esters[41] indicate that this acyl function is transferred via a concerted pathway. Stereochemical probes indicate that derivatives of sulfur acids at the tetravalent and hexavalent levels of oxidation transfer the acyl function via concerted mechanisms.[42] There is, however, ample preparative evidence for the stability of

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possible associative intermediates in sulfur acid acyl group transfer.[43]

Conclusions

Acyl group transfer reactions in solution should not be assumed to involve only addition or associative intermediates in their mechanisms. Discussion of mechanism for transfer of acyl groups between nucleophiles should seriously consider the concerted pathway as well as the stepwise mechanisms following dissociative and associative routes. Strongly basic donor and acceptor nucleophiles favor "tight" transition states whereas weakly basic nucleophiles encourage "open" or dissociative transition states. Concerted mechanisms of acyl group transfer are more common among derivatives of all acids than was previously supposed.

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Toward Molecular Magnets: The Metal–Radical Approach

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Molecular materials are characterized by being made up by discrete molecules. This structural property gives in principle many possibilities to modulate the bulk electrical, magnetic, and optical properties of the material by choosing appropriately the constituent molecules. At the same time, however, it is a challenge to develop synthetic strategies that allow the control of the spatial distribution of the molecules in the lattice. In fact, the bulk properties are always determined by cooperative interactions between the constituent molecules, which consequently must be assembled in the lattice in such a way as to maximize the bulk response.

Beyond the basic problem of establishing structure–property correlations, molecular materials appear as promising in order to develop new properties or novel associations of properties. As examples, we can mention

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the active research on organic materials with nonlinear optical properties[1] and the studies on organic conductors and superconductors.[2] In this framework, an area of growing interest is that of high-spin molecules[3–7] and molecular magnetic materials,[8,9] which aims at the synthesis of compounds that have spontaneous magnetization below a critical temperature. Molecular magnets are desirable because they may have magnetic properties associated with light weight (plastic magnets), solubility in organic solvents, or optical transparency, which could make them useful in the development of new electronic devices. Further, they provide the fun of the intellectual challenge to synthesize new classes of compounds that do not yet exist.

In this Account we provide a concise resume of magnetic phenomena, report briefly on the different strategies that have been developed up to the moment for designing molecular magnetic materials, and then summarize our own approach and the main results that

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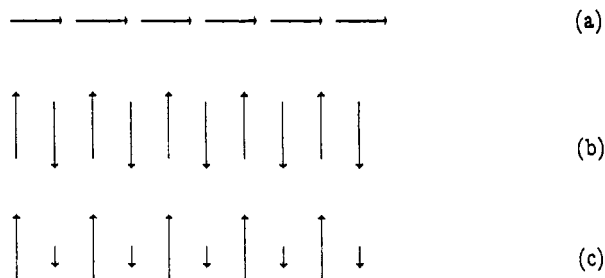
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Figure 1. Preferred directions of the spin alignment for ideal one-dimensional ferromagnets (a), antiferromagnets (b), and ferrimagnets (c).

have been obtained in this area.

Magnetic Materials

The number of different magnetic behaviors that can be observed in a solid is fairly large,[10] and indeed the family tree of magnetism has many branches. Nevertheless, five classes are of particular importance, namely, diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. The last three classes are characterized by the cooperative behavior of the spins. We will focus on both ferro- and ferrimagnetism, which give rise to spontaneous magnetization below a critical temperature. Iron is a well-known example of a ferromagnet, and lodestone of a ferrimagnet. In both cases, the spins in the lattice interact strongly with each other to give long-range order. In ferromagnets, the individual spins can be either all identical or different from each other, but the coupling is such that they all are parallel to each other in the ordered phase, as shown schematically in Figure 1 for a linear array. In both antiferromagnets and ferrimagnets, there are at least two kinds of different spins that are coupled antiparallel to each other. When the individual moments are different, there is a resultant nonzero magnetic moment (Figure 1). When the two different spins have identical moments, the magnetizations of the two sublattices cancel, and an antiferromagnet is formed.

In order to describe the interaction between two spins S_i and S_j, it is customary to refer to a coupling constant defined by the spin Hamiltonian $H = J(S_i \cdot S_j)$.[11] With this definition, the energy separation between a singlet and a triplet is J. A positive J means antiferromagnetic coupling (singlet lower); negative J means ferromagnetic coupling (triplet lower). The centers characterized by the spins S_i and S_j, respectively, interact with each other through a weak bonding interaction: if the orbitals containing the unpaired electron(s) on the two centers, the magnetic orbitals, are orthogonal to each other, then Hund's rule keeps the spins parallel to each other and parallel coupling between the two arises, while if they have nonzero overlap, the antiparallel alignment will be favored. The two spin centers may be also well separated from each other provided that intervening formally spin paired centers can transmit the interaction (superexchange).

In order to have a bulk ferromagnet, it is necessary that parallel coupling dominate on the scale of the lattice, but the orthogonality conditions are difficult to

impose on all the neighbors of a given spin. In other terms, avoiding some bonding interaction between the unpaired electrons represents a big problem. If the spins are different from each other, then the nonorthogonality of the magnetic orbitals is not too severe a problem, because an antiparallel alignment of the spins will lead to uncompensated moments and to a ferrimagnet.

Attempts have been made to obtain molecular-based magnets possessing spontaneous magnetization by designing systems with either parallel or antiparallel spin alignment. Although the critical temperatures reached so far are fairly low, it can be safely stated that our understanding of the requisites for a high-temperature magnet is much deeper now than it was a few years ago.

Several groups have followed an organic approach, but at the moment no bulk ferromagnet has been obtained, although some reports claim to have observed a fraction of ferromagnetic materials in polymers based on 1,3,5-triaminobenzene[12] or a nitroxide biradical.[13] However, reproducible chemical or physical characterization of the materials has not yet been achieved.

An organic/organometallic approach has been followed by Miller et al.[4,14-17] who synthesized a compound of formula [Fe(Me$_5$Cp)$_2$](TCNE) (Me$_5$Cp = pentamethylcyclopentadienyl; TCNE = tetracyanoethylene), which orders ferromagnetically at 4.8 K. In this case, it is suggested that the parallel alignment of the spins is achieved through a mechanism of virtual charge transfer between the two different spin centers of the compound.

An inorganic approach has been followed by Kahn et al.[18-21] and Drillon et al.,[22-26] who used metal ions bridged by closed-shell organic ligands. In this case, one-dimensional ferrimagnets were obtained, which in some cases ordered ferromagnetically at low temperature. The highest transition temperature seems to be 14 K at the moment.[27]

We are currently following an approach that is intermediate between organic and inorganic because the interacting magnetic centers are metal ions directly bound to stable organic radicals, such as the nitroxides.

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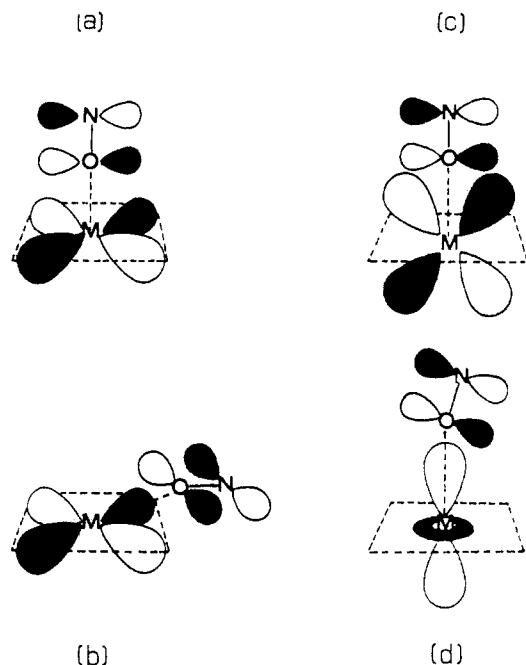(24) Drillon, M.; Coronado, E.; Fuertes, A.; Beltran, D.; Georges, R. *Chem. Phys.* 1983, *79*, 449.
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(a)   (c)

(b)   (d)

Figure 2. Schemes of possible interactions between the magnetic orbitals of a nitroxide and a metal ion.

Coordination Chemistry of the Nitroxides

Nitroxides are well-known stable organic radicals that have a N–O group with one unpaired electron in a π^* orbital roughly equally shared by the nitrogen and oxygen atoms.[28] These radicals have been widely used as spin-probes,[28] and their coordination chemistry has been reviewed previously.[29,30] In fact, the oxygen atom has a weak Lewis basicity and the nitroxides can be used as ligands toward many different metal ions. However, the nitroxides are rather poor ligands, and this sets large limitations on the nature of the additional ligands that are compatible with them.

When the nitroxide binds through its oxygen atom to a paramagnetic metal ion, two cases can occur: (i) the spins orient antiparallel to each other or (ii) the spins orient preferentially parallel to each other. The limit of case i is the formation of a strong covalent bond which totally pairs the spins; otherwise, if the levels of different total spin multiplicity are thermally populated, an antiferromagnetically coupled system is formed. Case ii corresponds to ferromagnetic coupling.

The sign of the coupling of a nitroxide directly bound to a metal ion is easily predicted on the basis of orbital overlap considerations.[31] If the orbitals containing the unpaired electrons on the metal and the radical have significant overlap, the coupling is antiferromagnetic, while if they are orthogonal to each other, the coupling is ferromagnetic.

In Figure 2 we show some possible relative orientations of magnetic orbitals leading to ferro- or antiferromagnetic coupling. In part a, the two orbitals are orthogonal to each other and the coupling is ferromagnetic. This situation occurs in a few copper(II)–nitroxide complexes, where the radical is in an axial

Table I
Typical Values of the Magnetic Coupling Constant J for Metal–Nitroxide Complexes

metal ion	type of coupling	$J,^a$ cm^{-1}
copper(II)[b]	AF	≥500
copper(II)[c]	F	−10 to 70
nickel(II)	AF	≥300
cobalt(II)	AF	≥300
manganese(II)	AF	150–300

[a] Positive J means antiferromagnetic coupling. The energy separation between singlet and triplet is J. [b] The nitroxide is an equatorial site. [c] The nitroxide in an axial site.

coordination site, and experimentally the triplet state has been found to lie 10–70 cm^{-1} below the singlet state.[31-34]

Situation b occurs in copper(II)–nitroxide complexes where the radical coordinates in an equatorial coordination site. If the M–O–N angle is different from 180°, substantial overlap occurs and the coupling must be antiferromagnetic. Experimentally the singlet has been found to be the ground state,[35-38] and no evidence of thermal population of the triplet has been found, indicating that it is at least 500 cm^{-1} above the ground state, and perhaps more. Therefore the problem remains open of whether the two spins are completely paired in a covalent bond or the metal–ligand interaction is more correctly described as an exchange interaction.

Cases c and d occur in complexes of nickel(II), cobalt(II), and manganese(II), and they invariably lead to strong antiferromagnetic coupling. The magnetic properties of nickel(II),[39,40] cobalt(II),[40] and manganese(II)[41,42] hexafluoroacetylacetonate (hfac) adducts with the nitroxides of formula $M(hfac)_2(RNO)_2$ have indeed shown that the ground state has zero, one, and three unpaired electrons, respectively, but other spin levels originated by the exchange interaction are thermally populated. A clear evidence for this was found in $Mn(hfac)_2(proxyl)_2$ (proxyl is 2,2,5,5-tetramethyl-pyrrolidinyl-1-oxy). The antiferromagnetic interaction between the spin of manganese, $S = {}^5/_2$, with the two $S = {}^1/_2$ spins of the two radicals yield one $S = {}^3/_2$, two $S = {}^5/_2$, and one $S = {}^7/_2$ state. The magnetic data showed that $S = {}^3/_2$ is the ground state, with the $S = {}^5/_2$ states at 525 and 735 cm^{-1}, respectively.[41] EPR confirmed this order by showing a spectrum typical of $S = {}^3/_2$ at low temperature and of $S = {}^5/_2$ at room temperature.[42]

More detailed evaluation of the overlap of the magnetic orbitals and consequently of the extent of mag-

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netic coupling between metal ions and radicals can be obtained by extended Hückel calculations.[31,43] In Table I we review the type of magnetic coupling observed in some metal–nitroxide complexes.

From Zero-Dimensional to One-Dimensional Antiferromagnets

Simple nitroxides can interact with one metal ion at a time; therefore, they cannot easily form extended magnetic structures. A clear example of this limitation is provided by $Cu(hfac)_2TEMPOL$[33,34,44] (TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-N-oxy), which has the structure 1. The radical has two oxygen atoms,

1
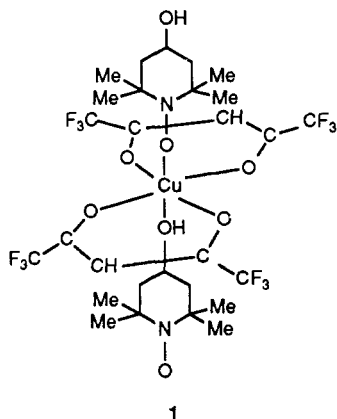
which bind to two different metal ions, forming a linear chain. The N–O group, which has the unpaired electron, is ferromagnetically coupled to the copper ion to which it is bound with $J = -13$ (5) cm^{-1}, but the coupling with the other nearest-neighbor copper ion is much weaker and antiferromagnetic, $J' = 0.053$ (1) cm^{-1}. In practice, $Cu(hfac)_2TEMPOL$ has a chain structure but the magnetism above 4 K is that of a weakly coupled metal–radical species.

We sought easy-to-handle radicals which offer better possibilities of building extended magnetic structures. It occurred to us that the nitronyl nitroxides, (NIT)R = 2-substituted 4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide, of general formula[45–47]
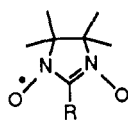
have one unpaired electron, which is delocalized on the two equivalent N–O groups; therefore, the exchange interaction operative between one oxygen and a metal ion must be transmitted without attenuation to the other oxygen atom. If the two oxygen atoms of the N–O groups bind to two different metal ions, a polymeric structure can be formed, with effective pathways to transmit the magnetic interactions between the metal ions. Ideally one would like to build three-dimensional structures of connected metal ions and radicals, but even if this goal has not yet been achieved, even one-dimensional structures, which are easier to assemble,

Chart I

can provide interesting results, as we will show below. A further advantage of these ligands is that, on varying R, the steric and electronic characteristics are varied, thus allowing in principle for some flexibility in the design of magnetic materials.

With these considerations in mind, we started a systematic investigation of the coordination behavior of nitronyl nitroxides and found that indeed the radicals can bind in several different ways to metal ions as shown in Chart I. In I they bind with one oxygen atom to one metal ion, yielding discrete mononuclear complexes (nuclearity is referred to the metal).[31,32,43] These compounds are not very interesting for our final purposes, but they provided useful information on the type and the extent of magnetic interaction between nitronyl nitroxides and metal ions. When a (NIT)R ligand binds to one metal ion, its coordination behavior and magnetic properties are similar to those of simple nitroxides.

In II, the radicals bind with one oxygen to one metal, while the other oxygen interacts weakly with another radical,[48] forming magnetic chains. In III, they bind with the two oxygen atoms to two different metal ions: in this case, chains can be formed, either ferromagnetic[49] or ferrimagnetic,[50] depending on the nature of the metal ion. In IV, they bind with one oxygen atom to two different metal ions, and each metal ion is bound to two radicals, with four spins arranged at the vertices of a diamond. The second oxygen atom then interacts with the oxygen atom of another radical, thus forming antiferromagnetic chains.[51]

A practical realization of structure II of Chart I has been observed in $CuCl_2((NIT)Ph)_2$,[48] where the copper(II) ion coordinates to two chlorides and two (NIT)Ph molecules in a square plane. The coupling between the three spins is antiferromagnetic, and the magnetic data at room temperature indicate the pres-

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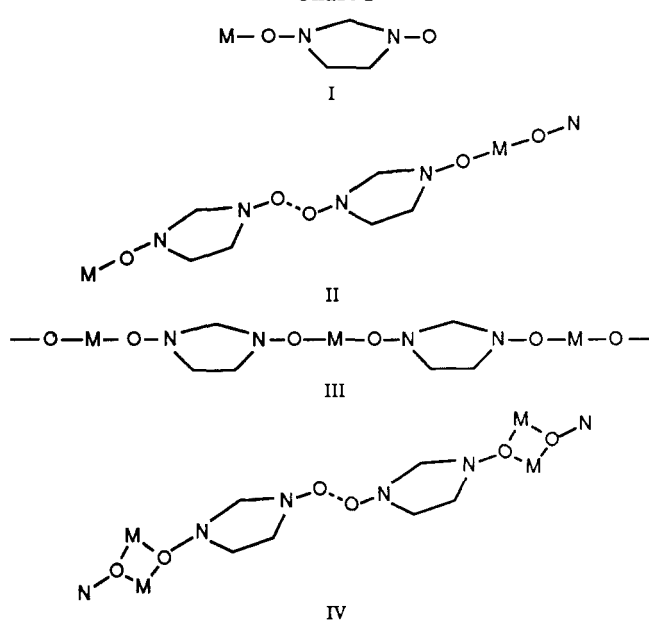
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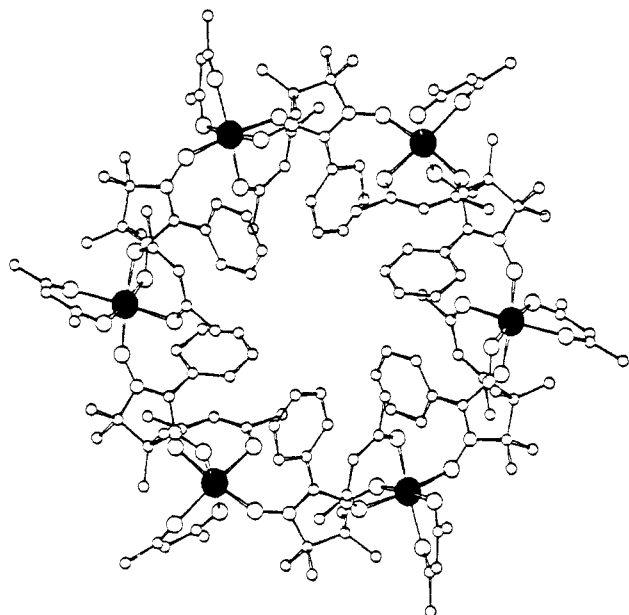
Figure 3. Structure of the $[Mn(hfac)_2(NIT)Ph]_6$ molecule. The fluorine atoms are omitted for the sake of clarity.

ence of one unpaired electron. The nitrogens of two noncoordinated N–O groups are 3.56 Å from the oxygen atoms of another molecule and are bonded in such a way that the π^* orbitals of two neighboring radicals overlap, suggesting a strong antiferromagnetic coupling between the $CuCl_2((NIT)Ph)_2$ molecules. Indeed the low-temperature behavior of this compound is that of an antiferromagnetic chain of spin $S = {}^1/_2$.

The coordination IV has been observed in [M-$(hfac)_2(NIT)R]_2$ where M = Ni and Co and R = ethyl and isopropyl.[51] The coupling is strongly antiferromagnetic within the M_2O_2 clusters, but, since the spins are different, the ground state is magnetic. For instance, when M = nickel(II), the isolated metal ion has two unpaired electrons and the ground state for the cluster of four spins is $S = 1$. However the coupling between the noncoordinated N–O groups is antiferromagnetic also in this case, and indeed the magnetic properties at low temperature are those of antiferromagnetic chains.

When the nitronyl nitroxides bind as bidentate ligands toward two metal ions, according to III, both oligonuclear spin clusters and chains can be formed. An interesting example of the former is provided by [Mn-$(hfac)_2(NIT)Ph]_6$,[52] which has the ring structure shown in Figure 3 with an overall S_6 symmetry. Rings like this have long been used by theorists[53,54] in order to approximate the thermodynamic properties, including magnetic susceptibility, of one-dimensional materials, and $[Mn(hfac)_2(NIT)Ph]_6$ is a practical realization of a ferrimagnetic ring. The effective magnetic moment is temperature dependent, and below 30 K, it is close to that expected for $S = 12$, $\mu_{eff} = 24.5\mu_B$ vs $25\mu_B$, a clear indication that the spins are indeed antiferromagnetically coupled. This interpretation is confirmed by magnetization measurements.

Recently a manganese cluster has been shown to have a $S = 14$ ground state.[55] It must be noted that one of

the suggested strategies for the synthesis of molecular-based ferromagnets is that of assembling high-spin building blocks, but the two clusters with the highest spin multiplicity ever reported do not show any magnetic phase transition and stay paramagnetic down to 4.2 K.

From One-Dimensional Ferro- and Ferrimagnets to Three-Dimensional Magnets

In linear chain compounds formed according to III in Chart I, the coupling can be such as to align the neighboring spins either parallel or antiparallel to each other. In the former one-dimensional ferromagnets are formed, while in the latter, one-dimensional ferrimagnets are formed. The effective moments of both kinds of materials are expected to diverge at low temperature, as a consequence of the alignment of the spins along the chain.

In a one-dimensional material, long-range order can be achieved only at 0 K,[56] but at low temperature, the spins are highly correlated so that even at finite temperatures the effective spin on each magnetic center may become quite large. As a consequence, even weak interchain interactions, which are always operative in real one-dimensional materials, may drive three-dimensional order and a magnetic phase transition.

The first one-dimensional magnetic material that we synthesized was $Cu(hfac)_2(NIT)Me$,[49] which behaves as a one-dimensional ferromagnet with a coupling constant of -25.7 (1) cm^{-1}. The effective magnetic moment at 300 K, $2.8\mu_B$, is slightly higher than the value expected for uncorrelated spins, and on lowering of the temperature, it increases indefinitely and at 4 K is $4.9\mu_B$. This means that at 4 K the effective spin, defined as the S value of a normal paramagnet with the same g value, has grown to almost 3.

Measurements on $Cu(hfac)_2(NIT)Me$ below 4 K indicate that μ_{eff} keeps increasing and at 1.2 K a significant deviation from ideal one-dimensional behavior is observed, which can be accounted for by a simple molecular field model which requires that the chains are weakly antiferromagnetically coupled. Therefore in this case the attempts to obtain three-dimensional ferromagnetic order apparently failed.

The ferromagnetic coupling between copper(II) and a radical is relatively weak;[49] therefore, we sought to take advantage of the larger antiferromagnetic coupling constants that are expected for nickel(II) and manganese(II) complexes, and aimed at the synthesis of one-dimensional ferrimagnets. $Ni(hfac)_2(NIT)R$[39] and $Mn(hfac)_2(NIT)R$[50] with R = Me, Et, iPr, nPr, and Ph have such a behavior. In Figure 4, we plot the effective magnetic moment vs T for $Mn(hfac)_2(NIT)iPr$, whose unit cell is shown in Figure 5. At 20 K, the effective magnetic moment is $22.1\mu_B$, corresponding to an effective spin for the manganese radical pair of ca. 11.

A quantitative analysis of the temperature dependence of the magnetic susceptibility for both types of compounds can be performed by using the formulas reported for ferrimagnetic chains, either for classical spins[57] or for alternating quantum and classical spins.[58]

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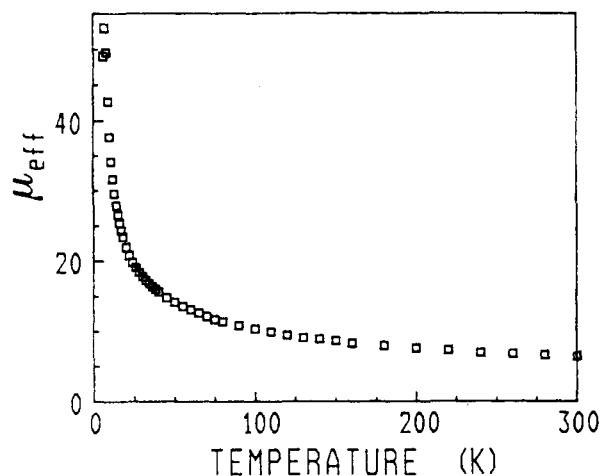
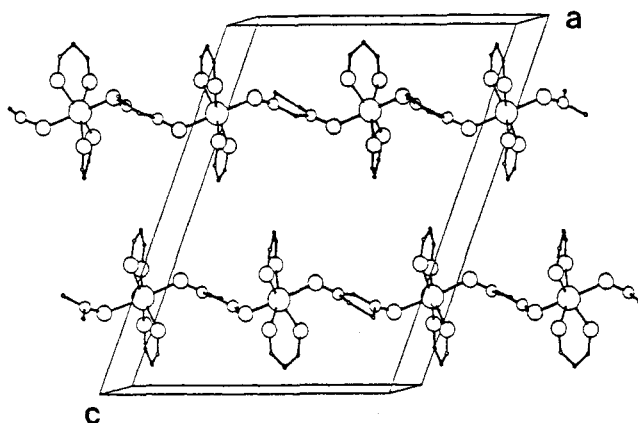**Figure 4.** Temperature dependence of the effective magnetic moment of Mn(hfac)$_2$(NIT)iPr.

Figure 5. View of the unit cell of Mn(hfac)$_2$(NIT)iPr. The CF$_3$ and CH$_3$ groups have been omitted for the sake of clarity. The chains develop parallel to the *c* axis.

Figure 6. Experimental susceptibility vs temperature for Mn-(hfac)$_2$(NIT)iPr along three orthogonal axes.

A good agreement was obtained by using *J* values of 424 cm^{-1} for the nickel and in the range 210–330 cm^{-1} for the manganese derivatives. The experimental data could be reproduced in this way only down to 20 K. Below this temperature, the experimental points are higher than the calculated ones, suggesting ferromagnetic phase order.

Indeed a magnetic phase transition can be observed in very weak applied fields. The experimental susceptibility vs temperature for single crystals of Mn-(hfac)$_2$(NIT)iPr is shown[59] in Figure 6. The critical temperature is 7.6 K, and the transition is ferromagnetic, as shown by the temperature dependence of the susceptibility parallel to *b*, the easy axis, i.e., the direction of preferred spin orientation. Additional evidence of the ferromagnetic nature of the transition was obtained by saturation measurements. Similar ordering was observed for Mn(hfac)$_2$(NIT)Et[60] at 8.1 K, for Mn(hfac)$_2$(NIT)nPr[60] at 8.6 K, and for Ni(hfac)$_2$-(NIT)Me[39] at 5.3 K. Therefore, these materials can be described as ferromagnetically ordered ferrimagnetic chains.

The origin of the ferromagnetic phase transition observed in all the above compounds is attributed to the dipolar interaction between chains. In fact, we could calculate the transition temperature with a simple formula that relates the spin correlation length, which is essentially a measure of the efficiency of the exchange along the chain, and the lattice dipolar energy.[59] Similar conclusions were reached also through the critical exponent γ, which was found[59] to be close to the value expected for the dipolar uniaxial ferromagnet. This result is not unexpected, because, despite the strong coupling along the chain, the compounds stay paramagnetic down to rather low temperature. In fact, the bulky hexafluoroacetylacetonates effectively shield the chains, and no obvious exchange pathway is available. The lower transition temperature observed for the nickel compared to the manganese derivatives can be qualitatively explained by the smaller spin of the former, which makes the dipolar interaction less effective.

The spin alignment of Mn(hfac)$_2$(NIT)iPr in the ordered phase was determined through magnetic anisotropy experiments,[59] which showed that the favorite direction of the spins is orthogonal to the chain axis. Similar conclusions can be reached from the analysis of the EPR spectra in the paramagnetic phase, which are a very useful complementary tool for the investigation of magnetic materials.[61]

The observed spin orientation is typical of ideal one-dimensional ferrimagnets, i.e., systems in which the exchange interaction is isotropic and strong along the chain and vanishingly small between chains. The combined effect of exchange and dipolar interaction along the chain is to orient preferentially the spins as shown in Figure 1 for ferro- and ferrimagnets, respectively. The two behaviors are understood by taking into account the nature of the exchange and dipolar interactions. The dipolar interaction tends to keep the spins parallel to each other along the chain. When the exchange coupling is ferromagnetic, both interactions keep the spins parallel to each other along the chain, while when the exchange coupling is antiferromagnetic, this

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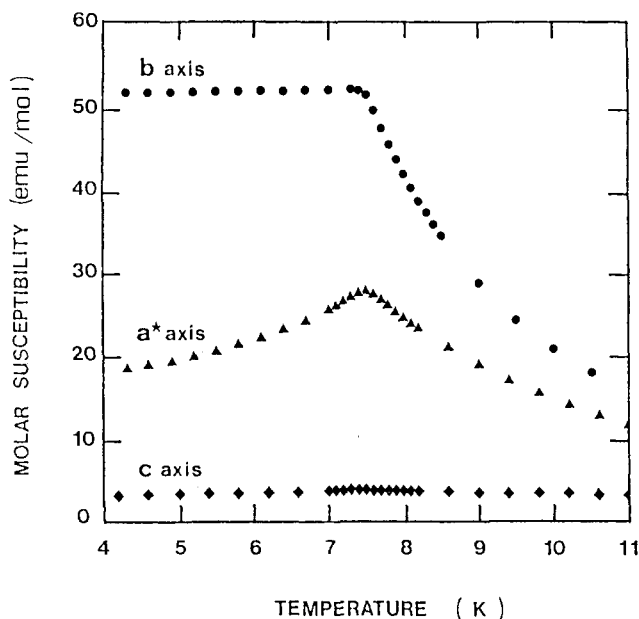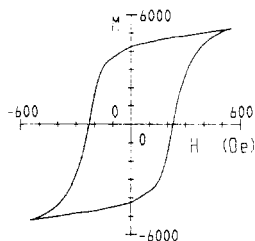(60) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 3314.

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Figure 7. Hysteresis loop of [Mn(pfbz)$_2$]$_2$(NIT)Me at 4.2 K. The molar magnetization is expressed in emu mol^{-1} G.

orients the spins antiparallel along the chain. As a result of the two contrasting interactions, the spins orient orthogonally to the chain. It is instructive to realize that these same considerations were used by G. N. Lewis to rationalize the spin pairing accompanying the formation of a covalent bond.[62]

The magnetic data of the manganese derivatives show that it is indeed possible to obtain molecular materials with spontaneous magnetization by using metal ions and nitronyl nitroxides as interacting centers. However, since the interchain coupling in the adducts of metal hexafluoroacetylacetonates with nitronyl nitroxides is so small, strategies must be developed to obtain greater intermolecular coupling. In principle, two synthetic possibilities can be considered, to change either the radicals or the metal complexes. Introduction of substituents on R may increase the possibilities of interacting with other metal ions or radicals.

Changing the metal complexes is in general possible, the limitation being that they must keep a relatively strong Lewis acidity due to the low coordinative capacity of the nitroxides. The metal hexafluoroacetylacetonates, which are very useful to bind to nitroxides, are not the ideal for short and efficient contacts between the metal ions.

Reacting manganese(II) pentafluorobenzoate, Mn(pfbz)$_2$, with nitronyl nitroxides, we obtained com-

pounds of formula [Mn(pfbz)$_2$]$_2$(NIT)R (R = Me, Et),[63] which were found to undergo a transition to three-dimensional magnetic order at 24 and 20.5 K, respectively. The compounds have a spontaneous magnetization below the transition temperature, but it is not clear if it is ferrimagnetic or antiferromagnetic with spin canting. The hysteresis loops have a large coercive field and remnant magnetization, Figure 7. Unfortunately, these compounds eluded our attempts to grow crystals, and no structural magnetic correlation can be established. However, it is apparent that substituting hfac with pfbz, which is expected to provide efficient exchange pathways between the metal ions, can increase the transition temperature dramatically.

Conclusions

The strategy of building bulk magnets starting from paramagnetic metal ions bound to paramagnetic ligands has been found to yield encouraging results. It has been found that parallel spin alignment is much more probable than it was believed up to some years ago,[9,64,65] but antiparallel interactions may also be exploited to give ferrimagnets. Nitroxides have been investigated to some extent, but additional improvements may be foreseen with more complex starting ligands. Radical anions[66,67] also deserve to be taken into consideration; those of nitrogen bases and semiquinones may also be suitable ligands. Thus, it appears that the field of metal–radical interactions will be actively investigated in coming years.

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