

Low-dimensional polynuclear complexes and high-spin molecules: towards molecular magnets

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Abstract

Coordination chemistry allows the synthesis of new molecules which show cooperative magnetic phenomena, behaving like *magnets*. Two main ways of synthesizing these systems have been developed: a) low-dimensional complexes (1-D or 2-D) which are linked in the crystal net and so give ferromagnetic long-range order and b) isolated molecules with high-spin ground state and strong anisotropy, which have a long relaxation time. Two different series of molecular magnets were prepared and characterized, following these approaches:

a) The pseudohalide ligands (azido, thiocyanato and selenocyanato) are good bridging ligands which give easily tunable magnetic interactions between paramagnetic metal ions like Cu^{II}, Ni^{II} or Mn^{II}. With Cu^{II} and Ni^{II} these compounds are rarely studied outside the field of molecular magnetism and they do not give rise to molecular magnets. Nevertheless they allow magneto-structural correlations to be studied in greater depth. In contrast, Mn^{II} ion with azido and pyridine-derivative ligands easily gives one- or two-dimensional systems with long-range order at low temperature, owing to *canting* phenomena which show cooperative ferromagnetism. They are, thus, *molecular magnets*.

b) New oxo-bridged manganese carboxylate chemistry was also developed. We focused our attention on dodecamanganese(III,IV) of general formula [Mn₁₂O₁₂(2-Xbenzoato)₁₆(H₂O)₄] (X = F, Cl, Br, Me). These new complexes were compared with their acetato and benzoato analogues. They are all superparamagnetic molecules, with high-spin ground state (close to S_T = 10) and strong anisotropy, which gives a hysteresis loop and blocking temperature close to 4K. The most particular feature is the presence of a non-zero *out-of-phase* (imaginary) component in their *ac* susceptibility performed in zero field. The maximum in this imaginary component is frequency-dependent, indicating superparamagnetic behavior. Thus, these Mn₁₂ complexes have a property rarely associated with small molecular species: they also are molecular magnets.

Key words: Molecular magnets, polynuclear complexes, high-spin molecules, low-dimensional complexes

Resum

La química de coordinació pot donar lloc a noves molècules que presenten fenòmens magnètics cooperatius i es comporten com a *imants*. S'han pogut desenvolupar dues vies per sintetitzar aquests sistemes: a) complexos de baixa dimensionalitat (1-D o 2-D) units en el cristall de tal manera que donen ferromagnetisme tridimensional i b) molècules aïllades amb estat fonamental de spin elevat i alta anisotropia, la qual cosa origina temps de relaxació llargs. Amb aquestes perspectives, s'han preparat i caracteritzat dues sèries diferents d'imants moleculars:

a) Els lligands pseudohalur (azidur, tiocianat i selenocianat) són bons lligands pont que donen interaccions magnètiques fàcilment modulables entre ions metàl·lics com Cu^{II}, Ni^{II} i Mn^{II}. Amb Cu^{II} i Ni^{II}, aquestes interaccions rarament van més enllà del magnetisme molecular, i no donen lloc a imants moleculars. Es tracta d'espècies interessants perquè permeten aprofundir en el camp de les relacions magnetoestructurals. En canvi, amb Mn^{II}, el lligand pont azidur, junt amb la presència de lligands bloquejants derivats de la piridina, dona fàcilment sistemes mono- o bidimensionals que presenten ordenament magnètic a llarga distància, a causa de fenòmens de «*canting magnètic*». Es tracta, doncs, de veritables imants moleculars.

b) També s'ha desenvolupat la química de nous carboxilats de manganès amb pont oxo. La nostra atenció s'ha centrat especialment en la sèrie dels dodecamanganesos (III,IV) de fórmula [Mn₁₂O₁₂(2-Xbenzoato)₁₆(H₂O)₄] (X = F, Cl, Br, Me). Els nous complexos s'han comparat amb els acetato i benzoato ja descrits. Tots ells són espècies superparamagnètiques amb un estat fonamental de spin molt elevat (S_T = 10) i alta anisotropia, que presenten cicle d'histèresi i temperatura de bloqueig magnètic prop de 4 K. L' característica més important i peculiar és la presència d'un component imaginari (*out-of-phase*) en les mesures de susceptibilitat *ac*. El màxim d'aquest component imaginari depèn de la temperatura, la qual cosa indica precisament el caràcter superparamagnètic. Per tant, aquestes molècules Mn₁₂ presenten propietats rarament associades a les petites molècules: són realment imants moleculars.

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Coordination Chemistry has become one of the main areas of Inorganic Chemistry due to the potential applications of the new complexes [43]. The fields of homogeneous catalysis (organometallic chemistry), photochemistry, mixed-valence systems, synthesis of new polydentate ligands with specific properties, magnetochemistry, supramolecular chemistry, bioinorganic chemistry, and superconducting chemistry, belong to the general field of Coordination Chemistry. In some cases, the difference between Coordination Chemistry and Solid State Chemistry is very subtle, especially when the properties of the coordination compounds studied depend on the arrangement of these complexes in the crystal net. For example, the magnetic and/or conducting properties of most inorganic solids are borderline between Coordination Chemistry and Solid State Chemistry. At present, however, these differences are more academic than real.

The main aim of our group «Magnetic Interactions and Molecular Magnetism» (Departament de Química Inorgànica; Universitat de Barcelona) is to synthesize and characterize new polynuclear complexes formed by paramagnetic first-row transition ions, in order to study magneto-structural correlations and to synthesize new molecules with potentially interesting magnetic properties.

An extraordinary evolution has taken place in all the groups working on molecular magnetism: from the discrete polynuclear molecules synthesized and studied to improve our understanding of the mechanism of magnetic couplings [15,42] to the synthesis and characterization of new low-dimensional materials (one- or two-dimensional) which may show ferromagnetic long-order cooperative phenomena (*molecular magnets*) [1,4,5,12, 15,19]. Research into discrete polynuclear molecules has not declined but rather has acquired a new dual perspective: a) to obtain new synthetic models of bioinorganic systems like enzymes, the photosynthesis, [20] and b) to synthesize new paramagnetic clusters with high spin in the ground state and strong anisotropy so that superparamagnetic molecules, which may also be used as *molecular magnets*, can be formed [3,36].

The goal of our group is to develop classic molecular magnetism towards magnetic materials:

a) the synthesis and full characterization of new molecular species with 3-D ferromagnetic interactions (long-range order).

b) the synthesis and full characterization of new molecular species with high nuclearity, high-spin ground state and strong anisotropy.

In both cases, we attempted to advance in the field of molecular magnets. Up to now, not only in our group but also in other research groups worldwide, the development of the former has been more successful than the development of the latter.

Two paths were followed: the ferromagnetic approach *i.e.* 3-D ferromagnetic coupling, very difficult to predict and tune, between discrete low-dimensional systems, and the

ferrimagnetic approach *i.e.* new 3-D non-compensate anti-ferromagnetic couplings (ferrimagnetism), much easier to predict and tune since natural couplings are more frequently antiferromagnetic. Working with this hypothesis, it was logical to assume that we might reach the synthesis of new antiferromagnetic systems, which had no relevance to magnetic materials, but which would allow us to carry out new magneto-structural correlations between new structures, molecular orbital theories and experimental magnetic properties.

This study is divided in these lines.

Results and discussion

New ferrimagnetic species

Molecules with two kinds of metal ions play an important role in molecular magnetism [15]. This is because the types of interaction between two spin carriers A and B within a molecular unit are much more diverse when A and B are different and, secondly, with several kinds of magnetic centers, lattices with quite peculiar spin topologies can be designed. Several reviews of these heteropolymetallic systems have been written [14,16]. Up to now, only the intramolecular interactions within an A-B heterodinuclear molecule have been examined. Thus the coupling between different ions like Cu^{II}-Ni^{II} or M^{II}-Cu^{II}-M^{II} (M^{II} = Cu, Ni, Mn) with appropriate ligands that generate intramolecular antiferromagnetic coupling is essentially ferrimagnetic [22]. The use of different blocking ligands (amines) allowed the synthesis, X-ray structural determination and magnetic and e.p.r. studies of new *ferrimagnetic* discrete molecules. By selective choice of the terminal ligands, these heteropolynuclear complexes can be used as «complexes as ligands» [37] following a stepwise strategy to synthesize new large clusters with special spin topologies. Indeed, as pointed out by Kahn [16], in molecular magnetism not only local spins associated with metal ions, but also the molecular spins associated with molecular units as a whole are important. It turns out that the interaction between two such molecular units may differ from the interaction between two metal ions belonging to different molecular units.

For example, working with the neutral molecule [Cu(oxpn)] or the anionic species [Cu(pba)]²⁻ (Figure 1), the nature of the magnetic coupling in Cu-Cu, Cu-Ni or Cu-Mn dinuclear entities or Cu-Cu-Cu, M-Cu-M (M = Ni^{II}, Mn^{II}) trinuclear entities is antiferromagnetic, owing to the good overlap between the magnetic orbitals of the two metal ions through the corresponding molecular orbital of the oxamidate bridge. This new heteropolynuclear species may be linked to form new low-dimensional systems with bridging intermolecular ligands like N₃⁻, SCN⁻, SeCN⁻ and NO₂⁻ in a ferromagnetic mode (Figure 2) [27,31]. Unfortunately, these systems are not molecular magnets, even though the intermolecular coupling is ferromagnetic. However, the very rare case of stabilization of S_T = 0 ground state due to this intermolecular ferromagnetic coupling has been observed. This stabiliza-

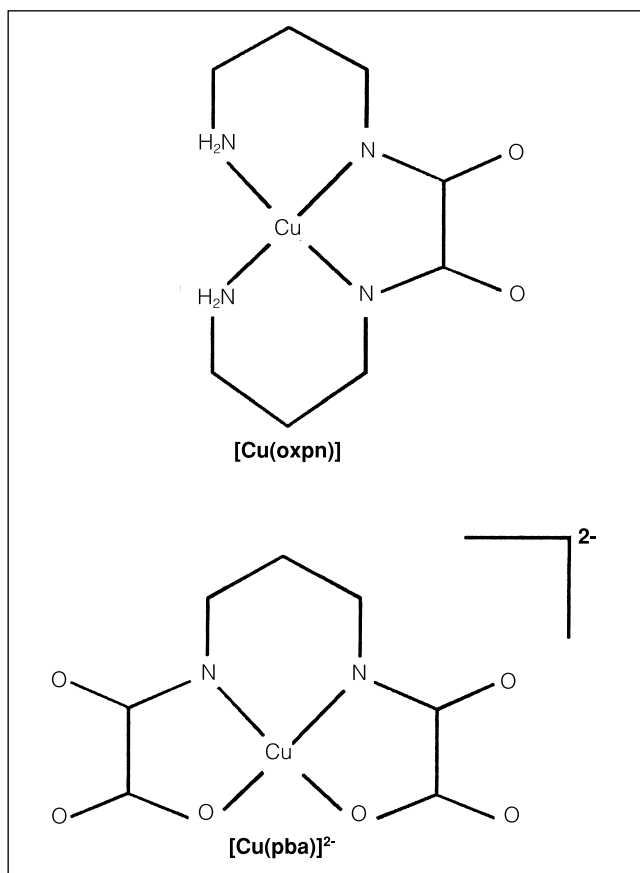


Figure 1. Schematic drawing of the neutral complex [Cu(oxpn)] and the dianionic complex [Cu(pba)]²⁻ as starting products for ferrimagnetic systems.

tion of a «diamagnetic» ground state is due to the topological arrangement of the individual spins in the crystal net (Figure 2). The ferromagnetic coupling between ferrimagnetic systems giving the stabilization of a singlet ground state is rare and must be studied with accuracy. The mathematical calculations for fitting J parameters (antiferromagnetic within the molecules and ferromagnetic between the molecules) and g values are now being developed by our group.

New ferromagnetic species

Bridging ligands can easily give ferromagnetic coupling (according to both our experience and literature data). Although this ferromagnetic coupling is not always predictable, we chose pseudohalide ligands: azide, cyanate, thiocyanate and selenocyanate. With these bridging ligands new mono, di and tridimensional systems with Cu^{II}, Ni^{II} and Mn^{II} were obtained.

New discrete ferromagnetic species with N_3^- or $S(Se)CN^-$ bridging ligands

When N_3^- anions act as bridging ligands there are two possible coordination modes: *end-to-end* (or 1,3) and *end-on* (or 1,1) (Figure 3a). Normally, the *end-to-end* coordination mode gives antiferromagnetic coupling, and the *end-on* gives ferromagnetic coupling. Working with different commercial amines and maintaining the Ni^{II}/amine/azide in 1/2/1

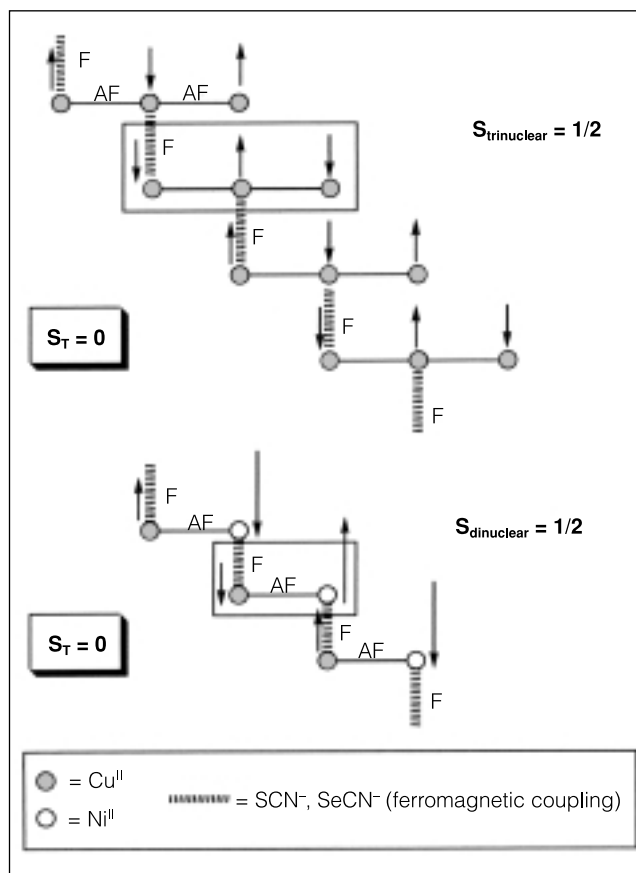


Figure 2. Schematic drawing of the one-dimensional complexes obtained from precursors of Figure 1 (intramolecular antiferromagnetic coupling and intermolecular ferromagnetic coupling between the polynuclear entities). The whole system is ferrimagnetic with $S_T = 0$.

ratio, several ferromagnetic discrete molecules have been synthesized and characterized. These molecules are normally dinuclear with a spin ground state $S_T = 2$ (Figure 4a) [6]. All these complexes show the peculiarity of a second-order Jahn-Teller effect, which causes a distortion (asymmetrization) of the theoretical Ni-(N_3)₂-Ni rhombus at low temperature. This second-order Jahn-Teller effect is due to a mixing of the partially occupied magnetic molecular orbitals, which, when the symmetry of the system is reduced, belong to the same symmetry species in the point group of the molecule. This asymmetrization causes a magnetic change in the susceptibility measurement at the temperature of the asymmetrization [6]. If the bond angles at high and low temperature are known, this magnetic change can be explained by molecular orbital calculations.

With the amine 2-hydroxo-1,3-propanediamine, a nearly regular square tetranuclear complex was obtained, with a spin ground state $S = 4$ [23] (Figure 4c). This relatively high spin, together with the anisotropy due to Ni^{II}, can give interesting magnetic phenomena at low temperature, which we are studying at the moment.

With other pseudohalides (SCN^- and $SeCN^-$) new ferromagnetic dinuclear species were synthesized [39]. All of them have two terminal amine ligands on each nickel atom and their core is always very similar: $[Ni(\mu-NCS)_2Ni]^{2+}$ with

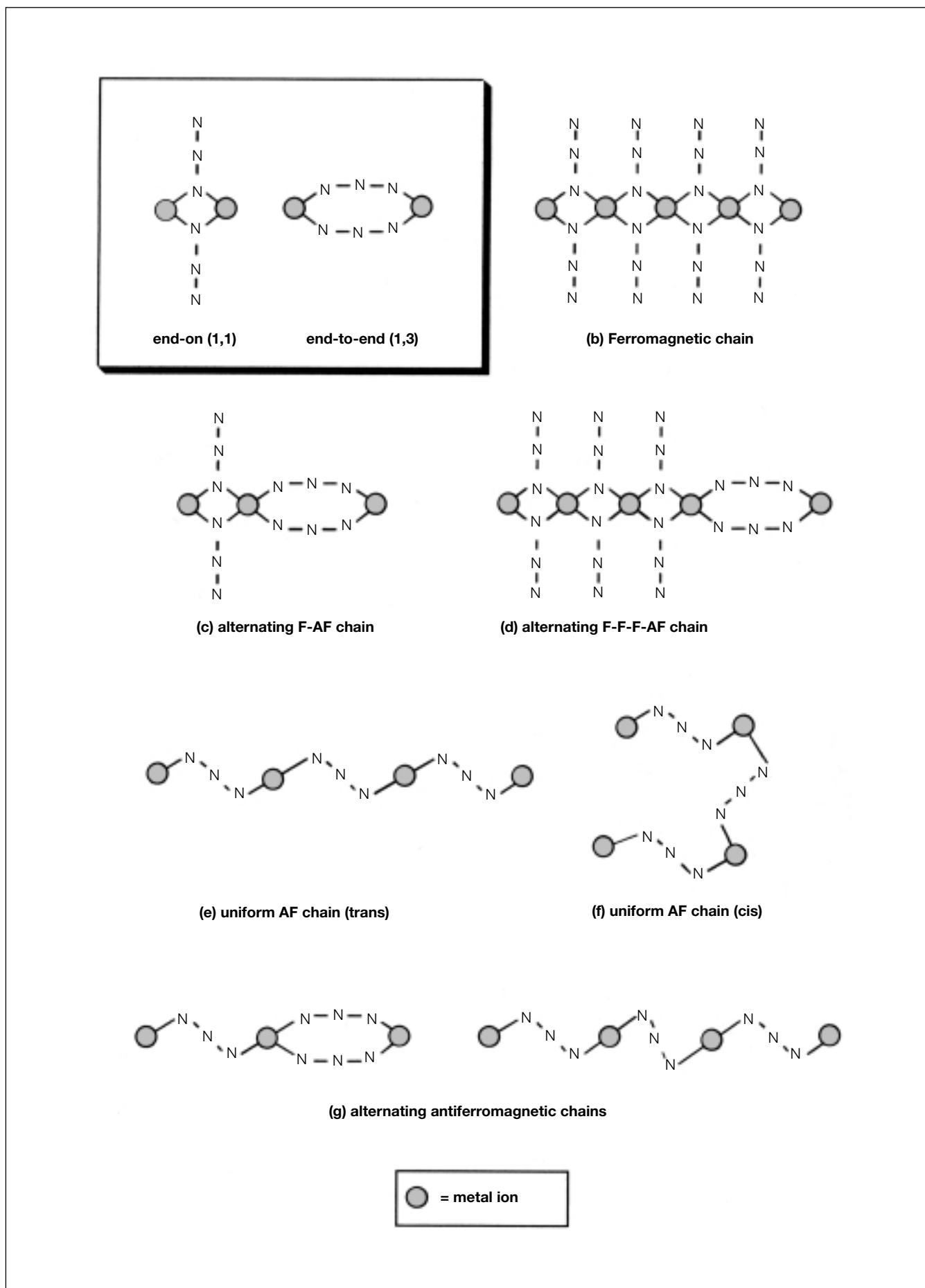


Figure 3. Scheme of the different coupling modes for azido bridging ligands, giving dinuclear (a) or one-dimensional systems (b-h).

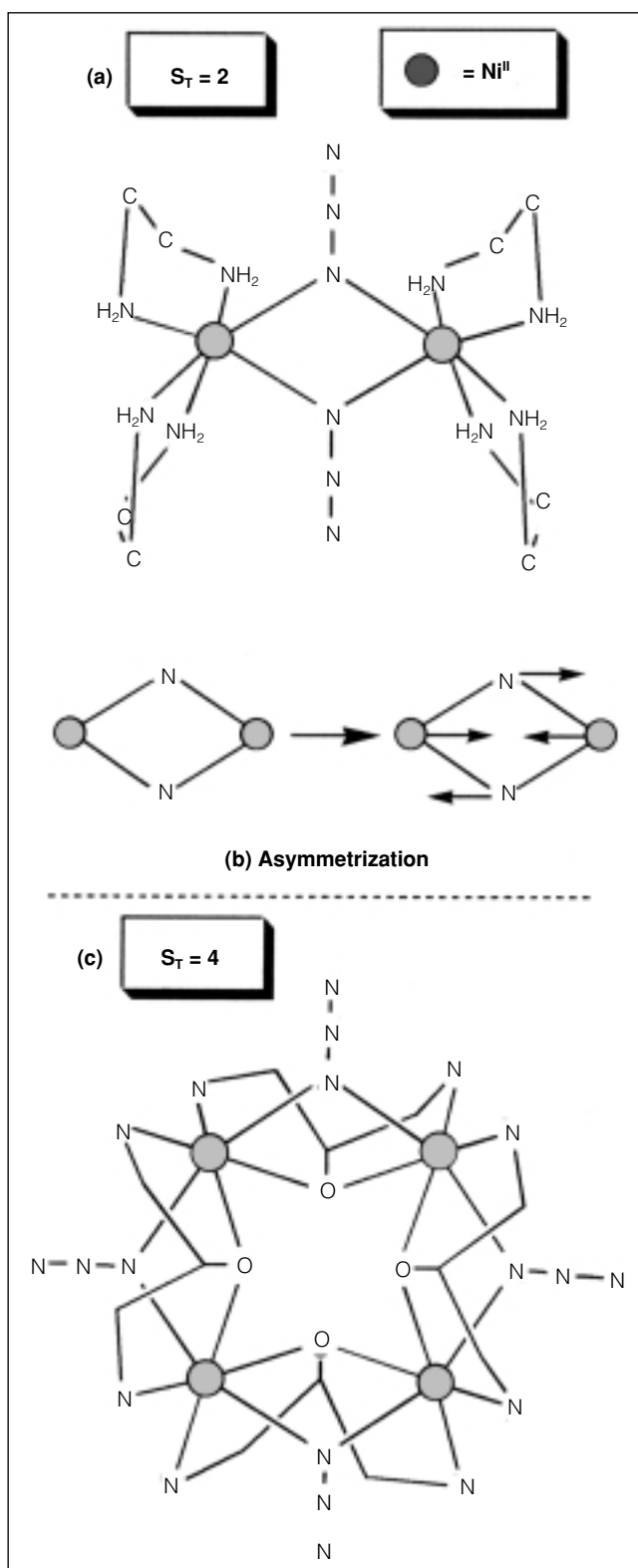


Figure 4. An example of a dinuclear ferromagnetic system (a) and a tetranuclear ferromagnetic system (c), with their spin ground states (S_T).

the Ni-NCS and Ni-SCN angles always close to 180° and 90° , respectively (theoretical angles for which maximum ferromagnetism is expected) (Figure 5a). The magnetic properties are almost independent of the terminal amines used in the synthesis.

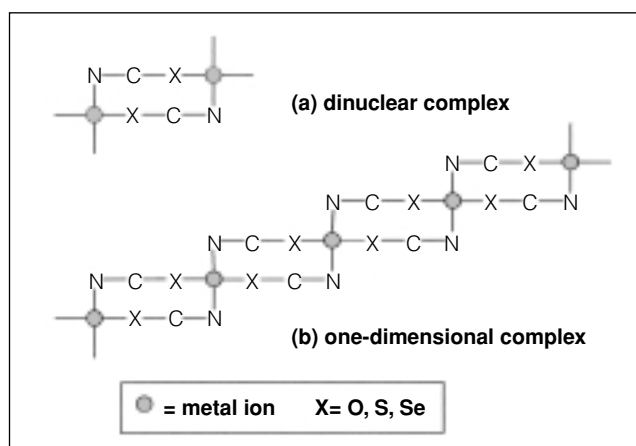


Figure 5. Scheme of the different coupling modes for cyanato, thiocyanato and selenocyanato bridging ligands, giving dinuclear (a) or one-dimensional systems (b).

One-dimensional ferromagnetic systems with N_3^- or $\text{S}(\text{Se})\text{CN}^-$ bridging ligands.

When the working ratio indicated above was 1/1/2 instead of 1/2/1, new one-dimensional ferromagnetic species with formula $[\text{Ni}(\text{amine})(\mu\text{-N}_3)_2]_n$ or $[\text{Ni}(\text{amine})(\mu\text{-SCN})_2]_n$ were characterized [25,40]. The central core, important magnetically, is the same as that mentioned above for the dinuclear complexes: when the bridging ligand is the azide ion it shows the *end-on* coordination mode (Figure 3b); when the bridging ligand is the thiocyanate or selenocyanate ion, the M-N-C and M-S-C bond angles are close to 180° and 90° respectively (Figure 5b), as in the dinuclear complexes. The only difference is the presence of one terminal amine ligand instead of two and the lack of any counter-anion. Thus the experimental ferromagnetic coupling is logical. With Mn^{II} , only one ferromagnetic one-dimensional complex with azido bridging ligand was characterized [11] (Table 1; Figure 3b).

New species with ferromagnetic-antiferromagnetic alternation

With the $M/\text{amine}/\text{azide}$ ratio indicated above (1/1/2), not only were new ferromagnetic chains $[\text{M}(\text{amine})(\mu\text{-N}_3)_2]$ obtained but also, depending on the amine used in the synthesis, new ferromagnetic-antiferromagnetic species were synthesized. This was predictable because until now it has not been possible to tune the coordination mode of the azido bridging ligand (*end-to-end* or *end-on*). Thus, the packing effects (hydrogen or Van der Waals bonds) can force the stabilization of each coordination fashion. The alternation can be very simple, F-AF [29] (Figure 3c) or much more complicated such as, for example, F-F-F-AF (Figure 3d) [30]. In all these cases, when $M = \text{Ni}^{\text{II}}$, the magnetic data were interpreted and fitted by numerical extrapolation of $S = 1$ rings of finite length. For these calculations, an isotropic Heisenberg system with quantic spin $S = 1$ was assumed.

With Ni^{II} and the 2,2'-dimethyl-propanodiamine ligand, a unique new two-dimensional system with ferro-antiferromag-

netic alternation was obtained. This complex can be represented as a linkage of ferromagnetic $[\text{Ni}(\text{amine})(\mu\text{-N}_3)_2]$ dinuclear entities by one azido bridging ligand in *end-to-end* (antiferromagnetic) coordination mode (Figure 6a). This linkage is extended through one layer and the layers are linked by hydrogen and Van der Waals forces. The interest of this system lies in its magnetic properties: it shows a *canting* phenomenon at low temperature [18]. *Canting* behavior can be defined as antiparallel spins canted at a small angle. The total resulting from these small vectors is not nil when the *canting* angle is different from zero. This *canting* gives the complex the characteristics of a molecular magnet (hysteresis loop, for example).

With Mn^{II} , N_3^- and various monodentate pyridine derivatives, other 2-D systems with ferro-antiferromagnetic alternation were also synthesized (Figure 6b) [11]. These new systems also act as molecular magnets due to *canting* phenomena at low temperature. Magneto-structural correlations were developed by comparing their magnetic results with other simpler Mn^{II} systems reported in the literature.

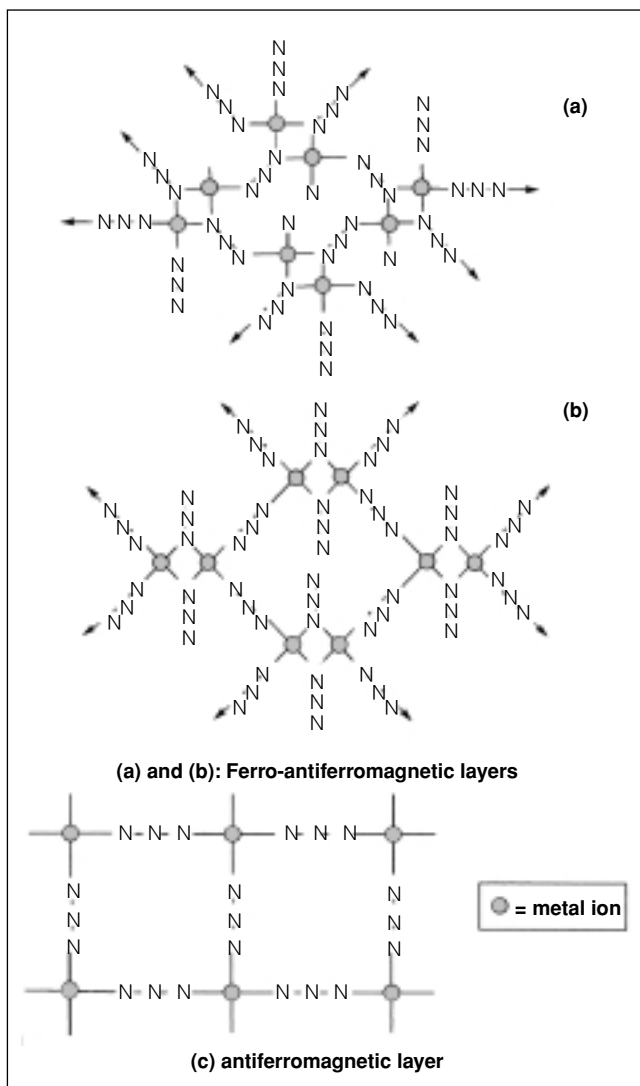


Figure 6. Scheme of different coordination modes giving two-dimensional systems with azido bridging ligands, for Ni^{II} and Mn^{II} central ions.

New species with antiferromagnetic coupling: magneto-structural correlations

We have indicated above that the azide bridging ligand can adopt two coordination modes (*end-to-end* or *end-on*) (Figure 3a) and that it is impossible to predict, at the present stage of our research, which coordination mode will be adopted. Indeed, several systems were prepared in which the coordination mode of the azide bridging ligand is *end-to-end* giving antiferromagnetic coupling. In these new systems, the corresponding magneto-structural correlations were developed by relating the experimental magnetic data and theoretical molecular orbital calculations. The following systems should be noted:

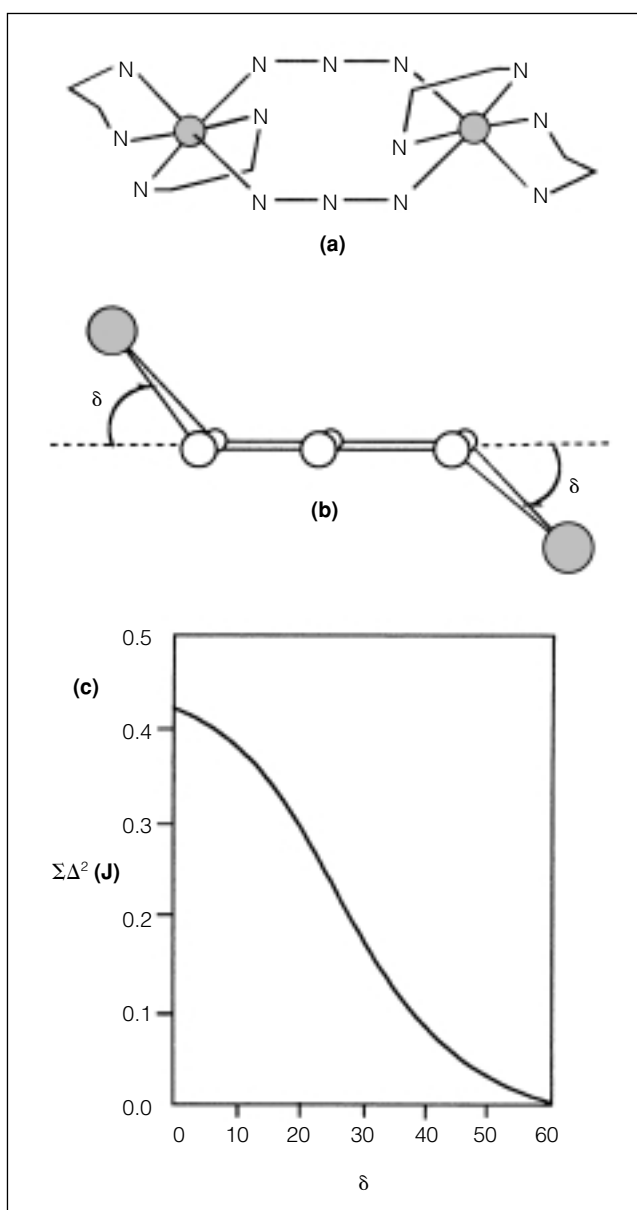


Figure 7. Schematic drawing of a dinuclear antiferromagnetic complex with azido bridging ligands (a); dihedral angle, δ , which contributes to the antiferromagnetic coupling (b) and diagram of the energy gap created by the molecular magnetic orbitals vs the dihedral angle δ . The antiferromagnetic coupling (J) is proportional to this energy gap ($\Sigma \Delta^2$).

Dinuclear systems

All these complexes are nickel(II) and their formula is $[\text{Ni}_2(\text{amine})_4(\mu_{1,3}\text{-N}_3)_2]\text{X}_2$ (X = perchlorate or hexafluorophosphate). An example of these complexes is given in Figure 7a. From these complexes, some of which were synthesized for the first time and others were taken from the literature, a new relationship was developed between the exchange coupling parameter, J (in cm^{-1}) and the structural data [24].

The main factor determining the J value is the $[\text{Ni}-(\mu\text{-N}_3)_2\text{-Ni}]$ dihedral angle (Figure 7b). The results of extended Hückel molecular orbital calculation are shown in Figure 7c as $\Sigma\Delta^2$ vs δ , Δ being the gap created between the symmetric and antisymmetric combinations of Ni^{II} magnetic orbitals ($z^2 \pm z^2$ and $x^2 - y^2 \pm x^2 - y^2$) and δ the $\text{Ni-N}_3\text{-Ni}$ dihedral angle. According to all magnetochemical theories [15] J_{AF} is proportional to this gap ($J_{\text{AF}} \propto \Sigma\Delta^2$). Experimental data corroborate this model. The more planar the structure is (dihedral angle δ close to 0°), the more antiferromagnetic the coupling. When this dihedral angle increases, the J value decreases [24].

One-dimensional systems

If it is impossible to predict the coordination mode of the azido-bridging ligand, it is also impossible to predict whether, in a given reaction, the complex formed will be discrete or low-dimensional (starting with the same reagent ratio). Indeed, a large number of one-dimensional systems with different polydentate amines were obtained and structurally characterized. However, depending on the amine and counter-anion used in the synthesis, these chains can have the bridging azido ligands in *trans* (Figure 3e) [7] or *cis* (Figure 3f) [8,28] position. Extended Hückel molecular orbital calculations on model complexes have shown that the main factors which determine the J value are: the Ni-N-N angle and the $\text{Ni-N}_3\text{-Ni}$ torsion angle. As indicated for dinuclear complexes, J_{AF} is proportional to $\Sigma\Delta^2$ (Δ = energy difference between the corresponding magnetic orbitals). In Figure 8 the variation of Δ^2 (or J) as a function of the Ni-N-N angle and the $\text{Ni-N}_3\text{-Ni}$ torsion angle is shown. When the Ni-N-N angle is close to 110° the coupling is maximum, which is consistent with the experimental data. When the torsion angle δ is close to 0° , the antiferromagnetic coupling is the strongest, again in accordance with the experimental data. When this torsion angle δ increases, the J value decreases.

That the J parameters depend on the Ni -azido angles can be checked with one-dimensional systems in which the structural parameters (angles) alternate in the chain. Indeed, we synthesized new alternating systems with Ni^{II} and Mn^{II} . Before our results alternating systems had been reported only for Cu^{II} ($S = 1/2$). Two typical examples are schematized in Figure 3g [8,38]. In all these cases, the magneto-structural correlations previously developed with uniform chains were corroborated. A unique case is produced by the blocking N,N,N',N' -tetramethylethylenediamine [26]. In the chain there are two alternating coordinations: three *end-on* groups (with a very small Ni-N-Ni angle) and one

end-to-end azido group. The fit of the susceptibility curve was very good, assuming two AF parameters instead of one ferromagnetic coupling owing to the presence of three *end-on* azide bridging groups. This is the first case for which this anomalous behavior has been reported and we are attempting to synthesize similar new complexes to corroborate this magnetic behavior. Finally, the clearest alternating antiferromagnetic system is a Ni^{II} chain formed by oxalato and azide

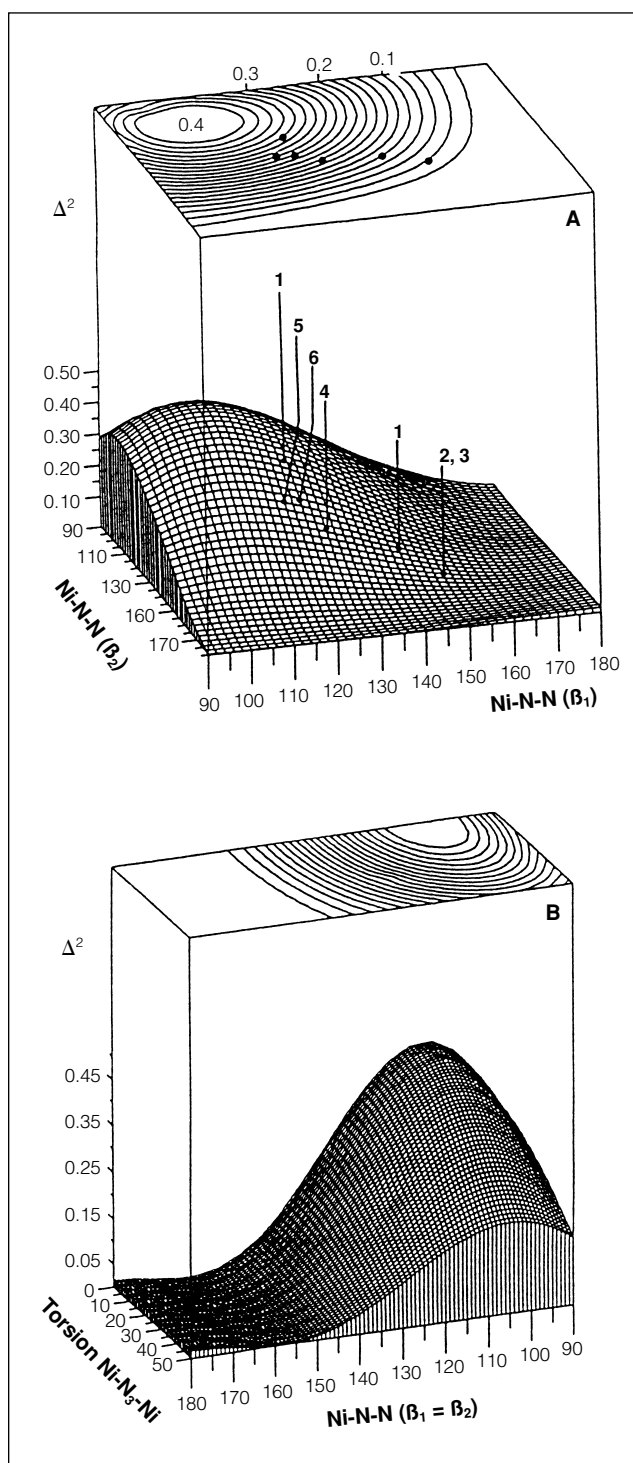


Figure 8. Diagram of the energy gap created by the molecular magnetic orbitals vs the Ni-N-N angle (A) and vs the $\text{Ni-N}_3\text{-Ni}$ torsion angle for a given Ni-N-N angle (B). The antiferromagnetic coupling (J) is proportional to this energy gap ($\Sigma\Delta^2$).

Table 1. Main low-dimensional Mn^{II} complexes of general formula [Mn(L)(μ-N₃)₂]_n with their structure and magnetic properties.

Blocking ligand (L)	Structure	Magnetic behavior
<i>ONE-DIMENSIONAL COMPLEXES</i>		
2-benzoylpyridine	double bridge 1,1 (Figure 3 b)	Molecular F; no long-range order
3-benzoylpyridine	alternating double bridge 1,1 and 1,3 (Figure 3c)	Molecular F-AF; no long-range order
3-ethylpyridine	double bridge 1,3 (Figure 3g)	Molecular AF; no long-range order
2-pyridone	double bridge 1,3 (Figure 3g)	Molecular AF; no long-range order
<i>BI-DIMENSIONAL COMPLEXES</i>		
3-acetylpyridine	1,3 and 1,1 bridging ligands (Figure 6b)	Molecular F-AF; long-range order («canting»)
4-acetylpyridine	1,3 bridging ligands (Figure 6c)	Molecular AF; long-range order («canting»)
4-cyanopyridine	1,3 and 1,1 bridging ligands (Figure 6b)	Molecular F-AF; long-range order («canting»)
methyl-isonicotinate	1,3 bridging ligands (Figure 6c)	Molecular AF; long-range order («canting»)
ethyl-isonicotinate	1,3 and 1,1 bridging ligands (Figure 6b)	Molecular F-AF; long-range order («canting»)

F = Ferromagnetism; AF = Antiferromagnetism

bridging ligands placed consecutively in the one-dimensional complex [9].

In all these cases, the magneto-structural correlations mentioned above make it very easy to assign the two different J values to the corresponding part of the one-dimensional molecule.

Bidimensional systems

If with Ni^{II} and polydentate amines it is very easy to obtain one-dimensional systems, with Mn^{II} and monodentate pyridine derivative ligands it was possible to isolate new antiferromagnetic two-dimensional systems [10] (Figure 6c). The susceptibility data and e.p.r. measurements indicate long-range order at low temperature, presumably due again to *canting* phenomena as mentioned above for other systems (Table 1),

New superparamagnetic species with high nuclearity and strong anisotropy

As indicated in the Introduction, one of our aims was the synthesis and characterization of new molecular species with high-spin and strong anisotropy. As the Ni^{II} ion shows little anisotropy (D parameter which reflect the typical e.p.r. silent behavior of Ni^{II} complexes), the Mn^{III} ion is the ideal cation for this kind of complex, due to its strong anisotropy created by the first order Jahn-Teller effect (four electrons in (t_{2g})³(e_g)¹ orbitals). For this reason, research was focused on polynuclear manganese(III) complexes in attempt to synthesize and study new high-spin and anisotropic molecules. According to the literature data, the most promising of the Mn^{III} complexes were the carboxylato-oxo complexes.

In recent years oxo-bridged manganese carboxylate chemistry has advanced considerably [1,4,12] for two main reasons. Di, tri, and tetranuclear complexes are important bioinorganically, as indicated above. Higher nuclearity products like Mn₆ [34], Mn₈ [41], Mn₁₁ [21], Mn₁₂ [33] and Mn₁₈ [35] have also been characterized structurally and studied magnetically owing to their peculiar characteristics as precursors or models of magnetic materials and, in some cases, as new molecular magnets. In all cases, as Christou says, serendipity has probably provided a helping hand, be-

cause in most cases precise nuclearity could not have been predicted from the reagents used.

These high nuclearity oxo-bridged manganese complexes are relevant for various reasons.

1) Fundamental information about single-domain magnetic oxides could be forthcoming from the characterization of discrete high-nuclearity oxo-bridged metal complexes. Even in the known magnetite, Fe₃O₄, single-domain particles behave as paramagnets when their diameters are less than 20 Å. In paramagnets the magnetic moments of the metal ions act independently of each other. Magnetic particles with diameters in the range of 20-300 Å are superparamagnetic. In a superparamagnet all the individual magnetic moments are aligned parallel (or antiparallel) as a result of the magnetic exchange interactions, but the net magnetization of a superparamagnet rapidly changes direction as a result of thermal fluctuation. Magnetic particles with diameters larger than 300-400 Å have greater magnetic exchange interactions and, as a result, they show hysteresis and permanent magnetization (ferromagnetism). Access to a series of well-characterized high-nuclearity oxide-bridged metal complexes would lead to a better understanding of the paramagnet/ superparamagnet/ferromagnet interfaces.

b) Molecules with large numbers of unpaired electrons are potential building blocks for molecular-based magnetic materials [3,33,36]. The search for molecules with a large number of unpaired electrons is being pursued in both the organic and inorganic areas. In the inorganic area manganese chemistry has, undoubtedly, been studied most and has given the most promising results. For example, a hexanuclear complex, [Mn^{II}₆(hfac)₁₂(NITPh)₆] (hfac = hexafluoroacetylacetonate; NITPh = a nitronyl-nitroxide radical) that has an S_T = 12 ground state, was prepared [2]. Goldbert *et al.* reported the preparation and characterization of (Me₄N)₄[Mn₁₀(biphen)₄O₄Cl₁₂] (biphen = 2,2-biphenoxide). This Mn^{II}₆Mn^{III}₄ complex was shown to have a S = 14 ground state [13]. The complex [Mn₁₂O₁₂(acetato)₁₆(H₂O)₄] has an S_T = 10 ground state, and the benzoato derivative has an S_T = 10 or 9 ground state, depending on whether or not it has some interstitial molecules in the crystal lattice [33]. Most interestingly, these Mn₁₂ complexes are the only molecular

species known to exhibit a non-zero out-of-phase (imaginary) component in their *ac* susceptibility performed in zero applied field. In addition, measurements performed at various frequencies show that the temperature at which the maximum in the imaginary component occurs is frequency-dependent. Paramagnets display an *out-of-phase ac* response only in the presence of an external magnetic field. In contrast, materials with spontaneous magnetization below some critical temperature (T_c) can show an *out-of-phase* response in zero applied field, but the temperature at which the maximum occurs is not frequency-dependent. Frequency dependent maxima have been observed to date only for superparamagnetic species. Thus, these Mn_{12} complexes behave unusually for small molecular species.

Given the importance of high-nuclearity species and the serendipitous nature of their discovery in most cases, some of the reported reagents that give good results should be changed in order to try to improve control and to understand of the methodology for their rational synthesis, better. In this study, the results obtained by Christou's group at the University of Indiana (USA) for the dodecanuclear complexes with acetato or benzoato bridges were reproduced with halobenzoate derivatives.

With the 2-fluoro, 2-chloro, 2-bromo and 2-methylbenzoic derivatives several Mn^{III} mixed-valence Mn^{III} - Mn^{IV} clusters with different nuclearity like trinuclear $[Mn_3O(X\text{-benzoato})_6(py)_3]$ [32] $[Mn_4O_2(X\text{-benzoato})_7(bpy)_2]^{0,+1}$, $[Mn_4O_3Cl_4(X\text{-benzoato})_3(py)_3]$, $[Mn_6O_2(X\text{-benzoato})_{10}(py)_4]$ have been

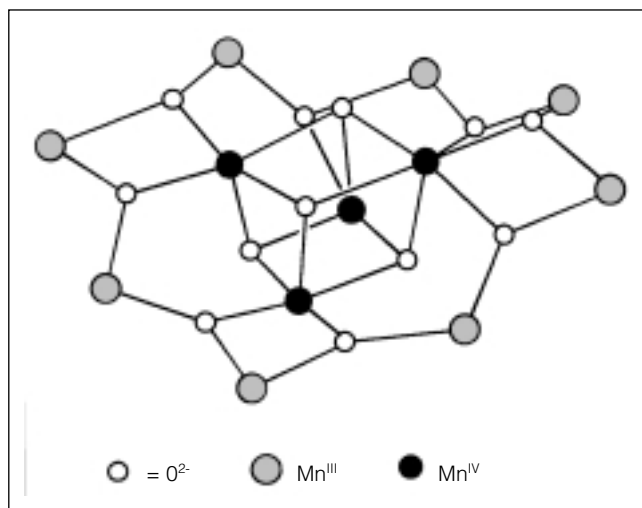


Figure 9. Schematic drawing of the central $Mn_{12}O_{12}$ core for a $[Mn_{12}O_{12}(\text{carboxylato})_{16}(\text{H}_2\text{O})_4]$ complex..

synthesized and characterized (Albela, B. PhD Thesis. Universitat de Barcelona, December 1996). All these compounds show anisotropy, but the spin-ground state is not high enough to give superparamagnetic properties, at least up to 2K. It is remarkable that the hexanuclear mixed-valence complexes have a spin ground state of $S = 0$, indicating that high nuclearity it is not equivalent to high-spin, owing to the compensation of different spins in the molecule. These small clusters can be used as building blocks for synthesizing new large clusters. For example, the trinuclear Mn_3O complexes can

give the Mn_{12} complexes, by oxidation with MnO_4^- , but with low yield. They can easily be obtained by replacing the acetato bridging ligand in the $[Mn_{12}O_{12}(\text{acetato})_{16}(\text{H}_2\text{O})_4]$ [17] with a carboxylate that is more acidic than the acetate in a non-aqueous solvent like CH_2Cl_2 or toluene [33]. With this method the 2-F, 2-Cl, 2-Br and 2-Me complexes were obtained and characterized. The crystal structure of the 2-Cl and 2-Me was solved, indicating that their cores $Mn_{12}O_{12}$ are very similar (Figure 9). The 2-Cl derivative differs in crystal packing from the other dodecamanganese compounds: the molecules of the acetato, benzoato and 2-methylbenzoate are aligned in the crystal net while the 2-Cl (and presumably the 2-Br owing to its great similarity) is the first in which the molecules are placed perpendicular to each other in the net. The $\chi_M T$ vs T curves are characteristic (Figure 10a): they show a value of *ca* $18 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature and, on decreasing the temperature, a maximum is reached at *ca* 20 K (between 45 and $50 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ depending on the carboxylate), after which there is a decrease. This maximum reached at low temperature may indicate that these systems have a relatively high-spin ground state. A magnetization study at various field values (from 20 to 50 kG) in the temperature range 2-5 K was carried out, indicating that the system may have a high spin value in all cases. Besides, if only the ground state was populated at these low temperatures, the non-superimposability of the curves recorded in different fields would indicate the presence of zero-field splitting effects in the ground state, which is an indirect measurement of the anisotropy of the system (Figure 10b). Field-Cooled (FC) and Zero-Field-Cooled (ZFC) magnetization experiments show a blocking temperature (at which the paramagnetic phase becomes ferromagnetic) close to 4 K (Figure 10c). Finally, all four new complexes show hysteresis loops at 2 K (Figure 10d), typical of ferromagnetic behavior, with jumps at several fields, which may indicate that at these fields the relaxation process becomes faster, probably due to resonant tunneling of the magnetization. Working with *alternating current (ac)* they show real and imaginary components which are frequency-dependent (Figures 10e,f). The spin-ground state can be determined from the plateau ($T = 6\text{-}10 \text{ K}$) in the $\chi'_M T$ (χ'_M is the real part or *in-phase* component of the *ac* susceptibility) versus T plot, by applying the Curie law for $g = 2.00$. A large S_T value, between 8 – 10, was obtained for all compounds. A rapid decrease in $\chi'_M T$ at lower temperature was observed for all compounds (Figure 10e). At the same time, a peak in the χ''_M (imaginary part or *out-of-phase* component) versus T plot appeared (Figure 10f). These features were indicative of slow relaxation of the magnetization. The temperature at which the maximum in χ''_M occurred correlated well with the temperature at half the decrease in the $\chi'_M T$ versus T plot, as expected for these systems. It is called blocking temperature (T_c), since below it the magnetization of the complex cannot stay in phase with the oscillating field and the system is thus «blocked». Moreover, the position of the *out-of-phase* (χ''_M) peaks and that of the $\chi'_M T$ fall were frequency-dependent. These phenomena are typical of superparamagnetic species, as indicated above. This superparamagnetism is attributable to the large

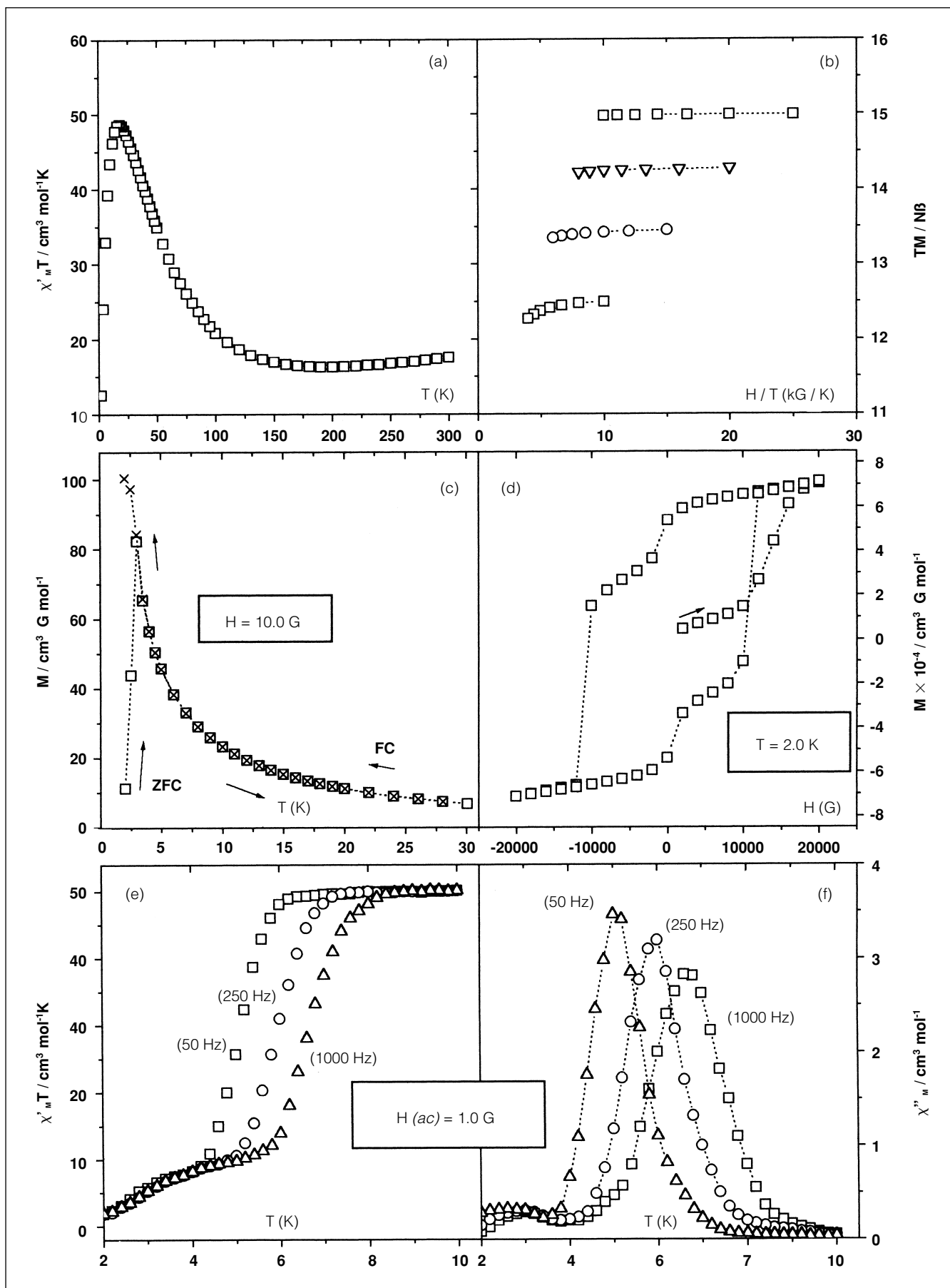


Figure 10. Magnetic measurements for a $[\text{Mn}_{12}\text{O}_{12}(\text{carboxylato})_{16}(\text{H}_2\text{O})_4]$ (carboxylato = 2-chlorobenzoato) complex, showing its peculiar characteristics as molecular magnet: (a) $\chi'_M T$ vs T ; (b) isofield magnetizations; (c) field-cooled and zero-field cooled magnetization; (d) hysteresis cycle; (e) *in-phase* $\chi'_M T$ vs T and (f) *out-of-phase* $\chi''_M T$ vs T (see Text for the explanation).

magnetic anisotropy of the complexes. Each molecule has a high-spin ground state ($S_T = 8-10$) which shows appreciable zero-field splitting (ZFS), and the splitting of the level is such that the two components with maximal multiplicity are the lowest in energy. This ZFS arises from the single-ion ZFS of all the Mn^{III} in the outer ring of the molecule, whose Jahn-Teller axes are aligned, which leads to a large ZFS in the ground state. If an $S_T = 10$ ground state is considered, at low temperature only the $M_S = \pm 10$ level of this $S_T = 10$ may be populated, and the spin-up and spin-down levels are separated by a large anisotropy barrier due to the high value of D , the axial ZFS. So, at low temperature, at which thermal agitation is low, a long time may be needed to reorient the magnetization of the system, since the spin component must pass from the $M_S = -10$ state to -9 , then to -8 , up to $M_S = 0$, which is the highest in energy, and then descend gradually to $M_S = +10$. Consequently, long relaxation times may be observed, which may give rise to the unusual magnetic properties found in these complexes. However, this behavior has only been associated with isolated molecules rather than cooperative effects among them.

Finally, these dodecamanganese complexes are very stable in non-aqueous solvents, which suggests that they might be used as a starting point for the synthesis of new unexpected clusters with higher nuclearity and higher spin ground-state. 1H -NMR studies were performed which corroborate this stability and determine that the structure is maintained in solution. Electrochemical studies were performed in CH_2Cl_2 . The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were similar for all complexes. All showed three features on the reduction side: the first was quasi-reversible and the following two were irreversible. In all cases quasi-reversible oxidation was observed, and when the potential sweep was increased a second oxidation was detected, which was irreversible. This creates the possibility of synthesizing new reduced or oxidized ionic clusters separated in the crystal net by counterions, like those reported by Christou [33b] which led to the hypothesis that magnetic behavior is inherent to the molecular cluster and not due to intermolecular interactions. This and the possibility of isolating new larger clusters derived from these dodecamanganese derivatives are two major challenges for the future.

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About the author

Doctor in Chemistry (1974) and Professor in Inorganic Chemistry since 1986 at the University of Barcelona. Since 1970 his research has been conducted in several fields of Coordination Chemistry: synthesis and characterisation of complexes with oxoanions like dithionato, sulfato, etc. as ligands; kinetic studies of solid state polynuclear compounds with cyanide as bridging ligand; synthesis and conductivity studies of square-planar complexes with sulfur derivative ligands and, finally, synthesis, characterisation and study of magneto-structural correlations in polynuclear complexes derived from first-row transition metal ions. At present he is leading a group (Magnetic Interactions and Molecular Magnetism) at the Inorganic Chemistry Department of University of Barcelona. The members of his team have collaborated with the main groups devoted to the magnetochemistry of molecular systems, including those led by Dr. Olivier Kahn (Orsay, France), Dr. Jean-Jacques Girerd (Orsay, France), Dr. Michel Verdaguer (Paris, France), Dr. Marc Drillon (Strasbourg, France), Dr. Dante Gatteschi (Firenze, Italy) and Dr. George Christou (Bloomington, Indiana, USA).

The aim of the group is the synthesis of molecular systems to develop magneto-structural correlations and to attempt to obtain new species that can act as magnetic materials, such as discrete and low-dimensional systems, which may show cooperative phenomena at low temperature, and discrete clusters with high spin and strong anisotropy that show superparamagnetic behavior. The group is also devoted to the synthesis of discrete polynuclear systems that can be envisaged as models of certain bioinorganic systems.

