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Magnetism of Lanthanides in Molecular Materials with Transition-Metal Ions and Organic Radicals

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I. Introduction

Rare-earth ions are characterized by large unquenched orbital angular momentum associated with the internal nature of the valence f orbitals. In fact, with the exception of gadolinium(III) and europium(II), which have an f^7 electron configuration and an orbitally nondegenerate ground state, all the rare-earth ions have orbitally degenerate ground states, which are split by spin−orbit coupling and crystal-field effects. Since crystal-field effects are smaller and spin−orbit coupling larger for f electrons compared to the d electrons of transition-metal ions, the orbital component of the magnetic moment is much more important for the rare-earth ions compared to the transition-metal ions. The magnetic properties of rare-earth ions are strongly influenced by this, in particular the magneto-crystalline anisotropy, which is in general large. This is one of the reasons why rare earths are widely used in magnet technology. Some examples of this are provided by the $SmCo_5$ and $Nd_2Fe_{14}B$ permanent magnets, which have found large market use in the past few years.

Although the theory of the paramagnetic properties of rare-earth ions has long been developed, the presence of the large unquenched orbital angular momentum has not allowed the development of simple models for a rational analysis of the structural magnetic correlations, analogous to the Goodenough−Kanamori rules[1] or the Kahn−Briat[2] and Hay−Hoffmann[3] molecular orbital oriented models. This is essentially due to the fact that the simplified spin Hamiltonian approaches which have been so useful for understanding and parametrizing the magnetic interactions in compounds containing transition-metal ions cannot be used in the presence of orbital degeneracy. Further, the internal nature of the f electrons gives rise to weak magnetic interactions, which also make the analysis of the experimental data more difficult. Fundamental theories should be used, but this is still difficult for open-shell systems with sizable relativistic effects.

Molecular magnetic compounds have been recently developed to a large extent,[4−7] and suitable strategies have been worked out to obtain new materials with expected properties, like molecular ferro- and ferrimagnets, organic magnets, single-molecule magnets, high-spin molecules, etc. An advantage of molecular compounds, compared to those based on continuous lattices, is that it is relatively easy to obtain systems containing isolated pairs of magnetic centers, with different relative orientations of the so-called magnetic orbitals, in such a way that the structural features responsible for the magnetic coupling clearly emerge.

The efforts for obtaining molecular magnets containing rare-earth ions have been comparatively less numerous because the interactions in pairs of f electrons are expected to be small, producing measurable effects at extremely low temperatures, but the number of new reported compounds in which rare-earth ions are magnetically coupled to transition-metal ions and/or organic radicals is rapidly increasing. The rationale for this approach is that the interaction of the f electrons with the more expanded s, p, or d electrons should be stronger than that with other f electrons, thus producing measurable effects at high temperatures, and the problem of orbital degeneracy may be limited.

We review here the structure and magnetic properties of molecular compounds containing rare-earth ions coupled to d ions and organic radicals. In particular we will briefly recall the paramagnetic properties of rare-earth ions; then we will develop effective Hamiltonians for describing the interactions between rare-earth ions and transition-metal or

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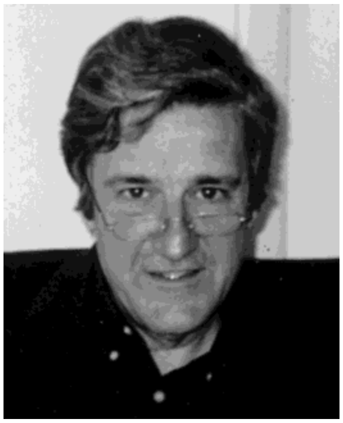
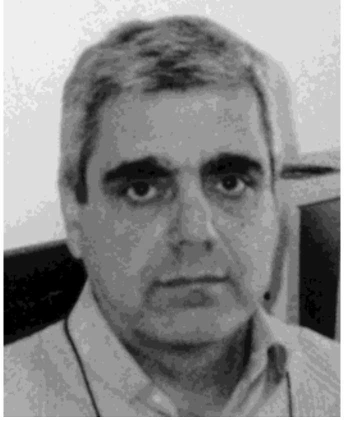


Dante Gatteschi was born in Florence, Italy, in 1945. He graduated in Chemistry at the University of Florence in 1969. He became assistant of Professor Sacconi in the same university, and in 1980 became Professor of Inorganic Chemistry here in the Faculty of Pharmacy. His research interests lie in the electronic structure of low-symmetry transition-metal complexes, in EPR spectroscopy of transition-metal ions, and more recently in molecular magnetism. During the past few years he has focused on the magnetic properties of large spin clusters, stressing their role as nanosize magnets, which allowed for the first time the observation of quantum tunneling effects of magnetization in molecular clusters. He is the author of more than 400 publications in international journals, of one book on *EPR of Exchange Coupled Systems,* and the editor of several books on molecular magnetism. In 1979 he was awarded by the Italian Chemical Society the Nasini prize, reserved for young inorganic chemists, and in 1992 the Magnetic Resonance award of the same Society.



Cristiano Benelli was born in Florence, Italy, in 1947. He graduated in Chemistry at the University of Florence in 1971, and in 1983 he became Professor of Inorganic Chemistry in the Faculty of Engineering in the same university. At the beginning of his scientific work his research interests were dedicated to analyzing the magnetic and spectroscopic properties of transition-metal complexes. In a second stage he focused his research on the study of the exchange mechanism of heterometallic couples with particular interest in 3d–4f systems. He is the author of more than 100 publications in international journals.

organic radical centers, specializing them to interactions involving ions, like gadolinium(III), whose total orbital momentun is equal to zero. Finally, we will survey the structures and the magnetic properties of the reported molecular compounds comprising rare-earth ions coupled to transition-metal and organic radicals, dividing them in zero-, one-, and two-dimensional, depending on the structural features of the rare-earth ions. In other words we classify the compounds according to the number of structurally correlated rare-earth ions (finite and infinite in one and two dimensions, respectively).

Table 1. Ground State, *g* Values, and Room Temperature χ Values for Trivalent Lanthanide Ions

trivalent ion	configuration	ground state	g_J	χT (emu mol^{-1} K)
Ce	f^1	$^2F_{5/2}$		0.80
Pr	f^2	$3H_4$	4/5	1.60
Nd	f^3	$4I_{9/2}$	8/11	1.64
Pm	f^4	$5I_4$	3/5	0.90
Sm	f^5	$^6H_{5/2}$	2/7	0.09
Eu	f^6	$7F_0$		
Gd	f^7	$8S_{7/2}$	2	7.88
Tb	f^8	$7F_6$	3/2	11.82
Dy	f^9	$^6H_{15/2}$	4/3	14.17
Ho	f^{10}	$5I_8$	5/4	14.07
Er	f^{11}	$^4I_{15/2}$	6/5	11.48
Tm	f^{12}	$3H_6$	7/6	7.15
Yb	f^{13}	$2F_{7/2}$	8.7	2.57

II. Spin States of Rare-Earth Ions

The magnetic properties of rare-earth ions are well-known and dominated by the internal nature of the f orbitals, which give rise to strong unquenched orbital angular momentum, and by spin–orbit coupling. The trivalent ions are characterized by f^n configurations, which give rise to ^{2S+1}L multiplets, split by spin–orbit coupling to give J states

$$E(^{2S+1}L_J) = (\lambda/2)[J(J+1) - L(L+1) - S(S+1)] \tag{1}$$

where J is defined by the angular momentum summation rules

$$|L - S| \leq J \leq L + S \tag{2}$$

and $\lambda = \pm\zeta/2S$. ζ is the spin–orbit coupling constant which ranges between 600 and 3000 cm^{-1} throughout the series, the highest values corresponding to the heaviest rare earths. The + sign applies for $n < 7$ and the − sign for $n > 7$. The ground states for the different rare-earth ions are reported in Table 1. Equation 1 and the sign of the spin–orbit coupling constant λ imply that in the ground-state $J = L - S$ for $n < 7$ and $J = L + S$ for $n > 7$. For f^7 ions, like gadolinium(III), $L = 0$ and $S = 7/2$ and the orbital momentum is completely quenched in the ground state.

The g factor of the Zeeman Hamiltonian of a given J multiplet is given by

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \tag{3}$$

In general, the lowest lying J multiplet is well separated from the excited ones. The most notable exceptions are europium(III) and samarium(III). The former has a ground $^7F_0$ state, with $^7F_1$ at ca. 350 cm^{-1}, and the latter a ground $^6H_{5/2}$ with $^6H_{7/2}$ at ca. 700 cm^{-1}.

Crystal-field effects are small, in such a way that the magnetic susceptibility only differs from the free ion value at low temperature, while at room temperature the free ion expression is a very good approximation. The typical χT values for the various lanthanide(III) ions are given in Table 1 together with the g values of the ground multiplet.

In the isolated ions, crystal-field effects split the J multiplets, the splitting typically being comparable to thermal energy. The paramagnetic properties of the ions therefore are determined by the thermal population of the split components of the low-lying J multiplets, and large deviations from Curie law must be anticipated at low temperature. The approximation which is often done for transition-metal ions with an orbitally nondegenerate ground state that the magnetic moment is temperature independent cannot be used for rare-earth ions. In a coupled system containing a rare-earth ion coupled to an orbitally nondegenerate transition-metal ion, the observed deviation from Curie law can be due to both the single-ion effect of the rare-earth ion and the coupling between the two ions, and no simple model has so far been produced to unravel the two contributions. In the following we will show how some attempts have been done to obtain independent information on the crystal-field effects on the rare-earth ions by using diamagnetic substitution methods.

III. Models for the Magnetic Coupling of f and s, p, d Electrons: Spin Hamiltonians

The interaction between a S state ion like gadolinium(III) and an orbitally nondegenerate d ion or an organic radical can be treated using the well-known spin Hamiltonian

$$H = J\, S_{\mathrm{Gd}} \cdot S_1 \qquad (4)$$

where S_{Gd} is the spin operator associated to gadolinium and S_1 is the spin operator associated with the other magnetic center. It must be remarked at the outset that with this spin Hamiltonian positive J means antiferromagnetic and negative ferromagnetic coupling. The spin levels follow the law

$$E(S) = (J/2)[S(S+1) - S_{\mathrm{Gd}}(S_{\mathrm{Gd}}+1) - S_1(S_1+1)] \qquad (5)$$

where S is defined by the angular momentum addition rules

$$|S_{\mathrm{Gd}} - S_1| \leq S \leq S_{\mathrm{Gd}} + S_1 \qquad (6)$$

The energy levels can be expressed as a function of one parameter, which can be obtained with acceptable reliability from the analysis of the magnetic properties. For instance, in the case $S_1 = 1/2$, two total spin states are allowed, namely, $S = 4$, which is the ground state for ferromagnetic coupling, and $S = 3$, which is the ground state for antiferromagnetic coupling. The separation between the two levels is $4J$.

The value of J obtained from the analysis of the experimental data, for instance by fitting the temperature dependence of the magnetic susceptibility, determined by the change in population of the $S = 3$ and 4 levels, is then compared with more fundamental theories. At the basis of all the treatments is the early model developed by Anderson[8] about 50 years ago. Reducing a complex theory to extremely simplified terms one has to take into consideration the magnetic orbitals, i.e., the ones containing one unpaired electron. If the two orbitals on the two different centers have a nonzero overlap, then the spins will pair with an antiferromagnetic coupling, while if the orbitals are orthogonal to each other, the spins will tend to be parallel to each other (ferromagnetic coupling). If more magnetic orbitals are present, the contributions of all the possible pairs will have to be taken into account. In the language of Anderson, these interactions are called exchange or superexchange interactions, depending on whether the two magnetic centers are in direct contact or they are bridged by a formally diamagnetic moiety. It is apparent that the above simple considerations indicate that what we call exchange or superexchange interaction is just a form of weak bonding between the two magnetic centers. In recent years many developments have become available on the possibility of actually calculating the magnetic coupling using molecular orbital theory. It must be recalled that these calculations are by no means simple, because the exchange interactions are weak, ranging typically from 10^0 to 10^2 cm^{-1}. The first attempts were made at the semiempirical level (Extended Hückel),[3] while now ab initio methods of variable complexity are successfully used.[9-13]

Complex as they can be, both the spin Hamiltonian and the rigorous approaches rely on one assumption, that the ground states of the two interacting centers are orbitally nondegenerate. When this condition breaks down, as it happens for the rare-earth ions, it is, so far, impossible to make any accurate estimation of the energy levels generated by the magnetic interaction. The problem is that one should take into account explicitly spin−orbit coupling, low-symmetry crystal-field effects, and vibronic (phonon) coupling. To our knowledge, this has not yet been made at the rigorous level, but even at the spin Hamiltonian level many complications arise.[14,15] In fact, the Hamiltonian (eq 4) implies that the total spin S is a good quantum number, i.e., in the absence of an applied magnetic field the M components of S have the same energy and states with different S cannot be admixed. This means that all the directions in space are equivalent. However, if orbital moment is present, in principle the three directions in space are no longer equivalent, and even in zero field there will be a preferred direction. In other terms, the energy of the state will depend on the M component and a zero field splitting will be observed.

The first detailed treatment of the interactions involving one orbitally nondegenerate ion, like iron(III), and an orbitally degenerate rare-earth ion was performed by Levy[16] in an attempt to rationalize the exchange interactions in garnets. The inclusion of orbital degeneracy makes the spin Hamiltonian (eq 1) insufficient to describe the interactions. A convenient form uses irreducible tensor operators[17] $T_q^{[k]}$

$$H = \sum_{k=0}^{2l} \sum_{q=-k}^{k} \alpha_{kq} T_q^{[k]}(i) s(i) \cdot S(\mathrm{TM}) \qquad (7)$$

where i indicates the ith electron of the rare-earth ion and S(TM) is the spin operator of the transition-

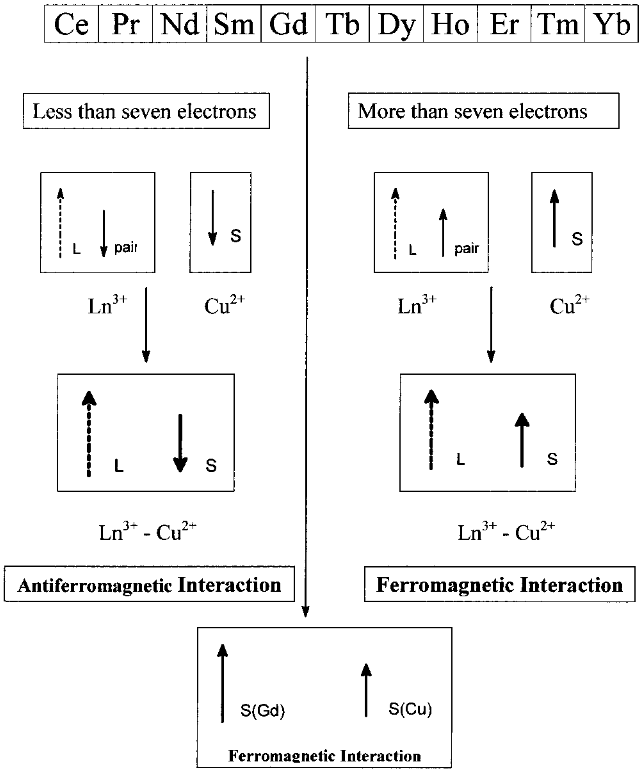


Figure 1. Scheme of the interactions between rare-earth ions and copper(II) ions. It is assumed that the spin–spin interaction is unaltered throughout the series.[87]

metal ion. Instead of the one-parameter J there are now $(2l + 1)(l + 1)$ adjustable parameters. It is apparent that in this way the meaningful fit of the experimental parameters becomes extremely difficult if not impossible. Further, it is necessary to perform anisotropic measurements, because the Hamiltonian (eq 7) is intrinsically anisotropic. Some results were later reported for holmium and ytterbium garnets.[18,19]

Sometimes simplified arguments have been used to rationalize the properties of series of rare-earth compounds.[20,21] In the previous section we showed that the relative orientations of the spin and orbital moments are reversed for f^n configurations with less and more than seven electrons, respectively. If it is assumed that the spin–spin interaction is of the same sign throughout the series, then the overall interactions changes sign for $n < 7$ and $n > 7$, respectively. The argument is graphically depicted in Figure 1. If, for instance, the spin–spin interaction is ferromagnetic, the overall coupling between the rare-earth ion and copper(II) is antiferromagnetic for $n < 7$ and ferromagnetic for $n > 7$.

IV. Nature of the Magnetic Coupling Involving Gadolinium(III)

The first molecular compounds containing gadolinium(III) ions coupled to copper(II) ions were found to be ferromagnetically coupled.[22,23] The result was surprising[24] and aroused some skepticism. It must be recalled that in all cases the coupling constants are small and the effects of the magnetic susceptibility can be observed only at very low temperature, where experimental control may be difficult to achieve. Further support to the observation of ferromagnetic coupling came[25,26] from compounds comprising gadolinium(III) and nitronyl nitroxide ligands, NITR.[27]

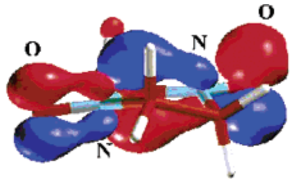
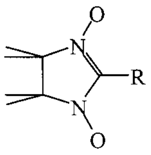


Figure 2. Sketch of the π^* magnetic orbital of a nytronil nitroxide.



NITR

In the superexchange mechanism the presence of overlap between the magnetic orbitals of the gadolinium(III) and the second paramagnetic center gives antiferromagnetic coupling, while the presence of orthogonal orbitals gives ferromagnetic contribution. In principle, it is possible to decompose the experimentally determined coupling constant J in a sum of terms

$$J = \frac{1}{n_1 n_2} \sum_i J_{f_i - o} \tag{8}$$

where f_i indicates an f magnetic orbital of gadolinium(III) and o the magnetic orbital either of copper(II) or of the radical. n_1 is the number of unpaired electrons on gadolinium (seven) and n_2 the number of unpaired electrons on the other magnetic center (1 in the present case). Since the copper ion is in an elongated octahedral coordination, the magnetic orbital is $d_{x^2-y^2}$ in nature, while in the nitronyl nitroxide radical it is a π^* orbital as sketched in Figure 2. It may be expected that at least one nonzero f–o overlap is present, yielding an antiferromagnetic pathway. A maximum of six orthogonal pairs of orbitals may be present. These in principle give rise to ferromagnetic coupling or to no coupling at all, depending on whether f_i and o have zones of suitable orbital density or not. It must be remembered that the condition of zero overlap between the two orbitals may be met either because no overlap at all is present or because regions of overlap density of opposite sign are present. In the former case there is no coupling (this case corresponds to orbitals at infinite distance); in the latter the ferromagnetic coupling will be larger the larger the overlap density. In this frame the overall ferromagnetic coupling may originate from the fact that the number of ferromagnetic pathways is larger than that of antiferromagnetic ones. However, in low-symmetry compounds one would feel that the antiferromagnetic pathways are relatively more numerous than the in high-symmetry ones. Therefore, an overall antiferromagnetic coupling would be expected. A similar situation holds for manganese(II) compounds, which generally yield an overall weak antiferromagnetic coupling.[28] However since the f orbitals are effectively shielded from the ligand orbitals, the effective overlaps are very close to zero.

A first attempt to justify the coupling using a different mechanism was made by the Florence group,[29] who suggested that a spin polarization description might be appropriate. In this scheme it is considered that the overlap of the *o* magnetic orbital of copper(II) or radical is relatively larger with the empty d or s orbitals of gadolinium(III) than with the f orbitals. Therefore, a fraction of unpaired electron is transferred into the empty orbitals, keeping the spins of the electrons in the f orbitals parallel to itself according to the Hund's rule. This is indeed a generalization of the Goodenough–Kanamori[1] rule, suggesting a ferromagnetic pathway when a magnetic orbital of one site has nonzero overlap with an empty orbital of the other site. This coupling was first observed in manganites, and recently it has been discovered to be involved in the colossal magnetoresistance effects.

The rationale for this is that a fraction of unpaired electron is transferred into the empty orbital with the same spin it had in the starting magnetic orbital. Now, according to Hund's rule, this fraction of unpaired electron will keep the spins of the magnetic electrons of the second center parallel to its own spin, thus establishing a ferromagnetic coupling. The suitable empty orbitals of gadolinium(III) can in principle be either the 6s or the 5d orbitals. The former were suggested by Gatteschi et al.[29,30] and the latter by Kahn et al.[31]

An elementary semiquantitative treatment was suggested by Kahn et al.[20] for the copper case. The energy difference, Δ, between the $S = 3$ and $S = 4$ states originating from the interaction between the gadolinium(III) and copper(II) can be expressed as

$$\Delta = 8k^0_{\mathrm{f-5d}} + \text{two-site ionic integrals} \qquad (9)$$

where $8k^0_{\mathrm{4f-5d}}$ is a mean one-site exchange integral. Defining as U' the energy gap between the gravity centers of the $S = 3$ and $S = 4$ states and the ground configuration, as defined in Figure 3, this is the energy cost associated with the transfer of one electron from the 3d orbital of copper to the empty 5d gadolinium(III) orbital. Allowing for the admixture of the ground and of the charge-transfer excited configuration, the energy separation between the lowest lying $S = 3$ and $S = 4$ levels, J, is given by

$$J = \frac{\beta^2_{\mathrm{5d-3d}}}{4U'^2 - \Delta^2} \qquad (10)$$

where $\beta_{\mathrm{5d-3d}}$ is the transfer integral for an electron moving from the 3d orbital of copper to the 5d orbital of gadolinium. Since the 5d orbitals of gadolinium are diffuse, therefore relatively more reactive toward the environment than the 4f orbitals, this correction may be important.

A semiquantitative attempt was made for calculating the exchange coupling constant using eq 10. The value of Δ was estimated from the energy separation between the ^7D and ^9D states corresponding to the $4f^75d^1$ configuration of gadolinium(III), 8488 cm^{-1}; that of U' was estimated from the difference in ionization potentials of gadolinium(III) and copper(II), namely, 120 000 cm^{-1}, while the transfer integrals were calculated using the Extended Hückel approach. In this way a value close to 5 cm^{-1} was obtained, in fair agreement with the experimental data, confirming at least the feasibility of the suggested ferromagnetic exchange pathway.

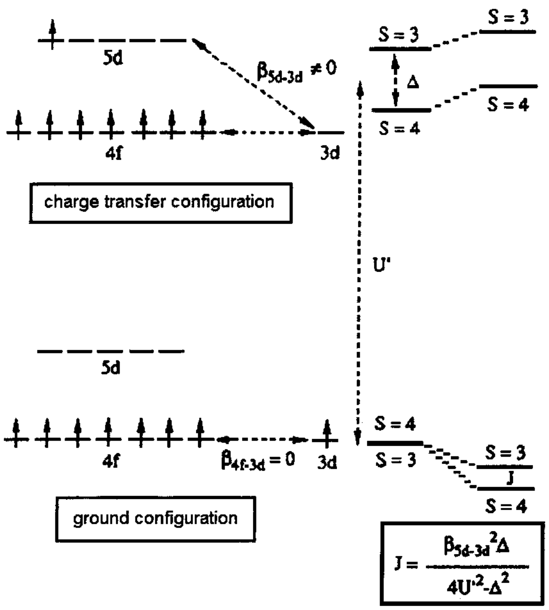


Figure 3. Scheme of the ground and charge-transfer configuration relevant to the exchange mechanism in gadolinium(III)–copper(II) species: (left) unperturbed configuration; (right) effect of their admixture.[20]

To our knowledge the only example of DFT calculation on dinuclear species containing RE ions and d ions is that reported by Yan et al.[32] They investigated three dinuclear compounds involving gadolinium(III) coupled to copper(II), low-spin iron(III), and chromium(III). They used DFT calculations coupled to the broken symmetry approach developed by Noodleman. In this frame the J coupling constant is calculated from the energy difference between the high-spin state, E_{HS}, and the broken symmetry state, E_{BS}, according to[10,33,34]

$$E_{\mathrm{HS}} - E_{\mathrm{BS}} = -J/2[-S_{\max}(S_{\max} + 1) + \Sigma_S A_1(S)S(S + 1)] \qquad (11)$$

where the sum is over all the coupled S states and $A_1(S)$ is the square of the Clebsch–Gordon coefficient. The broken symmetry state is calculated within the spin-unrestricted formalism by assigning up spin to gadolinium and down spin to the other metal ion. For both copper(II) and low-spin iron(III), eq 11 gives $E_{\mathrm{HS}} - E_{\mathrm{BS}} = (7/2)J$, while for chromium(III) $E_{\mathrm{HS}} - E_{\mathrm{BS}} = (21/2)J$. The calculations were performed by using the Amsterdam density functional package version, without taking into account any relativistic correction. The molecular structure was taken from the X-ray crystal structure determination without any correction. The observed and calculated coupling constants are given in Table 2. The agreement between experimental and theoretical values can be considered as

Table 2. Magnetic Coupling Constants J (cm^{-1}) for Some Gd−M-Coupled Species

compound	J_{exp}	J_{calcd}
$GdCu(OTf)_3(bdmap)_2(H_2O)\cdot THF$	−5.8(4)	−7.2
$[Gd(C_4H_7ON)_4(H_2O)_3][Fe(CN)_6]\cdot 2H_2O$	−1.48(6)	−16.2
$[Gd(C_4H_7ON)_4(H_2O)_3][Cr(CN)_6]\cdot 2H_2O$	−0.80(4)	−40.6

good for the copper(II) derivative, while for the other two compounds only the sign is correct, while the actual values scale by almost 2 orders of magnitude. The data were analyzed also for the delocalization−polarization mechanism, but no information is given concerning the possible involvement of empty 5d orbitals.

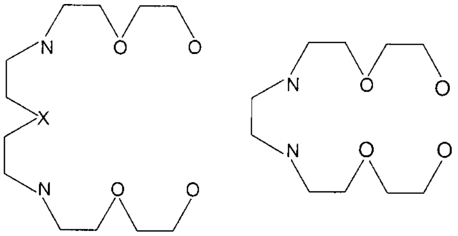
More recently, several examples of antiferromagnetic coupling have been reported for gadolinium(III) complexes with organic radicals and also with copper complexes.[35−37] The organic radicals which yield antiferromagnetic coupling are stronger ligands than the originally reported nitronyl nitroxide ferromagnetic couplers, and it has been suggested that this stronger donor ability may allow the direct interaction of the radical orbitals with the f orbitals. DFT models have been recently used with much success in the calculations of the magnetic properties of 3d metal ions and organic radical coupled systems,[38−41] but to our knowledge no report is available concerning systems with f orbitals. Preliminary data of this laboratory on gadolinium(III) semiquinonate derivatives invariably give an antiferromagnetic coupling, but much larger than the experimental ones. In no case the calculations provided ferromagnetic coupling, even with the NITR radicals. More experimental and theoretical work is needed in order to understand the mechanism of magnetic coupling involving gadolinium(III).

V. Zero-Dimensional Systems

A. Systems Involving Transition-Metal Ions

The nature of the magnetic interaction between rare-earth and other paramagnetic centers has been studied for several years in ionic systems such as garnets. In molecular systems the first paper describing an isolated molecule containing paramagnetic 3d and 4f ions appeared in the literature in 1975.[42] Unfortunately, neither the structural features nor the magnetic properties of the systems described in the paper were fully characterized. Only 10 years after this first attempt, new molecules containing Gd(III) and Cu(II) were synthesized by reacting tetradentate copper(II) Schiff's bases with $Gd(ClO_4)_3$.[22]

Following this first example, several systems containing 4f−3d pairs of interacting metal ions were synthesized in the following years. Paticular interest has been devoted to the synthesis of well-isolated discrete bimetallic RE−transition-metal ion complexes to get direct information on the nature of the exchange magnetic interaction. Due to the tendency of RE ions toward high coordination numbers, the preparation of a simple bimetallic system required very often specific ligands such as, for instance, asymmetric compartmental ligands as sketched below.



By using this kind of ligand, Costes et al. were able to synthesize the first example of a fully characterized isolated gadolinium(III)−copper(II) dinuclear species,[43] as previously reported examples of similar molecules were not structurally characterized by means of X-ray diffraction.[44−46] The copper(II) ion occupies in the molecules, as in most of these types of systems, the N_2O_2 compartment, while the RE ion enters the O_4 compartment (Figure 4). The coordination of the 4f ion is completed by solvent molecules and counterions. The four atoms CuO_2RE network forms, in general, a plane, while the coordination around the copper varies from almost planar,[43] to distorted tetrahedral,[47] five,[37,48] or six coordination.[49] In these systems the gadolinium(III)−copper(II) distance within the molecules is around 3.5 Å, while the intermolecular distance between paramagnetic centers is around 7−8 Å. The magnetic behavior of this class of compounds is characterized by the presence of a ferromagnetic Gd−Cu interaction with an intensity that in any case is well above the intensity expected for a purely dipolar interaction. The maximum value of the coupling constant evaluated on the basis of an HDVV approach is 10.1 cm^{-1}.[49] Only in one molecule was a weak antiferromagnetic interaction (J = 0.49 cm^{-1}) observed, and in this case the presence of a more complex pattern for the exchange mechanism was not completely ruled out.[37] By analyzing the whole series of compounds, Costes et al.[49] proposed a correlation between the magnitude of the magnetic interaction and the exponential of the dihedral angle between the two halves (Gd−O−Gd and O−Cu−O) of the bridging core.

A different synthetic approach was followed by Kahn et al. to synthesize Gd−Cu dinuclear species.[50] The systems were obtained by reacting Gd(hexafluoroacetylacetonate)$_3$ with Cu(N,N'-ethylenebis-salicylideneiminate): in the presence of 1-methylimidazole, well-isolated dinuclear species were obtained whose magnetic properties were interpreted on the

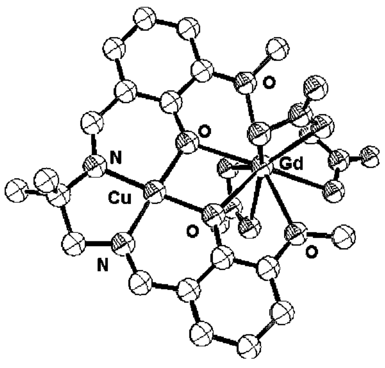


Figure 4. ORTEP view for [(1,2-bis((3-methoxysalicylidene)amino)-2-methyl-propanato)Cu(II)Gd$(NO_3)_3$]$\cdot Me_2CO$.[43]

basis of a ferromagnetic interaction ($J = -5.08$ cm^{-1}). In the absence of the imidazole, the molecules are packed in the crystal so close to each other that the intermolecular Cu−Cu distances are similar to the Gd−Cu intramolecular separations, and therefore, the presence of relevant Cu−Cu magnetic interactions prevented a well-defined analysis of the magnetic properties of these systems. Recently similar systems were reported where, on varying the Schiff base around the copper(II) ions, the presence of the imidazole is no longer necessary to stack the dimers well apart, and again the magnetic intramolecular interaction has been observed to be ferromagnetic in nature ($J = -1.91$ cm^{-1}).[51]

In most cases the reported systems contain Gd−Cu pairs especially to avoid the problem of the unquenched orbital momentum of the RE which are not gadolinium(III). One of the rare examples of systems containing the anisotropic 4f ions has been reported by Kahn et al. by using Cu Schiff's base reacted with RE nitrates (RE = Ce, Gd, Tb, Dy, Ho, Er).[52] The Gd derivatives showed a very strong ferromagnetic interaction ($J = -17.32$ cm^{-1}), while the presence of crystal effects on the other RE ions masked the magnetic interaction between paramagnetic centers. The reaction of Cu(2,6-bis[(dimethylamino)methyl] 4-methylphenolato)$_2\cdot$H$_2$O with Pr(hexafluoroacetylacetonate)$_3$ gave a dinuclear species where Cu and Pr were bridged by two oxygen atoms. The magnetic data were not analyzed in detail, even if the presence of antiferromagnetic exchange is suggested without any quantitative approach.[53]

Often the copper(II) ion is replaced by the nickel(II) ion, but due to the planar environment generated by the compartmental ligand, the nickel ion is in the low-spin state and, therefore, is diamagnetic. Sometimes this characteristic has been used to define in a more precise way the magnetic behavior of the RE present in the molecule, especially when the RE is not gadolinium. The rationale for this is the assumption that the crystal-field effects on the rare-earth ions, responsible for the non-Curie behavior associated with the f electrons, may be experimentally obtained by measuring the temperature dependence of the RE−Ni system. In other words, it is assumed that the crystal-field effects around the RE ions are the same for the nickel and for the copper derivative. Deviations of the susceptibility calculated as the sum of the RE−Ni and copper contributions are attributed to the magnetic interaction between RE ion and copper. Using this approach,[54] the nature of the magnetic interaction in Cu−RE dinuclear species has been analyzed. The magnetic exchange was reported to be ferromagnetic in nature when RE = Gd, Tb, Dy, Ho, and Er and antiferromagnetic with RE = Ce, Nd, and Sm, while no relevant magnetic interaction was observed with RE = Eu and Pr.

A system containing a magnetically interacting Gd−Ni pair has been synthesized by using [2,2′-[2,2′-dimethyl-1,3-propanediylbis(nitrilomethyldyne)]bis(6-methoxyphenole)]. This compartmental ligand is able to coordinate a nickel(II) ion in the inner site with a distorted octahedral environment, while gadolinium(III) ion occupies the external site. Analysis of the temperature dependence of the magnetic susceptibility and of the magnetic field dependence of the magnetization allowed the authors to state that the complex has a $S = 9/2$ ground state which derives from a Gd−Ni ferromagnetic interaction with a coupling constant of -3.6 cm^{-1}.[55]

Cryptate ligands with a cavity of suitable size are often able to allocate more than one metal ion. Tris(2-aminoethyl)amine was reacted with 2,6-diformyl-4-chlorophenol in the presence of Gd(II) ions. The product of this reaction was added to a methanol/DMF solution of Ni(II) perchlorate, and the green crystalline precipitate was analyzed by means of X-ray diffraction and electrospray mass spectroscopy. The system contains well-isolated Gd−Ni pairs, and their magnetic properties are consistent with the presence of a ferromagnetic interaction between the two metal ions. The fitting procedure gave a coupling constant value of -0.56 cm^{-1}. The lower value of J with respect to the one observed in the previously described dimer was attributed to a larger dihedral angle (O−Gd−O, O−Ni−O).[56]

By reacting Ni(II) ion in an octahedral environment generated by the podand amine phenol ligand 1,1,1-tris(((2-hydroxybenzyl)amino)methyl)ethane with RE perchlorate (RE = La, Dy, Yb), isolated dinuclear species where obtained and fully characterized.[57] The magnetic data were interpreted on the basis of a very simple model which did not take explicitly into account the orbital contribution: the overall behavior is described in terms of an antiferromagnetic Ni−RE interaction whose intensity increases with decreasing ionic radius of Ln(III) ions.

In the literature there are a few reports of systems including interacting Co(II) ions with Gd(III) ion in a compartmental ligand and Gd(III), Tb(III), Dy(III)[58] linked by pivalate ligands.[59] In this case there is an additional complication for the interpretation of the magnetic data because cobalt(II) also has also an unquenched orbital contribution. In both cases the authors concluded that the magnetic behavior may be rationalized on the basis of ferromagnetic interactions, but the approximation of neglecting the orbital contribution seems too strong to make these results fully reliable. When the components of the pairs have a ground state without any orbital contribution, it is always possible to define the nature of the magnetic exchange: in the case of Gd−VO dinuclear species obtained by using a compartmental ligand, the magnetic interaction was observed to be antiferromagnetic.[60]

In the case of chromium acetylacetonate bridged to RE ions (RE = Eu, Gd, Tb, Yb, Lu) by an oxalate group,[61] the analysis of magnetic data for Gd derivative was made on the basis either of pure intermolecular interaction and inter- and intramolecular interactions. By using this second approach the final result was not conclusive about the nature of the magnetic interaction as the coupling constant varies from -0.09 to 0.02 cm^{-1} as a consequence of a similar small variation of the other fitting parameters. The magnetic data for the other RE are indicative of the presence of a strong magnetic interaction, but it was not possible to define its nature and intensity.

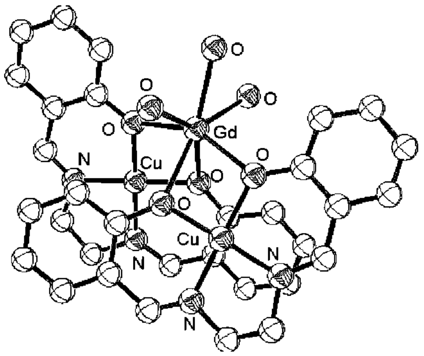


Figure 5. ORTEP view of the cation $[(N,N'\text{-ethylenebis(salicylaldiminato)Cu})_2\text{Gd}(H_2O)]^{3+}$.[22]

The synthesis of a system containing interacting 3d and 4f ions has been developed following two different approaches: one strategy is based on the use of complexes containing a transition-metal ion as a ligand toward lanthanide ions; alternatively, ligands and salts containing 3d and 4f ions are mixed together to prepare in a single step the final compound. In any case the high coordination number preferred by rare-earth ions led to the formation of clusters containing several paramagnetic centers.

The types of metal complexes used as ligands in the first attempts were two slightly different Schiff base derivatives containing copper(II) which were reacted with Gd perchlorate yielding complexes with a Cu_2Gd magnetic core.[22] The asymmetric units in the crystals of the two complexes consist of three-nuclear species where two copper(II) ions are bonded to one gadolinium(III) ion by two bridging oxygen atoms as shown in Figure 5. Two molecules of the starting Schiff bases are also included in the crystals as solvating molecules. The analysis of the magnetic susceptibilities measured down to 4.2 K were performed, including both Gd−Cu and Cu−Cu magnetic interactions. The data are indicative that a ferromagnetic interaction is operative between the lanthanide and transition-metal ions while an antiferromagnetic exchange is active between the two 3d ions. This result was quite surprising both for the nature of the magnetic interaction and for the intensity: both of these features are indicative of a complex magnetic exchange mechanism. The presence of two additional paramagnetic units in the crystal could contribute to some extent to mask the actual magnetic properties of the compounds. In an attempt to simplify the system, a new compound obtained by using a different copper Schiff base [*N*,*N'*-1,3-propylene-bis(salicylaldiminato)]Cu(II)] and $Gd(NO_3)_3$ was reported where the asymmetric unit is similar to those previously reported but without the additional monomeric Cu(II) complex in the cell. The analysis of the magnetic behavior on varying the temperature confirmed substantially the previous coupling scheme.[23,62]

By using $RE(\text{hexafluoroacetylacetonate})_3$ (RE = Gd, Dy), a cluster with a Cu_2RE_2 magnetic core was produced as a consequence of the hydrolysis of the organic ligand.[29] The four magnetic ions occupy alternatively the corner of a rhombus, and the magnetic data can be interpreted on the basis of ferromagnetic Gd−Cu and Gd−Gd antiferromagnetic interactions. If the possibility of a Cu−Cu interaction is included in the coupling scheme, this interaction is antiferromagnetic, but no substantial improvement of the fit was observed. An attempt was also made to analyze the data of the dysprosium derivative by using Levy's approach.[19] The experimental data were nicely reproduced, but the large number of parameters required by the model prevented any conclusive analysis. A similar molecular structure was observed in the $[CuLGd(hfac)_2]_2$ complex (H_3L = 1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylidene amino)ethane). The temperature dependence of magnetic susceptibility and of the magnetization was interpreted on the basis of an $S = 8$ ground state originated by Gd−Cu ferromagnetic interactions, whose intensity was not determined.[63]

A $RECu_5$ magnetic core (RE = Gd, Dy, Ho) was observed in a system synthesized by reacting Cu-(*N*,*N'*-bis(3-aminopropyl)oxamidate) with RE nitrate in a 4:1 ratio.[64] Even with some slight differences, these complexes can be described as formed by the RE ion which is surrounded by the eight oxygen atoms of four oxamidato groups while the two nitrogen atoms of these groups are coordinated two by two around the four copper(II) ions. A detailed analysis of the magnetic properties of the Gd derivatives led to the conclusion that the ground spin state is 11/2, as confirmed by magnetization measurements. This spin state can be justified on the basis of a ferromagnetic Gd−Cu exchange with $J = -0.85\ \text{cm}^{-1}$ with a weak antiferromagnetic Cu−Cu interaction. The unquenched orbital angular momentum in the ground states of Dy(III) and Ho(III) made the analysis of the magnetic characteristic of these systems very difficult: even an Ising approach requires a very high number of parameters. Therefore, the presence of a ferromagnetic Dy−Cu interaction could only be postulated.

The "one-step" strategy of synthesis gave polymetallic systems with higher nuclearity and a large variety of structures even if, sometimes, the final compounds had a magnetic core similar to those previously described as in the case 2,2-dimethylpropane-1,3-diamine ligand.[65] The Cu_2Gd complex shows the usual coupling scheme of a Cu−Gd ferromagnetic and Cu−Cu antiferromagnetic interaction.

One of the most successful ligands in this field is pyridonate molecule, largely employed by Winpenny's group. Adding gadolinium perchlorate to a solution containing deprotonated 2-hydroxypyridine and copper nitrate gave green crystals whose asymmetric unit contains an octahedral arrangement of four Cu and two Gd atoms.[66] The hydroxypyridine acts as a bridge binding via the oxygen atom to Gd and Cu atoms and via the nitrogen atom to a second Cu atom. The magnetism of the system was interpreted on the basis of ferromagnetic Gd−Cu exchange within a Cu_2-Gd subunit. Since below 170 K the magnetic moment falls, these subunits are probably antiferromagnetically coupled to each other. If a 6-substuituted 2-pyridonate is used, a large variety of Cu RE systems can be obtained with a very different Cu:RE ratio up to the very fascinating $Cu_{12}La_8(\mu_3\text{-OH})_{24}$

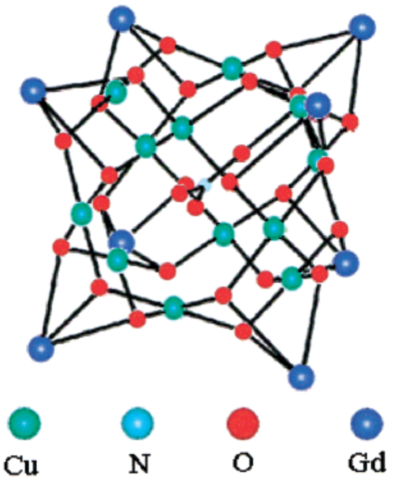


Figure 6. $[Cu_{12}La_8(\mu_3\text{-}OH)_{24}(NO_3)]^{23+}$ core of complex $[Cu_{12}La_8(\mu_3\text{-}OH)_{24}(NO_3)_{21.2}$(6-chloro-2-pyridone)$_{13}(H_2O)_{5.5}]$-$[NO_3]_{2.8}\cdot$2(6-chloro-2-pyridone): La, purple; Cu, green; N, blue; O, red.[67]

core [Figure 6].[67] If the substituent in the 6 position is chlorine, magnetic clusters with Cu_2Gd_2, Cu_4Gd_2, Cu_3Gd have been synthesized.[68] The basic coupling schemes used in the interpretation of the magnetic data are reported below, while the various Cu−Cu interactions were assumed to be antiferromagnetic as observed in the lanthanum analogues. The fitting to experiments was performed with the aim of using the lowest number of parameters and showed the existence of ferromagnetic Gd−Cu exchange mechanisms with coupling constants ranging from 0.11 to 3.51 cm^{-1}. An analysis of these results together with literature data on similar systems showed a nice correlation between the magnitude of the Gd−Cu exchange coupling and the exponential of the Gd−Cu distance. Systems containing 3d ions different from copper are not very common: one example has been obtained with an approach similar to those previously described using Ni(II) and Co(II) salts and Er, Dy, and Gd lanthanide ions.[69] The magnetic core is formed by an RE_2−(3d ion)$_2$ ring where the heterometallic pairs are bridged by three μ_2 oxygen atoms. The magnetic data of Er_2Ni_2 and Gd_2Co_2 were analyzed: no fit to experiment was performed due to the lack of a suitable model to account for the presence of orbitally degenerate states. The low-temperature data could suggest the presence of a weak antiferromagnetic interaction. A similar system has been synthesized using pivalate ligand, which includes manganese(III) and gadolinium(III) ions:[70] the structure consists of a manganese(III) di-μ-oxo-bridged dimer, each oxide further bridging to a gadolinium(III) ion in a fashion which recalls a chair or a distorted butterfly. The magnetism of this cluster is dominated by a strong Mn−Mn antiferromagnetic interaction ($J_{Mn-Mn} = 62.91$ cm^{-1}), while a ferromagnetic interaction is suggested for the Gd−Mn exchange coupling ($J_{Gd-Mn} = -2.44$ cm^{-1}) with a dipolar Gd−Gd interaction. Actually these data which show the presence of a ferromagnetic interaction within Gd and a 3d ion different from copper require further experimental confirmation.

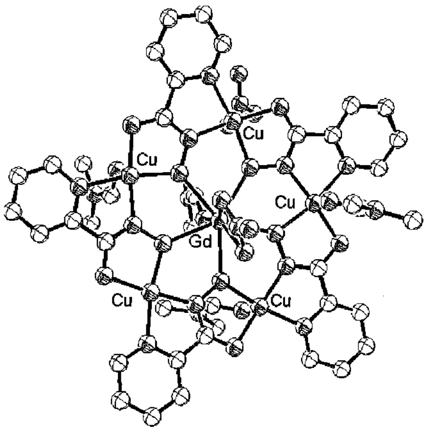


Figure 7. ORTEP view of {Gd(NO$_3$)$_3$[Cu(picoline hydroxamate)$_5$]$_5$(DMF)$_5$}.[71]

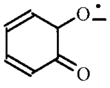
A system very different from those described until now was synthesized in Pecoraro's group in the framework of research on the properties of the so-called "metallacrowns".[71] As shown in Figure 7, the metallacrown forms a pentagonal-planar arrangement of five copper(II) or nickel(II) ions with a single RE ion in the center (RE = La, Nd, Sm, Eu, Gd, Gd, Dy, Ho, Er, Yb). The only system analyzed in some detail in the solid state was the Gd derivative, and the usual scheme of weak ferromagnetic Gd−Cu and antiferromagnetic Cu−Cu interaction was found to be operative. An analogous system showing a "wheel" structure has been synthesized using *N*-carboxymethyl-*N*-(2-carboxypheyl)glycine acid (H_3L) as the ligand. The asymmetric unit in the crystal consists of $[Cu_6PrL_6]^{3-}$ clusters where each praseodymium(III) ion is surrounded by six copper(II) ions bridged through the oxygen atoms of the carboxylato groups. The observed magnetic data are indicative of the presence of an anomalous magnetic behavior. Unfortunately, they are not clear enough to define which is the dominant effect among crystal-field splitting of Pr^{3+} ion, antiferromagnetic coupling of the six Cu^{2+} ions around the rare-earth ion, any kind of Pr−Cu magnetic exchange.[72] When iminodiacetic acid is used as the ligand, clusters with the same RE/Cu ratio but different molecular structure have been isolated. The magnetic behavior of the $TbCu_6$ cluster was analyzed in comparison with the magnetic properties of the $LaCu_6$ isomorphous system. In the 100−25 K temperature range, an increase of the $\chi_M T$ values was observed. This feature can derive neither from the depopulation of the crystal-field levels of Tb^{3+} nor from the Cu−Cu coupling which is antiferromagnetic as derived from the study of the La-containing cluster. The authors attributed this increase to the presence of a Tb−Cu ferromagnetic exchange interaction whose intensity was not detemined.[73]

The use of zwitterionic ligands derived from betaine allow very interesting heterometallic clusters of high nuclearity to be produced. The first example of these systems was produced by using pyridine−betaine, and the final product of the reaction with copper nitrate and RE nitrate (RE = Y, Nd, Gd) in aqueous solution containing $NaClO_4$ gave crystals of formula $[Cu_{12}RE_6(\mu_3\text{-}OH)_{24}$(pyridine−betaine)$_{12}(ClO_4)]$-$(ClO_4)_{17}\cdot nH_2O$.[74] The Cu−RE metal framework can be described as formed by the six RE ions positioned at the vertexes of a regular nonbonding octahedron and the 12 copper(II) ions located at the midpoints of the 12 octahedral edges. Each bridging oxygen atom is linked to one RE ion and two Cu ions. The magnetic behavior of the yttrium derivative shows an $S = 0$ ground state which is indicative of antiferromagnetic interactions between the copper ions. No detailed analysis of the dependence on temperature of the magnetic moment of the Nd derivative is reported. The data of the Gd system are very close to the expected value for noninteracting magnetic centers down to 50 K. No explanation is reported on the contrast of this result with the interaction observed in the Y-derivative. Even the decrease of the magnetic moment observed below 50 K is analyzed. Complexes with analogous stoichiometry and molecular structure have been synthesized using chloroacetic acid and RE = La, Nd.[59] The cluster containing lanthanum shows the usual antiferromagnetic coupling between the copper resumed in a Curie−Weiss constant of −11.5 K. For the Nd system, the presence of a ferromagnetic Cu−Nd interaction is suggested but not proved.

Using pure betaine, various complexes have been obtained where the organic part of the cluster is slightly different but all contain the Cu_2RE_2 core (RE = La, Ce, Gd, Sm).[75] The copper(II) ion is quadruply bridged to the RE atom by the μ_2-carboxylate group of betaine ligand: the Cu−RE distances vary between 3.803 and 3.595 Å. The temperature dependence of the magnetic moment of gadolinium derivative is analyzed simply on the basis of the Curie−Weiss law: the θ value is indicative of a weak overall antiferromagnetic behavior of the system, but no indication of the nature and intensity of the Gd−Cu interaction is proposed.

B. Systems Involving Organic Radicals.

Several compounds have been reported in which RE ions are directly bound to stable organic radicals containing oxygen donor atoms. The organic radicals correspond to the nitronyl nitroxide and semiquinone derivatives, respectively.



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The nitronyl nitroxide radicals, when there are no additional donor atoms in the R residue, are weak ligands which can interact only with relatively strong Lewis acids.[27] This condition is met by metal hexafluoroacetylacetonates (hfac) as well documented for transition-metal ions and confirmed by RE ions. The first reported compounds had formulas $RE(hfac)_3(NITR)_2$, with RE = Eu, Gd.[76,77] The only compound containing one radical bound to a RE ion was $Eu(hfac)_3(NITiPr)(H_2O)$, isomorphous to the gadolinium derivative.[30] The latter showed evidence for a weak ferromagnetic coupling, $J = -0.65$ cm^{-1}. Weak ferromagnetic coupling was observed also with compounds formed with the NIToPy and NITpPy derivatives, as shown in Table 3[78] ranging from −0.17 to −3.03 cm^{-1}. Also, 1:2 species were reported with R = Ph and Et.

Table 3. Coupling Constants in Gadolinium(III) Nitronyl Nitroxide-Coupled Species (cm^{-1})

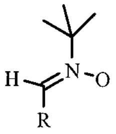
compound	$J_{\mathrm{Gd-rad}}$	$J_{\mathrm{rad-rad}}$
$[Gd(hfac)_3(NITiPr)(H_2O)]$	−0.60	
$[Gd(hfac)_3(NIToPy)]$	−3.03	
$[Gd(hfac)_3(NITpPy)]$ (J)	−1.78	
$[Gd(hfac)_3(NITpPy)]$ (J')	−0.17	
$[Gd(hfac)_3(NITPh)]$	−1.23	5.1
$[Gd(hfac)_3(NITEt)]$	−0.50	4.3

The gadolinium−radical coupling was found to be ferromagnetic, but a nonzero antiferromagnetic coupling between the radicals had to be included in the fit in order to reproduce the experimental data. The existence of the long-range antiferromagnetic coupling between the radicals mediated by the RE orbitals was confirmed by the magnetic properties of europium(III) and yttrium(III) derivatives

Sutter et al. investigated[79] the structure and magnetic properties of $[RE(NITtrz)_2(NO_3)_3]$, with RE = Y, La, Gd. The coupling between the radicals was found to be $J = 3.1$ cm^{-1} for the yttrium derivative and 6.8 cm^{-1} for the lanthanum derivative. The gadolinium derivative has a ground $S = 9/2$ state. The temperature dependence of χT was fit with the following coupling constants: $J_{\mathrm{Gd-R}} = -6.1$ cm^{-1}, $J_{\mathrm{R-R}} = 7.0$ cm^{-1}.

Lescop et al. in 1999 reported[35] $Gd(NITBzImH)_4(ClO_4)_3 \cdot 2THF \cdot 2H_2O$, where the RE ion is eight coordinate. The donor atoms are four oxygen and four nitrogen atoms of four different NIT ligands. The temperature dependence of the magnetic susceptibility showed evidence of intramolecular antiferromagnetic coupling. The ground state corresponds to $S = 7/2$ for the above derivative, while for the analogous NITMeBzImH derivative $S = 3/2$. The fit of the temperature dependence of the susceptibility of the two compounds provided $J_{\mathrm{Gd-R}} = 1.8(3)$ cm^{-1}, $J_{\mathrm{R-R}} = 7.2(5)$ cm^{-1} for the former and $J_{\mathrm{Gd-R}} = -3.8(2)$ cm^{-1}, $J_{\mathrm{R-R}} = 5.6(2)$ cm^{-1} for the latter.

A procedure used with transition-metal ions in order to have independent information on the crystal-field effects of anisotropic rare earths is that of substituting the paramagnetic metal ion with a diamagnetic one. In the case of organic radicals, this is much less obvious. An ingenuous attempt was made by Sutter et al. by replacing the nitronyl nitroxides[80] with a nitrone species, as sketched below.



The idea is that the diamagnetic ligand gives essentially the same crystal-field effects as the organic radical, without of course giving rise to magnetic interactions. The nitrone in other terms is the organic equivalent of zinc or yttrium and lanthanum for the inorganic substituents. The nitrone strategy has been followed for the holmium derivative, showing that the interaction between that RE ion and the NITR radical is weak ferromagnetic.

Antiferromagnetic interactions were also observed in $[Gd(Hbpz_3)_2(DTBSQ)] \cdot 2CHCl_3$, where $Hbpz_3$ =

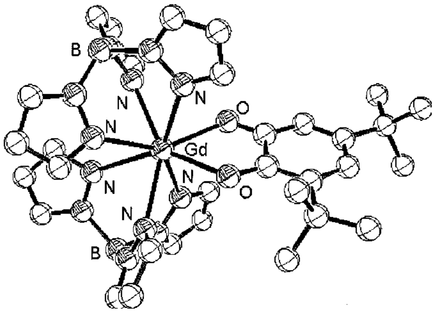


Figure 8. ORTEP view of [Gd(hydrotris(pyrazolyl)borate)$_2$(3,5-di-*tert*-butylsemiquinonato)].[36]

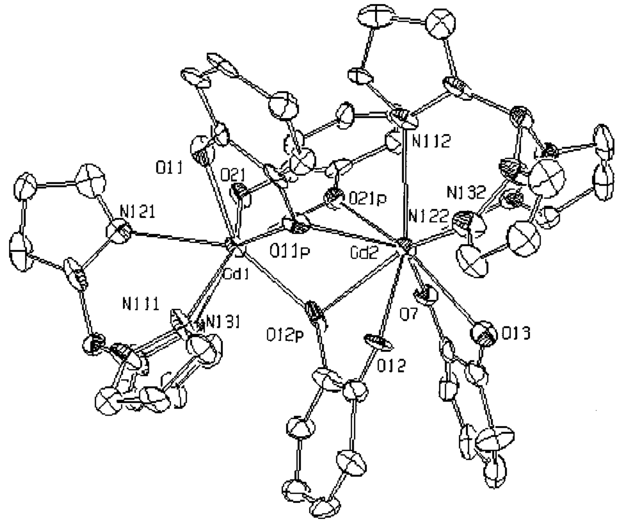


Figure 9. ORTEP view of [Gd$_2$(hydrotris(pyrazolyl)borate)$_2$(3,5-di-*tert*-butylsemiquinonato)$_4$]$\cdot$2CHCl$_3$. For clarity, hydrogen atoms and the *tert*-butyl group were omitted.[81]

hydrotris(pyrazolyl)borate and DTBSQ = 3,5-di-*tert*-butylsemiquinonato, which has a ground $S = 3$ state.[36] The structure of [Gd(Hbpz$_3$)$_2$(DTBSQ)] is shown in Figure 8. The coupling constant $J = 11.4$ cm^{-1} is the largest so far reported for interactions involving gadolinium(III) and radicals or transition-metal ions.

An interesting example of formation of an asymmetric dinuclear species is provided by [Gd$_2$(HBpz$_3$)$_2$(DTBSQ)$_4$]$\cdot$2CHCl$_3$, whose structure[81] is shown in Figure 9 The formation of the asymmetric species occurs by spontaneous symmetry breaking in solution. One gadolinium ion is eight coordinate, while the other is nine coordinate, the Gd−Gd distance being 3.755 Å. One of the semiquinonate ligands is chelating one gadolinium ion, while the other three bridge the two metal ions using one oxygen. The nature of the ground spin state is difficult to predict. The temperature dependence of the magnetic susceptibility clearly shows the presence of antiferromagnetic interactions and suggests an $S = 0$ ground state with an excited $S = 7$ lying very close to it. The existence of a low-lying $S = 7$ state has been confirmed by HF EPR spectra, like the ones recorded at 240 GHz depicted in Figure 10. At high temperature the spectra show only a broad feature centered at $g = 2$, corresponding to the envelope of many transitions corresponding to the various populated spin multiplets. On decreasing temperature, the presence of several well-defined features becomes apparent. At 4.2 K the spectrum simplifies again, with the appearance of features corresponding to crystallites with the z axis parallel to the static magnetic field at low field and perpendicular features at high field. This is typical of S spin multiplets in which crystal-field interactions leave the $M = \pm S$ components lying lowest. In fact, the spectra were satisfactorily simulated using $S = 7$, $D = -0.0465$ cm^{-1}, and $E = 0.0052$ cm^{-1}. The large spin state and the negative zero-field splitting provide an effective barrier for the reorientation of the magnetization of ca. 3 K. It is a pity that this is not the actual ground state; otherwise, this might have been the first single-molecule magnet containing rare-earth ions. This is however an indication that, despite the weak couplings, it might be possible to achieve this goal in the future.

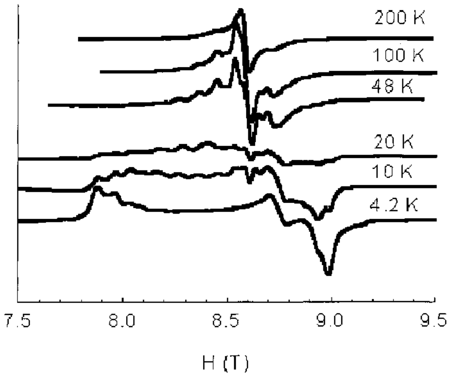


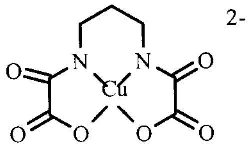
Figure 10. Temperature evolution of HF-EPR spectra of [Gd$_2$(hydrotris(pyrazolyl)borate)$_2$(3,5-di-*tert*-butylsemiquinonato)$_4$]$\cdot$2CHCl$_3$ recorded at 240 GHz between 200 and 4 K.[81]

The temperature dependence of χT and the magnetization at low temperature were fit with two different models. In both cases the three semiquinone bridges, considered as equivalent, $J_{\mathrm{Gd-SQb}}$, the coupling between the gadolinium with the nonbridging semiquinone, $J_{\mathrm{Gd-SQnb}}$, and the semiquinone-semiquinone, $J_{\mathrm{SQ-SQ}}$, considered as equivalent, were included. In model A, a molecular field correction was included, while in model B a Gd−Gd interaction was added. In both cases equivalent fits of the data were obtained, and in both cases many different multiplets lie at low energy. In particular, the fit with model B, which requires $J_{\mathrm{Gd-SQnb}} = 1.75$ cm^{-1}, $J_{\mathrm{Gd-SQb}} = 0.35$ cm^{-1}, $J_{\mathrm{SQ-SQ}} = 12.85$ cm^{-1}, and $J_{\mathrm{Gd-Gd}} = 0.08$ cm^{-1}, gives a ground $S = 0$ state with excited states ranging from $S = 1$ to $S = 7$ within 2.7 cm^{-1}. This is a clear example of the many difficulties met in attempts to fit the magnetic properties of RE compounds, where crystal-field and exchange effects are often of comparable size.

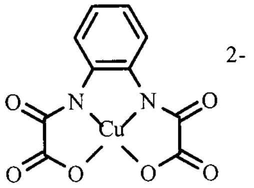
VI. One-Dimensional Systems

A. Transition-Metal Ion Derivatives

Simple one-dimensional compounds comprising rare-earth ions and transition-metal ions have not been so far reported, but several ladder-like or tube-like examples are available. The systems were obtained using as transition-metal building blocks the $[Cu(pba)]^{2-}$ and the $[Cu(opba)]^{2-}$ moieties.



$[Cu(pba)]^{2-}$



$[Cu(opba)]^{2-}$

The former generally yield strongly solvated crystals containing several water molecules, while the latter allows reactions in organic solvents to be performed rather than in water. A structurally well-characterized sample is $Tm_2[Cu(opba)]_3 \cdot xDMF \cdot yH_2O$ ($x \sim 10$, $y \sim 4$), $Lad(Tm_2Cu_3opba)$ (Lad = ladder-like structure),[82] which is obtained by grinding the copper(II) precursor $Na_2[Cu(opba)] \cdot 3H_2O$ with the appropriate rare-earth nitrate in a mortar, dissolving the mixture in DMF, and then allowing a slow crystallization at 70 °C. The side pieces of the ladder consist of TmCu (opba) moieties developing along the b axis of the orthorhombic $P2_12_12_1$ space group, while the rungs are formed by Cu(opba) moieties bridging two RE ions. The scheme of the structure is shown in Figure 11. Also, derivatives with the Cu(pba) moiety have been reported,[83−87] $Lad(RE_2Cu_3pba)$, following a different procedure in which the crystals are grown by slow diffusion in a H-shaped tube at room temperature, using equimolar aqueous solutions of $Na_2[Cu(pba)] \cdot 6H_2O$ and rare-earth chloride. Similar compounds were also reported with the analogous nickel(II) derivative,[88] $Lad(RE_2Ni_3opba)$.

A variation on the ladder theme is provided by compounds of formula $RE_2[Cu(pba)]_3 \cdot 20H_2O$, $Tub(RE_2M_3pba)$ (Tub = tubular-like structure), which were obtained with the same procedure described above but allowing slow crystallization at 70 °C. Their structure, sketched in Figure 12, can be described as generated by putting two ladders parallel to each other. Of the four possible rungs connecting the four side pieces, only two are present at a given level, alternated by a rotation of 90° with those of the following levels.

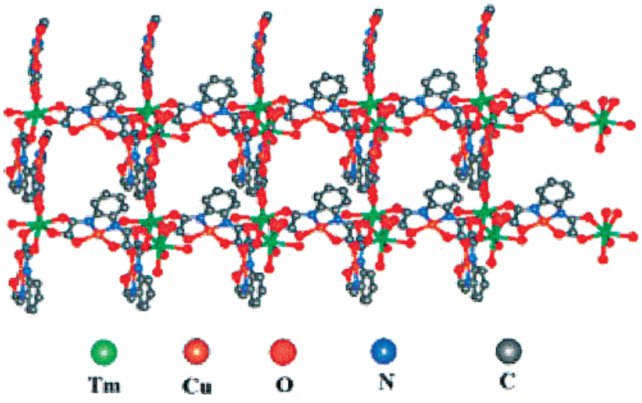


Figure 11. Scheme of the ladder structure in $Tm_2[Cu(o\text{-phenylenebis(oxamato)})]_3 \cdot 4H_2O \cdot 10DMF$.[82]

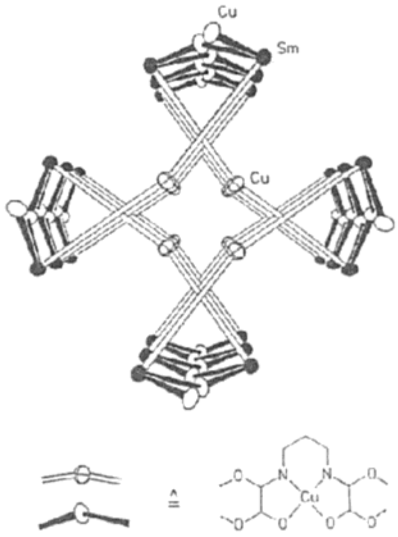


Figure 12. Schematic representation of the structure of $Sm_2[\{Cu(1,3\text{-propylenebis(oxamato)})\}_3] \cdot 23H_2O$: view along the c axis of the unit cell.[89]

The compounds with the diamagnetic yttrium(III) and lanthanum(III) ions show only a weak coupling between the copper(II) ions, antiferromagnetic in nature. A quantitative measurement of the coupling constant has not been performed but it must be small, presumably on the order of 0.1 cm^{-1} for lanthanum and negligibly small for yttrium. The coupling is assumed to be transmitted through the diamagnetic rare-earth ions via a superexchange mechanism. The difference between the two diamagnetic metal ions in transmitting the interaction is associated with the more diffuse nature of the orbitals of lanthanum compared to yttrium. The mechanism would be similar to that which makes the superexchange interaction transmitted by sulfur larger than that transmitted through oxygen. It must be recalled that lanthanum(III) is isoelectronic with iodide and yttrium(III) with bromide.

The χT value of $Tub(Eu_2Cu_3pba)$ is said to tend to zero at low temperature. This is surprising because an odd number of copper ions is present in the formula, and no evidence of antiferromagnetic order is provided. The gadolinium(III) derivative follows a Curie−Weiss law with $\theta = 1.2$ K, indicating that the chains behave as one-dimensional ferromagnets,[89] confirming the usual coupling in Gd−Cu pairs.

With the other paramagnetic RE ions, several different behaviors are observed. In particular, for $Lad(Dy_2Cu_3pba)$, χT is 29.5 emu mol^{-1} K, in agreement with the value expected for uncoupled Dy_2Cu_3 moieties. Below 10 K, χT rapidly increases as shown in Figure 13, reaching 90 emu mol^{-1} K at 1.8 K, suggesting a ferromagnetic coupling. Evidence for similar coupling is reported for the terbium(III) and erbium(III) derivatives.

The magnetic properties of the analogous opba derivatives are similar but not identical.[88,90] For instance, both the yttrium and lanthanum derivatives[82] show a substantially temperature-independent χT value, suggesting an exceedingly small coupling. χT was found to decrease on decreasing T for RE = Ho, Er, Tm, Yb. Since crystal-field effects of the rare-earth ions provide a similar temperature dependence, in the absence of further experimental data it is not

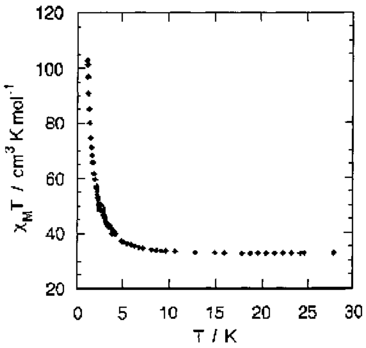


Figure 13. χ_M vs *T* plot for $Dy_2[\{Cu(1,3\text{-propylenebis-}(oxamato)\}_3]\cdot 23H_2O$ [83]

possible to conclude whether the observed behavior is due to crystal-field effects or antiferromagnetic coupling between the rare-earth and the transition-metal ion. For RE = Tb and Dy, χT initially decreases on decreasing temperature, goes through a minimum at 10 K for Dy and at 20 K for Tb, and then rapidly increases on decreasing temperature. This behavior suggests that significant spin correlation builds up along the ladders, indicating magnetic exchange. However, the observed minimum may be compatible with either ferro- or antiferromagnetic behavior.

The synthesis of the zinc(II) derivatives[91] allowed the authors to obtain independent information on the crystal-field and or exchange interactions involving the RE ions. χT of the gadolinium derivative goes from 15.7 emu mol^{-1} K at room temperature to 14.8 at 2 K. In principle, this decrease may be due to weak crystal-field effects expected for the *S* ion, to weak intraladder antiferromagnetic coupling, or to weak interladder interactions. In the Gd_2Cu_3 derivative on the other hand, χT goes from 16.9 emu mol^{-1} K at room temperature to 66 emu mol^{-1} K at 2 K. At 1.75 K, the system shows a transition to three-dimensional magnetic order. Analogous measurements on the Dy_2Zn_3 derivative allowed the crystal-field contribution of dysprosium to χT to be estimated. In Figure 14 is plotted χT for Dy_2Cu_3 and Dy_2Zn_3 and the difference Δ. Δ is essentially constant down to 50 K, the value corresponding nicely to the contribution of three uncoupled copper ions, then it rapidly increases, suggesting a ferromagnetic coupling. A similar behavior was observed for terbium, while for the thulium and holmium derivatives a less clear-cut behavior was observed.

Another kind of ladder-type of architecture was observed in systems obtained by reacting, in tetramethoxysilane gel, Ln nitrate (Ln = La, Ce, Pr, Nd) with $(NH_4)_3[Cr(oxalate)_3]\cdot 3H_2O$.[92] The magnetic behavior is similar for all the compounds, which show a decrease in the $\chi_M T$ values on lowering the temperature. This pattern is attributed essentially to the splitting of the electronic levels either on Cr(III) or Ln(III) assuming in any case the presence of a weak exchange interaction. The data for the neodymium derivative shows a minimum in the $\chi_M T$ curve which the authors claim as a signature of a ferrimagnetic system, but the analysis of the magnetic properties does not supply any another detail.

$[M(CN)_6]^{3-}$ ion (M = Fe, Mn, Cr) showed the capability of acting as a bridging unit toward lanthanide ions. The crystal structures of these systems show nice chains, where M^{3+} and Ln^{3+} (Ln = Gd, Sm) ions alternate regularly forming one-dimensional systems where, eventually, some hydrogen bond is present between chains.[93−96] Unfortunately the characterization of the magnetic properties is generally not detailed enough to define correctly the magnetic dimensionality of these interesting systems.

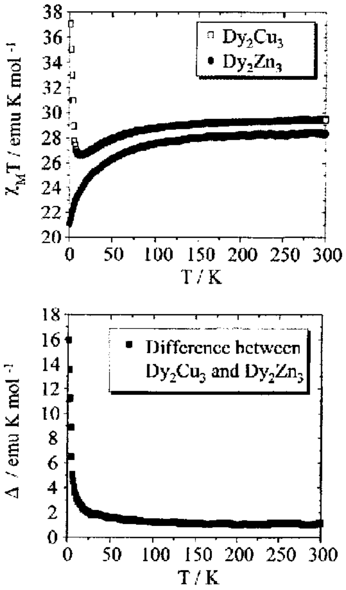


Figure 14. χ_M vs *T* plot for $Dy_2[Cu(o\text{-phenylenebis}(oxamato))]_3\cdot 4H_2O\cdot 10DMF$.[91]

B. Organic Radical Derivatives

Simple one-dimensional materials are easily obtained using rare-earth hexafluoroacetylacetonates and nitronyl nitroxides, $RE(hfac)_3NITR$.[76,97,98] A typical structure is shown in Figure 15. The RE ions are bound to the oxygen atoms of two nitronyl nitroxides, and each radical bridges two different RE ions. Such a spin topology is well-known for transition-metal ions, where one-dimensional ferro- and ferrimagnets have been reported.[27] Since the exchange interaction between the transition-metal ion and the radicals is fairly strong, ranging from −20 cm^{-1} for copper(II) to 300 cm^{-1} for manganese(II), strong intrachain spin correlation is observed at low temperature. In some cases a transition to three-dimensional magnetic order is observed; in others, when the metal ion has a strong Ising-type magnetic anisotropy, slow magnetic relaxation sets in at temperatures higher than the critical temperature.[99]

The magnetic properties of the yttrium and europium derivatives show evidence of antiferromagnetic coupling between the organic radicals mediated by the RE ions.[76,97] In particular, $Y(hfac)_3NITEt$ was found to behave as a one-dimensional Heisenberg antiferromagnet, with $J/k = 6.5$ K. Since the radicals are expected to be very isotropic and the chains are very well shielded from one another, the compound is expected to be a textbook example of a Heisenberg antiferromagnet. This was confirmed by ^1H longitudinal relaxation rate measurements performed in the range 7−60 MHz between room temperature and 4.2 K.[100] NMR data are very sensitive to interchain

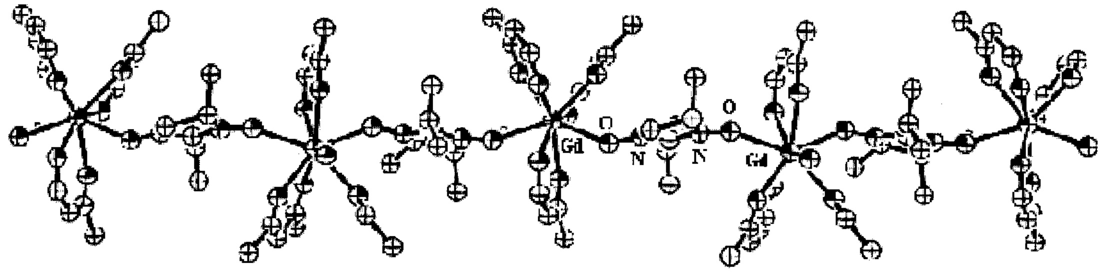


Figure 15. ORTEP view of [Gd(hexafluoroacetylacetonate)$_3$ (2-isopropyl-4,4,5,5-tetramethyl imidazoline-1-oxyl-3-oxide)].[77]

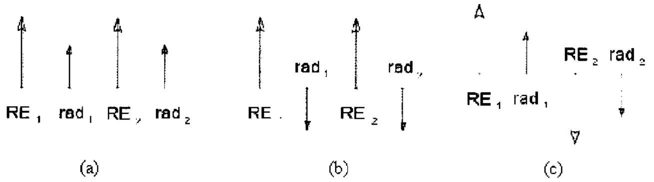


Figure 16. Sketch of the preferred spin alignment in Gd−NITR chain for (a) nn ferromagnetic coupling; (b) nn ferromagnetic coupling; (c) nnn dominant antiferromagnetic coupling.

interactions. In fact, for an ideal one-dimensional Heisenberg antiferromagnet, the ^{1}H relaxation rate is expected to vary linearly with the inverse square root of the NMR frequency.[101] This behavior has been experimentally observed for Y(hfac)$_3$NITEt in the range 8−80 MHz. The experiments were performed on polycrystalline powders, and no deviation from linearity was observed down to the lowest available frequency. This means that interchain interactions are weaker than the NMR quantum, thus indicating an upper limit of 3×10^{-3} K.

The most thoroughly investigated series is Gd(hfac)$_3$NITR.[76,77,97,98,102] The main feature of this series of compounds is that χT is either monotonically increasing or decreasing from room temperature down to very low temperature. Now, the former possibility is certainly qualitatively not surprising, because if the gadolinium and radical spins are ferromagnetically coupled, χT is expected to increase on decreasing temperature. However the antiferromagnetic behavior is at first sight difficult to understand. In fact if the interaction between gadolinium(III) and NITR is antiferromagnetic, when the correlation length increases one would expect to observe a ferrimagnetic behavior, due to the noncompensation of the RE ($S = 7/2$) and the radical ($S = 1/2$) spins. A pictorial sketch is shown in Figure 16. If the interaction between nearest neighbors is antiferromagnetic at 0 K, all the gadolinium spins would be up and the radical spins would be down. Clearly the difference between the two magnetic sublattices is not zero, and spontaneous magnetization is observed. This means that for both ferro- and antiferromagnetic nearest neighbor (nn) coupling χT diverges at low temperature and does not decrease as experimentally observed. Clearly some additional interaction must be included in order to justify the experimental data. From the analysis of the experimental data of oligonuclear compounds it is known that antiferromagnetic interactions are operative between the radicals. Remember that also in the isomorphous chains containing yttrium and europium instead of gadolinium the NITR radicals were observed to be moderately antiferromagnetically coupled. Weak antiferromagnetic interactions between the gadolinium ions were observed in the dinuclear species containing semiquinone ligands.[81] If next-nearest-neighbor antiferromagnetic interactions are present, the spins tend to be frustrated. This means that the preferred spin orientation cannot be described through simple up−down descriptions. The term is mutuated from psychology and means that a given spin is subject to two different pressures which tend to give a different behavior.

To understand this point let us consider a set of four spins as shown in Figure 16c. If we take the spin of R1 up, the spin of Gd1 must be also up, due to the ferromagnetic nn interaction. Now the spin of R2 for the same reason must be up, but if we take into account the next-nearest-neighbor, nnn, antiferromagnetic interaction, it must be down. The same considerations hold for Gd2. Here is the spin frustration. If the spins can only be up or down, then a compromise must be achieved, and this can occur by breaking the weakest bond. If this is the nn ferromagnetic coupling, the lowest energy orientation of the spins is two-spin-up−two-spin-down as shown in Figure 16c.[98] If, on the other hand, the nn ferromagnetic interactions dominate, then the preferred spin orientation is as shown in Figure 16c. Finally, if the spin-up−spin-down condition is relaxed but the spins can be oriented at relative angles different from 0° or 180°, then helical arrangements may be observed.

A simplified quantitative description can be achieved by assuming Ising-type magnetic anisotropy. This means that each spin is forced to be either up or down by a large uniaxial anisotropy. In general, the magnetic interaction between two spins can be described by the Hamiltonian

$$H = J_x S_{1x} S_{2x} + J_y S_{1y} S_{2y} + J_z S_{1z} S_{2z} \qquad (12)$$

If $J_x = J_y = J_z$ the interaction is isotropic or Heisenberg if $J_x = J_y \neq 0$; if $J_z = 0$ the interaction, is termed XY; if $J_x = J_y = 0$, $J_z \neq 0$, then the interaction is termed Ising.

The Ising model is certainly not appropriate to an isotropic system like Gd(hfac)$_3$NITR, but it has the advantage of simplicity. It has been quantitatively developed by Rettori et al.,[103] who used transfer matrix formalism to calculate the thermodynamic properties. In fact, they were able to satisfactorily reproduce the temperature dependence of χT, in particular the antiferromagnetic features.

The quantitative treatment in the Heisenberg limit is much more difficult to perform, while the use of

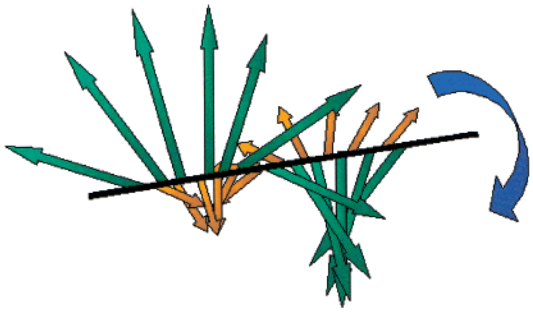


Figure 17. Bloch walls in a Gd−radical chain.

the XY formalism is much more tractable and can be considered as much more realistic than the Ising one. In this scheme the ground state is not described by the two-spin-up−two-spin-down scheme but rather the preferred spin orientation will describe a helix whose pitch depends on the ratio between the nn to nnn interactions. The ground state has a 2-fold chiral degeneracy.[104−106] This means that the helices can be either clockwise or anticlockwise, and the two states obviously have the same energy in the absence of applied magnetic fields. At 0 K, the correlation length of the spin diverges, giving rise to ordered infinite helices. At finite temperatures when the correlation length of the spins does not diverge, there will be segments characterized by clockwise and segments characterized by counterclockwise turn of the spins, separated by domain walls as depicted in Figure 17.

Specific heat measurements on Gd(hfac)$_3$NITiPr showed[104] a λ-type anomaly at 2.09 K characterized by a very small latent heat which must be associated with a magnetic phase transition. However, there is no anomaly observed in the temperature dependence of the magnetization, ruling out a conventional magnetic phase transition. In fact, Villain suggested[107] in 1978 that it might be possible to observe a chiral magnetic phase transition in chiral magnets. The nature of the phase transition can be described as due to the fact that at a given temperature all the chains show either clockwise or counterclockwise spin arrangement. This does not correspond to long-range order. In a given chain the correlation length does not go to infinite but all the ordered segments have the same chirality. This is true for all the chains, but there is no translation symmetry. The transition can be described as the onset of a collection of parallel corkscrews all turning in the same way but with random phases.

In recent years interest toward chiral magnets has rapidly developed, especially with the observation of magnetochiral effects.[108] Molecular magnets containing rare-earth ions might be good candidates to observe new magnetic properties.

When gadolinium is substituted by other paramagnetic rare-earth ions, different magnetic behaviors are observed.[109] In particular, for Dy(hfac)$_3$NITEt, a transition to weak ferromagnetic order is observed at ca. 4 K.[102,110] The simplest way of understanding the nature of a weak ferromagnet is that of imagining two identical sublattice antiferromagnets. The spins in one sublattice are up with those in the other down. If the angle is exactly 180°, the magnetizations of the two sublattices are exactly compensated and an antiferromagnetic state is achieved. However, if some anisotropy is present, then the angle may differ from 180°, as shown in Figure 18. It is apparent that the two magnetizations will no longer be exactly compensated and a nonzero magnetic moment arises. The larger the deviation from 180°, the larger is the noncompensated moment. Therefore, a weak ferromagnet is a canted antiferromagnet. To observe an angle different from 180° for the spins, it is necessary to introduce magnetic anisotropy, like in Hamiltonian eq 12. The anisotropy is associated with the orbital motion of the electrons.

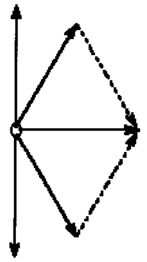


Figure 18. Spin canting determining a weak ferromagnetic behavior.

The critical temperature observed for Dy(hfac)$_3$-NITEt is surprisingly high considering that the intrachain interactions are relatively weak and that the chains are reasonably well shielded one from the other. For the sake of comparison, for Mn(hfac)$_2$NITR in which the intrachain interaction is on the order of 300 cm^{-1} the critical temperature for magnetic order is in the range 4−8 K.[27]

Magnetic phase transitions were observed also for the Tb, Ho, and Er derivatives. The critical temperature is 1.7 K for Tb, 3.2 K for Ho, and 1.2 K for Er.[109]

VII. Two-Dimensional Materials

Two-dimensional structures containing lanthanide ions coupled to transition-metal ions or radicals are still exceedingly rare, but very recently two compounds have been reported, and it may be easy to foresee that more will follow soon.

By slow diffusion of $K_3[M(CN)_6]$, M = Fe, Co, and bpym, 2,2′-bipyrimidine, with $Nd(NO_3)_3$ in a 1:1:1 molar ratio in aqueous solution, Gao et al.[111] obtained compounds of formula $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ which have a unique 2D structure. It consists of a 2D net with alternating fused rows of rhombus-like $Fe_2Nd_2(CN)_4$ rings and six sided $Fe_4Nd_4(CN)_8$ rings. A sketch of the structure is shown in Figure 19. The comparison of the magnetic properties of the cobalt(III) derivative, where the transition-metal ion is diamagnetic, with the iron(III) derivative suggests that the coupling between iron(III) and neodymium(III) is ferromagnetic. However, no evidence of long-range magnetic order is observed down to 2 K. Rather, unexpectedly the cobalt derivative showed a puzzling behavior of the ac susceptibility measured in the presence of an applied field of 2 kOe. In fact, while measurements at zero field showed normal paramagnetic behavior, those in the presence of a field showed evidence of slow paramagnetic relaxation, analogous to that observed in spin glasses or

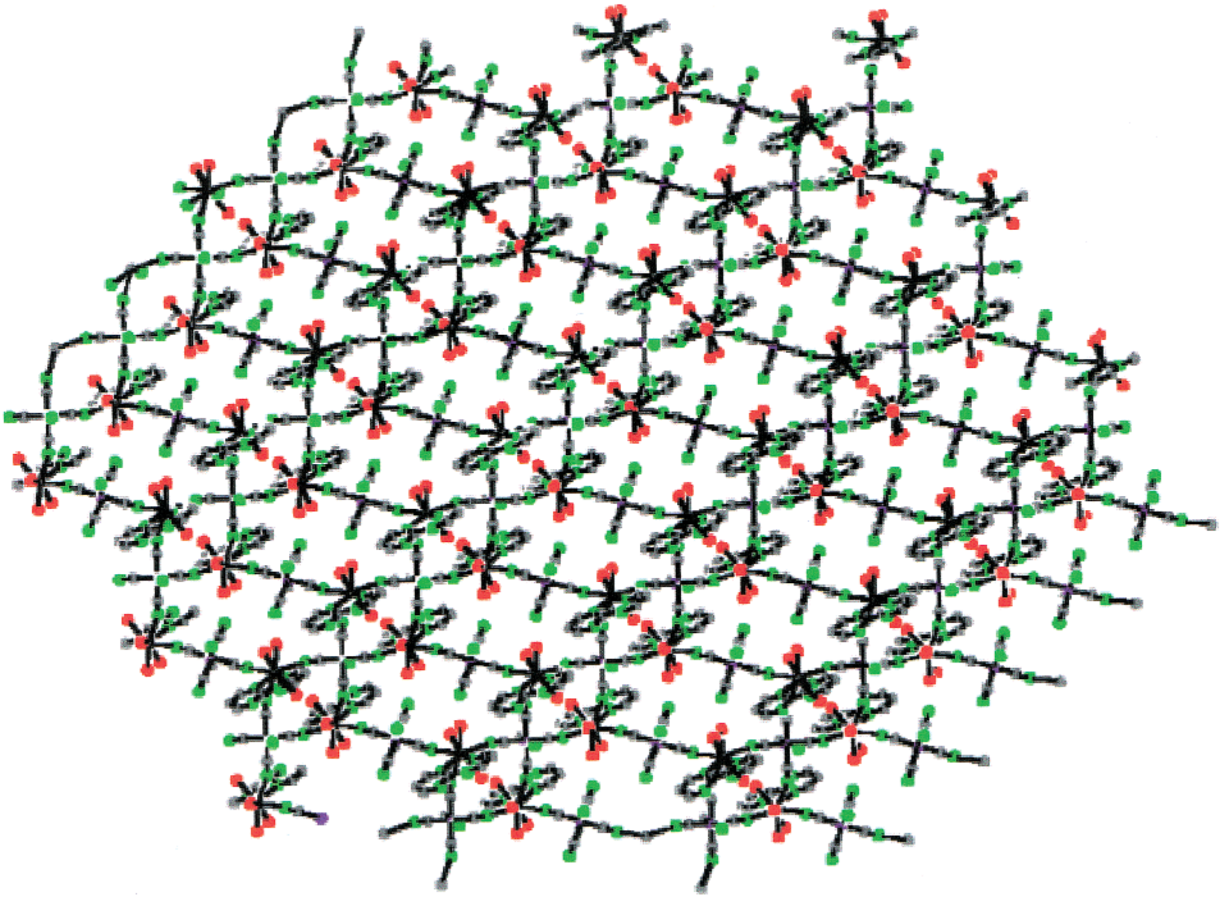


Figure 19. ORTEP view of the structure of [NdFe(2,2′-bipyrimidine)$(H_2O)_4(CN)_6$].[111]

superparamagnets. This behavior was tentatively attributed to spin glass behavior generated by spin frustration. More experimental work is needed. This strategy of synthesis is rather flexible: on changing the capping ligand toward the lanthanide ions it is possible to obtain a slightly different compound based on various arrangements of the chains where the $[M(CN)_6]^{3-}$ ions (M = transition-metal ion) act as a bridging unit between rare-earth ions. For instance, if DMF (*N*,*N*′-dimethylformamide) is used in the presence of chromium(III) cyanide and gadolinium(III) nitrate, a two-dimensional bimetallic array with a brick-wall-like structure is obtained. The magnetic behavior is interpreted on the basis of a Gd−Cr antiferromagnetic interaction with an overall ferrimagnetic behavior which derives from the uncompensated spins.[112] A similar crystal structure was observed in two samarium(III) derivatives.[113] Due to the presence of the orbital contribution in the Sm ground state, the analysis of the magnetic data is not easy as the observed decrease of $\chi_M T$ on lowering the temperature in both the compounds should be due to the superposition of thermal depopulation of the excited state of Sm and/or the Sm−Cr magnetic interaction. The detailed analysis of the magnetic behavior was not conclusive in determining the nature of the magnetic interaction but showed in one case a magnetic phase transition below 4.2 K and a coercive field of 100 Oe at 1.85 K while for the other derivative no long-range magnetic order was observed. Using 2,2′-bipyridine as the capping ligand, systems with the same general formula were obtained starting from $Ln(NO_3)_3$ (Ln = Gd, Y) and $K_3[M(CN)_6]$ (M = Fe, Co).[114] The crystal structure showed the presence of chains of transition-metal and lantanide ions bridged by cyano groups and the chains connected through hydrogen bonds to form layers. Since the separation between the various metal ions in the chain is comparable with the nearest interchain and interlayer separations, these systems can be regarded as an anisotropic 3D magnetic system with a weak interlayer interaction to make these systems exhibit magnetic long-range order as it is possible to derive from the magnetic susceptibility and heat capacity measurements. The magnetic relaxation is field dependent and unusually slow and qualitatively resembles those in single-molecule magnets as Mn_{12}−Ac.[115]

A typical honeycomb structure was reported[116,117] for a compound obtained by reacting in a sealed tube two DMF solutions of $NdCl_3 \cdot 6H_2O$ with $Na_2[Cu(opba)]$. Partial hydrolysis of the copper compound during the reaction affords some oxalate, ox, yielding a compound of formula $\{Nd_2[Cu(opba)_{0.5}(ox)]_3 \cdot 9DMF\} \cdot 4.5DMF$. The honeycomb structure is shown in Figure 20 with the Nd ions at theconjunctions of the hexagons and the copper ions along the sides. The magnetic properties were measured down to 2 K. The extrapolation to 0 K of the χT curve goes to zero, a rather unusual result for a two-dimensional magnetic compound with an odd number of unpaired electrons. It is suggested that this is due to accidental cancellation at low temperature of the moment associated to two Nd and three Cu. Analogous results were

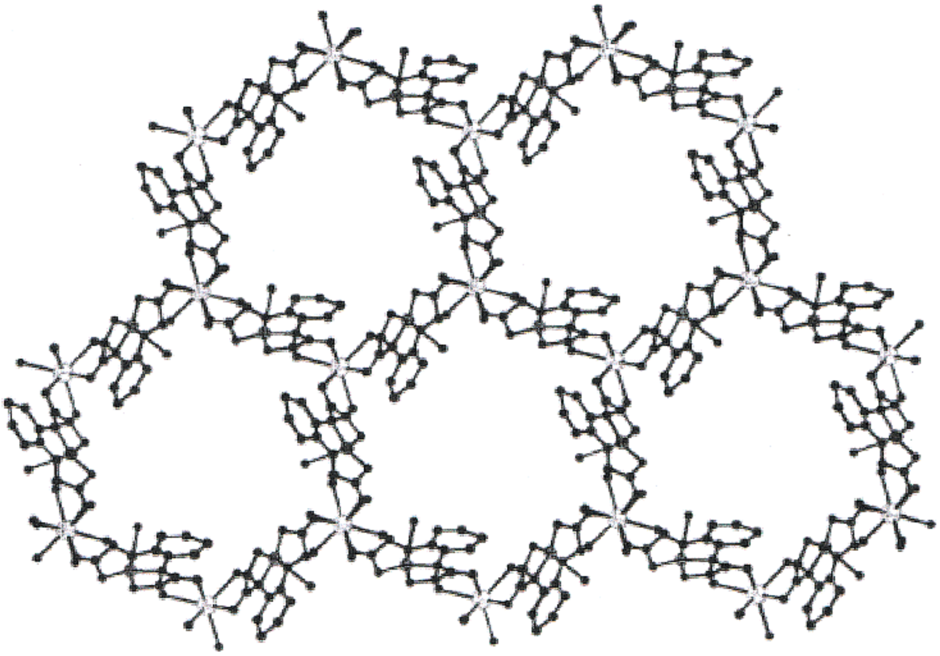


Figure 20. ORTEP view of $\{Nd_2[Cu(o\text{-phenylenebis(oxamato)})_{0.5}(oxalato)]_3\cdot 9DMF\}\cdot 4.5DMF$.[117]

observed in compounds with analogous formula but with a ladder-like structure.[118]

On the borderline of molecular magnets can be cited Prussian blue like derivatives.[119] $[SmFe(CN)_6]\cdot 4H_2O$ and $[TbCr(CN)_6]\cdot 4H_2O$ have a three-dimensional structure, which gives important magnetic properties. In fact, the former orders as a ferrimagnet at ca. 3.5 K with strong coercive field, while the latter has the highest critical temperature reported so far ($T_C = 11.7$ K) for 4f−3d molecule-based magnets. These compounds are a clear indication that provided the proper conditions are developed, interesting magnetic properties can be observed in compounds containing rare-earth and transition-metal ions.

VIII. Conclusions and Perspectives

The understanding of the magnetic interactions involving rare-earth ions in molecular magnets is still far from being satisfactory. The key point is the role of the orbital contribution, which introduces many complications, in particular large magnetic anisotropies. It is necessary to gather a large number of experimental data, and isotropic measurements are not particularly well suited in order to obtain the information which is needed to reconstruct the full map of the magnetic interactions. Ideally one should use UV−Vis spectra in order to obtain information on the crystal-field effects on the individual RE ions; anisotropic magnetic measurements down to very low temperature on pure and diamagnetically substituted species, EPR spectra, and inelastic neutron scattering experiments on single crystals can also provide much additional insight in the low-lying levels. It must be stressed that the number of sophisticated physical measurements which can be performed on molecular compounds has dramatically improved in the past few years, and it is perhaps time that a complete effort is made to characterize some particularly well-suited set of compounds. Further, it can be expected that soon DFT or similar calculations will finally provide the necessary insight taking into account the relativistic effects which are so important for rare-earth ions. We feel that in the next few years these concerted efforts will finally provide a clear view of the magnetic interactions involving rare-earth ions.

IX. Acknowledgments

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X. References

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