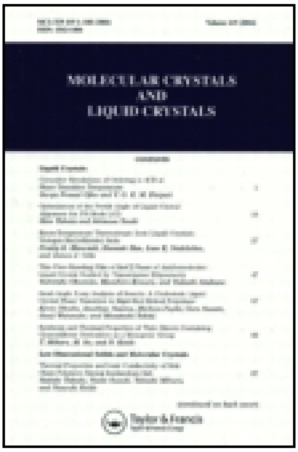


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetism of Materials Formed by Metal Ions and Radicals

Andrea Caneschi [a] , Dante Gatteschi [a] & Roberta Sessoli [a]
[a] Department of Chemistry, University of Florence, 50144, Florence, Italy

To cite this article: Andrea Caneschi , Dante Gatteschi & Roberta Sessoli (1996): Magnetism of Materials Formed by Metal Ions and Radicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 177-194

To link to this article: http://dx.doi.org/10.1080/10587259608042189

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 177–194
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

MAGNETISM OF MATERIALS FORMED BY METAL IONS AND RADICALS

ANDREA CANESCHI, DANTE GATTESCHI and ROBERTA SESSOLI
Department of Chemistry, University of Florence, 50144-Florence, Italy

Abstract We briefly review, showing some examples, the current state of magnetic materials containing transition metal and lanthanide ions coupled to nitronyl nitroxide organic radicals. Results obtained with a purely organic ferromagnet, NITSMe, are also illustrated. The case of one molecule containing Mn(II) ions and nitronyl nitroxide radicals co-ordinated in a monodimensional structure motiv and possessing non-linear optical activity together with 3D magnetic phase transition is showed. Unusual behavior observed in monodimensional linear chains containing lanthanide ions and nitronyl nitroxide radicals is presented and discussed. Proofs of the excitation of "chiral" domain walls, predicted by I. Harada in 1984, have been found in these frustrated spins systems through specific heat and low temperature low field magnetic measures. Thermodynamic properties were reproduced by using the transfer matrix calculation formalism.

Nitronyl nitroxides, NITR, are central molecules in molecular ferromagnetism, because they have provided important breakthroughs both in pure organic[1-7] and inorganic[8-10] materials. In fact our laboratory reported the ferromagnetic behavior below 24 K of $[M(pfbz)_2]_2NITR$, where pfbz = pentafluorobenzoate, in 1989,[11] and Kinoshita and co-workers described the ferromagnetic behavior of the β-phase of $NITp(NO_2)Ph$, in 1991.[12]

After these initial successes very large number of investigations were undertaken in order to increase the critical temperatures. We are still active in this area, both trying to develop new purely organic ferromagnets, and to employ the NITR radicals as ligands towards rare earth ions with the aim to obtain new classes of magnetic materials. In the purely organic ferromagnetism area we investigated the role of sulphur atom, which we expected to be able to transmit exchange interactions at relatively long distances, due to the diffuse electronic cloud. We wish to review here below the properties of 2-(4-thyomethyl- phenyl)-4,4,5,5-tetramethyl imidazoline-1-

oxyl-3-oxide, NITSMe. This radical, whose structure is shown in Figure 1, crystallises in the monoclinic system, $P2_1/a$ space group with the following lattice parameters: a = 9.437(2), b = 19.827(2), c = 8.516(2) Å, β = 113.66(1)°, Z = 4.[13]

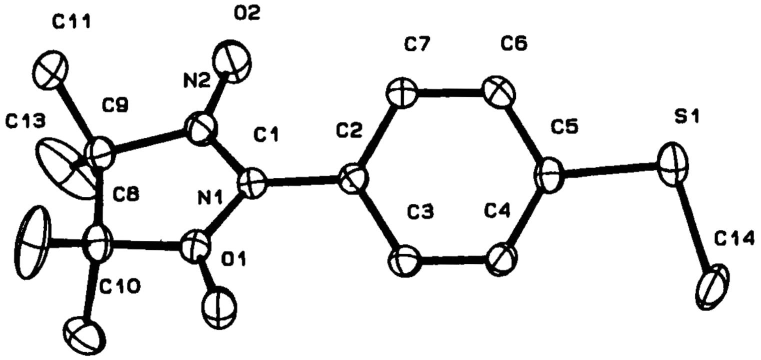


FIGURE 1 ORTEP view of the asymmetric unit of NITSMe.

The intramolecular bond lengths compare well with those reported[14-18] for other substituted phenyl nitronyl nitroxides and the angle between the five membered ring and the phenyl ring is 32.2(2)°, because the repulsion between the N-bonded oxygen and the aromatic hydrogen atoms, as found for similar nitronyl nitroxide radicals,[14-18] prevents the nitronyl nitroxide group from being coplanar with the phenyl ring. It is important to notice that the S1-C5 bond, 1.765(4) Å, is about 35 pm shorter than that expected for a single carbon-sulphur bond; this can be justified by a partial delocalization of the unpaired electron which leads to write a resonance formula with a double bond connecting S and C5. At the same time the bond length of the sulfur atom with the methyl group is longer of 40 pm of the normal value.

The relative orientations of the molecule in the unit cell allow to individuate a plane formed by the stacking of the five membered rings, almost parallel to each other along the *a* axis. The shortest intermolecular contacts relevant to the magnetic properties of NITSMe are those involving the NO group of a molecule and the C3 and C4 phenyl atoms, see Figure 2,
of the molecules related by glide planes (x+1/2; y-1/2, z and x-1/2, y-1/2, z); they range between 3.7 and 4 Å. This kind of contacts is the origin of ferromagnetic interactions in other nitronyl nitroxide radicals.[19-20] The ferromagnetic interactions were attributed to overlap between the positive spin density of the NO group of one molecule and the spin density of opposite sign of the benzene carbon atoms of another one. In NITSMe such kind of contacts give rise to a two dimensional network of ferromagnetic

interactions, while a 3D one is required in order to observe bulk magnetic ordering. The shortest contact between different planes occurs between the sulfur atom and a methyl group of an imidazoline ring belonging to a radical molecule of an adjacent plane, ranging between 4.3 and 4.6 Å.

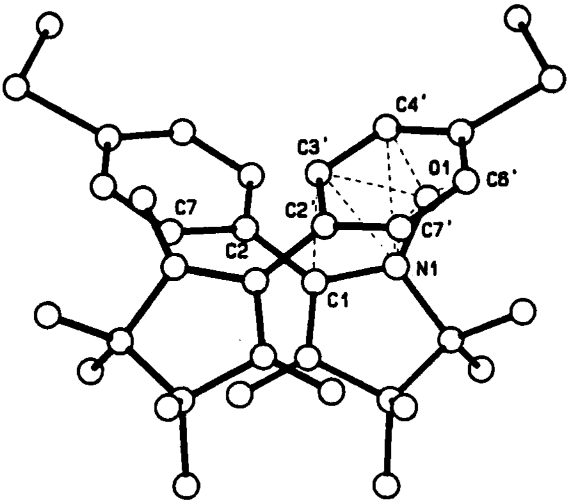


FIGURE 2 Short intermolecular distances between molecules of NITSMe related by the glide plane x+1/2, y+1/2, z.

NITSMe shows ferromagnetic interactions[21] at low temperature that give rise to magnetic order at 0.2 K, as shown by the divergence of χ' and correspondingly by the onset of χ'' as reported in Figure 3. The fit of the susceptibility data according to a square planar Heisenberg model of S=1/2 coupled spins with correction due to the inter-planes interaction,[22] yield the following parameters: J=-0.35 K (in plane) and J=-0.042 K (inter-planes). Since the dipolar energy calculated for the ordered system in the easy ferromagnetic configuration is very low, 0.004 cm^{-1}, the magnetic transition must be driven by the inter-plane interaction given by the contact of the sulfur atom with the methyl carbon atom of the imidazoline ring. Simple Extended Hückel calculations have shown[21] that the HOMO orbital in NITSMe has a large electronic density both on the NO group and the sulfur atom and that an important magnetic density should be induced on the sulfur atom. Experiments of polarised neutron diffraction performed on similar nitronyl nitroxide radicals,[23-24] namely NITPh, NITpPy and IMPh, see also Figure 4, show the presence of a sizeable positive spin density on the methyl carbons of the imidazoline ring. The same mechanism of spin polarisation observed for intraplanar interaction must be operative: the interaction between the two spin densities of opposite sign gives rise to the ferromagnetic interplanar coupling

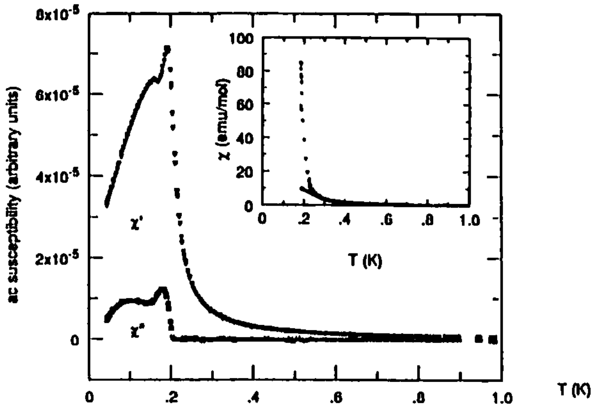


FIGURE 3 Real (χ') and imaginary (χ'') ac susceptibility for NITSMe. In the inset M/H vs. T data for H = 4 and 288 Oe.

responsible of the ferromagnetic phase transition experimentally observed. Molecules like NITSMe seem to be promising to obtain higher T_C for magnetic transition because the presence of a diffuse electronic cloud on the sulphur atom allow sufficiently strong ferromagnetic interactions even at long distances.

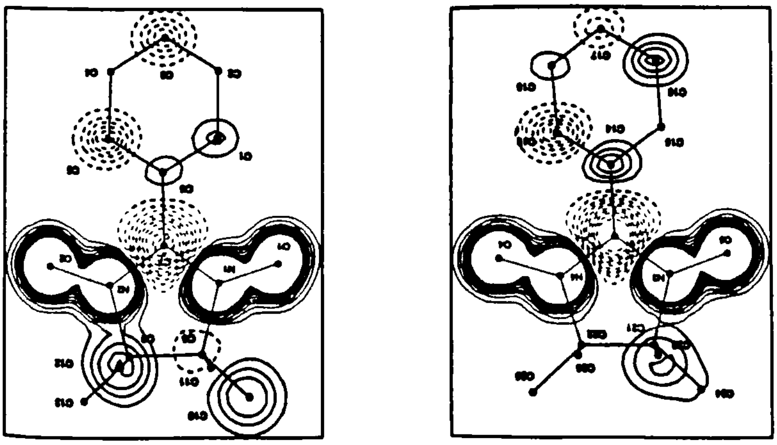


FIGURE 4 Spin density maps for the NITPh radical.

The nitronyl nitroxide radical family has been subject of study not only for its own magnetic properties but also for the ability to act as ligands that, due to the equivalence of the two NO positions, can easily transmit the magnetic interaction through the ONCNO atoms sequence.[10,25] The co-ordination modes of NITR which can originate extended structure are shown in Figure 5. Among them particularly well investigated are systems of the (a) type where radicals and metal ions regularly alternate in linear chains. A large series of compounds of formula $M(hfac)_2NITR$ (where hfac= hexafluoroacetylacetonate) have been

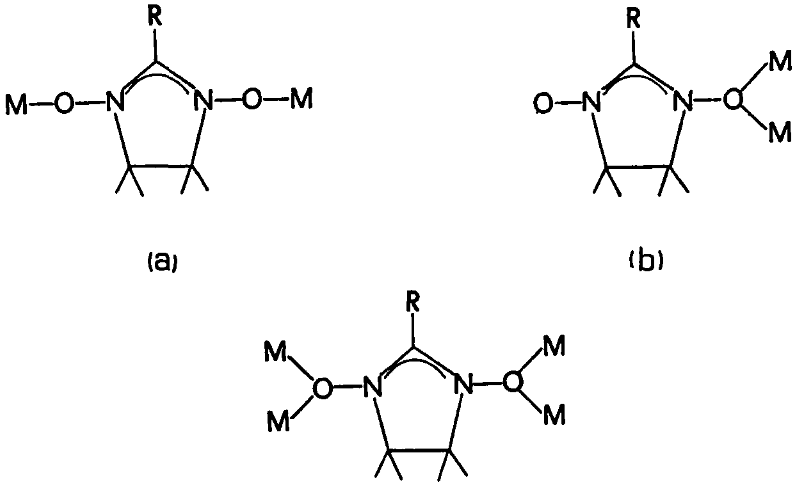


FIGURE 5 Possible coordination ways for the NITR radical family.

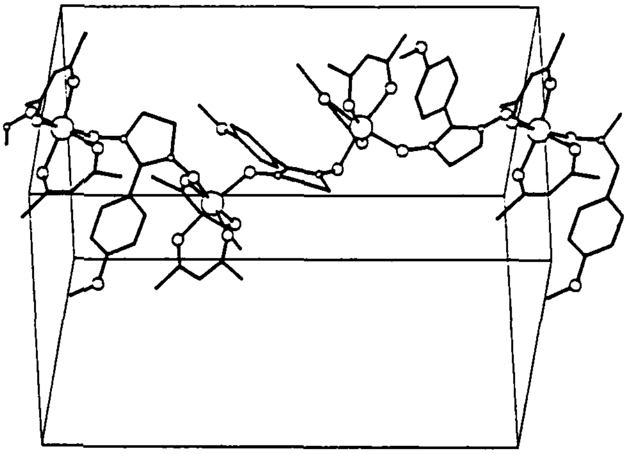


FIGURE 6 Simplified PLUTO view of the unit cell of $Mn(hfac)_2NITPhOMe$.

reported.[10,25] Some of them proved to be ideal examples of one-dimensional magnetic materials like ideal Heisenberg antiferromagnets, when M=Zn(II),[26] ferromagnets, when M=Cu(II),[27-29] and ferrimagnets, for M=Co(II),[30] Ni(II),[30] Mn(II).[31-33] In particular we would like to describe hereafter the study performed on the Mn(hfac)$_2$NITPhOMe compound,[34] where NITPhOMe = 2-(4'-methoxyphenyl)-4,4,5,5-tetramethyl imidazoline-1-oxyl-3-oxide. This compound has the structure shown in Figure 6; the NITPhOMe radical co-ordinates in cis-position two different Mn(II) ions forming in this way a trigonal helix. The variation of χT as function of the temperature is reported in Figure 7. It increases from a room temperature value of 5.5 emu mol^{-1} K, higher than expected for uncorrelated spins, 4.75 emu mol^{-1} K, monotonically to low temperature where, after an abrupt increase in the region of 20 K, it reaches a value as high as 260 emu mol^{-1} K. Due to the antiferromagnetic nature of the coupling interactions the absence of a minimum in the χT curve is indicative of a J value higher then 92 cm^{-1}.[35] The behavior was satisfactorily reproduced using the formulae

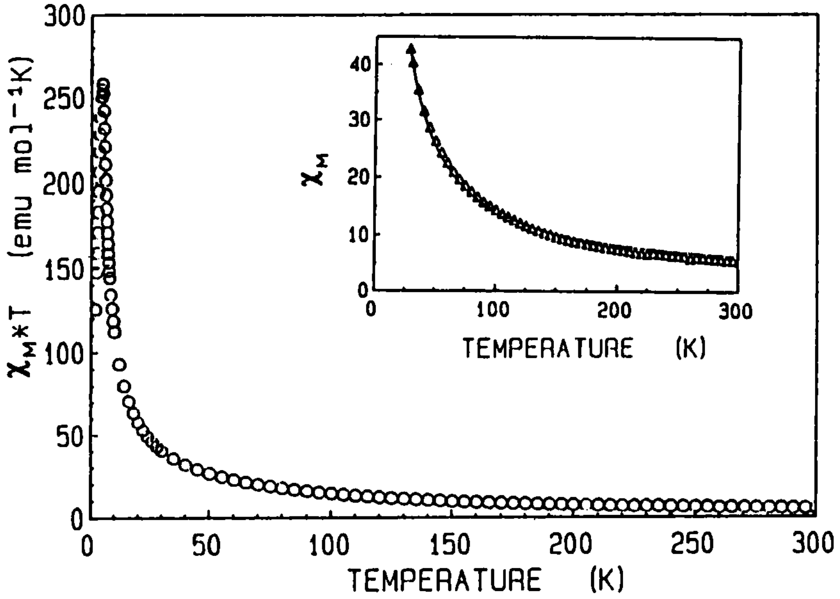


FIGURE 7 Temperature dependence of the product of the χT for Mn(hfac)$_2$ NITPhOMe. In the inset are reported the calculated values with the best fit parameters, J = -344 cm^{-1}.

for Heisenberg chains[36] with an antiferromagnetic exchange constant J = 344(1) cm^{-1} and g = 2. The Hamiltonian being defined as $\mathbf{H} = J\Sigma S_i \cdot S_{i-1}$. The material undergoes a magnetic phase transition at 5.5 K as suggested by the divergence of χ' and the onset of χ'' reported in Figure 8. The bulk ferrimagnetic order is not the only appealing property from a "technological" point of view. In fact due to the low symmetry of the molecule and to its crystallisation in the acentric $P3_1$ space group the compound is optically active. Moreover the presence of electron donor (O-Me) and electron acceptor (NIT) substituents on the phenyl ring, gives a large electrical polarizability to the molecule, and the compound posses a sizeable non-linear optical activity. The Second Harmonic Generation activity of $Mn(hfac)_2NITPhOMe$ was measured and was found[16] to be about one hundredth of that of m-nitroaniline. Although it is not very large it indicates that molecular magnets can show the coexistence of properties which usually are not observed in one material.

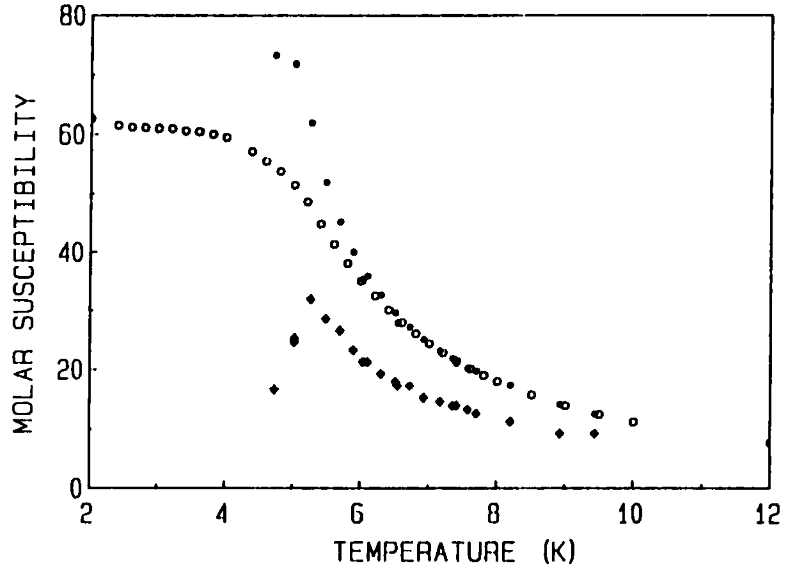


FIGURE 8 Magnetic susceptibility for $Mn(hfac)_2NITPhOMe$: (○) susceptibility measured in 100 Oe external field; (●) real part of the ac susceptibility measured at 333 Hz and zero static filed; (◆) imaginary part of the ac susceptibility.

Nitronyl nitroxides radicals can bind also trivalent rare earth ions forming linear chains.[38-43] In particular a few compounds of formula $RE(hfac)_3$, where RE = Eu(III),[37,41] Gd(III),[37,38,40,41] Yb(III), Ho(III), Dy(III),[39] Er(III), and R = Ph, Me, Et, iPr, nPr, were synthesised and characterised. Linear chain compounds containing

Y(III)[41] or Eu(III),[37,42] , which structure is shown in Figure 9, can be used to test the magnetic interactions between two radicals connected by a non-magnetic rare earth ion. Figure 10 shows χ vs.T behavior for $Y(hfac)_3NITEt$. The presence of a maximum in the χ curve suggests the antiferromagnetic nature of the interaction between the radicals. The best fit using the expression valid for Heisenberg S=1/2 chains gives a J value of 4.51 cm^{-1} with g = 2.01. It can be expected that the antiferromagnetic super exchange mechanism responsible for the coupling of the radicals in these compounds is present also in the chain compounds with magnetic metal ions.

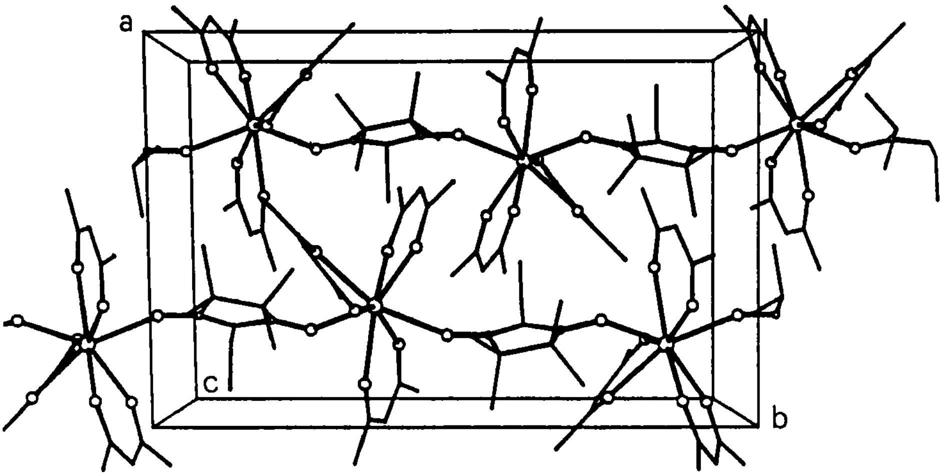


FIGURE 9 PLUTO view of $Eu(hfac)_3NITEt$. Fluorine atoms are omitted for the sake of clarity.

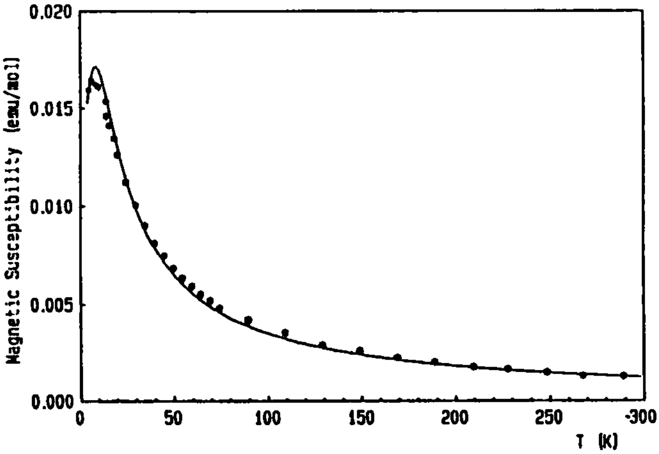


FIGURE 10 χ vs. T for $Y(hfac)_3NITEt$. Fit parameters are reported in the text.

In order to check the kind of interaction to be expected between the radical and rare earth ions we studied another test compound, namely $Gd(hfac)_3(NITEt)_2$,[43-45]. The magnetic properties are reported in Figure 11 in the form χT vs. T. A global ferromagnetic interaction is clearly observed. It is attributed to the interaction between the unpaired electrons of the two radicals and the seven unpaired electrons of the Gd(III) ion. The model to reproduce the magnetic data uses a Hamiltonian of the type $H = J(S_{Gd}S_{rad1} + S_{rad2}S_{Gd}) + J'S_{rad1}S_{rad2}$. The cluster of three spins has been considered symmetric because gadolinium-radical distances are very similar to each other (232.7(5) and 233.7(5) pm respectively) and also the metal-oxygen-nitrogen angles, which have been found to have large influence on the magnetic coupling,[10] are very close to each other (141.1(2)° and 144.6(2)° respectively). The best fit value was obtained with g = 2.049(2), J = -0.50(4) and J' = 4.3 cm^{-1}. The mechanism we propose for this interaction is shown in th e following scheme. We can imagine that the electron of the radical is transferred in the *s* or *d* empty orbitals of the rare earth, and here it polarises, according to the Hund's rule, the electrons of the more internal *f* orbitals in a ferromagnetic way, giving rise to the experimental behavior observed.

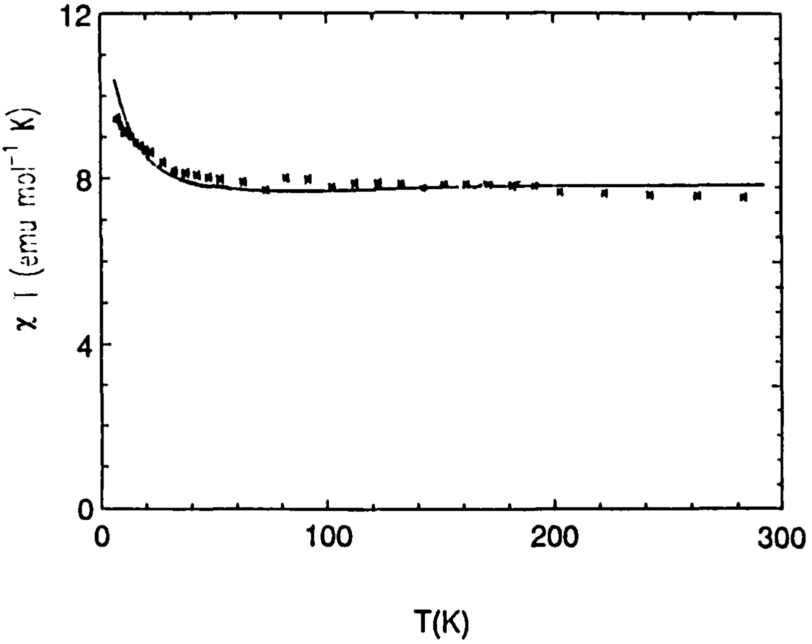
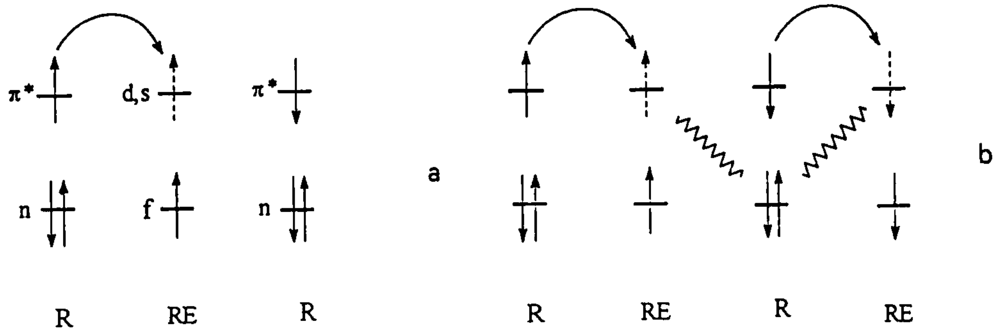


FIGURE 11 χT vs. T for $Gd(hfac)_3NITEt_2$.



Moving to the chains three limit behaviors are expected for dominant nearest neighbor, nn, interactions. In the limit of no interaction a Curie behavior is expected, while ferro- or ferrimagnetic chains will form for ferro- or antiferromagnetic coupling respectively. The analysis of complexes containing only one Gd(III) ion and two radicals described before showed that the nn coupling is ferromagnetic, suggesting that ferromagnetic chain should form. However the four χT curves shown in Figure 12 corresponding to Gd(hfac)$_3$NITR

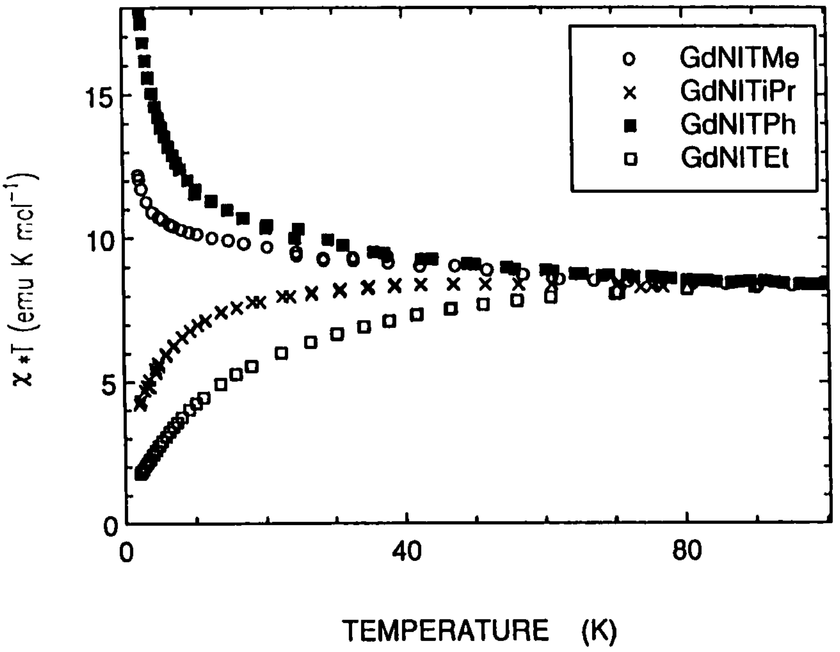


FIGURE 12 χT vs. T variation observed for Gd(hfac)$_3$NITR compounds chains, with R = Me, Et, Ph; iPr, do not agree with this prediction In fact only when R=Me or Ph, χT increases on decreasing the temperature, in qualitative agreement with a ferromagnetic chain, while when R = Et or iPr χT decreases on decreasing the temperature, like in antiferromagnetic chains. Moreover no large differences are present in the structures, shown in Figure 13, to justify the differences in the χT behavior.

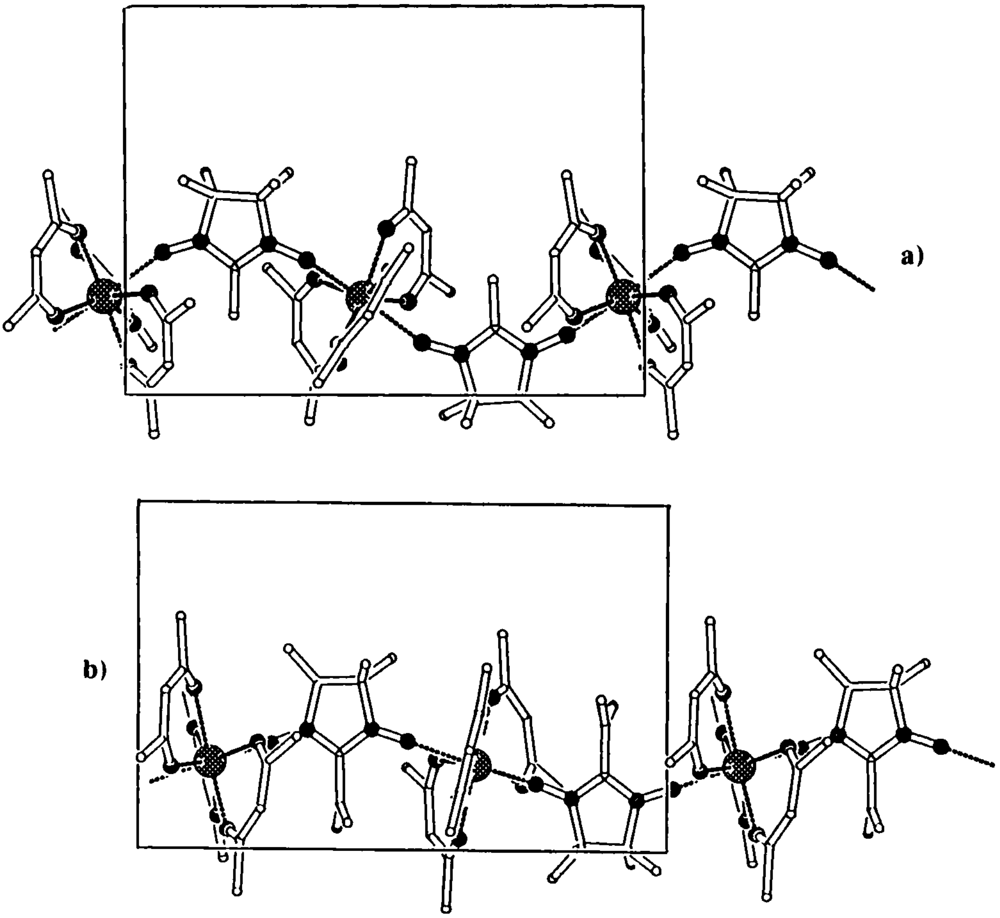
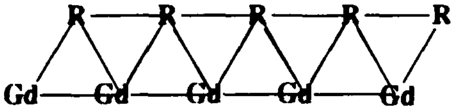


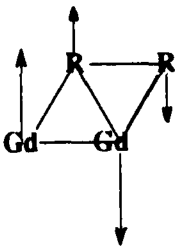
FIGURE 13 Simplified view of a) $Gd(hfac)_3NITMe$ and b) $Gd(hfac)_3NITiPr$ compounds.

The presence of antiferromagnetic interactions between radicals through the rare earth is not sufficient to justify the observed overall antiferromagnetic behavior of $Gd(hfac)_3NITEt$ and $Gd(hfac)_3NITiPr$. Also an antiferromagnetic nnn interaction between gadolinium ions has to be operative and the proposed mechanism for it is reported in part b of the precedent scheme. In the excited state that is responsible of the exchange mechanism the unpaired electron of the radical is transferred in the s or d orbitals of the rare earth and the radical behaves like a normal dimagnetic ligand connecting paramagnetic centres which can interact through the standard super exchange mechanism, being now the electronic cloud of the rare earth ions much more spread around. Except for accidental orthogonality this interaction is expected to be antiferromagnetic in nature. The electronic properties of the nitronyl-nitroxide radicals surely play a fundamental role as such long distance nnn interactions have not been observed in similar chain compounds where the S=1/2 that alternates with the rare earth is that of copper(II).[46]

The introduction of antiferromagnetic nnn interactions in the chains has the consequence of introducing spin frustration in the system because the gadolinium and radical spins are under the conflicting influence of antiferromagnetic interactions as often observed in triangular spin topologies.[47] In fact from the point of view of the magnetic interactions the system can be described as the chain of triangles schematised below. It is easy to realise that not all the interactions can be satisfied simultaneously.



In qualitative terms we may assume that frustration is relieved in the case of dominant nnn interaction, if the spins on the gadolinium and on the radical orient as show below in such



a way that only one of the two nn ferromagnetic interactions and both the antiferromagnetic nnn ones are satisfied. We can describe the ground state of the chain as a two-spins up two-spins down spin arrangement which is globally antiferromagnetic, in qualitative agreement with one of the two of the observed sets of data. The actual preferred spin orientation will depend on the relative values of the nearest and next nearest interactions therefore all the possibilities comprised between the ferromagnetic and the antiferromagnetic chain limits are available.

Quantitative calculations were performed with the standard formula for ferromagnetic linear chains[48] with only nn interaction for the two sets of data showing the increase of the χT value, R= Me and Ph, but no acceptable agreement with the experimental data was found. Better results were obtained for compounds where R = Et or iPr, the two sets of data showing a monotonic decrease of χT on decreasing temperature, with the assumption that the nn interaction is zero. In this case the system is idealised as two independent antiferromagnetic chains of radicals and gadolinium ions respectively. Reasonable agreement was found with $J_{Gd\text{-}Gd} = 0.5\ cm^{-1}$ and $J_{rad\text{-}rad} = 10\ cm^{-1}$.

A better level of approximation can be reached considering the spins as Ising spins even if this is not a very good approximation due to the isotropic nature of the spins of the radical and the gadolinium ion. This treatment has the advantage of simplicity and can provide some semiquantitative informations about the system whose thermodynamic properties were calculated using the transfer matrix calculation formalism.[49] The Ising model confirmed the two-spin up and two-spin down ground state and produced reasonable fit of the χT values.

A further improvement of the approximation is achieved treating the spins as XY spins, within the transfer matrix formalism again. The spins are classical planar rotators in the XY plane, perpendicular to the chain direction. According to this model the preferred spin orientation corresponds to a helix along the structural direction of the chain. The relevant parameters for expressing the type of magnetic ordering expected for the system are: $\delta = |J_{Gd\text{-}Gd}|S^2(J_{Gd\text{-}rad}\ S\ s)$, $\delta' = |J_{rad\text{-}rad}|S^2(J_{Gd\text{-}rad}\ S\ s)$, $\cos\theta = 1/2(\delta + \delta')$ where S and s are the values of the spin of the gadolinium and radical respectively, θ is the angle between adjacent spins. Low values of θ calculated for Me and Ph derivatives, mean less frustrated system and lead to an increase of the χT value while high value of θ are indicative of high degree of frustration and as a consequence, the χT value is calculated to decrease on decreasing temperature. Good fits were obtained for all the four systems. In Figure 14 we report the results for the Et derivative.

These systems allowed us to test for the first time the Harada's prediction, which assumes significant contribution of "chiral" domain walls to the thermodynamic properties of a magnetic chain with competing exchange interactions.[51-52] In fact Harada proposed that

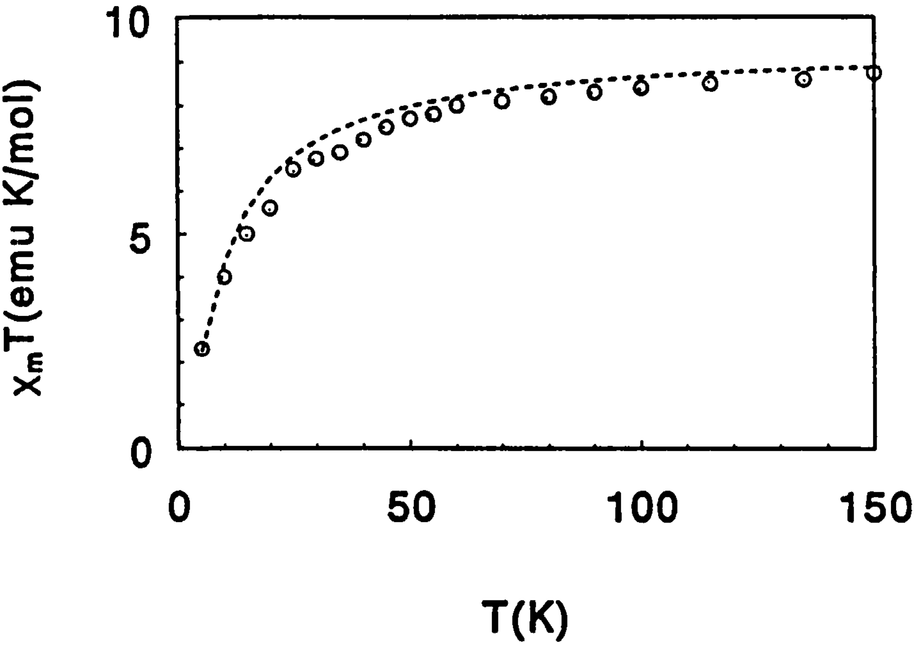


FIGURE 14 Fit of the χT data for Gd(hfac)$_3$NITEt chain using ther following parameters: $J_{Gd\text{-}rad}$ = 1 cm^{-1}, $J_{Gd\text{-}Gd}$ = -0.5 cm^{-1}, $J_{rad\text{-}rad}$ = -10 cm^{-1}, by using numerical transfer matrix calculation formalism.

the competition between nn ferromagnetic coupling and nnn antiferromagnetic coupling can produce a helical phase, whose two fold degeneracy, the clock-wise and counter-clock-wise turns of spins along the chain direction, leads to the excitation of topologically stable chiral domain walls separating two domains of opposite chirality. Up to now other compounds with such competitive interactions were available but did not possess all the requirements requested by the theory to get helical short range order, i.e. a sufficiently high ratio between nnn and nn exchange couplings, a very weak uniaxial anisotropy, and a very weak interchain interaction. We have measured the specific heat, via adiabatic low-temperature calorimetry, for the four compounds in the range 0.2-5 K, Figure 15. In this range of temperature the magnetic contribution is expected to be dominating over the lattice one. The two compounds with weak frustration, R = Me or Ph, show a λ-type anomaly around 0.6 K, indicating the onset of three dimensional long range order, in close agreement with the low temperature susceptibility data that show, with both dc and ac magnetic measurements, the presence of a ferromagnetic phase transition. The two compounds with strong frustration, R = Et or iPr, present small peaks centred around 2 K. It is impossible to believe that the two compounds undergo a 3D phase transition at such a high temperature because it will require a too strong interchain interaction and, as a definitive proof, no indications of transition are present in the ac and dc measurements. So the peaks observed could be attributed to the excitation of chiral domain walls, separating two domains of opposite chirality. Numerical transfer matrix calculations of the thermodynamic properties, i.e. magnetic susceptibility and magnetic specific heat, of these one dimensional magnets with spins S=7/2 and s=1/2 alternating along the chain and with competing nn ferromagnetic interactions and nnn antiferromagnetic interaction were performed and the results are in agreement with the experimental data.[53] Also for the two systems with low frustration, chiral domain walls can contribute to the magnetic specific heat but the related peaks should be centred at very low temperature, since the excitation energy of a wall decrees with decreasing δ and δ', but in the real system, i.e. the two compound with R=Me and Ph, the peaks due to non-linear excitation can be covered by the 3D λ-type anomaly.

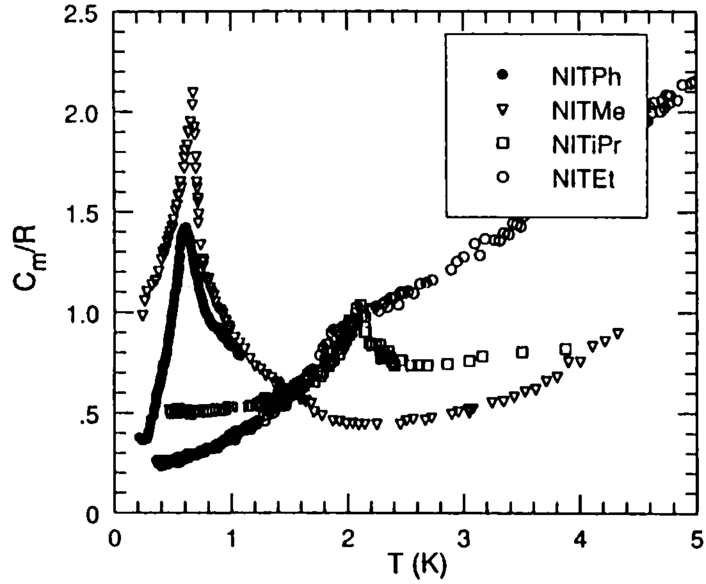


FIGURE 15 Measure of the specific heat, via adiabatic low temperature calorimetry for the Gd(hfac)$_3$NITR compounds.

In the field of molecular magnetism the stable nitronyl-nitroxide radicals have played a key role providing the first example of pure organic ferromagnetism.[12] The selected examples we have reported give an idea of the richness of magnetic behaviors that can be encountered by exploiting the coordination capability of these radicals. The number of radicals or radical containing compounds being synthesised is increasing very fast, however some field are still almost unexplored as, for instance, that of the magneto-optical properties of these compounds. In fact, even if the molecular magnetic materials here described are not candidate to substitute the traditional ones based on metals or metal oxides, more sophisticated devices can in principle be designed by exploiting the association of bulk magnetism with the richness variety of chemical and physical properties of the radicals.

ACKNOWLEDGEMENT

Thanks are due to A. Rettori of the Department of Physic of the University of Florence, Italy, and M.G. Pini, I.E.Q.-C.N.R., Florence, Italy, for theoretical calculation performed on rare earths linear chains, to J. Bartolomè and F. Bartolomè of the I.C.M. de Aragon, CSIC Universidad de Zaragoza, Spain, for performing low temperature calorimetry measurements, and C. Paulsen C.N.R.S., C.R.T.B.T., Grenoble, France, for low temperature magnetic measurements. Finacial support by the E.C. program Human Capital and Mobility through contract ERBCHRXDCT920080 "Magnetic Molecular Materials" and from the C.N.R., Italy are gratefully acknowledged.

REFERENCES

1. J. Veciana, J. Ciruieda, C. Rovira, J. Vidal-Gancedo, Adv. Mater., 7, 221, (1995).
2. F.L. Pratt, R. Valladares, J. Caulfield, I. Deckers, J. Singleton, A.J. Fisher, W. Hayes, M. Kurmoo, P. Day, T. Sugano, Synth. Metals, 61, 171 (1993).
3. K. Awaga, T. Inabe, Y. Maruyama, Chem. Phys. Lett., 190, 349 (1992).
4. K. Awaga, T. Inabe, Y. Maruyama, T. Nakamura, M. Matsumoto, Chem. Phys. Lett., 195, 21 (1992).
5. T. Sugano, M. Tamura, M. Kinoshita, Y. Sakai, Y. Okashi, Chem. Phys. Lett., 200, 235 (1992).
6. P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama, M. Kinoshita, Chem. Phys. Lett., 190, 349 (1992).
7. K. Inoue, H. Iwamura, Chem. Phys. Lett., 207, 551 (1993).

8. Molecular Magnetic Materials edited by D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio (Kluwer Academic, Dordrecht, The Netherlands, 1991).
9. Mol Cryst. Liq. Cryst. Special Issue, 232-233, edited by H. Iwamura, J. S. Miller, 332, (1993).
10. A. Caneschi, D. Gatteschi, P. Rey, Progr. Inorg. Chem., 39, 331 (1991).
11. A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli, J. Am. Chem. Soc., 111, 785 (1989).
12. a)M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi, M. Kinoshita, Chem. Phys. Lett., 186, 401 (1991); b) Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, K. Kinoshita, M. Ishikawa, Phys. Rev. B, 46, 8906 (1992).
13. A. Caneschi, F. Ferraro, D. Gatteschi, A. le Lirzin, E. Rentschler, Inorg. Chim. Acta, in press.
14. W. Wong, S.F. Watkins, J. Chem. Soc. Chem. Commun., 888 (1973).
15. A. Caneschi, D. Gatteschi, A. le Lirzin, J. Mater. Chem., 4(2), 319 (1994).
16. L. Angeloni, A. Caneschi, L. David, A.C. Fabretti, F. Ferraro, D. Gatteschi, A. le Lirzin, R. Sessoli, J. Mater. Chem., 4(7), 1047 (1994).
17. A. Caneschi, D. Gatteschi, E. Rentschler, R. Sessoli, Gazz. Chim. Ital., 125, 283 (1995).
18. W.R. Blackmore, S.C. Abrahams, Acta Cryst., 8, 329 (1955)
19. K. Yamaguchi, M. Okumura, J. Maki, T. Noro, H. Namimoto, M. Nakano, T. Fueno, Chem. Phys. Lett., 190, 353 (1992).
20. K. Yamaguchi, M. Okumura, M. Nakano, Chem. Phys. Lett, 191, 237 (1992).
21. A. Caneschi, F. Ferraro, D. Gatteschi, A. Le Lirzin, M. Novak, E. Rentschler; R. Sessoli, Adv. Mater., 7(5), 476 (1995).
22. The Hamiltonians for each couple of nearest neighbor spins are $H = JS_i \cdots S_j$ and $H = J'S_i \cdots S_k$, respectively for spins in the same and adjacent planes.
23. G.W. Neely, G.C. Hatch, R.W. Hreiligk, J. Am. Chem. Soc., 96, 652 (1974).
24. A. Zhuledev, V. Barone, M. Bonnet, B. Delly, A. Grand, E. Ressouche, P. Rey, R. Subra, J. Schweizer, J. Am. Chem. Soc., 116, 2019 (1994).
25. A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, Acc. Chem. Res, 22, 392 (1989).
26. A. Caneschi, D. Gatteschi, R. Sessoli, C.I. Cabello, P. Rey, A.L. Barra, L.C. Brunel, Inorg. Chem., 30, 1882 (1991).
27. C.I. Cabello, R.L. Carlin, A. Caneschi, D. Gatteschi, P. Rey, R. Sessoli, Inorg. Chem., 29, 2582 (1990).
28. A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, J. Am. Chem. Soc., 109, 2191 (1987).
29. A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, C.I. Cabello, J. Mater. Chem., 2, 1283 (1992).
30. A. Caneschi, D. Gatteschi, J.P. Renard,P. Rey, R. Sessoli, Inorg. Chem., 28, 2940 (1989).
31. A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli, Inorg. Chem., 28, 3314 (1989).
32. A. Caneschi, D. Gatteschi, P. Rey, R. Sessoli, Inorg. Chem., 27, 1756 (1988).
33. A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli, Inorg. Chem., 28, 1976 (1989).
34. A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, Inorg. Chem., 30, 3162 (1991).
35. A. Glisez, M. Verdaguer, J. Am. Chem. Soc., 106, 3727 (1984).

36. J. Seiden, J. Phys. Lettrs (Paris), 44, L947 (1964).
37. C. Benelli, A. Caneschi. D. Gatteschi, R. Sessoli, Inorg. Chem., 32; 4797 (1993).
38. C. Benelli, A. Caneschi. D. Gatteschi, R. Sessoli, J. Appl. Phys., 73, 5333 (1993).
39. C. Benelli, A. Caneschi. D. Gatteschi, R. Sessoli, Adv. Mater., 4, 504 (1992).
40. C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, Inorg. Chem., 29, 4223 (1990).
41. C. Benelli, A. Caneschi, D. Gatteschi, P. Rey, L. Pardi, Inorg. Chem., 28, 3230 (1989).
42. C. Benelli, A. Caneschi, D. Gatteschi, P. Rey, L. Pardi, Inorg. Chem., 28, 275 (1989).
43. C. Benelli, A. Caneschi, A.C. Fabretti, D. Gatteschi, L. Pardi, Inorg. Chem., 29, 4253 (1990).
44. C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, D.P. Shum, R.L. Carlin, Inorg. Chem., 28, 272 (1989).
45. C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, Angew. Chem. Int. Ed. Engl., 26, 913 (1987).
46. a) O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batail, M. Guillot, Inorg. Chem., 31, 110 (1992); b) O. Guillou, O. Kahn, K. Boubekeur, P. Batail, Angew. Chem. Int. Ed. Engl., 31, 626 (1992).
47. J. Vannimenus, G. Toulouse, J. Phys. C: Solid State Phys., 10, L537 (1977).
48. J.C. Bonner, M.E. Fisher, Phys. Rev., A135, 646 (1964).
49. M.G. Pini, A. Rettori, Phys. Rev. B., 48, 3240 (1993).
50. C. Benelli, D. Gatteschi, R. Sessoli, A. Rettori, M.G. Pini, F. Bartolomè, J. Bartolomè, J. Magn. Magn. Mat., 140-144, 1649 (1995).
51. I. Harada, J. Phys. Soc. Jpn., 53, 1643 (1984).
52. I. Harada, H.-J. Mikeska, Z. Phys. B-Condensed Matter, 72, 391 (1988).
53. C. Benelli, D. Gatteschi, R. Sessoli, A. Caneschi, A. Rettori, M.G. Pini, F. Bartolomè, J. Bartolomè, C. Paulsen, in preparation.