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Magnetism in Florence

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CONTENTS

ABBREVIATIONS

amoxa	*N*,*N'*-(2-aminomethyl)-2-(methylpropyl)oxamidate
ATP	adenosine-5'-triphosphate
bipy	2,2'-bipyridine
bz	benzoate
CTH	dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaxacyclotetradecane
DTBSQ	3,5-di-*tert*-butyl-*o*-semiquinone
en	ethylenediamine
F_3bzac	benzoyltrifluoroacetylacetonate
hapen	*N*,*N'*-ethylenebis(*o*-hydroxyacetophenoniminato)
hfac	hexafluoroacetylacetonate
Hiz	imidazole
IMHR	1-hydroxy-2-R-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole
IMMe	2-methyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy
IMPh	2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy
IMR	2-R-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy
iz	imidazolate
$Me_3[12]N_3$	2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene

napy	1,8-naphthyridine
NITEt	2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITiPr	2-i-propyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITMe	2-methyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITnPr	2-*n*-propyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NIToPy	2-2′-pyridyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITPh	2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITPhOMe	2-4′-metoxyphenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITpPy	2-4′-pyridyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide
NITR	2-R-4,4,5,5-tetramethyl-dihydro-1H-imidazol-1-oxy-3-oxide
oxal	oxalate
oxam	oxamate
pba	propylene-1,3-bis oxamato
phen	1,10-phenanthroline
PROXYL	2,2,4,4-tetramethyl-pyrrolinyl-1-oxy
py-NO	pyridine-*N*-oxide
quin	quinoline
SALen	*N*,*N*′-ethylenebis(salicylideneiminato)
SALMe	*N*-methyl-salicylideneiminate
SALMedpt	bis[3-(salicylideneimino)propyl]methylamine
SALtn	*N*,*N*′-1,3-propylenebis(salicylaldiminato)
Satn	*N*-(3-aminopropyl)salicylaldiminato
TCCat	3,4,5,6-tetrachlorocatecolate
TCSQ	3,4,5,6-tetrachlorosemiquinone
TEMPO	2,2,6,6-tetramethyl-piperidinyl-1-oxy
TEMPOL	2,2,6,6-tetramethyl-piperidinyl-1-oxy-4-hydroxy
tetren	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
tren	tris(2-aminoethyl)amine

A. INTRODUCTION

When Barry Lever and Ivano Bertini asked us to contribute to the special issue of *Coordination Chemistry Reviews*, dedicated to Professor Luigi Sacconi on the occasion of his 80th birthday, we thought it was a good idea to review briefly the main achievements of Sacconi and his school in the field of magnetochemistry. In fact, one of the features of the Florence school of inorganic chemistry is the keen interest in the magnetic properties of metal complexes. We well remember our first steps in research under the guidance of Sacconi when the first question he put to use whenever we took to him some new compound was: "what is the magnetic moment?" Sacconi feels himself very much a magnetochemist, and the main books on the shelf in his laboratory were Selwood's *Magnetochemistry* [1] and Bhatnagar and Mathur's *Physical Principles and Applications of Magnetochemistry* [2]. He had himself assembled the Gouy balance used in the laboratory when we started, and which could perform measurements down to liquid nitrogen temperature. Much later, he assembled the newer Faraday balance apparatus, taking advantage of an extended visit of Professor Brian Figgis to Florence.

Inevitably Sacconi's magnetochemical background has largely influenced our own research, as will be shown by this article, and has ultimately determined our interest in molecular-based magnetic materials. It has also had a big influence on the bioinorganic chemistry interest of Bertini and collaborators and in general on the subsequent achievements of all his former students and pupils.

This article is intended to be a tribute to Sacconi as a magnetochemist, reviewing his early and later achievements in this area, and making mention of our subsequent results in this field in order to testify to the continuity of the school.

B. THE ORIGINS

The origin of Sacconi's interest in the magnetic properties of coordination compounds stems from Pauling's magnetic criterion of bond character. The first paper he published in which magnetic moments are reported appeared [3] in the Bulletin of the Accademia Nazionale dei Lincei, the most prestigious Italian academy, in 1949. It is a note in Italian which was presented by Prof. V. Caglioti, who would have been Sacconi's mentor. The title is *Ricerche magnetiche su alcuni complessi dell'uranio(IV) a numero di coordinazione otto* (Magnetic investigation on some eight coordinated uranium(IV) complexes) and it reports the magnetic moments of some β-diketonates. The measurements were performed with a Bhatnagar interferometer balance. Evidence was found that all the compounds had two unpaired electrons. The interest in the magnetic measurements lay in the controversy, which at that time was still open, on the electronic configuration of uranium(IV). In fact, the original assumption of the $6s^2 6p^2 6d^2$ configuration had been rejected in favour of a $5f^2 6s^2 6p^6$ configuration. The magnetic data, which showed the presence of two unpaired electrons, were interpreted as evidence in favour of the latter configuration.

Among Sacconi's first papers are those reporting investigations on molybdenum blue where magnetic measurements are coupled to the determination of electrical conductivity [4,5]. From the very beginning, the tendency of Sacconi to couple synthetic work with sophisticated physico-chemical techniques appears clear.

In 1954, Cini and Sacconi published details on an apparatus for the accurate measurements of magnetic susceptibility [6], which was mainly used for diamagnetic substances. In particular accurate measurements on a series of alcohols allowed the authors to obtain the diamagnetic susceptibility of the CH_2 groups [7].

At the same time, Sacconi used magnetic measurements as important tools in order to obtain structural and bonding information on various series of transition metal complexes [8]. In particular, the first reports on Schiff base complexes were published in 1952 [9,10]. The interest in this class of compounds must have had its origin in the florentine tradition where Schiff operated between 1853 and 1915, the date of his death.

C. COORDINATION CHEMISTRY AND MAGNETISM

The end of the 1950s corresponds to the dramatic development of coordination chemistry, and Sacconi enters the fight for the understanding of the anomalous behaviour of the magnetic moments of nickel(II) salicylaldiminates. In the background is the choice of the proper theoretical model for the description of the bonding in nickel(II) complexes. According to Pauling's valence bond scheme, the paramagnetic complexes, either tetrahedral or octahedral, are ionic, while the diamagnetic complexes are square planar and covalent.

At that time, it was well known that the diamagnetic bis(*N*-methylsalicylaldiminato) nickel(II) becomes paramagnetic when dissolved in non-coordinating solvents such as benzene or chloroform [11]. The starting hypothesis of the presence of a spin-equilibrium between a diamagnetic square planar form and a paramagnetic tetrahedral form was ruled out on the basis of experimental evidence such as the presence of paramagnetism in the melt and the concentration and temperature dependence of the effective magnetic moment in solution. The magnetic behaviour was attributed to an association mechanism leading to a polymeric structure where the nickel(II) ions are in an octahedral environment [12].

On the other hand, working on other derivatives of the salicylaldimines, where different substituents were introduced in different positions in the aromatic ring, Sacconi was able to obtain the definitive evidence, based on magnetic and spectrophotometric measurements and X-ray analysis, that the main equilibrium was between a tetrahedral and a planar form, even if a further equilibrium with associated forms is sometimes present [13]. The influence of the nature of the substituent, the temperature, and of the concentration on the diamagnetic/paramagnetic species equilibrium was also explored [14]. A similar study was also performed on the analogous copper(II) derivatives, showing a greater tendency of this metal ion to assume a tetrahedral structure [15].

Another relevant contribution of Sacconi's group to classical coordination chemistry was the study of five coordination. When this research project started, very few five-coordinated complexes had been reported and among them high-spin derivatives were quite rare: the *N*-(methylsalicylaldiminato)cobalt(II) complex, described by Sacconi and coworkers in 1965, was the first high-spin cobalt complex whose five coordination was confirmed by a complete X-ray analysis [16,17].

This achievement was the starting point for a systematic analysis of all the factors which determine the chemical and physical properties of the compounds exhibiting this peculiar coordination number. By using ligands specifically designed to favour five coordination, a wide series of 3d derivatives was synthesized with a large variety of donor atoms sets and coordination geometry varying smoothly from trigonal bipyramidal to square pyramidal. Particular attention was devoted to determine the magnetic behaviour of the complexes: the analysis of their magnetism by means of the crystal field model [18] allowed the establishment of clear correlations between the nature of the ligand atoms, geometrical features, and the spin ground states of the 3d five-coordinated complexes [19].

D. SPIN EQUILIBRIA

Sacconi always showed interest in the magnetic properties of complexes exhibiting spin equilibria [20], although he did not publish many examples of such behaviour. An interesting example of genuine spin equilibrium is that presented by the bis-(isothiocyanato)[*N*-(2-(diphenylphosphino)ethyl)-*N'*,*N'*-diethylethylendiamine]-cobalt(II) complex, whose magnetic moment varies smoothly from 2.16 μ_B at 79 K to 4.32 μ_B at 418 K. A careful analysis of the temperature dependence of magnetic susceptibility, EPR spectra and crystal structure excluded the presence of an intermediate spin state and showed, therefore, that the magnetic behaviour is due to a disordered spin state [21].

Beyond this, Sacconi worked out some simple rules in order to predict the spin state of cobalt(II) and nickel(II) complexes in various coordination geometries [22], and also to determine the conditions under which spin equilibria might occur [20].

E. PARAMAGNETIC NMR

The development of paramagnetic NMR in Florence is well documented by the contributions of Bertini et al., Luchinat et al., and Scozzafava et al. in this issue; therefore only a brief mention will be made here. The first paper of the Florence group in this area was a collaboration with J.D. Thwaites on the spectra of high-spin nickel(II) complexes with Schiff bases, members of the series of five-coordinate complexes which at that time were in the forefront of research on transition metal complexes [23].

Our interest in this area came later and we reported some of the first examples of NMR spectra of dinuclear paramagnetic metal complexes, where we noticed the effect of the presence of a fast-relaxing metal ion which allowed recording the spectra of protons close to slow-relaxing metal ions, which otherwise would have been too broad to be detected. We also suggested that this technique might be useful in the investigation of the environment of metallo-proteins. Indeed, this was a good prophecy [24].

The last developments in this area, beyond bioinorganic chemistry, are associated with the investigation of single crystals of one-dimensional molecular ferrimagnets. In this case, NMR provided unique information on the spin dynamics and on the extent of magnetic interaction between neighbouring chains in the solid state [25].

F. EPR

The origin of the development of EPR spectroscopy in Florence is associated with the studies on ligand field spectra of copper(II) complexes, namely on complexes with geometries intermediate between square planar and tetrahedral, and pseudo-octahedral Jahn–Teller distorted chromophores.

The former line was later extended to the investigation of the properties of chromophores with geometries intermediate between square pyramidal and trigonal bipyramidal [26]. In fact, in this case, it was shown that EPR is an extremely powerful tool for monitoring the distortion of copper(II) complexes from the ideal geometries appropriate to five coordination. The idea beyond this useful correlation is extremely simple and is best described by referring to the reference frame described in Fig. 1.

The transition from a square pyramid to a trigonal bipyramid is performed by moving two ligands which are trans to each other, varying the α angle from 90° to 120°. The ground state in square pyramidal geometry is described as x^2-y^2, and the g values are expected to be $g_z > g_x, g_y > 2.00$. The ground state in trigonal bipyramidal geometry is described as a linear combination of x^2-y^2 and z^2, and the g values are expected to be g_z, $g_y > g_x \approx 2.00$. Since, in both limiting geometries, g_z does not vary significantly and g_x typically varies from 2.08 to 2.00, the g most sensitive to distortions is g_x, as shown in Fig. 2. This value is therefore a sensitive probe of the coordination environment around copper(II) in five-coordinate geometries [26].

Among the Jahn–Teller distorted copper(II) chromophores in the 1970s,

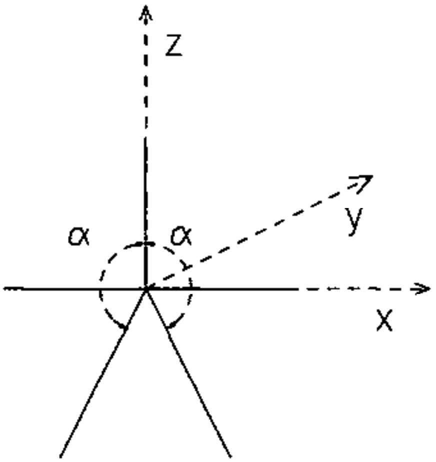


Fig. 1. Reference frame for pentacoordinate copper(II) complexes.

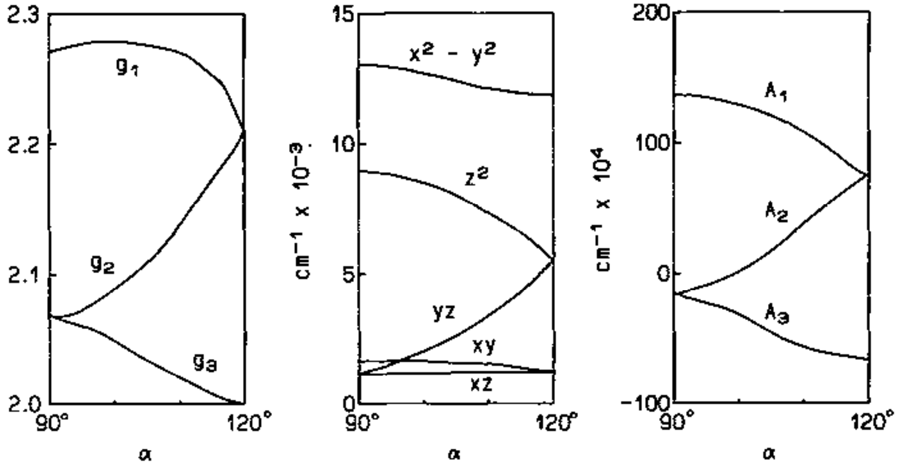


Fig. 2. Energy level diagram for the C_{2v} five-coordinate copper(II) complexes as a function of the α angle (see text); g and A dependence on the angle α (from left to right).

$K_2PbCu(NO_2)_6$ [27] and $Cu(en)_3SO_4$ [28] were extremely interesting because, crystallizing with T_h and D_3 site symmetry, respectively, they seemed to contradict the Jahn–Teller theorem. However, single crystal polarized electronic and EPR spectra showed that copper(II) indeed undergoes the usual elongated octahedral distortion, and that the high symmetry observed in the room-temperature X-ray crystal structure determination is actually the result of a dynamic averaging of three distorted coordinations.

One of the characteristics of the EPR investigations performed in Florence is that of using magnetically non-dilute compounds. The basis of this method was the idea that dilution in a diamagnetic host might change the geometrical parameters around the metal ion, thus making correlations between structure and properties associated with the electronic structure of the metal ions more difficult. Of course the use of magnetically non-dilute compounds destroys much information contained in the EPR spectra of magnetically dilute ones. However, it provides useful information about intermolecular exchange: for instance, it became clear how, in many cases, wrong assignments had been made of the coordination environments of copper(II) complexes on the basis of EPR spectra of magnetically non-dilute solids which provided $g_\perp > g_\parallel$, but with the latter larger than 2.00. This situation generally occurs with intermolecular exchange, which averages the true molecular $g_\perp$ and $g_\parallel$ values of antiferrodistortively ordered octahedra, as shown in Fig. 3 [29].

The other main theme in EPR spectroscopy is that of high-spin cobalt(II). High-spin cobalt(II) generally has rather fast electronic relaxation rates at room temperature in all the possible coordination environments. As a consequence, EPR spectra can be observed generally only in the liquid helium temperature range, a fact which made high-spin cobalt(II) difficult to investigate before low temperatures

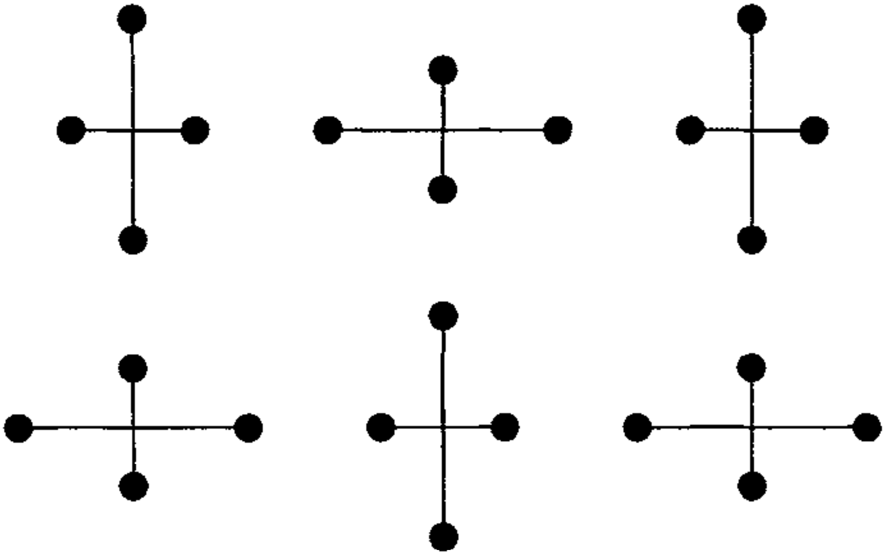


Fig. 3. Antiferrodistortive arrangement of tetragonally distorted six-coordinated chromophores. The other two bonds are orthogonal to the plane.

became available to chemical laboratories. In fact, when we started our systematic investigations of the EPR spectra of high-spin cobalt(II) complexes, very few chromophores had been investigated. In practice, not much more than the pioneering works of Abragam and Pryce on octahedral chromophores was available [30].

We investigated high-spin cobalt(II) chromophores in different coordination geometries [31–40], always associating EPR and electronic spectra, and calculating the energy levels with an angular overlap approach [41], which took into account low symmetry effects. The main results of these investigations, beyond realizing how sensitive cobalt(II) is to low symmetry effects, is that the EPR spectra can be used to provide unequivocal evidence of a given coordination environment only in special cases. In fact, for the purpose of classification, the cobalt(II) complexes can be divided into two classes, the octahedral and square pyramidal on one side, and the tetrahedral and trigonal bipyramidal on the other. The former have orbitally degenerate, while the latter have orbitally non-degenerate ground states. As a consequence, the spectra of the latter tend to be "normal", either with $g_{\parallel} \approx 2$ and $g_{\perp} \approx 4$, or $g_{\parallel} \approx 6$, $g_{\perp} \approx 0$, while those of the latter show large deviations from these limits [42].

G. OLIGONUCLEAR COMPLEXES

The work performed on dinuclear complexes has been essentially aimed at understanding the relation between the spin Hamiltonian parameters of the pairs, compared with those of the individual metal ions. This work has been performed on homo- and hetero-nuclear pairs, the latter corresponding either to isolated complexes or to species diluted into lattices of homonuclear pairs [43,44].

One of the first purposes of the investigation of the EPR spectra of these pairs was that of establishing the relationships between the spin Hamiltonian parameters of the ion pairs and those of the individual ions. Assuming that the isotropic exchange term is dominant on anisotropic terms in the spin Hamiltonian, these relations are easily found and our group in Florence extensively studied these predictions [45–47]. It was indeed found that, whenever the real systems conform to the conditions required by the theoretical treatment, the spin Hamiltonian parameters are linear combinations of those of the individual ions. The use of heteronuclear pairs has been extremely useful in this respect. In fact, while the g values of the pair for homonuclear pairs are expected to be identical to the g value of the single ion, for heteronuclear pairs the **g** tensor of the pair is indeed a linear combination of the **g** tensors of the two ions. In particular, the g values can be algebraically summed, and a **g** tensor can occur with a plus or a minus sign. In this way, consistent deviations from the values observed for single ions can be observed. In this respect, copper(II)–manganese(II) pairs are extremely illuminating. In fact, the two states which can originate from their interactions, $S=2$ or $S=3$, have g values of

$$g_3=(4/5)g_{\mathrm{Mn}}+(1/5)g_{\mathrm{Cu}}$$

$$g_2=(6/5)g_{\mathrm{Mn}}-(1/5)g_{\mathrm{Cu}}$$

High-spin manganese(II) is expected to have an isotropic $g\approx 2.00$, while copper(II) has an anisotropic g, larger than 2.00. As a consequence, g_2 is expected to be smaller than 2.00, not as a result of spin–orbit coupling, but as a result of the antiparallel alignment of the copper(II) and manganese(II) spins. This is exactly what has been observed in a few cases [48–50].

Once the method was found to work well, it became possible to use the relationships between spin Hamiltonian parameters of the pairs and of the individual ions in order to obtain the spin Hamiltonian parameters of ions which cannot easily be obtained in a direct way. For instance, nickel(II) is generally a very difficult ion to observe in an EPR experiment, due to unfavourable spin lattice electronic relaxation, and/or to large zero field splitting. However, when nickel(II) is coupled to copper(II), the pair has an odd number of electrons and the EPR spectra become generally observable. By measuring the **g** tensors of the pairs and obtaining independent information on the **g** tensor of copper, for instance by recording the spectra of copper(II)–zinc(II) pairs, it is possible to calculate the **g** tensors of nickel(II). Some of the results are summarised in Table 1. It is apparent that, when the nickel(II) ions are in octahedral or square pyramidal geometries, the calculated **g** tensors are close to those expected on the basis of ligand field theory, but in the case of trigonal bipyramidal coordination, the calculated **g** tensors are too large. Corrections are needed when the zero field splitting is not negligible compared with the isotropic

TABLE 1

g values for nickel(II) complexes derived from EPR spectra of Cu–Ni pairs

Chromophore	Coord. Geom.	g_1	g_2	g_3	Ref.
NiO_4N_2	Octahedral	2.18	2.20	2.21	54
NiN_4O_2	Octahedral	2.16	2.17	2.21	55
NiO_4O_2	Octahedral	2.20	2.24	2.24	56
NiO_4O_2	Octahedral	2.26	2.26	2.26	57
NiN_2O_2Cl	Sq. Pyram.	2.12	2.32	2.38	58
NiO_2Cl_2O	Sq. Pyram.	2.17	2.36	2.48	59
NiN_3O_2	Trig. Bipyr.	2.06	2.09	2.61	60

exchange contribution, and/or orbital degeneracy is still present in the ground state [51–53]. This is a point which is still largely overlooked when spectra of pairs, or of larger aggregates, are taken into consideration.

Although in this short resume' we have now focused on the **g** tensors, similar relationships also hold for the hyperfine (or superhyperfine) tensors. EPR data have also been used to check these relations, but NMR is the technique providing the most stringent test because the signs of the hyperfine tensors can then be easily obtained.

The other fundamental parameter in the EPR pair spectra is the zero field splitting tensor, **D**. This is certainly much more difficult to analyze than the **g** or **A** tensors, because it has several different contributions present. In fact, if the individual ions have $S > 1/2$, they have individual zero field splitting tensors, which contribute to **D** according to rules similar to those previously discussed for **g** and **A**. Further, in this case there is also a contribution which is associated with the interaction, which has no counterpart with the latter. This interaction-determined zero field splitting, which is present even with two $S = 1/2$ spins, is on its own given by the sum of two contributions, one associated with exchange, and the other with dipolar interaction. Both contributions are theoretically expected to be present, but they cannot be separated one from the other except on the basis of some model.

In the literature, it has been customary to estimate the order of magnitude of the exchange-determined contribution with the Moriya formula [61]

$$D \propto \frac{\Delta g^2}{gJ}$$

where Δg is the deviation of the g value of one ion from the free electron value. This equation was obtained with a second-order perturbation treatment taking into account the admixture of excited states into the orbitally non-degenerate state ground state via spin–orbit coupling. However, it assumes that the exchange interaction between one ion in the ground state and the other in the excited state is the same as the interaction between the two ions in the ground state. We have shown, through extensive experimental work, that this assumption is completely untenable for ions such as copper(II) which have sizeable spin–orbit coupling [62–69].

In fact, analysis of the zero field splitting tensors of a series of dinuclear copper(II) complexes of the general structure shown schematically in Fig. 4 provided the following conclusions: (a) the principal axis of the zero field splitting tensor is *not* parallel to the copper–copper direction, as would be expected for dominant dipolar interaction, but parallel to the highest g value, as expected for dominant exchange interaction; (b) the value of the zero field splitting is not proportional to J, as predicted by the simple Moriya formula. In fact, a good correlation was found by assuming that the zero field splitting parameter D for a dinuclear complex of geometry shown in Fig. 4 can be expressed as [69]

$$D_{\mathrm{ex}}^{zz}=\frac{(g_{\parallel}-g_e)^2 J_{x^2-y^2,xy}}{2}$$

$$D_{\mathrm{ex}}^{xx}=\frac{(g_{\perp}-g_e)^2 J_{x^2-y^2,yz}}{2};\quad D_{\mathrm{ex}}^{yy}=\frac{(g_{\perp}-g_e)^2 J_{x^2-y^2,xz}}{2}$$

where $J_{x^2-y^2,xy}$, $J_{x^2-y^2,yz}$, and $J_{x^2-y^2,xz}$ are the exchange coupling constants relative to the interaction between one ion in the ground x^2-y^2 orbital and the other ion in an excited state, to be compared with J, which is relative to the interaction between the two ions with one unpaired electron in the ground x^2-y^2 orbital. When this is taken into account, a nice correlation is found between the copper–copper distances in di-μ-oxo bridged complexes and D_{ex}^{zz}, as shown in Fig. 5.

In the early days, a method was suggested to relate the exchange interaction with the angular overlap parameters of the two interacting metal ions [70]. The advantage of this method, in principle, is that of relating the metal–metal interaction to the spectroscopic parameters of the two metal ions. More sophisticated approaches

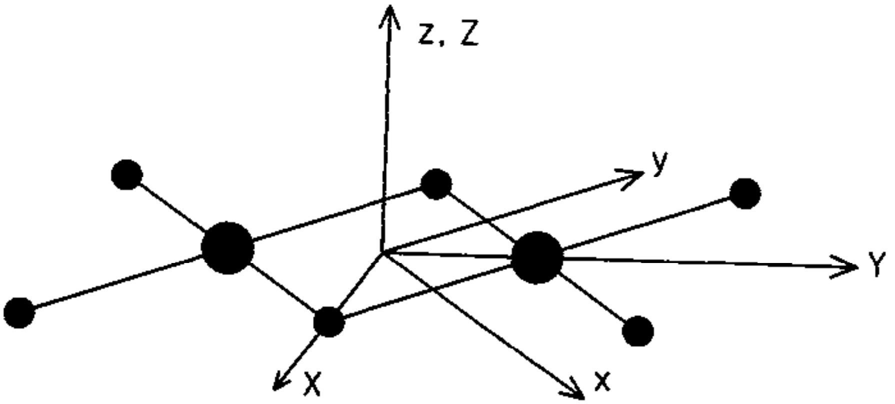


Fig. 4. Orientation of the principal axes of the **D** (X, Y, Z) and **g** (x, y, z) tensors in square planar copper(II) dimers.

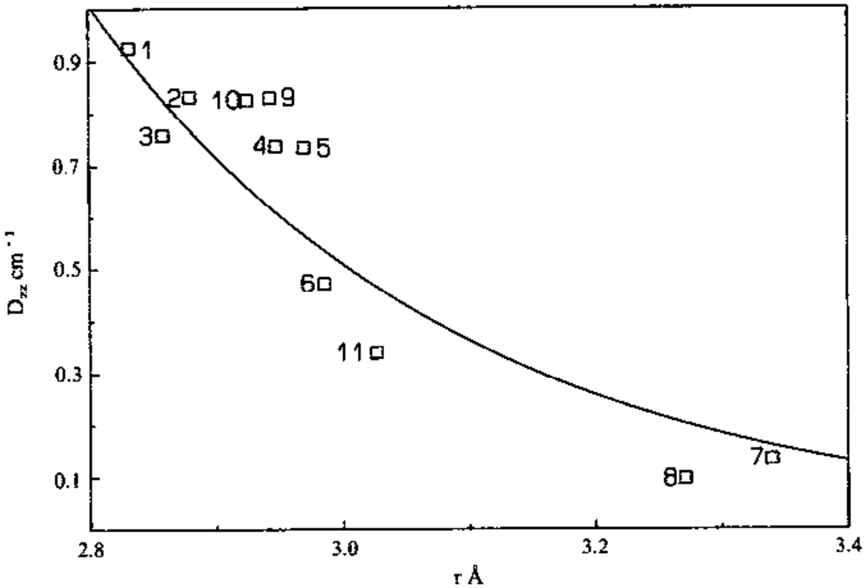


Fig. 5. $\mathbf{D}_{zz}$ exchange values vs. copper–copper distance with the calculated curve for exponential regression for the following compounds: (1) $(\mu\text{-OH})_2(\text{bipy})_2\text{Cu(II)}(\text{NO}_3)_2$ [75]; (2) $(\mu\text{-OH})_2[(\text{bipy})\text{Cu(II)}]_2$sulphate-pentahydrate [76]; (3) $(\mu\text{-OH})_2[(\text{bipy})\text{Cu(II)}]_2(\text{ClO}_4)_2$ [77]; (4) $(\mu\text{-OH})_2\text{-}[(\text{tetren})\text{Cu(II)}]_2(\text{ClO}_4)_2$ [78]; (5) $(\mu\text{-OH})_2[(\text{tetren})\text{Cu(II)}]_2(\text{ClO}_4)_2$ [79]; (6) $(\mu\text{-OH})_2[(2\text{-methylimidazole})_2\text{Cu(II)}]_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2$ [80]; (7) $(\mu\text{-py-N-O})_2[(\text{py-N-O})\text{Cl}_2\text{Cu(II)}]_2$ [81]; (8) $(\mu\text{-py-N-O})_2[\text{Cl}_2(\text{H}_2\text{O})\text{Cu(II)}]_2$ [82]; (9) dipiperidinium bis-[(μ-methoxo)bis(2,4-dinitrophenolato)Cu(II)]-2-methanol [83]; (10) dipiperidinium bis[(μ-methoxo)bi-(2,4-dinitrophenolato)-Cu(II) [83]; (11) bis[μ-2-(diethylamino)ethanolato]$\text{Br}_2\text{Cu(II)}$ [84].

have been used, employing the SW Xα method within a broken symmetry scheme. In this way, the exchange coupling constants of the $\text{Cu}_2\text{Cl}_6^{4-}$ dimers have been calculated and satisfactorily compared with experiment [71]. Applications of these methods are reviewed by Bencini et al. in this issue.

Finally, a remarkable example of a mixed valence dinuclear complex is provided by $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^+$ whose structure [72] is shown in Fig. 6. Formally it contains a nickel(II) and a nickel(I), i.e. two magnetic ions. The magnetic and EPR properties indicate a ground $S=3/2$ state with no evidence of thermal population of excited states, even at room temperature. Parallel alignment of the two unpaired electrons of nickel(II) and of the electron of nickel(I) is therefore achieved. Although ferromagnetic coupling cannot be excluded, it is more probable that double exchange [73] is operative in this compound.

Double exchange can be classified as a spin polarization mechanism associated with electron transfer. In fact, when one electron moves from nickel(I) to nickel(II) it is forced to be spin-down as sketched in Fig. 7. This mechanism has acquired noteworthy importance in recent years when a similar mechanism has been advocated for justifying the magnetic properties of iron–sulphur proteins [74]. $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^+$ has become the archetypal model for double exchange.

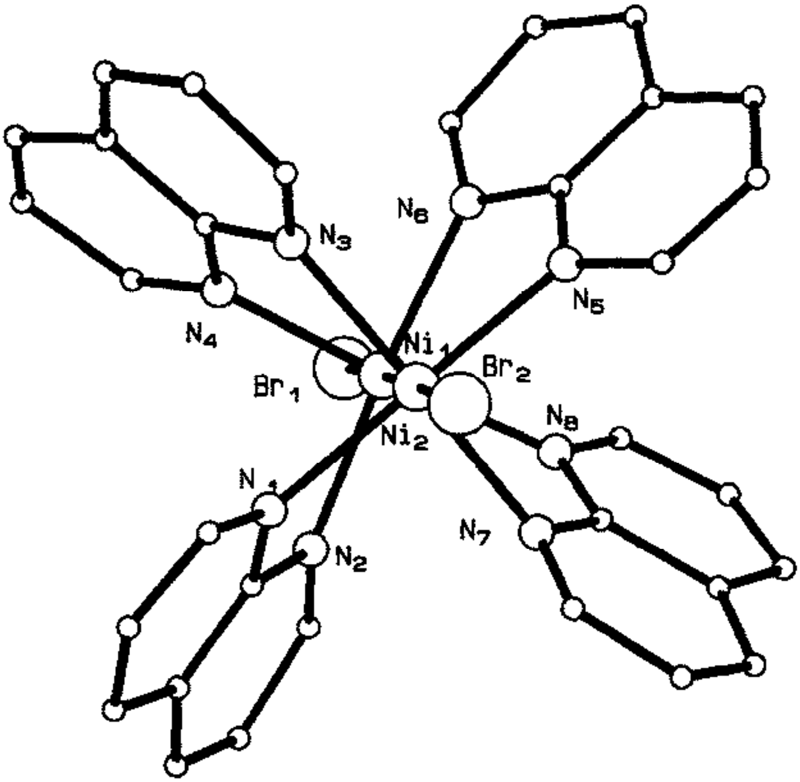


Fig. 6. PLUTO view of the $[Ni_2(napy)_4Br]^+$ cation.

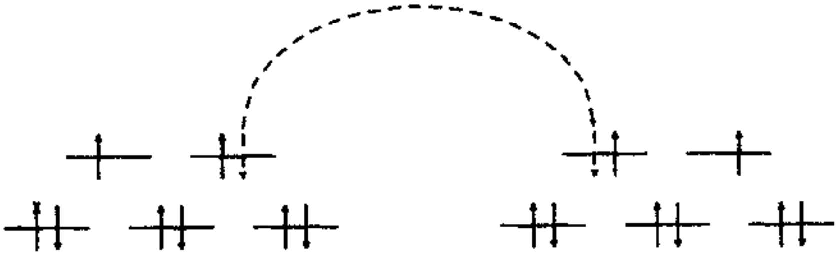


Fig. 7. Electron transfer in a d^8–d^9 pair.

H. MAGNETIC MATERIALS

The last developments in the investigation of the magnetic properties of compounds based on metal complexes in Florence is directed toward the design and synthesis of bulk magnetic materials. To this aim, some work on model systems has been performed to identify the most suitable building blocks to form a three-dimensional ferro- or ferri-magnet. This research is in line for the development of molecular-based materials, which are understood as possible candidates for a new generation of materials for which the techniques of molecular chemistry can be employed to fine tune the properties [85].

A necessary preliminary step to assemble a bulk ferromagnet is that of understanding the conditions under which two spins can interact with each other to give preferential parallel spin alignment. We have found several examples of ferromagnetic coupling between the spins, and they are collected in Table 2 [86–95]. More examples will be provided in the next section on lanthanide ions.

The ferromagnetic coupling observed in the complexes containing Cu–VO and Cu–Ni pairs is easily justified on the basis of the orthogonality between the σ and π orbitals of the metal ions [96]. In fact, in the Cu–VO case, the copper unpaired electron is in a x^2-y^2 orbital and that of vanadium is in an xy orbital [86]; in the Cu–Ni case, nickel is octahedral while copper is tetrahedral, with consequent mismatch of the magnetic orbitals. Ferromagnetic coupling was also observed in copper–nickel pairs obtained by doping copper benzoate, a compound with the well-known copper acetate-type structure. In that case, the observed coupling was justified on the basis of the orthogonality of the nickel z^2 and copper x^2-y^2 orbitals, which should be enough to more than compensate the antiferromagnetic coupling between the x^2-y^2 orbitals [87].

The most spectacular results, however, are observed when the metal ions are bound directly to stable organic radicals acting as ligands. The radicals actually used are shown in Fig. 8. In some cases, the ferromagnetic coupling is so large that the spin clusters are in the ground state at room temperature with no evidence of population of excited states, so that only a lower limit to the value of J can be given [90,94,97,98]. Again, the conditions under which ferromagnetic coupling can be established are easily understood: the magnetic orbitals on the metal ions must be orthogonal to the π orbitals of the radicals. This, of course, can occur when the π

TABLE 2

Exchange constants for some ferromagnetic coupled compounds

Compounds	J[a]	Ref.
Cu–VO–Cu	$\simeq 90$	86
$(Ni,Cu)(bz)_2(quin)_2$	$\simeq 20$	87
$[Cu(ATP)(bipy)]_2$	0.15	88
$Ni(CTH)CuCl_4$	$\simeq 70$	89
$[Ni(CTH)DTBSQ]PF_6$	>300	90
$[Cu(Me_3[12]N_3)(TCCat)]$	140	91
$Cu(hfac)_2TEMPOL$	13	92
$Cu(hfac)_2NITMe$	25.7	93
$Cu(hfac)_2IMPh$	400	94
$Mn(hfac)_2NITpPy$	1	95

[a] In cm^{-1}. In the fitting procedure the spin Hamiltonian $H = JS_1S_2$ was used.

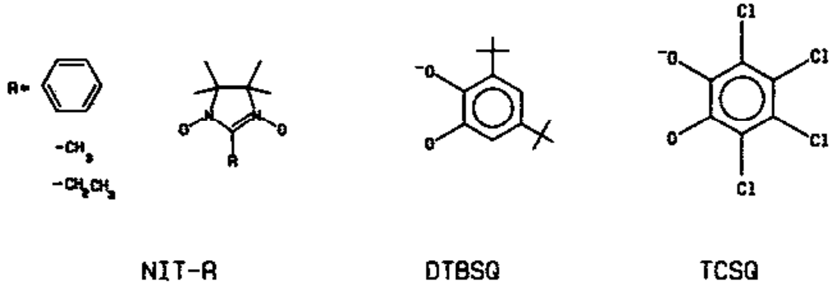


Fig. 8. Stable organic radicals used as paramagnetic ligands towards 3d and 4f ions.

orbitals of the radical are not directly involved in the bonding with the metal ion [90].

The very weak ferromagnetic coupling observed between manganese(II) and NITpPy when the radical is bound to the metal ion through its pyridine nitrogen atom should be discussed. Since the unpaired spin density on the radical is essentially localized on the two NO groups, the coupling observed in this case must be determined by a spin polarization mechanism. Similar considerations will be required to justify the coupling with lanthanide ions [95,143].

The presence of ferromagnetic coupling is necessary to assemble a ferromagnet; however it is possible to assemble a ferrimagnet by using individual building blocks which are antiferromagnetically coupled, but have different individual magnetic moments. Again, these conditions can easily be met when either two different types of metal ion or a metal ion and an organic radical are brought into interaction. In Table 3 we survey the principal types of antiferromagnetic coupling we have observed in bimetallic and in metal–radical pairs.

We have particularly concentrated on metal–radical systems to obtain extended structures, which eventually order magnetically at low temperatures. The principal classes of magnetic materials so obtained are summarized in Table 4 [119–130].

It is apparent that a great variety of different materials can be obtained. In fact, if the metal ions are diamagnetic, both antiferro- and ferro-magnetic chains have been reported [119,120]. More complex behaviour is observed when the metal ions are paramagnetic: with copper, ferromagnetic chains are observed with NITR radicals, while with TEMPOL, alternating ferro–antiferromagnetic chains were reported [92,124]. Complex antiferromagnetic behaviour was observed with $CuCl_2NITPh_2$, where the three spins in the formula unit are antiferromagnetically coupled, leaving one unpaired electron. Further coupling through the radicals forms one-dimensional antiferromagnets [130].

Perhaps the most interesting compounds are the one-dimensional ferrimagnets formed by NITR radicals with manganese(II), cobalt(II), and nickel(II) salts [123–127].

The $Mn(hfac)_2NITR$ system is the most thoroughly investigated. These materi-

TABLE 3

Exchange constants in some antiferromagnetically coupled complexes

Compounds	$-J^a$	Ref.
[NaVOSALen]BPh$_4$	0.15	99
Cr(CTH)TCSQ	>500	100
{MnCTHCu(bpa)}(CF$_3$SO$_3$)$_2$	36.6	101
[Mn(F$_3$bzac)NITMe]$_2$	142	102
Mn(hfac)$_2$(TEMPO)$_2$	154	103
Mn(hfac)$_2$(PROXYL)$_2$	210	104
Mn(hfac)$_2$(NITPh)$_2$	180	105
Mn(hfac)$_2$(NITiPr)$_2$	330	106
Mn(hfac)$_2$(NITMe)$_2$	187	105
Mn(hfac)$_2$NITEt	260	107
Mn(hfac)$_2$NITnPr	260	107
Ni(CTH)MnCl$_4$	1.2	89
Ni(benzoate)$_2$(quinoline)$_2$	250	86
Ni(hfac)$_2$(NITPh)$_2$	≃400	108
Ni(hfac)$_2$(NITEt)$_2$	300	109
Ni(hfac)$_2$(PROXYL)$_2$	400	103
[Co$_2$(tren)$_2$OH](ClO$_4$)$_3$	38	110
CoSALMe	9.8	111
[Cu(SALMedpt)Cu(hfac)$_2$]$_2$	6.6	112
[Cu$_2$(phen)$_2$(oxam)](NO$_3$)$_2$	400	113
[Cu$_2$(phen)$_2$(oxal)](NO$_3$)$_2$	330	113
Cu(iz)$_2$(Hiz)$_8$(ClO$_4$)$_4$	117	114
CuCl(iz)(Hiz)$_2$	84	115
Cu$_2$(amoxa)(Cu$_3$COO)$_2$	431.7	116
[Cu(hfac)$_2$]$_3$(NITEt)$_2$	>500	117
Cu(hfac)$_2$NITPh	>500	118

[a] In cm^{-1}. In the fitting procedure, the spin Hamiltonian $H = JS_1S_2$ was used.

als order magnetically in the range 4–8 K, as a consequence of dipolar coupling between the chains. At high temperature, the magnetic resonance spectra are textbook examples of one-dimensional behaviour, which shows up in the EPR (magic angle behaviour of the linewidth, lineshape intermediate between Lorentzian and Gaussian, *g*-shifts) and in the NMR (relaxation rate proportional to the inverse square root of the resonating frequency) [25,131].

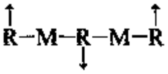
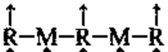
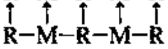
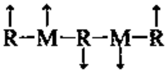
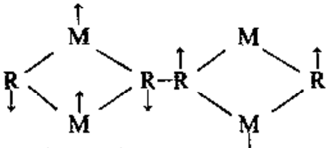
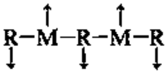
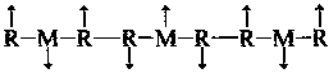
Mn(hfac)$_2$NITPhOMe has the unusual helix structure shown in Fig. 9, which provides it with optical activity and second-order non-linear optical activity [131].

I. LANTHANIDE COMPLEXES AND MATERIALS

In developing our research on molecular magnetic materials, we could not avoid using systems containing rare-earths, even though the 4f elements have never

TABLE 4

Low-dimensional magnetic materials formed by metal ions and NITR, IMH radicals

	M	R	J^a	Ref.
	Rh_2	NITMe	200	119
	Zn	NITiPr	12.2	120
	Y	NITEt	5	121
	Eu	NITEt	12	121
	Rh_2	IMMe	−5	119
	Cu	MITMe	−26	122
		NITiPr	−22	123
	Cu	TEMPOL	13	92
			−0.5	124
	Ni,Co	NITEt	≈300	125
	Mn	NITR	≈300	126–128
	Ni	NITR	424	129
	Cu	NITPh	300	130

[a] In cm^{-1}.

been very popular in Sacconi's lab. The bulk magnetic properties of materials containing lanthanides are influenced mainly by the nature of exchange interactions involving these ions and by the anisotropy of their ground states.

For a better understanding of the exchange mechanisms and the role of the ground state anisotropy, we decided to attempt a molecular approach to the problem: we tried to synthesize simple compounds where the rare earths were in close contact with different paramagnetic centres. We used two different types of paramagnetic ligand: either the nitronyl-nitroxides described in the previous section [133,134] and copper(II) Schiff base complexes whose ability to act as ligands was well established [135–137]. When a radical was used, it was possible to obtain complexes with either a 1:1 or 2:1 radical–lanthanide ratio, as shown in Fig. 10, depending on the nature of the R substituent. When the Cu(II) Schiff bases were used, only molecules with a 2:1 Cu–rare earth ratio were isolated (Fig. 11).

Analysis of the magnetic properties of these systems was restricted to those containing gadolinium(III) as this ion has an orbital singlet ground state and, therefore, it is possible to use the isotropic spin Hamiltonian approach to deal with the magnetic properties of its derivatives. All the compounds showed a common feature: the exchange interaction involving gadolinium(III) was always found to be

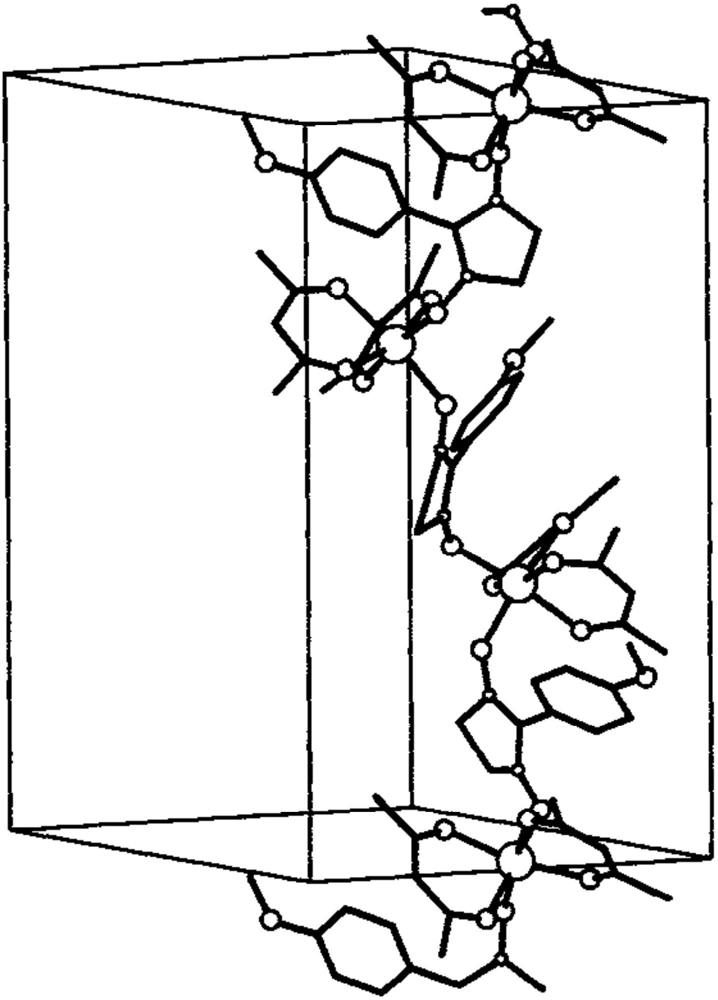


Fig. 9. Schematic view of the unit cell for Mn(hfac)$_2$NITPhOMe. Fluorine atoms are omitted for clarity.

ferromagnetic in nature and its intensity was definitely higher than that expected for a simple dipolar interaction [138]. Further, in the systems where two $S = 1/2$ paramagnetic centres are present, they are coupled in an antiferromagnetic fashion, as confirmed by magnetic measurements performed on derivatives where gadolinium(III) is substituted by diamagnetic ions such as yttrium(III) or europium(III) [121] (see Table 5).

The model we propose to rationalize the experimental evidence is based on the possibility of a spin transfer through the empty 6s orbital on the gadolinium ion. This exchange mechanism can justify both the antiferromagnetic exchange operative between the $S = 1/2$ species and the ferromagnetic Gd–radical or Cu(II) coupling. In

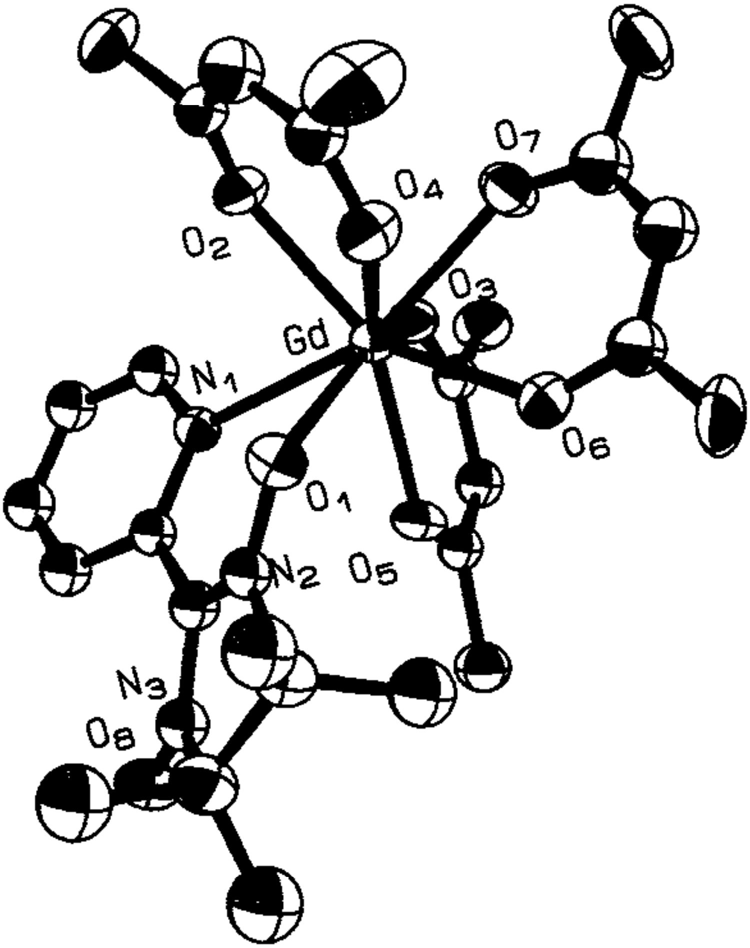


Fig. 10. ORTEP view of the asymmetric unit of Gd(hfac)$_3$NIToPy. Fluorine atoms are omitted for clarity.

the latter case, the transfer of a fraction of an unpaired electron into the 6s orbital will force the seven unpaired electrons, by Hund's rule, to align parallel to that of the paramagnetic ligand. The final ferromagnetic exchange is therefore determined by the third rule of Goodenough and Kanamori [143,144].

If gadolinium(III) is substituted by any other rare earth, the analysis of the magnetic properties is not straightforward due to the presence of orbitally degenerate ground states for the 4f ions. The model we are testing is derived by one previously proposed [145] to interpret the properties of magnetic iron garnets. Due to the low symmetry of our compounds, a large number of parameters is required to reproduce, for instance, their magnetic properties: nine parameters come from the necessity of taking into account crystal field effects and ten are required to introduce the magnetic

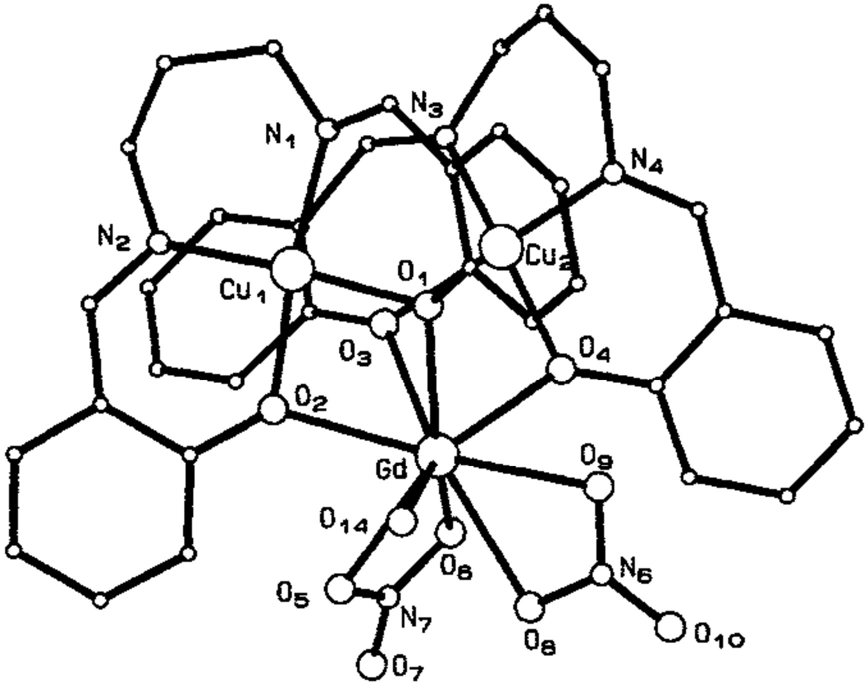


Fig. 11. PLUTO view of the asymmetric unit of $[(CuSALtn)]_2Gd(H_2O)(NO_3)_3$.

TABLE 5

Coupling constants[a] in gadolinium nitronyl-nitroxide and gadolinium–copper coupled species

Complex	$J_{RE-1/2}$[a]	$J_{1/2-1/2}$[a]	Ref.
1:1			
$[Gd(hfac)_3(NITiPr)(H_2O)]$	−0.60	–	138
$[Gd(hfac)_3(NIToPy)]$	−3.03		142
$[Gd(hfac)_3(NITpPy)]$	−1.78		142
$[Eu(hfac)_3(NITEt)]$	12.0		121
$[Y(hfac)_3(NITEt)]$	4.51		121
1:2			
$[Eu(hfac)_3NITEt_2]$		17.6	134
$[Eu(hfac)_3NITPh_2]$		16.3	133
$[Gd(hfac)_3NITEt_2]$	−0.50	4.3	134
$[Gd(hfac)_3NITPh_2]$	−1.23	5.1	133
$[(CuSALtn)_2Gd(H_2O)(NO_3)_3]$	−1.2	3.6	136
$[(CuSALen)_2Gd(H_2O)(ClO_4)_3]$	−7.4	12.2	137
$[(Cuhapen)_2Gd(H_2O)(ClO_4)_3]$	−5.3	4.2	137
$[Gd(hfac)_3CuSatnOH]_2$	−2.8	2.6	138

[a] In cm^{-1}.

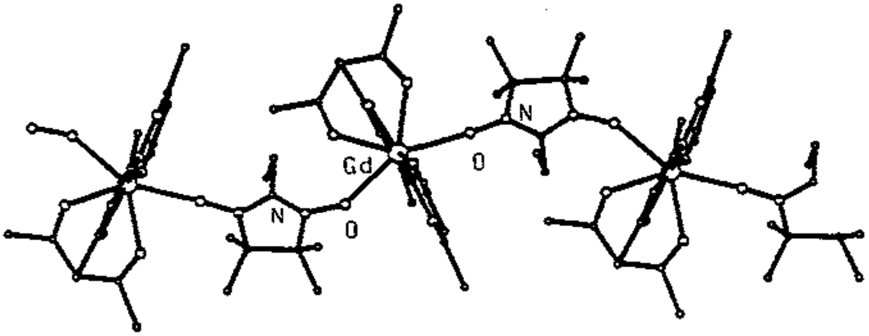


Fig. 12. PLUTO view of the unit all of $Gd(hfac)_3NITEt$. Fluorine atoms are omitted for clarity.

interaction involving the rare earth. The only test we have performed so far was on a system containing dysprosium(III)–copper(II) pairs and our model was able to reproduce nicely the magnetic behaviour of the system [139].

Using appropriate nitronyl-nitroxides, we synthesized novel one-dimensional magnetic materials where gadolinium(III) and organic radicals regularly alternate to form chains of $S = 7/2$ and $S = 1/2$ spins as shown in Fig. 12 [140,141]. Beyond the fact that these materials are among the very rare examples of low-dimensional lanthanide systems, their uncommon feature involves the temperature dependence of their magnetic susceptibility. At room temperature, the observed value of the effective magnetic moment is close to that expected for uncorrelated spins and remains almost constant down to approximately 80 K. Below this temperature, a steady decrease in its value was observed: at the lowest temperature reached (1.33 K), the magnetic moment measured is well below the value expected for antiferromagnetic coupling between the metal and radical spins. This behaviour is probably due to non-negligible next-nearest-neighbour interactions: an Ising treatment of the data which explicitly includes this type of interaction was able to reproduce the experimental patterns. The full set of nearest-neighbour and next-nearest-neighbour interactions supports the presence at 0 K of a "two spin up–two spin down" ground state which might be considered as a diamagnetic state [142].

J. CONCLUSIONS

This short review has not been able to cover all the aspects of magnetism in Florence. However, we hope it has shown how the roots of Sacconi's work has fed a tree whose branches are still growing.

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We wish to express our gratitude to Prof. Sacconi for putting us in such an exciting field.

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