) compounds were synthesized and characterized in order to obtain insight into the nature of the [$M^{3+}-Ln^{3+}$] magnetic coupling.

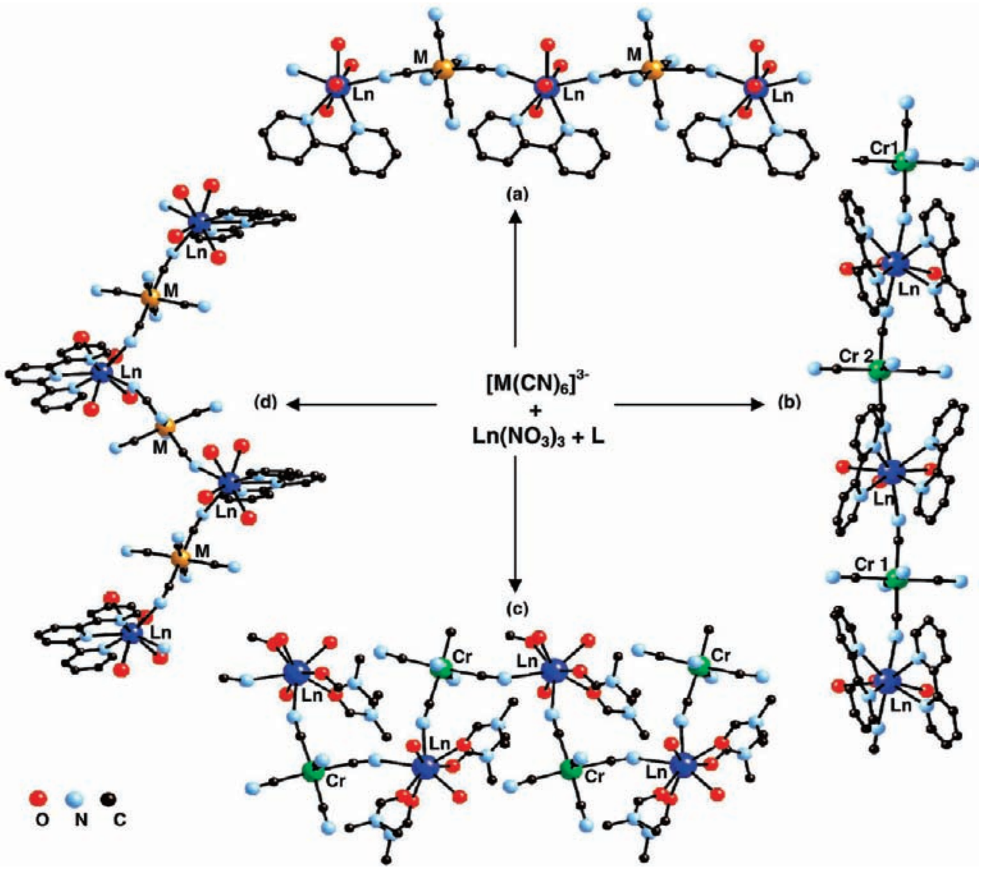
(a) *trans*-$[Ln(H_2O)_4(bpy)(\mu\text{-}CN)_2M(CN)_4]_n \cdot XnH_2O \cdot 1.5n$-bpy ($M^{3+}$ = Fe and Ln^{3+} = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; M^{3+} = Co and Ln^{3+} = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb; $X = 4$ or 5).[61,62a] Their crystallographic analysis revealed that all confine isomorphous 1-D polymers (Scheme 3a). The chains show an alternation of $Ln(H_2O)_4(bpy)$ and $M(CN)_6$ (M^{3+} = Fe, Co) units linked by cyanide bridges in the trans geometry and running along the structure in a perfect zigzag path. The bipyridine of crystallization adopts two different stereoconfigurations. One of them is not planar, showing a dihedral angle (N−C−C−N) in the range of 16.6−17.7°. The other configuration is planar, and the same dihedral angle is 180°. A supramolecular 3-D network is given by hydrogen bonds and $\pi-\pi$ interaction. The analysis of the eight-vertex coordination polyhedron of the lanthanide cations in these complexes was analyzed by continuous-shape measures (CShMs).[63] The results of the CShM approach indicate that the polyhedron of the lanthanide ions is in the middle of the minimal distortion path between two ideal geometries: square antiprism and triangular dodecahedron. The bite angle of the bpy ligand is responsible for the deviation of the minimal distortion path between the two ideal geometries. The magnetic studies of the *trans*-$[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Fe(CN)_4]_n \cdot 5nH_2O \cdot 1.5n$bpy complex show weak ferromagnetic 3-D ordering. Susceptibility measurements were carried out in a range of low magnetic fields (Figure 15). When the magnetic field decreased from 1000 to 10 Oe, the maximum susceptibility increases from 2.5 to 33 $cm^3\ mol^{-1}$ K. Zero-field cooling (ZFC)−field cooling (FC) measurements at 50 Oe indicate the onset of weak ferromagnetic 3-D ordering at 3.5 K (Figure 16). The hysteresis cycle was measured at 2.5 K (Figure 16, inset). The coercivity field $\chi_M T$ was ca. 137 Oe, and the remnant magnetization was $M_r = 0.08N\mu_B$. For the *trans*-$[Dy(H_2O)_4(bpy)(\mu\text{-}CN)_2Fe(CN)_4]_n \cdot 1.5nbpy\cdot 4nH_2O$ complex, in a low magnetic field, was maximum at 2.5 K. When the magnetic field decreased from 400 to 20 Oe, the maximum value of $\chi_M T$ increased from 11.36 to 12.63 $cm^3\ mol^{-1}$ K, which indicates the onset of weak ferromagnetic 3-D ordering. The ac magnetic susceptibility shows a small frequency dependence of the peaks, attributed to the glassy behavior of the magnetically ordered state (Figure 17). ZFC−FC measurements at 20 Oe show a bifurcation point at 2.5 K. The $Ln^{3+}-Fe^{3+}$ interaction is antiferromagnetic in [Gd−Fe] (−0.77 cm^{-1}) and [Tb−Fe]; there is no sign of any significant interaction in [Eu−Fe], [Ho−Fe], [Er−Fe], and [Tm−Fe] complexes, and the interaction remains unresolved for the [Fe−Yb] complex.

(b) *trans*-$[Ln(H_2O)_3(bpy)_2(\mu\text{-}CN)_2Cr(CN)_4]_n \cdot 4nH_2O \cdot 3.5n$bpy ($Ln^{3+}$ = La, Ce, Pr, Nd).[64] Their crystallographic analysis revealed that all confine isomorphous 1-D polymers (Scheme 3b). The Ln^{3+} ion is nine-coordinated. The chain is made up of alternating $Cr1(CN)_6-Ln(H_2O)_3(bpy)_2-Cr2(CN)_6$ fragments. These complexes show a 3-D supramolecular structure consisting of an intricate array of hydrogen bonds involving contributions from the coordination and crystallization of water molecules. The most notable is a water decamer $(H_2O)_{10}$ built around a cyclic hexameric core with an inversion center in the middle of the ring, which represented another new mode of association of water molecules. The $Ln^{3+}-Cr^{3+}$ interaction is antiferromagnetic in [Ce−Cr] and unresolved for [Pr−Cr] and [Nd−Cr].

(c) *trans*-$[Ln(H_2O)_4(bpy)(\mu\text{-}CN)_2Cr(CN)_4]_n \cdot 3.5nH_2O \cdot 1.5n$bpy ($Ln^{3+}$ = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).[64,65] These complexes are isomorphous with those obtained using $[Fe(CN)_6]^{3-}$ instead of $[Cr(CN)_6]^{3-}$, as described in Scheme 3a. For the *trans*-$[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Cr(CN)_4]_n \cdot 3.5nH_2O \cdot 1.5n$bpy complex, susceptibility measurements at low temperature were carried out at a range of low magnetic fields (Figure 18). When the magnetic field decreased from1000 to 50 Oe, the $\chi_M T$ value increased from 14.32 to 37.53 $cm^3\ mol^{-1}$ K at 2 K, which indicates the onset of a weak ferromagnetic 3-D ordering. In the ac measurements, a signal of χ'' appears, but a maximum in the χ'' vs T curve is not observed. We thus conclude that the magnetic transition temperature, T_c, is lower than 2 K (Figure 18, inset). The $Ln^{3+}-Cr^{3+}$interaction is antiferromagnetic in [Nd−Cr], [Sm−Cr], [Gd−Cr] (−1.06 cm^{-1}), [Tb−Cr], [Dy−Cr], [Ho−Cr], [Er−Cr], and [Tm−Cr] and negligible in [Eu−Cr] and [Yb−Cr].

(d) *cis*-$[Ln(H_2O)_2(DMF)_4(\mu\text{-}CN)_2Cr(CN)_4]_n \cdot nH_2O$ (Ln^{3+} = Gd, Sm).[57b,65] Their crystallographic analysis revealed that its structure is composed of 1-D polymers (Scheme 3c). The

Scheme 3



chains show an alternation of $Ln(H_2O)_4(DMF)_4$ and $Cr(CN)_6$ units linked by cyanide bridges in the cis geometry with respect to Cr^{3+} ions. The Ln^{3+} ion is eight-coordinated. The chains are self-assembled through hydrogen bonds into a 3-D network. For the [Gd−Cr] complex, the magnetic interaction is antiferromagnetic ($-0.52\ cm^{-1}$), and for the [Sm−Fe] complex, it is proposed to be ferromagnetic.

(e) *trans*-$[Ln(H_2O)_4(terpy)(\mu\text{-}CN)_2M(CN)_4]_n$ (M^{3+} = Fe and Ln^{3+} = La, Sm; M^{3+} = Co and Ln^{3+} = Sm).[66] Their structures consist of 1-D chain polymers (Scheme 3d). The chains show an alternation of $Ln(H_2O)_4(terpy)$ and $M(CN)_6$ (M^{3+} = Fe, Co) units linked by cyanide bridges in the trans geometry. The [Ln−M−Ln] trinuclear entities run along the chain in a zigzag path. The coordination number of the Ln^{3+} ion is nine. Complexes [Sm−Fe] and [Sm−Co] are isomorphous. The Sm−M distances along the chain are the same, but in complex [La−Fe], there are two different La−Fe distances. Because each Sm^{3+} ion in the [Sm−M] complexes is related to its neighbor by a glide plane, there are two enantiomeric coordination spheres in an achiral chain. In the [La−Fe] complex, each La^{3+} ion is related to its neighbor by the inversion center at the Fe^{3+} ion that bridges them; hence, there are two enantiomeric coordination spheres in the achiral trinuclear unit. For the three complexes, the supramolecular structure is created by hydrogen bonds. The magnetic interaction in the [Sm−Fe] complex is negligible. Recently, Dunbar et al. reported on series of $Ln^{III}-M^{III}$ 1-D coordination polymers constructed by using a tridentate blocking ligand [2,4,6-tri(2-pyridyl)-1,3,5-triazine] and

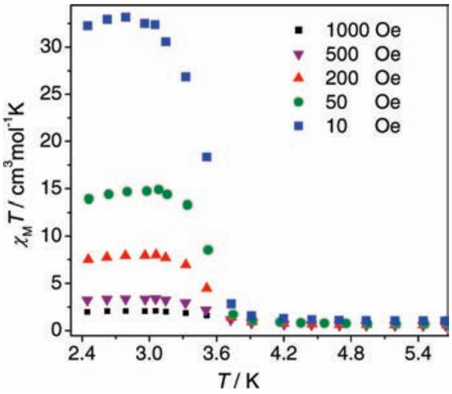


Figure 15. Thermal dependence at different low fields (from 1000 to 10 Oe) of $\chi_M T$ for $[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Fe(CN)_4]_n \cdot 5nH_2O \cdot 1.5n$bpy.

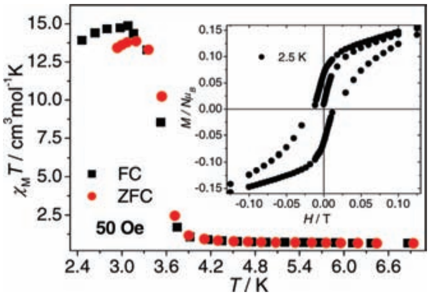


Figure 16. Thermal dependence of $\chi_M T$ for $[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Fe(CN)_4]_n \cdot 5nH_2O \cdot 1.5n$bpy cooled in zero field (ZFC) and in a field of 50 Oe (FC). Inset: Hysteresis cycle at 2.5 K for $[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Fe(CN)_4]_n \cdot 5nH_2O \cdot 1.5n$bpy.

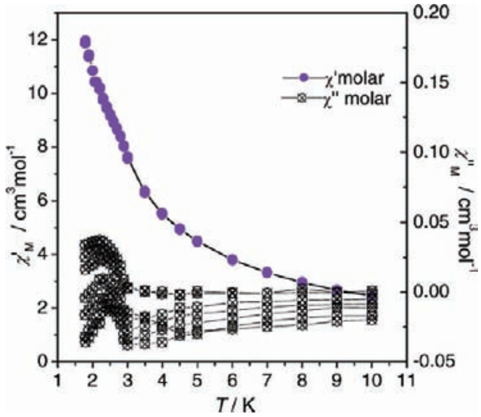


Figure 17. Plot of the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility of $[Dy(H_2O)_4(bpy)(\mu\text{-}CN)_2Fe(CN)_4)]_n\cdot 4nH_2O\cdot 1.5n$bpy at 1500, 1250,750, 500, 100, and 50 Hz.

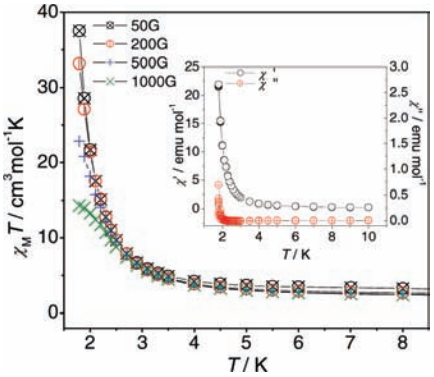


Figure 18. Thermal dependence at different fields of $\chi_M T$ for $[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Cr(CN)_4]_n\cdot 3.5nH_2O\cdot 1.5n$bpy. Inset: Plot in the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility at 1500, 1000, 750, 500, 100, and 50 Hz for $[Sm(H_2O)_4(bpy)(\mu\text{-}CN)_2Cr(CN)_4]_n\cdot 3.5nH_2O\cdot 1.5n$bpy.

$[M(CN)_6]^{3-}$ tectons (M = Fe, Cr).[41a] Within this series, the $Sm^{III}-Fe^{III}$ interaction was found to be ferromagnetic.

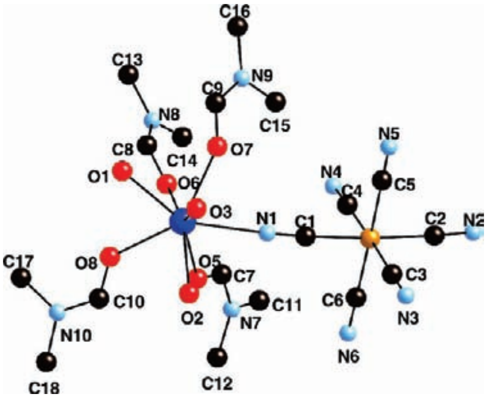
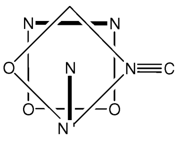


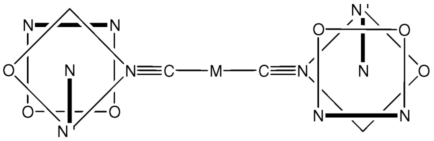
Figure 19. View of the dinuclear unit of $[Tm(DMF)_4(H_2O)_3(\mu\text{-}CN)Fe(CN)_5]\cdot 4H_2O$.

We must also recall that 3-D networks can be obtained with heterodinuclear or trinuclear complexes. So, with DMF, complexes formulated as $[Ln(DMF)_4(H_2O)_3(\mu\text{-}CN)M(CN)_5]\cdot nH_2O$ are isolated with M^{3+} = Fe, Co and all lanthanide ions except Pm and Lu with $1 \leq n \leq 2$.[67] Five complexes [Pr–Fe], [Tm–Fe], [Ce–Co], [Sm–Co], and [Yb–Co] have been structurally characterized, while X-ray powder diffractograms confirm the isostructurality all along the series. Their molecular structure consists of a cyano-bridged array of $M(CN)_6$ and $Ln(DMF)_4(H_2O)_3$ fragments forming heterobimetallic molecular entities linked by a CN^- bridging ligand (Figure 19). The Ln^{3+} ion is eight-coordinated with distorted dodecahedral geometry, and the $[M(CN)_6]^{3-}$ entity shows a distorted octahedral geometry. The neutral dinuclear units are linked by hydrogen bonds in a 3-D network that involves the five terminal CN^- groups of the $M(CN)_6$ fragment, the three water oxygen atoms of the $Ln(DMF)_4(H_2O)_3$ fragment, and the water molecules of crystallization. The $Ln^{3+}-Fe^{3+}$ magnetic interaction is antiferromagnetic in [Ce–Fe], [Nd–Fe], [Gd–Fe], and [Dy–Fe], ferromagnetic in [Tb–Fe], [Ho–Fe], and [Tm–Fe], and negligible in [Pr–Fe], [Eu–Fe], [Er–Fe], [Sm–Fe], and [Yb–Fe] systems.

With bpy, heterotrinuclear complexes formulated as *trans*-$[\{Ln(bpy)_2(H_2O)_4\}_2(\mu\text{-}CN)_2M(CN)_4][M(CN)_6]\cdot 8H_2O$ for M^{3+} = Fe and Ln^{3+} = La, Ce, Pr, Nd and for M^{3+} = Co and Ln^{3+} = Ce, Pr, Nd, Sm.[62b] The structures of the eight complexes involve trinuclear cations, $[\{Ln(bpy)_2(H_2O)_4\}_2(\mu\text{-}CN)_2M(CN)_4]^{3+}$, $[M(CN)_6]^{3-}$, and solvent water molecules. The structure of the centrosymmetric trinuclear cation consists of a cyano-bridged array of $M(CN)_6$ (M^{3+} = Fe, Co) and two $Ln(bpy)_2(H_2O)_4$ fragments. In the trinuclear cation, the metal atom is connected to two Ln^{3+} atoms through two trans-bridged cyano groups (Figure 20). The Ln^{3+} ion is nine-coordinated, and the M^{3+} ion shows a distorted octahedral environment. The analysis of the nine-vertex coordination polyhedra of the lanthanide cations in these complexes was by the CShMs proposed by Avnir et al.[63] The results indicate that the best stereochemical description of the lanthanide environments corresponds to a gyroelongated square pyramid. The conformation of the $Ln(DMF)_4(H_2O)_3$ unit is chiral (**A**). Because each lanthanide ion is related to the other one by the inversion center at the transition-metal atom that bridges them, there are two enantiomeric coordination spheres in an achiral trinuclear unit (**B**).



A



B

In the crystal lattice, the trinuclear cations are self-assembled through hydrogen bonds, thus giving an extensive 3-D network. The bpy ligands of neighboring trinuclear entities exhibit weak $\pi-\pi$ interactions, providing additional stabilization of the crystal structure. The magnetic interaction for the three trinuclear $[Ln_2Fe]$ (Ln^{3+} = Ce, Pr, Nd) units is negligible. It has to be noted that these low-nuclearity complexes have not been obtained with $Cr(CN)_6$ units.

The 3-D structures reported above involve hydrogen bonds. There are a few examples of 3d–4f complexes with 3-D networks and coordinative bonds only. They are obtained with multicarboxylate ligands under hydrothermal conditions.

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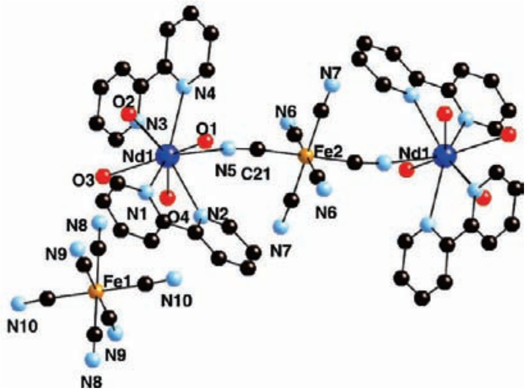

Figure 20. View of complex *trans*-$[Nd(bpy)_2(H_2O)_4(\mu\text{-}CN)Fe(CN)_6]$-$[Fe(CN)_6]$

So, the use of pyridine-2,6-dicarboxylic acid yields 3-D Ln−Mn zeolite-type materials,[68] pyridine-2,4,6-tricarboxylic acid 3-D Pr−Ni−Na open networks,[69] and iminodiacetate acid 3-D Ln−Cr interpenetrating structures.[70] Another interesting ligand is oxodiacetic acid (H_2oda), which can give a series of 3-D complexes $[Cu_3Ln_2(oda)_6(H_2O)_6\cdot xH_2O]_n$ that crystallize in a hexagonal system under hydrothermal conditions[71] or $[\{Mn(H_2O)_6\}\{MnGd(oda)_3\}_2]\cdot 6H_2O$ under classical preparation,[72] which is the first cubic Gd−Mn 3-D network where each gadolinium ion is linked to six manganese ions through anti−anti carboxylate bridges and each manganese ion to six gadolinium ions. A weak Mn−Gd ferromagnetic interaction is active in the three space directions.

Coordination Polymers Constructed from Oligonuclear 3d−4f Complexes as Nodes. Originating from Robson's seminal papers published in 1990,[73] the node-and-spacer approach is a widely used strategy for the construction of a large variety of coordination polymers. It relies upon the strong directionality of the coordination bonds established between the metal ions (nodes and connectors) and the exodentate ligands (spacers and linkers). Coordination polymers can be constructed from oligonuclear nodes as well.[74] The metal ions interact with the divergent ligand through their easily accessible coordination sites. The presence of two or more metal ions confers to the node a higher geometrical flexibility. Moreover, the metal−metal intra- and internode interactions can lead to new redox, electric, or magnetic properties.

The compartmental ligands derived from 3-methoxysalicylaldehyde and a diamine have been specially designed to obtain binuclear 3d−4f complexes, $[LCuLn(O_2NO)_3]$.[11] Their exceptional versatility as building blocks is due to the presence of two metal ions that differ drastically in their chemical behavior: the rare-earth cations are hard acids, with a strong oxophilic character and high coordination numbers, whereas Cu^{II} is a borderline acid with a marked tendency to adopt a more or less distorted square-pyramidal geometry. Consequently, they can interact selectively with various spacers.

The exodentate ligands with oxygen donor atoms are supposed to interact preferentially with the oxophilic 4f cations, while the exodentate ligands bearing nitrogen atoms will prefer the Cu^{II} ions. Indeed, various network topologies were obtained by employing spacers with only oxygen, only nitrogen, or both oxygen and nitrogen donor atoms.[75] For example, the reaction between $[LCuLn(O_2NO)_3]$ and the dianion of the acetylenedicarboxylic acid, acdca^{2-}, affords a 1-D coordination polymer, $[L^5Cu^{II}Gd^{III}(acdca)_{1.5}(H_2O)_2]\cdot 13H_2O$ [H_2L^5 = *N*,*N′*-propylenedi(3-methoxysalicylideneimine], in which the spacer interacts only with the gadolinium ions (Figure 21).[75a] The $\{L^5CuGd\}$ entities are alternatively bridged by one and two dicarboxylato ligands having different connectivity modes: with the single bridge, the acetylenedicarboxylato ligand acts as bischelating ligand toward two gadolinium ions, while with the double bridge, each carboxylato group acts as a unidentate ligand. The investigation of its magnetic properties reveals a ferromagnetic $Cu^{II}\cdots Gd^{III}$ intranode coupling ($J = 5.98\ cm^{-1}$) and antiferromagnetic interactions, mediated by the dicarboxylato linkers, between the resulting $S = 4$ spins.

The case of fumaric acid is particularly interesting. It has been shown that the nature of the resulting heterometallic complexes is influenced by (i) the degree of deprotonation of the dicarboxylic groups, (ii) the various connectivity modes exhibited by the carboxylato groups, and (iii) the $Cu^{II}-Ln^{III}$ and Ln^{III}−linker molar ratios. Three different types of coordination polymers were obtained by using the fumaric acid H_2fum: $[L^5Cu^{II}Gd^{III}(fum)_{1.5}(H_2O)_2]\cdot 4H_2O\cdot C_2H_5OH$, $[L^5Cu^{II}Sm^{III}(H_2O)(Hfum)(fum)]$, and $[L^5Cu^{II}Er^{III}(H_2O)_2(fum)]$-$(NO_3)\cdot 3H_2O$ (Figure 22). The gadolinium derivative is a 2-D network, the samarium one is a double chain, and the erbium derivative is a single chain. $[L^5Cu^{II}Gd^{III}(fum)_{1.5}(H_2O)_2]\cdot 4H_2O\cdot C_2H_5OH$ has the same stoichiometry as the 1-D acetylenedicarboxylato derivative described above, except the crystallization solvent molecules, but its structure is completely different: it is a 2-D coordination polymer with a brick-wall architecture. Each {Cu−Gd} entity is connected through fumarato bridges to three other heterobinuclear units. Two out of the three fumarato linkers connect the gadolinium ions from three {Cu−Gd} units, with each carboxylato group acting as a chelate. For the third fumarato linker, each

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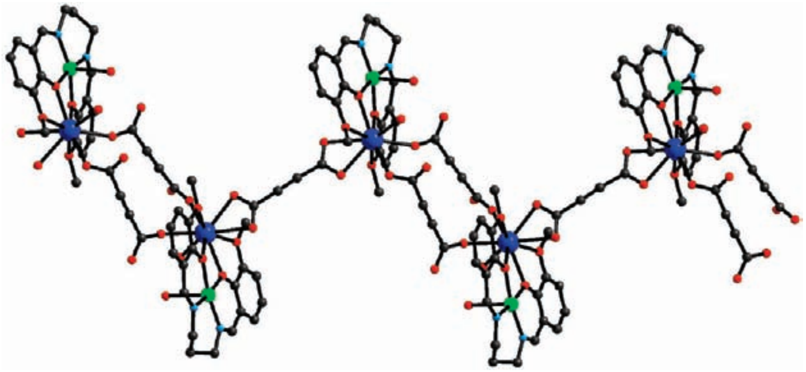

Figure 21. View of a chain constructed from ferromagnetic [Cu−Gd] nodes and acetylenedicarboxylato spacers (dark blue, gadolinium; green, copper; light blue, nitrogen; red, oxygen).

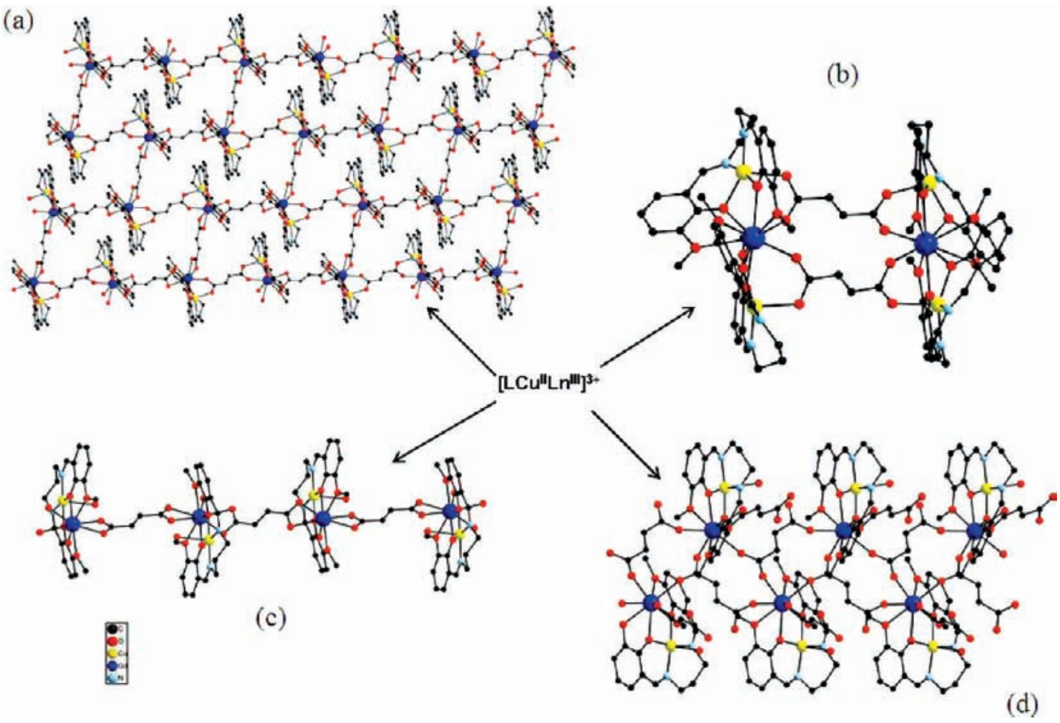

Figure 22. Coordination polymers obtained by using the anions of fumaric acid as spacers: (a) $^{2}{}_{\infty}[L^5CuGd(fum)_{1.5}(H_2O)_2]\cdot 4H_2O\cdot C_2H_5OH$ (2-D); (b) $[\{(L^5Cu)_2Sm\}_2fum_2](OH)_2$ (hexanuclear); (c) $^{1}{}_{\infty}[L^5CuEr(H_2O)_2(fum)](NO_3)\cdot 3H_2O$ (1-D, single chain); (d) $^{1}{}_{\infty}[L^5CuSm(H_2O)(Hfum)(fum)]$ (1-D, double chain).

carboxylato group bridges the Cu^{II} and Gd^{III} ions within the {Cu−Gd} building block (syn−syn bridging mode). The samarium derivative has been obtained by reacting the {Cu−Sm} precursor with fumaric acid. One of the fumaric acid molecules is fully deprotonated, while the other one is monodeprotonated. The fum^{2-} and $Hfum^{-}$ species are coordinated only to the samarium ions: the first one acts as a bridge, while the second one is a terminal ligand, with the chelating carboxylato group coordinated to samarium. The fum^{2-} ligand links simultaneously three samarium ions from three different {Cu−Sm} units: one carboxylato group bridges two samarium ions in anti−anti fashion, while the second one is coordinated through one oxygen atom to the third samarium ion. This results in a double chain. The $Hfum^{-}$ ion acts as a terminal ligand, being coordinated to a samarium ion (chelating mode). The reaction between $[L^5CuEr(NO_3)_3]$, fumaric acid (molar ratio 1:1), and LiOH leads to a different compound: $[L^5Cu^{II}Er^{III}(H_2O)_2(fum)](NO_3)\cdot 4H_2O$. In this case, only two out of the three nitrato ligands were replaced by one fumarato dianion. This results in a 1-D coordination polymer with the {Cu−Er} nodes connected by fum^{2-} bridges. By reaction of the mononuclear Schiff base Cu^{II} complex with samarium nitrate and fumaric acid in a 2:1:1 molar ratio (in the presence of LiOH), a hexanuclear complex based upon the $[Cu_2Sm]$ entity was formed: $[\{(L^5Cu^{II})_2Sm^{III}\}_2fum_2](OH)_2$. The two $\{Cu_2Sm\}$ moieties are linked through two fum^{2-} ions. Each carboxylato group acts as a bridge between the copper and samarium ions (the classical syn−syn bridging mode).

It is interesting to anticipate that this synthetic approach could be applied for the design of chains or sheets of SMMs by choosing the appropriate metal ions and linkers.

Bimetallic d−f complexes are also useful starting materials for obtaining coordination compounds with three different spin carriers (3d−3d′−4f, 2p−3d−4f, 3p−3d−4f, etc.), with the nitrato gropus being replaced by ligands carrying the third

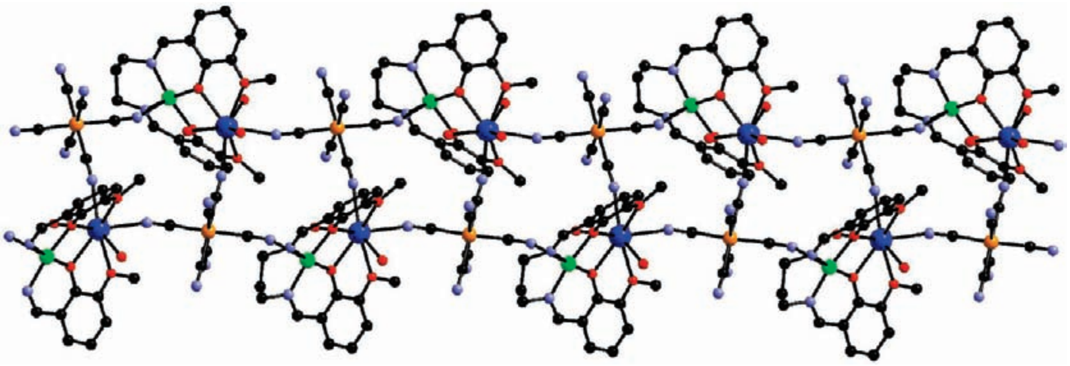

Figure 23. Perspective view of the 3d−3d′−4f coordination polymers [{L^5Cu}Ln(H_2O)$_3${M(CN)$_6$}]·4H_2O resulting by reacting [L^1CuLn(NO_3)$_3$] complexes with [M(CN)$_6$]$^{3-}$ ions (dark blue, lanthanide; green, copper; orange, iron; light blue, nitrogen; red, oxygen).

spin carrier. Such compounds are of high interest in molecular magnetism, providing both physicists and theoreticians exciting cases for investigation. The third spin carrier could add new properties/functions to the magnetic material. The number of such heterospin complexes is limited to only a few examples.

Heterotrimetallic 3d−3d′−4f complexes can be obtained by reacting [L^5CuLn(NO_3)$_3$] precursors with a metalloligand, for example, hexacyano complex anions, [M(CN)$_6$]$^{3-}$ (M = Cr, Fe, Co). A family of isostructural complexes, [{L^5Cu}Ln(H_2O)$_3${M(CN)$_6$}]·4H_2O, has thus been obtained.[75a,c] The [M(CN)$_6$]$^{3-}$ ion connects three metal ions (two Cu^{II} and one Ln^{III}), through three meridially disposed cyano groups, resulting in a ladder-type topology (Figure 23). The [$Cu^{II}Gd^{III}Co^{III}$] derivative gives information on the [Cu−Gd] interaction within the whole [$Cu^{II}Gd^{III}M^{III}$] family ($J_{Cu-Gd} = 7.24$ cm^{-1}, $H = -JS_{Cu}S_{Gd}$). The magnetic behavior of the [$Cu^{II}Gd^{III}Cr^{III}$] and [$Cu^{II}Gd^{III}Fe^{III}$] derivatives results from the combination of the following exchange interactions: Cu^{II}−Gd^{III} (ferro) and Gd^{III}−M^{III} (antiferro). The intranode ferromagnetic Cu^{II}−Gd^{III} interaction is overwhelmed by the Gd^{III}−Cr^{III} antiferromagnetic interactions. The simulation of the magnetic properties for chains with three different spin carriers is challenging.

A few other 3d−3d′−4f complexes are described.[60,76] All of them have been obtained following a stepwise synthetic procedure similar to the one described above, with the third metal ion being inserted by employing [M(CN)$_6$]$^{3-}$ ions. One of these compounds, [$Co^{II}_2Gd^{III}L_2(H_2O)_4${$Cr^{III}(CN)_6$}]·2$H_2O$ [H_2L = 2,6-di(acetoacetyl)pyridine], is a 3-D network exhibiting 3-D ferromagnetic ordering with $T_c = 15.4$ K. This is the highest critical temperature among PB analogues incorporating lanthanide ions.[76b]

The first 2p−3d−4f and 3p−3d−4f heterospin systems have been obtained by using respectively TCNQ$^{\bullet-}$ and [Ni(mnt)$_2$]$^{\bullet-}$ anionic radicals, which carry the third spin and can act as ligands (TCNQ$^{\bullet-}$ = radical anion of 7,7,8,8-tetracyano-*p*-quinodimethane; mnt = maleonitriledithiolato).[77] Let us recall here two examples: {CuL^5}$_2$Gd(TCNQ)$_2$]·TCNQ·CH_3OH·2CH_3CN and [{(CH_3OH)-CuL^6}{CuL^5}Gd(O_2NO){Ni(mnt)$_2$}][Ni(mnt)$_2$]·CH_2Cl_2 [H_2L^6 = *N,N′*-ethylenedi(3-methoxysalicylideneimine)]. The two compounds have been obtained by reacting the copper precursors, [CuL^5] or [CuL^6], with gadolinium nitrate and respectively LiTCNQ or (TBA)[Ni(mnt)$_2$] (TBA = *n*-tetrabutylammonium). The [Ni(mnt)$_2$]$^{\bullet-}$ radical anion bears mostly a 3p spin type. In the first compound, the TCNQ$^{\bullet-}$ ions are involved in both coordinative and stacking interactions.[77a] One TCNQ$^{\bullet-}$ radical is coordinated to the gadolinium atom. The second TCNQ$^{\bullet-}$ acts as a bridging ligand between Cu^{II} ions from neighboring [Cu_2Gd] units, resulting in infinite chains (Figure 24a). The third TCNQ$^{\bullet-}$ ion is uncoordinated. The stacked TCNQ$^{\bullet-}$ ions do not contribute to the magnetic moment because of their strong antiferromagnetic coupling. The Cu^{II} and Gd^{III} ions are ferromagnetically coupled ($J = +7.7$ cm^{-1}; $H = -J(S_{Cu1}S_{Gd} + S_{Gd}S_{Cu2})$.

The second compound, [{(CH_3OH)CuL^6}{CuL^6}Gd-(O_2NO){Ni(mnt)$_2$}][Ni(mnt)$_2$]·CH_2Cl_2, is a genuine example of a 3p−3d−4f heterospin complex.[77b] Its structure consists of cationic species, uncoordinated [Ni(mnt)$_2$]$^{\bullet-}$ ions, and solvent molecules. The cationic species are constructed out of two [Cu_2Gd] moieties bridged by two nitrato groups (each one acting as a chelate toward the gadolinium ion from a unit and monodentate toward the Cu2 ion from the other unit; Figure 24c). The Cu2 ions exhibit an elongated octahedral stereochemistry because their two apical positions are occupied by a nitrato oxygen atom and by a nitrogen atom arising from one [Ni(mnt)$_2$]$^{\bullet-}$ ion. The [Ni(mnt)$_2$]$^{\bullet-}$ units are stacked in tetramers, with the semicoordinated anions embracing the uncoordinated ones. The analysis of the magnetic behavior reveals the coexistence ferromagnetic and antiferromagnetic interactions: Cu^{II}−Gd^{III}, $J = +4.3$ cm^{-1}; Cu^{II} − [Ni(mnt)$_2$]$^{\bullet-}$, $J = -10$ cm^{-1}; [Ni(mnt)$_2$]$^{\bullet-}$ - [Ni(mnt)$_2$]$^{\bullet-}$, $J = -250$ cm^{-1}.

When the bicompartmental ligand is changed (L^5 instead of L^6), the interaction between [(CuL^5}$_2$Ln]$^{3+}$ and [Ni(mnt)$_2$]$^{\bullet-}$ leads to ionic compounds [{(CH_3CN)-CuL^5}$_2$Ln(H_2O)][Ni(mnt)$_2$]$_3$·2CH_3CN (Ln = Gd, Sm, Tb), with all of the [Ni(mnt)$_2$]$^{\bullet-}$ ions being uncoordinated (Figure 24b). Again, the Cu−Gd interaction was found to be ferromagnetic ($J = +4.1$ cm^{-1}), while the stacked [Ni(mnt)$_2$]$^{\bullet-}$ units are strongly antiferromagnetically coupled. When Gd^{III} is replaced by Tb^{III}, the system becomes

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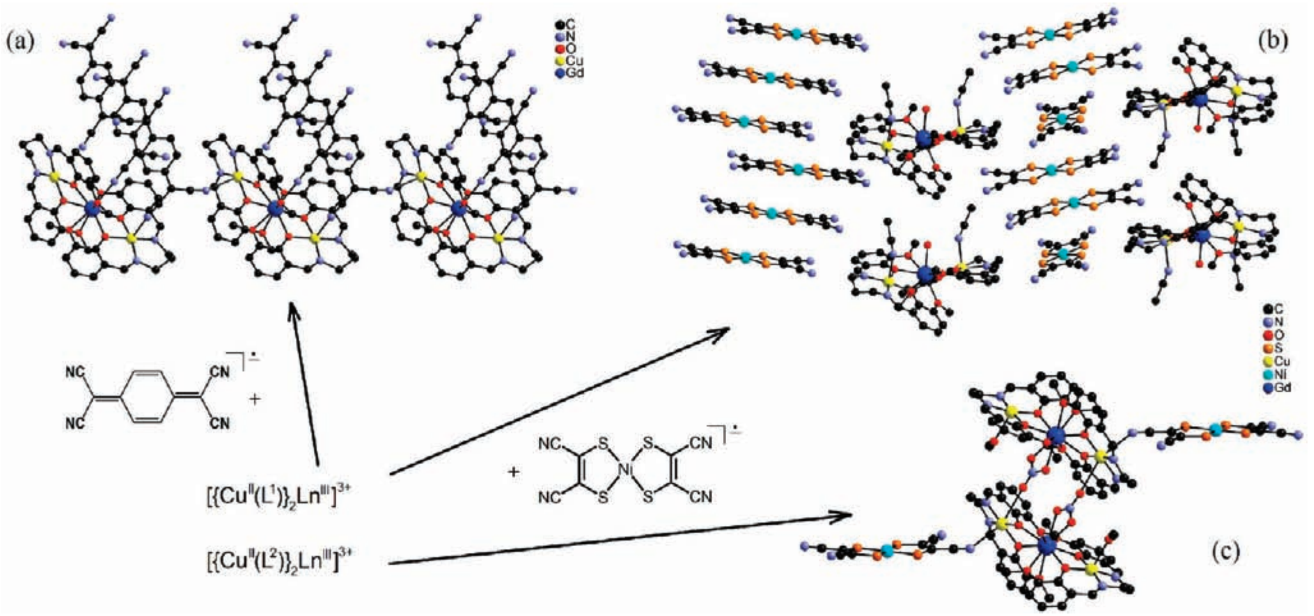

Figure 24. Heterospin (a) 2p−3d−4f and 3p−3d−4f systems: (a) $[\{CuL^5\}_2Gd(TCNQ)_2]\cdot TCNQ\cdot CH_3OH\cdot 2CH_3CN$; (b) $[\{(CH_3CN)CuL^5\}_2Ln(H_2O)][Ni(mnt)_2]_3\cdot 2CH_3CN$; (c) $[\{(CH_3OH)CuL^6\}\{CuL^6\}Gd(O_2NO)\{Ni(mnt)_2\}][Ni(mnt)_2]\cdot CH_2Cl_2$.

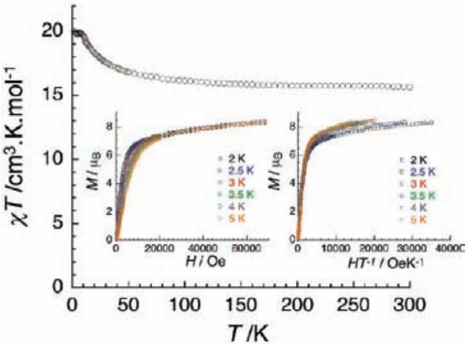

Figure 25. χT vs T plot at 1000 Oe for $[\{(CH_3CN)CuL^5\}_2Tb(H_2O)][Ni(mnt)_2]_3\cdot 2CH_3CN$. Inset: M vs H and M vs H/T plots measured between 2 and 5 K.

significantly anisotropic. The exchange interaction between Tb^{III} and Cu^{II} is found to be ferromagnetic. Magnetization versus field studies at different temperatures (M vs H/T plot) confirm the presence of anisotropy (Figure 25). In zero dc field, frequency-dependent ac susceptibility is observed below 10 K. The shape of this relaxation process is broad and does not look like a classical SMM behavior with a single relaxation process. A distribution of relaxation time might be present because of, for example, structural disorder, defects, or different intermolecular magnetic interactions.

In the above-described compounds, the 2p and 3p spin carriers do not contribute significantly to the magnetic behavior and do not bring another property. On the other hand, the use of dithiolene complexes $[M(mnt)_2]^{q-}$, with a noninteger average oxidized state, is very attractive in the design of multifunctional materials, by combining magnetic properties with molecular conductivity. In a series of recent papers, Yamashita et al. have shown that such mixed-valence metal dithiolene groups, $[M(mnt)_2]^{q-}$, which are either coordinated or uncoordinated to the magnetic moiety (manganese clusters with SMM behavior), bring electronic conductivity arising from the charge delocalization on the stacked $[M(mnt)_2]^{q-}$ units (M = Ni, Pt).[78] Their synthetic strategy can be extended toward other systems, including lanthanide-based molecular materials.

Conclusions

The compartmental Schiff base ligands with inner N_2O_2 and outer O_2O_2 coordination sites appear as the best quality ligands to isolate 3d−Gd heterodinuclear complexes (3d = Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, VO), to solve their structural determinations, mainly of the η^2-coordinated nitrate entities, and to study their magnetic behaviors. The results confirm that ferromagnetic 3d−Gd interactions are present in a large majority of these complexes and that the diphenoxo bridge is the best one for transmission of the 3d−4f magnetic interaction. Considering that the exchange mechanism is affected by the increased number of active 3d electrons, the J values decrease in going from copper to nickel, cobalt, and iron. It has also been shown that the magnitude of the exchange parameter, J, and in a few cases its sign are dependent on the bending of the $\{MO_2Gd\}$ core gauged by the dihedral angle defined as the angle between the two halves (OMO and OGdO planes) of the bridging network. The limiting case of no bending displays the largest ferromagnetic interaction, while the largest angles are associated with the lowest J values and in a few cases to antiferromagnetic interactions. This remark explains why the ferromagnetic VO−Gd interactions, with the vanadyl ion out of the N_2O_2 coordination site, are always weaker than the ferromagnetic Cu−Gd interactions and that the largest antiferromagnetic interaction has been detected in a VO−Gd complex.

Contrary to the magnetic properties of 3d−3d′ complexes, which are explained by an understanding of their orbital interactions, the mechanism responsible for the presence of

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general 3d−Gd ferromagnetic interaction is not so clearly documented. Gatteschi et al.[4] first proposed that spin-polarization factors resulting from orbital interaction between the 6s Gd orbital and delocalization tails of the 3d Cu orbitals on the ligand were responsible for that behavior. Then a configuration interaction based on the Goodenough model[79] and corresponding to a one-electron (or a fraction of electron) jump between the 3d Cu orbital and the vacant 5d Gd orbitals was advanced by Kahn et al.[5b] A more recent work on magnetic coupling in dinuclear gadolinium complexes[80] focuses the influence of the $4f^7$−5d exchange interaction on molecular orbitals with significant 5d-orbital character to facilitate stronger ferromagnetic coupling. The dominating role of a structural factor is a strong experimental argument in favor of a decisive contribution of the 5d Gd orbitals in the magnetism of the 3d−Gd complexes.

Because the 3d−Gd interaction is mainly ferromagnetic, association of these dinuclear synthons in keeping only 3d−Gd interactions and avoiding 3d−3d or Gd−Gd interactions is a nice way toward high-spin species. This bottom-up strategy has been exemplified by the synthesis of tetranuclear complexes with $S = 8$ ground states. Furthermore, introduction of anisotropic lanthanide ions such as terbium or dysprosium in place of gadolinium ions yields complexes that exhibit features typical of SMMs with both hysteretic behavior of the magnetization and frequency dependence of the ac magnetic susceptibility. The results published until now demonstrate the ability of 3d−4f complexes to increase ground spin states S and negative axial anisotropy D in order to increase relaxation times.

Perspectives

From a magnetic point of view, the understanding of the magnetic properties of complexes that involve 4f ions is still far from being satisfactory. Until now, the generality of Cu−Gd ferromagnetic coupling has been correlated with the large occurrence of approximate pseudo-C_{2v} geometry of these complexes. Within this symmetry, it has been demonstrated that the influence of interaction channels exhibiting orbital orthogonality prevails over the nonorthogonal ones. This would explain why antiferromagnetic Cu−Gd exceptions occur when the molecular asymmetry is advanced, as in lower symmetries. It would be interesting to synthesize complexes of different geometries in order to check the role played by geometry on the interaction parameters. Such comparisons should give a better understanding of the interaction mechanism and should confirm the role played by the 5d orbitals of the 4f ions.

The ligand strategy based on Schiff base complexes presents the quite interesting advantage of obtaining starting complexes with any transition metal of the first row. Because they also allow the introduction of anisotropy with 4f ions, it becomes clear that new complexes with anisotropy coming from the 3d ions or from the 3d and 4f ions will appear in the near future. It has to be noted that a first example has already been reported.[36]

Because the 3d−4f interactions are not very strong, the use of second and third transition metal ions characterized by more diffuse valence orbitals should be a way to enhance the exchange interaction between magnetic centers. Such an approach can be realized by assembling 3d−4f units with octacyanometallate bridging entities to yield 3d−4d−4f or 3d−5d−4f heterotrimetallic complexes, according to the strategy retained for the preparation of 3d−3d′−4f chains with hexacyanometallate bridges. Preliminary results[81] do confirm the feasibility of this approach that should be developed in the future. The association of three or more different spin carriers is a possible way toward multifunctional materials, which deserves to be further investigated.

The magnetic properties of the most rare-earth ions are strongly influenced by the orbital component of the magnetic moment, due to spin−orbit coupling of the f electrons compared with the ligand-field effects. Additionally, the ligand-field effects and the exchange interactions between the magnetic centers become relevant at the same temperature's range. This makes the analysis of the magnetic behavior of such compounds very difficult. The typical empirical approach, developed by one of us[15,28] and applied by several authors, is the most widely used to examine the nature of the magnetic interaction. On the other hand, more quantitative approaches have been developed using an isotropic exchange Hamiltonian.[82,83] Taking into account the above, it is necessary to gather a large number of experimental data to evaluate the crystal-field effects of each individual Ln^{3+} ion and to gain insight into the low-lying levels. Studies of f−d complexes and the corresponding diamagnetically substituted systems by using EPR (powder and single crystal), anisotropic magnetic measurements at very low temperatures, and inelastic neutron scattering on single crystals will be performed to help in the understanding of their magnetic behavior. We expect that, in the near future, DFT or similar calculations will help to obtain the information required to reconstruct the full map of the magnetic interactions in the f−d systems.

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