Magnetism of Large Iron-Oxo Clusters

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1 Introduction

Large iron–oxo clusters are well known materials which have been investigated for many years now in relation to the mechanisms of hydrolysis of iron in water solution.[1] In fact it was observed that hydrolysis products which are found in natural systems can be related to prototypes identified in synthetic media. Numerous minerals are formed by hydrolytic processes, such as haematite, goethite, ferrihydrite, lepidocrocite and maghaemite. The same processes are also observed in the mechanisms of biomineralization of iron.[2] In fact iron oxides or oxo hydroxides are found in many different living organisms, with different biological roles, as shown in Table 1. The iron oxide type materials found in biological systems are often observed in small particles, of size of a few nanometres. The best example is provided by ferritin, the iron storage protein, which is found in most living organisms. It is constructed of an array of polypeptide chains organized into a roughly spherical shell, which envelopes an inorganic core of approximate stoichiometry corresponding to ferrihydrite, $5Fe_2O_3{\cdot}9H_2O$, as schematically depicted in Fig. 1. The size of the inorganic core is about 7 nm.

The synthesis of large iron–oxo clusters has long been attempted with the aim to provide suitable models for the understanding of the above outlined mechanisms, but in recent years there have been additional reasons for interest in such compounds, associated with the investigation of the magnetic properties of these materials.[3–5] In fact the general trend towards interest in nanoscale objects has shown that in principle nanometer size magnets can be important both from the fundamental point of view, where they can provide examples of manifestation of quantum effects in large objects, and for their applications, where they can be in principle used for such diverse reasons as for optimal magnetocaloric effects and for magneto-optical devices.[6–8]

The general idea behind this interest is that with small particles it may be possible to store information with a higher density than by using large particles, as is common up to now. However the process of reduction of the size of the particles cannot continue indefinitely, because when the size becomes too small the particles cannot be any longer permanently magnetized. It is of significant interest to investigate the range of size, where the cross-over from permanent magnet to paramagnet occurs, because it can be expected to provide evidence of coexistence of quantum and classic phenomena.

Table 1 Iron oxides and oxo hydroxides found in living organisms

Oxide	Mineral	Location	Function
$5Fe_2O_3{\cdot}9H_2O$	Ferrihydrite	Ferritin Molluscs radula	Storage Structural
α-FeOOH	Goethite	Hemosiderin Molluscs radula	Storage Structural
γ-FeOOH	Lepidocrocite	Molluscs radula	Structural
Fe_3O_4	Magnetite	Magnetosomes Molluscs radula	Sensor Structural

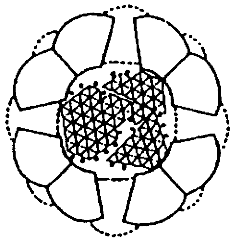

Figure 1 Scheme of the structure of ferritin. Apoferritin is a segmented protein shell with an outer diameter of 12.5 nm and an inner diameter of 7.5 nm. The inorganic core contained inside has a composition very close to that of ferrihydrite ($5Fe_2O_3{\cdot}9H_2O$).

Dante Gatteschi, born in 1945, graduated in Chemistry in 1969 in Florence in the Laboratory of Luigi Sacconi. He has spent all his academic life in the same University, where he was appointed Professor of General and Inorganic Chemistry in the Faculty of Pharmacy in 1980. His research interests are in the area of molecular magnetism.

Andrea Caneschi, born in 1958, graduated in Chemistry at the University of Florence in 1983 and obtained his Ph.D. in 1988 in the same institution under the supervision of Professor D. Gatteschi. He had a temporary position at the Università della Calabria in the period 1988–1990 then he became a researcher in the University of Florence.

Andrea Cornia was born in 1968 in Modena, where he graduated in Chemistry in 1992. In 1995 he completed his Ph.D. studies under the supervision of Professors A. C. Fabretti (Università di Modena) and D. Gatteschi. His research work involves the synthesis and magnetic characterization of high-nuclearity iron and manganese clusters.

Roberta Sessoli, born in 1963, graduated in Chemistry in 1987 at the University of Florence where she received a Ph.D in 1992 with a thesis on molecular magnetism under the supervision of Professor D. Gatteschi. Her major interests are the magnetism and magnetic resonances of large clusters and low dimensional materials.

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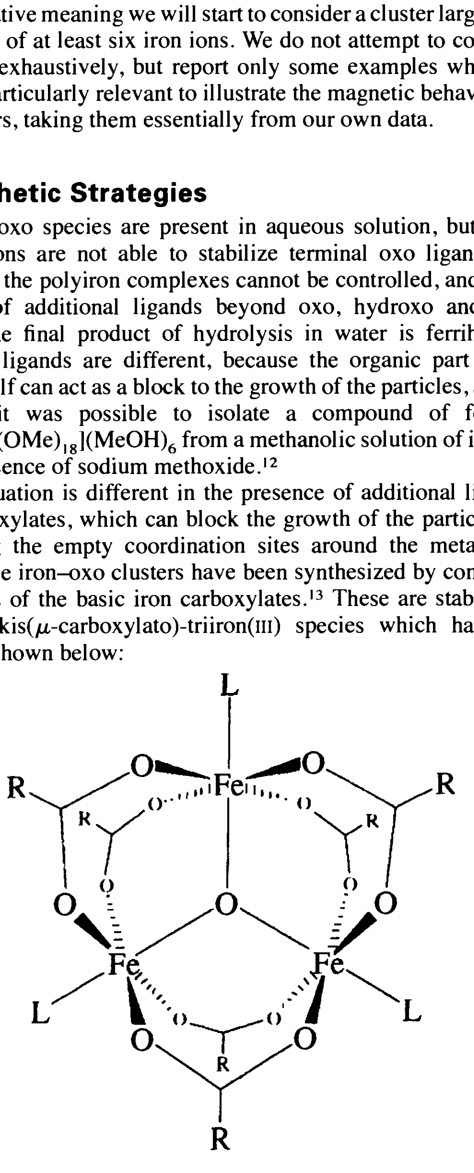
In principle it would be desirable to learn how to synthesize large iron–oxo clusters, by adding the iron ions one after the other, or in small blocks, but this is not yet possible, and growing large clusters is still much of an art. However many beautiful examples of large clusters have been structurally characterized.[9–11] The advantage of these systems over the small magnetic particles grown by physical techniques is that the molecular clusters are well defined objects, whose structures can be determined exactly, and all the particles are of course identical in the lattice. Furthermore they can often be dissolved with retention of their structures and embedded in polymeric matrices. In this way it is possible to investigate the magnetic properties of the individual clusters, reducing the magnetic interactions between them practically to zero by keeping the clusters far apart from each other.

This review aims to show some relevant examples of iron(III)–oxo clusters which have been structurally characterized and for which detailed magnetic data are available. Since 'large' has only a relative meaning we will start to consider a cluster large when it consists of at least six iron ions. We do not attempt to cover the literature exhaustively, but report only some examples which we feel are particularly relevant to illustrate the magnetic behaviour of the clusters, taking them essentially from our own data.

2 Synthetic Strategies

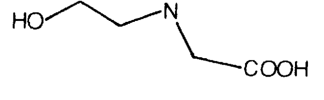
Polyiron–oxo species are present in aqueous solution, but, since iron(III) ions are not able to stabilize terminal oxo ligands, the growth of the polyiron complexes cannot be controlled, and in the absence of additional ligands beyond oxo, hydroxo and aquo ligands the final product of hydrolysis in water is ferrihydrite. Alkoxide ligands are different, because the organic part of the ligand itself can act as a block to the growth of the particles, and for instance it was possible to isolate a compound of formula $Na_2[OFe_6(OMe)_{18}](MeOH)_6$ from a methanolic solution of iron(III) in the presence of sodium methoxide.[12]

The situation is different in the presence of additional ligands, like carboxylates, which can block the growth of the particles, by occupying the empty coordination sites around the metal ions. Many large iron–oxo clusters have been synthesized by controlled hydrolysis of the basic iron carboxylates.[13] These are stable (μ_3-oxo)-hexakis(μ-carboxylato)-triiron(III) species which have the structure shown below:



The $[Fe_3O]^{7+}$ core can be used as a building block to give rise to larger clusters. For instance the decanuclear complex $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$ can be obtained[14] by a reaction between $[Fe_3O(O_2CCH_2Cl)_6(H_2O)_3](NO_3)_3{\cdot}4H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$. Similar strategies were used to synthesize clusters with eleven and sixteen iron(III) ions.[10]

The carboxylates are not the only co-ligands used to block the growth of the ferrihydrite particles. For instance using the ligand H_3heidi:



it was found[15] that, starting from solutions at pH 2.4, a compound of formula $[Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{10}(heidi)_8(H_2O)_{12}]$ $[Fe_{19}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_8(heidi)_{10}(H_2O)_{12}](NO_3)_4{\cdot}60H_2O$ was obtained.

Other ligands which have been used extensively are the polyketonates. In fact methanolysis of simple iron(III) salts in the presence of β-diketonates has proved to be an excellent route to Fe_2, Fe_3, Fe_4, Fe_6, and Fe_{10} clusters.[16,17] These systems contain OMe and β-diketonate ligands and provide some insight into the aggregation processes which take place in alcoholic media.

3 Selected Structures

3.1 Fe_6 Clusters

Several different types of Fe_6 clusters have been reported, which were classified as planar, twisted boat, chair, parallel triangles, octahedral and fused clusters.[18] Recently a new structure was reported[16] as shown in Fig. 2. The six iron ions define a ring, and they are bridged by μ_2-alkoxo ligands. The $[Fe_6(\mu_2\text{-}OMe)_{12}(dbm)_6]$ ring, [Fe_6 ring], where Hdbm is dibenzoylmethane, is a neutral species, but in the solid it crystallizes with NaCl. In fact the sodium ion is trapped in the centre of the iron ring, which acts like a crown ether complexing the alkaline ion. The six iron ions and the sodium ion are practically coplanar, with average deviations from the least squares plane of 2.4 pm. Therefore the compound can be formulated as $[NaFe_6(\mu_2\text{-}OMe)_{12}(dbm)_6]Cl$. An isostructural compound trapping a Li^+ ion has been isolated in our laboratory. NMR experiments have recently shown that the analogy between the Fe_6 ring and crown ethers is not only structural but also functional. In fact, when the lithium-containing compound is dissolved in chloroform in the presence of sodium ions, substitution of Li with Na takes place. A very interesting feature of the structure, and one which will be often encountered also with other iron–oxo clusters, is that the oxygen atoms of the bridges and of the β-diketonate ligands tend to form close-packed layers, similar to those found in the lattices of metal oxides and hydroxides. In fact the oxygen donors of [Fe_6 ring] are assembled essentially on two planes, with maximum deviations of 20 pm. The distances between the oxygen atoms compare well with those observed in the continuous lattices of the oxides and hydroxides. Therefore it can be concluded that a molecular cluster like that depicted in Fig. 2 is indeed a small piece of an iron hydroxide.

A variation on the theme of structures with iron ions lying

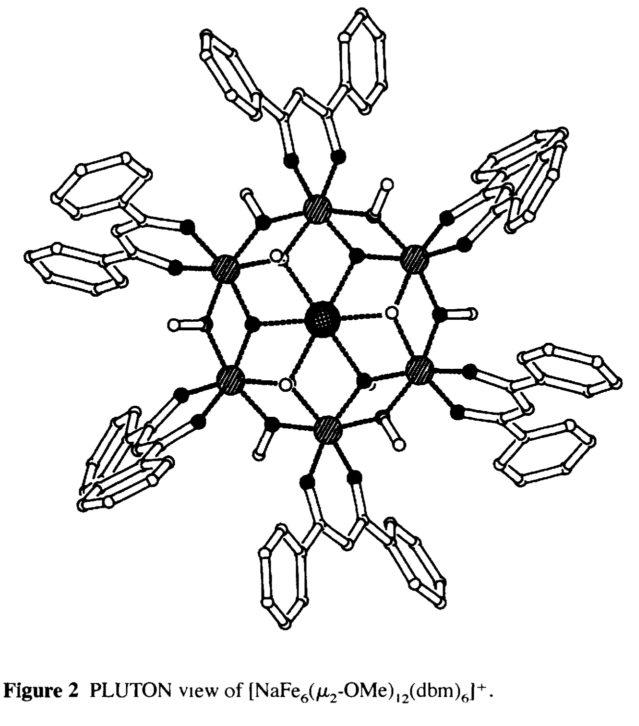


Figure 2 PLUTON view of $[NaFe_6(\mu_2\text{-}OMe)_{12}(dbm)_6]^+$.

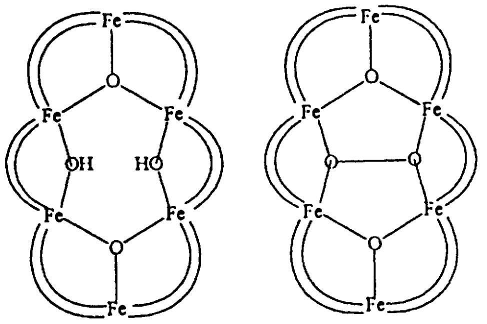


Figure 3 Schemes of the structures of the hexanuclear iron(III) clusters composed of two parallel triangles.

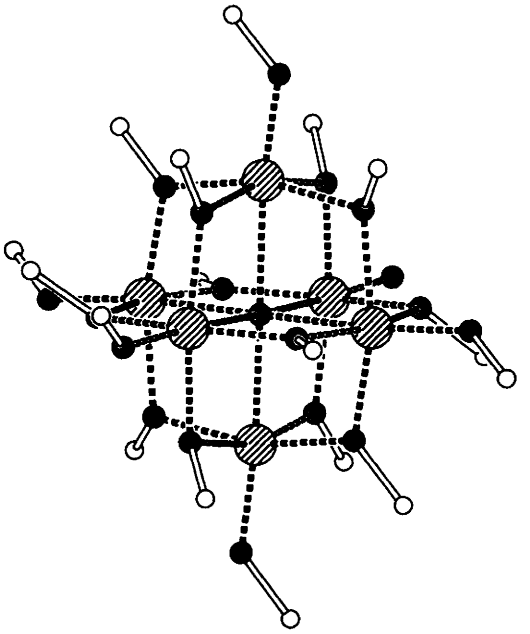


Figure 4 PLUTON view of $[Fe_6(\mu_6\text{-}O)(\mu_2\text{-}OMe)_{12}(OMe)_6]^{2-}$.

approximately on the same plane is provided by the compounds shown in Fig. 3. The two triangles in the Fe_6 clusters are defined by μ_3-oxo ligands, and they are connected by different ligands ranging from hydroxo to peroxo groups.[19–22]

Structures in which the iron ions define an octahedron have been observed in two clusters recently reported by Hegetschweiler *et al.*[12] The main feature of these two compounds, $[Fe_6(\mu_6\text{-}O)\{(OCH_2)_3(CMe)\}_6]^{2-}$ and $[Fe_6(\mu_6\text{-}O)(\mu_2\text{-}OMe)_{12}(OMe)_6]^{2-}$, $[Fe_6$ octahedra$]$, is that they contain a unique μ_6-oxo bridge. The structure of $[Fe_6(\mu_6\text{-}O)(\mu_2\text{-}OMe)_{12}(OMe)_6]^{2-}$is shown in Fig. 4. The close-packed structure of these compounds is very apparent; in fact there are three layers of oxygen atoms, in which the maximum deviation from planarity is 13 pm, and the iron ions are assembled in two planes in between the oxygen planes. Actually there are more oxygen layers, because the anions are capped by sodium ions. The cluster is therefore a nice example of a small part of a cubic close-packed structure.

3.2 Fe_8 Clusters

Wieghardt reported a cluster of eight iron(III) ions, $[(tacn)_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}Br_7(H_2O)]^+$, $[Fe_8]$, whose structure[23] is given in Fig. 5 (tacn is 1,4,7-triazacyclononane). The four central iron ions are connected by two μ_3-oxo bridges in a well known disposition, observed in a few tetranuclear structures, which has been called 'butterfly'.[24] The two iron ions connected by bis-μ_3-oxo bridges define the body of the butterfly, while the ions connected by single μ_3-oxo bridges define the wings. The overall symmetry of the cluster is D_2. In this case also the iron ions lie approximately on a plane which is sandwiched by two oxygen and nitrogen layers.

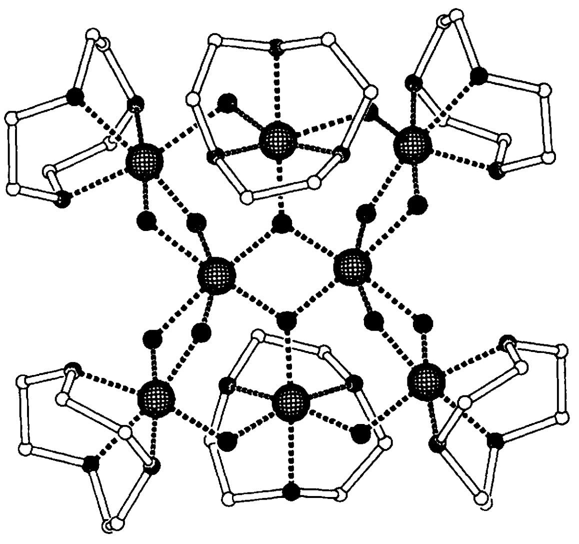


Figure 5 PLUTON view of $[(tacn)_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}Br_7(H_2O)]^+$.

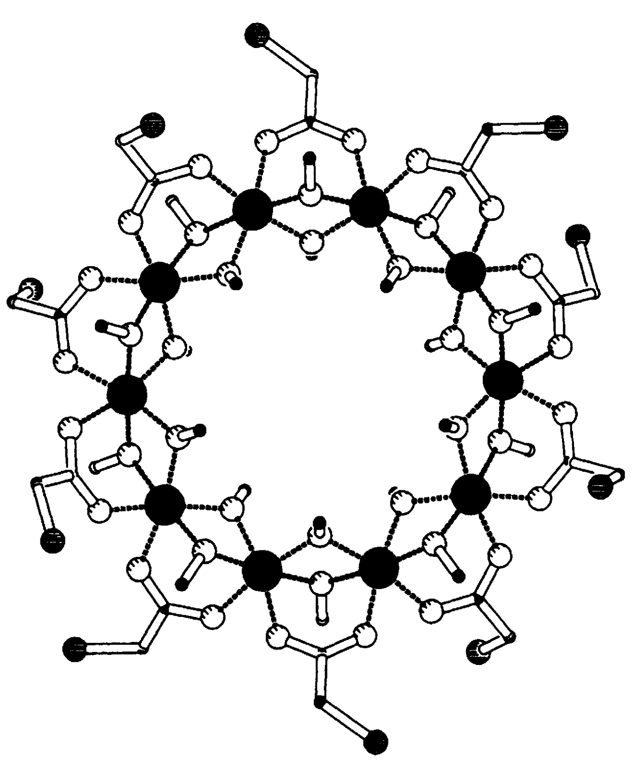


Figure 6 PLUTON view of $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$.

3.3 Fe_{10} Clusters

An interesting cluster containing ten iron(III) ions, with a ring structure, $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, $[Fe_{10}]$, named ferric wheel, was reported by Lippard *et al.*[14] a few years ago. The structure of the cluster is shown in Fig. 6. From the magnetic point of view this cluster, like $[Fe_6$ ring$]$, is a beautiful example of systems which can be used as models for the interpretation of the magnetic properties of linear chains. The iron ions are octahedrally coordinated and they are bridged by two methoxo and one carboxylate group.

3.4 Fe_{17} and Fe_{19} Clusters

The largest clusters so far reported contain seventeen and nineteen iron(III) ions respectively.[15] They crystallize together in the same

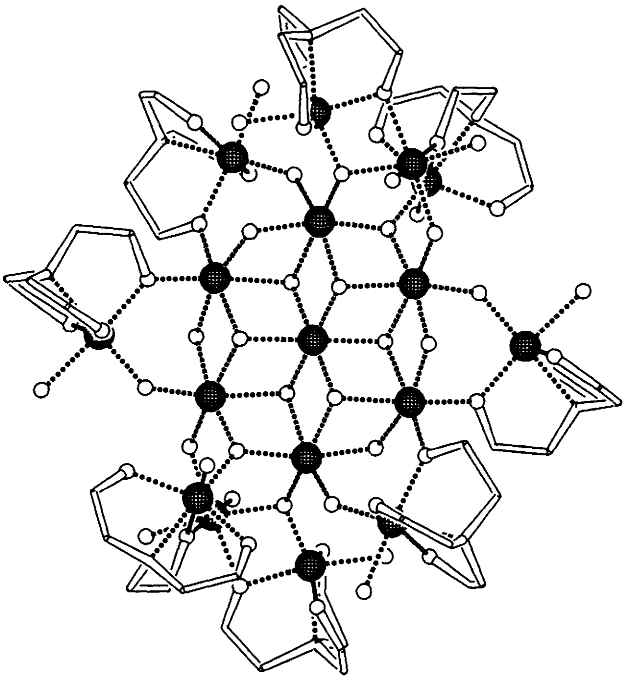


Figure 7 PLUTON view of $[Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{10}(heidi)_8(H_2O)_{12}]^{3+}$.

unit cell and have two formulae $[Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{10}(heidi)_8(H_2O)_{12}]^{3+}$, $[Fe_{17}]$, and $[Fe_{19}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_8(heidi)_{10}(H_2O)_{12}]^+$, $[Fe_{19}]$, respectively. The two clusters have very similar structures. That of $[Fe_{17}]$ is shown in Fig. 7. $[Fe_{19}]$ has two additional iron ions on the exterior of the cluster, but the central moiety of seven iron ions is identical in the two compounds. It is interesting to note that this central core of seven ions is very similar to that observed[16] in $[NaFe_6(\mu_2\text{-}OMe)_{12}(dbm)_6]^+$, provided that the sodium ion of the latter is substituted by an iron ion.

4 Magnetic Properties of the Clusters: Theoretical Considerations

Finite-size clusters can be considered to behave as complex paramagnets, in which there are in general strong to moderate interactions between the spins present in the cluster, and weak interactions between the clusters. In order to interpret the magnetic properties of the clusters it is customary to use a spin Hamiltonian in which the pairwise interactions between the different spins, *i* and *j*, are parametrized as in eqn. (1):

$$H=\Sigma_{i>j}J_{ij}S_i\cdot S_j \tag{1}$$

In the case of pairs the levels can be expressed as a function of the total spin *S*:

$$|S_1-S_2|\leq S\leq S_1+S_2 \tag{2}$$

with the energies:

$$E(S)=J/2\,[S(S+1)-S_1(S_1+1)-S_2(S_2+1)] \tag{3}$$

When $J<0$ (ferromagnetic coupling) the ground state has the maximum spin multiplicity $S=S_1+S_2$, while when $J>0$ (antiferromagnetic coupling) the ground state has $S=S_1-S_2$.

Use of this Hamiltonian for dimers yields the well known Bleaney–Bowers equation[25] for the magnetic susceptibility. Extention of eqn. (1) to large clusters is in principle easy, but in practice it rapidly becomes extremely difficult. In fact for a cluster of N spins characterized by individual quantum numbers S_i, the total number of states which form the Hamiltonian matrix is $(2S_i+1)^N$. For instance, for $S_i=5/2$, as appropriate for iron(III), when $N=8$ the number of states is already 1 679 616. Therefore the calculation of the spin levels, and of the magnetic susceptibility, becomes a formidable task. The best approach so far reported is that of using irreducible tensor operators, ITOs, which exploit at best the symmetry associated with the total spin.[26] However even in this case it is necessary to calculate 21 matrices (corresponding to the total spin values S ranging from 0 to 20), the largest of which, $S=5$, is of size 16 576×16 576.

Table 2 Symmetry classification of the total spin states of Fe_8 in the point group D_2

S	A	B_1	B_2	B_3	Total
20	1	—	—	—	1
19	2	1	2	2	7
18	10	6	6	6	28
17	22	18	22	22	84
16	60	50	50	50	210
15	118	108	118	118	462
14	243	225	224	224	916
13	419	401	420	420	1660
12	717	690	686	686	2779
11	1088	1061	1092	1092	4333
10	1614	1578	1568	1568	6328
9	2174	2138	2184	2184	8680
8	2841	2799	2780	2780	11200
7	3401	3359	3420	3420	13600
6	3927	3885	3854	3854	15520
5	4139	4097	4170	4170	16576
4	4155	4122	4076	4076	16429
3	3704	3671	3750	3750	14875
2	3019	3001	2940	2940	11900
1	1899	1881	1960	1960	7700
0	703	703	630	630	2666

A further reduction in the size of the matrices can be obtained using the point group symmetry of the cluster. For D_2 symmetry the results are as shown in Table 2.

In general the exchange interactions observed in oxo-bridged iron(III) ions are antiferromagnetic, with the general trend that J decreases in the order from oxo to hydroxo bridges. Since the corresponding iron–oxygen distances are shorter for the oxo than for the hydroxo bridges a simple way of taking into account the difference between the two types of groups is to use the average bond distance, P, or in the presence of multiple bridges the average bond distance relative to the shortest superexchange pathway. Gorun and Lippard found[27] a reasonable correlation for 34 compounds; we have now extended it to 50 compounds. The best fit equation, for P in Å and J in cm^{-1}, is:

$$J=3.25\times10^9\exp(-9.3P) \tag{4}$$

From Gorun and Lippard's work no correlation emerged between Fe–O–Fe angles and coupling constants. However, Kurtz[28] noted that in strongly coupled oxo-bridged diiron(III) complexes the J value is angle-dependent, linear bridges leading to stronger interactions. The same conclusion has been reached recently in the case of alkoxo clusters, in which substantially weaker interactions are present. Attempts were also made to find a theoretical justification for this, but they were not extended to very small angles, <100°, which can be observed in μ_3-oxo bridged systems. In some cases we were obliged to use smaller J constants for a given P value at small angles. Further work is needed in this area.

Large clusters are characterized by a large number of spin levels; therefore these will tend to merge into a continuum. When this occurs the system must cross over from complex paramagnetic to bulk magnetic behaviour. This transition must be expected to occur gradually. From a theoretical point of view we may imagine large clusters being built by adding metal ions one at a time. This path to infinity may occur in one, two, or three dimensions as suggested by Fig. 8. Linear clusters or rings can be models for one-dimensional magnetic materials, planar clusters for two-dimensional and finally three-dimensional clusters for bulk magnetic materials.

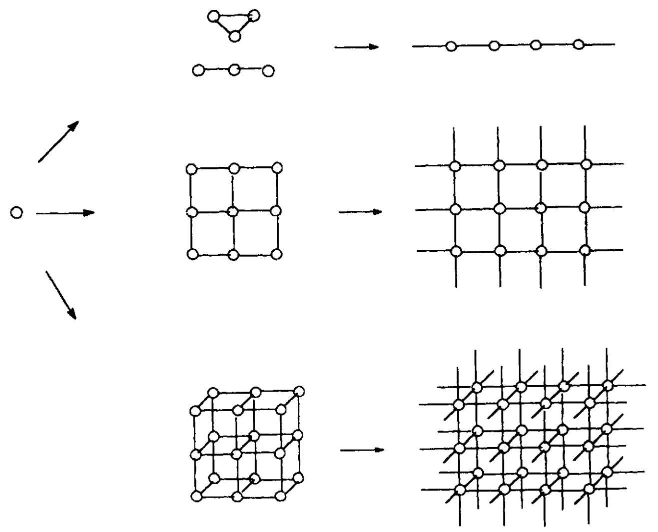


Figure 8 Schematic path to infinity in one-, two- or three-dimensions.

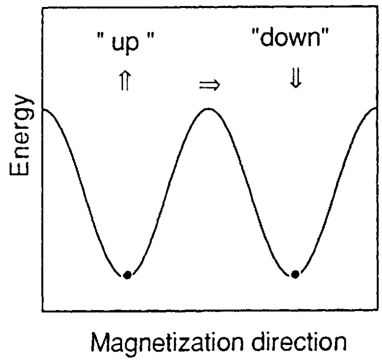


Figure 9 Representation of the energetic barrier that a particle must undergo to reorient its magnetization in the absence of an external magnetic field.

In this ideal process at some stage the interacting spins of the cluster will become frozen in a preferred orientation, corresponding to a ferro-, ferri-, or antiferromagnet, and the system becomes ordered. Associated with the ordering is the development of a magnetic anisotropy, which will dictate the spatial orientation of the magnetic moment. The origin of the anisotropy can be associated with the shape of the particle, to the contribution of the anisotropy of the individual ions, or a contribution associated with the magnetic interaction between the individual ions. For relatively large particles the anisotropy A can be assumed[29] to be proportional to the volume V of the particle:

$$A = CV \tag{5}$$

A represents the barrier that a particle must overcome in order to reorient its magnetization to the energetically equivalent position, in the absence of an external field, as shown in Fig. 9.

When A is large compared to thermal energy the magnetization will be blocked in one of the two minima, but when the barrier is small the magnetization will freely flip over from one minimum to the other. The ordered system will thus behave as a paramagnet, but one characterized by a large magnetic moment. A particle which behaves like this is called a superparamagnet. The relaxation of the magnetization τ follows a thermally excited process:

$$\tau = \tau_0 \exp(A/kT) \tag{6}$$

τ_0 is typically 10^{-11} s for ferromagnets like iron.

A given particle behaves like a bulk magnet when τ is larger than the characteristic time τ_c of the investigation technique used to monitor it. τ_c is 10^{-3}–10^{-1} s for ac susceptibility measurements and 10^{-8} s for Mössbauer spectroscopy. The temperature at which the relaxation time of the magnetization equals τ_c is called the blocking temperature of the superparamagnet, T_B.

In the case of clusters it can be thought that the first indication of bulk behaviour comes from a slow relaxation of the magnetization observed at low temperature. A further reason for interest in the investigation of the dynamics of the magnetization of the clusters at low temperature is that, since their size is intermediate between that of bulk objects, to which classical mechanics applies, and molecular objects, to which quantum mechanics applies, at very low temperature the inversion of the magnetization may be thought to occur by a tunnelling process. Indeed this is one of the reasons for the great interest of solid state physicists in this new kind of magnetic material.

5 Magnetic Properties of the Clusters: Experimental Results

5.1 Fe_6 Clusters

Here we will focus on the types which can be represented by the spin topologies depicted in Fig. 10. By spin topology we mean the set of exchange pathways which can be expected to be present between pairs of iron ions, on the basis of the presence of chemical bridges, like oxo groups connecting pairs of metal ions. In Fig. 10 we have not made any attempt to differentiate between different types of bridges, but we have considered them all as equivalent. Of course the differences in the intensities in the exchange interactions transmitted by the different bridges are of paramount importance in determining the actual magnetic properties of the individual clusters.

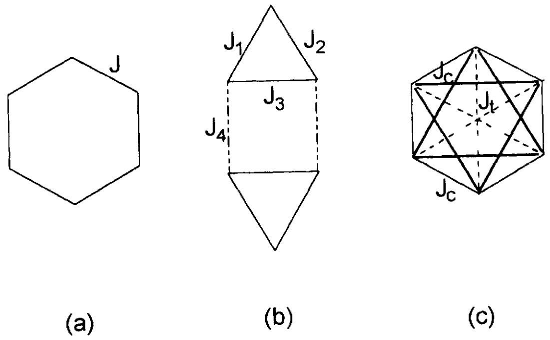


Figure 10 Possible spin topologies for hexanuclear clusters.

Up to now there is one cluster which has the spin topology (a). The magnetic properties of [Fe_6 ring] are rather obvious,[16] dominated by the antiferromagnetic interaction between the nearest-neighbour iron ions. The magnetic susceptibility of [Fe_6 ring] goes through a broad maximum at *ca.* 150 K, and then decreases rapidly. The comparison with the behaviour expected for infinite chains of iron(III) ions suggests a coupling constant $J \approx 20$ cm^{-1}. The quantitative fit of the magnetic properties of the cluster is less obvious, because the number of states to be calculated is very high, but the procedures outlined in Section 4 make it possible.

A satisfactory fit to χ *vs.* temperature yielded a coupling constant, $J = 20$ cm^{-1}, which agrees with the values observed in dinuclear complexes with similar bridges. A further proof of the goodness of the fit comes from the field dependence of the magnetization at very low temperature, which provided the energies of a few excited states. Indeed magnetization measurements in large clusters can provide a wealth of information as shown below.

The magnetization of [Fe_6 ring] was measured at 1.5 K in fields up to 52 T. At low field the magnetization is close to zero, but on increasing the field several steps are observed where the magnetization rapidly increases. The steps are equally spaced in field, as shown in Fig. 11. These data can be explained considering that the saturation magnetization of a paramagnet characterized by a ground spin state S is given by $M = g\mu_B S$. In a system like [Fe_6 ring] for

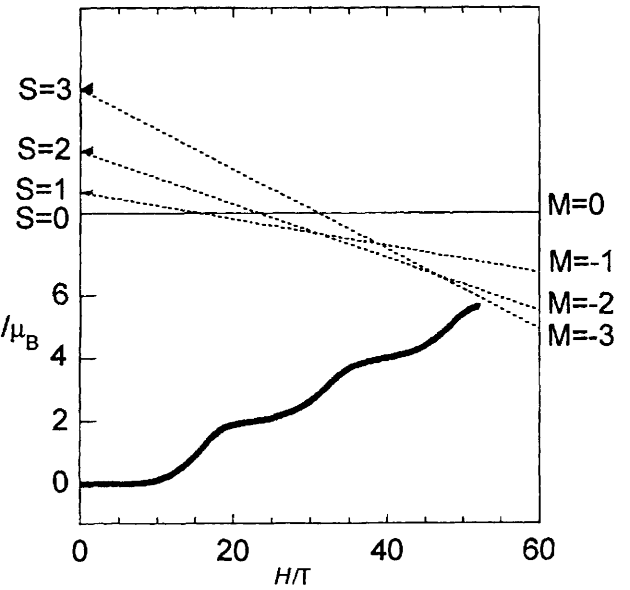


Figure 11 Spin crossover diagram for the first spin levels of [Fe_6 ring]; (O) experimental points.

very low fields the magnetization must be equal to zero, because the ground state has $S = 0$. However, on increasing the external field, the energies of the $M = -S$ components of all the excited S spin multiplets rapidly decrease, with slopes proportional to $-S$, as shown in Fig. 11. It is clear that up to 10 T the magnetization is close to 0. Above this limit it rapidly increases to reach the saturation value of $S = 1$. A further increase of the field determines a second step which reaches the magnetization of $S = 2$. Finally a third step gives the magnetization of $S = 3$. The inflection points of the magnetization curve are regularly separated in a field by about 16 T as clearly observable by the plot of the differential magnetization, d*M*/d*H*, *vs.* magnetic field, shown in Fig. 12.

If the lowest lying spin multiplets follow a Lande interval rule, *i.e.* they are given by eqn (7):

$$E(S) = (K/2)\, S(S+1) \tag{7}$$

it is easy to show[14] that the crossover points will occur at fields given by eqn (8):

$$B_{S,S+1} = K/g\mu_B \tag{8}$$

where $B_{S,S+1}$ is the field value at which the spin multiplets S and $S+1$ have the same energy. The consequence of eqns. (7) and (8) is that the crossover points will be observed at regular intervals in a field of $K/g\mu_B$. The calculated energies of the excited states correspond within experimental error to the observed ones.

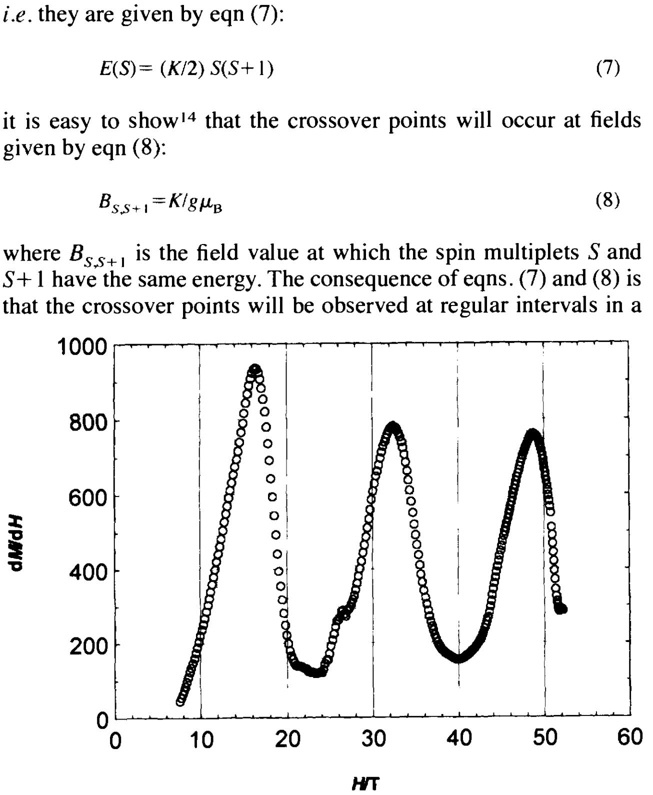


Figure 12 Differential magnetization, d*M*/d*H* (arbitrary units), *vs.* magnetic field at 1.5 K for [Fe_6 ring].

It might be asked why the lowest-lying S excited levels follow a Lande interval rule. The answer is rather simple: the lowest lying levels can be described to a good approximation by a spin configuration in which all the spins on the odd sites are up, and those on the even sites are down. In general the spins in the ring of $2n$ members can be partitioned into two sets, each containing n objects. The two sets will have identical intermediate spin $S_A = S_B = nS_i$. If the two intermediate spins are coupled to give the total spin S the energies of the levels according to eqn. (3) are given by eqn. (9):

$$E(S) = K/2\, [S(S+1) - S_A(S_A+1) - S_B(S_B+1)] \tag{9}$$

showing that the first excited states must follow a Lande interval rule. K is an effective coupling constant, which is related to J according to eqn (10):

$$K = 2J/n \tag{10}$$

K is expected to go to zero for large n, *i.e.* when the energy levels must merge to give a continuum.

There are quite a few Fe_6 clusters with the spin topology depicted in Fig. 10(b), and they have been shown[19–22] to give rise to several different ground spin states ranging from $S = 0$ to $S = 5$. The spin topology in this case shows the presence of two triangles, and these, in the presence of antiferromagnetic interactions, make it impossible to predict the nature of the ground state on the basis of up–down spins. In fact it is easy to see that if we put for instance spin (a) of Fig. 13 up and spin (b) down, there is no way that spin (c) can obey at the same time the antiferromagnetic interactions with the other two spins. This has been called spin frustration,[30] by analogy with the psychological term which applies to a person under the influence of two equally strong and opposing stimuli.

The most general scheme for the exchange interactions in centrosymmetric clusters with spin topology (b) is as depicted[31] in Fig. 10 (b).

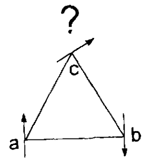


Figure 13 Schematic representation of the spin topology in an antiferromagnetic coupled triangle of spins.

In the following we will assume that J_1, J_2, and J_3 are similar to each other, and much larger than J_4. We will also assume that all are positive, corresponding to antiferromagnetic interactions.

In the most symmetric case, $J_1 = J_2 = J_3$, the ground state is always $S = 0$, so it is relatively unexciting. The same situation is achieved if it is assumed that $J_1 = J_2 \neq J_3$. Matters become much more interesting if it is assumed $J_1 = J_3 \neq J_2$. In this case the possible ground states are variable depending on the J_2/J_1 ratio, r. The calculated temperature dependence of the resultant μ_{eff} is shown in Fig. 14, for selected values of r. For $r = 1$ the ground state is $S = 0$, for $r = 0.7$ it is $S = 1$, for $r = 0.55$ it is $S = 3$, and for $r = 0.2$ it is $S = 5$. In fact when r tends to zero the spin frustration in the triangles is completely destroyed and the nature of the ground state is easily predicted with elementary spin up–spin down considerations.

The magnetic susceptibility[32] of the [Fe_6 octahedra] clusters, see Fig. 10c, reported by Hegetschweiler[12] gives a clear indication of a ground $S = 0$ state, which is steadily expected on the basis of qualitative considerations. The quantitative interpretation can be done in a simple way in this case, using the formalism first suggested by Kambe.[33] The energies of the levels are given by eqn. (11):

$$E(S) = J_c/2\, S(S+1) + |(J_t - J_c)/2|[S_{12}(S_{12}+1) + S_{35}(S_{35}+1) + S_{46}(S_{46}+1)] \tag{11}$$

where J_c is the coupling constant for two ions which are *cis* to each

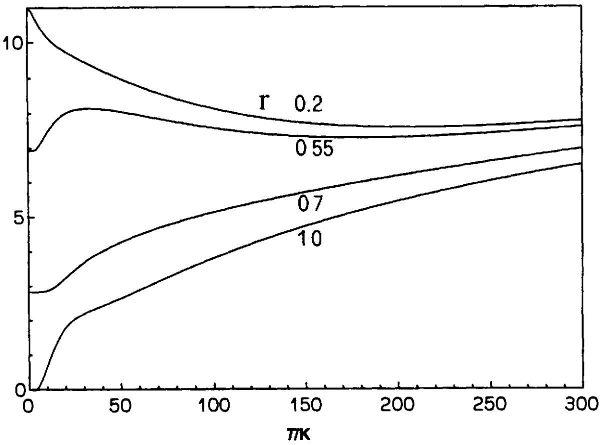


Figure 14 Calculated temperature dependence of the μ_{eff} for different *r* values.

other in the octahedron, and J_t the corresponding constant for two ions *trans* (S_1 and S_2, S_3 and S_5, S_4 and S_6) and S_{ij} is the intermediate spin resulting from the coupling of the *i* and *j* spins. The best fit values are $J_t = 21.2$ cm^{-1}, $J_c = 9.9$ cm^{-1}. The surprising feature is that despite the very long Fe–O distances involved in the μ_6 bridge the coupling constants are relatively large, certainly larger than would be expected on the basis of a largely accepted relation between Fe–O–Fe distance and coupling constant.[27]

The essential results of the investigation of the magnetic properties of Fe_6 clusters can be summarised as follows:

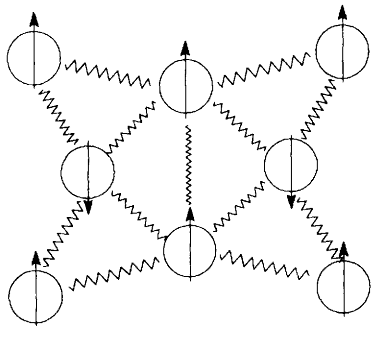
(*i*) The magnetic properties of Fe_6 clusters are those of paramagnets.
(*ii*) The quantitative interpretation of the magnetic properties can be arrived at using sophisticated extensions of the usual techniques.

In order to find deviations from simple paramagnetic behaviour it is necessary to extend the investigations to larger clusters.

5.2 Fe_8 Clusters

If the magnetic interaction transmitted by the oxo bridges is dominant in [Fe_8], the four central iron ions should be in an $S = 0$ ground state.[34] In fact the central butterfly of four iron ions has the wing–body interaction transmitted by oxo-bridges with exchange pathways close to 3.8 Å, and O–Fe–O angles close to 130°, while the body–body interaction corresponds to longer exchange pathways, 3.91(2), 3.96(2) Å, and much smaller angles [96.2(1)° and 97.3(1)°, respectively]. Therefore it can be concluded that spin frustration effects are not very important, and the ground state is $S = 0$.

The interactions with the external iron ions are determined by two different types of bridges, corresponding to one and two hydroxo groups, respectively. If the coupling constants are sufficiently different from each other it can be concluded that the ground state for the cluster must have $S = 10$, as shown in the Scheme 1.



Scheme 1

This is qualitatively confirmed by the temperature dependence of χT, which at room temperature is 20.06 emu mol^{-1} K, much smaller than expected for eight uncoupled $S = 5/2$ spins (35 emu mol^{-1} K), a clear indication of large antiferromagnetic coupling. The χT product increases on decreasing the temperature, showing that at low temperature the number of spins up is different from the number of spins down, *i.e.* the cluster is ferrimagnetic. High-field magnetization data at low temperature agree with an $S = 10$ ground state.

The quantitative fit of the magnetic properties was attempted using the ITO approach of Section 4. A reasonable agreement with experiment was found by setting $J_1 = 20$ cm^{-1}, $J_2 = 120$ cm^{-1}, $J_3 = 15$ cm^{-1}, $J_4 = 35$ cm^{-1}. J_1 corresponds to the body–body interaction in the central butterfly, J_2 to the wing–body interaction, J_3 to the bis-μ-hydroxo and J_4 to the single μ-hydroxo bridges. This is so far the largest cluster for which quantitative interpretation of the magnetic properties was achieved.

The nature of the ground state was confirmed[34] also by high frequency EPR data, recorded at 250 GHz and 4.2 K, which show 20 transitions. The spectra can be interpreted with $D = -0.191$ cm^{-1}, $E/D = 0.1675$. The sign of the zero-field splitting indicates that the *M* components with the highest possible value, namely $M = 10$, lie lowest in energy. This has the important consequence that the system becomes very anisotropic at low temperature (Ising type anisotropy, *i.e.* one easy axis), and the reorientation of the magnetization becomes very slow. In fact Mossbauer spectroscopy showed that the reorientation of the magnetization becomes slow on the time scale of the experiment, 10^{-8} s, at *ca.* 30 K, while ac susceptibility measurements, which have a time scale of 10^{-2} s, show similar results below 3 K. This behaviour is analogous to that of superparamagnets, and is entirely determined by the magnetic anisotropy of the cluster, which in its turn is mainly determined by single ion contributions.

These results are of extreme importance, because they confirm previous analogous findings in an Mn_{12} cluster,[35] which is the first reported case of molecular cluster with superparamagnetic-like behaviour showing magnetic hysteresis effects. Furthermore they show that superparamagnetic behaviour previously observed in larger iron oxo–clusters[4] must have been determined by an analogous mechanism, and not by the pseudo-three-dimensional structure of the particles. In fact [Fe_8] is essentially planar.

5.3 Fe_{10} Clusters

The magnetic properties[14] of [Fe_{10}] are simple to interpret, by analogy with those of the cyclic [Fe_6 ring] cluster described above. In fact assuming nearest-neighbour antiferromagnetic interaction, a ground $S = 0$ state would be expected. The magnetic susceptibility in fact goes through a maximum at *ca.* 65 K, while χT decreases from 32.2 emu mol^{-1} K at room temperature to 0.355 emu mol^{-1} K at 2.5 K. By analogy with simple dimers the maximum in χ suggests a coupling constant $J \approx 10$ cm^{-1}. The quantitative interpretation of the data is however impossible in this case, because the dimensions of the matrices are by far too large for us to be able to diagonalize them. However, by calculating the susceptibility for rings of 4, 6 and 8 $S = 5/2$ spins, we could extrapolate the curve to 10 spins, with a very good agreement between observed and calculated values. The coupling constant, $J = 9.6$ cm^{-1}, appears to be in the right range.

More interesting are the magnetization data for [Fe_{10}] obtained at 0.65 K. In fact in this case also, as for the cyclic [Fe_6 ring] cluster[16] described above, it can be expected that crossovers between different spin states are observed on increasing field. In Fig. 15 the magnetization in pulsed fields up to 40 T is shown.

The curve corresponds to the derivative of the magnetization as a function of the field. Therefore the peaks in Fig. 15 correspond to inflection points in the magnetization *vs.* field curve, *i.e.* they correspond to crossovers between different ground states with increasing *S*. The first peak in low field corresponds to the transition $S = 0 \rightarrow 1$, the second to $1 \rightarrow 2$, and the last at high field to $8 \rightarrow 9$.[1] The fact that the field separations between the different crossovers are always the same confirms a Lande interval rule up to $S = 9$. Using eqns (8) and (10) it is possible to calculate $J = 9.4$ cm^{-1}, in excellent agreement with the value calculated from the susceptibility.

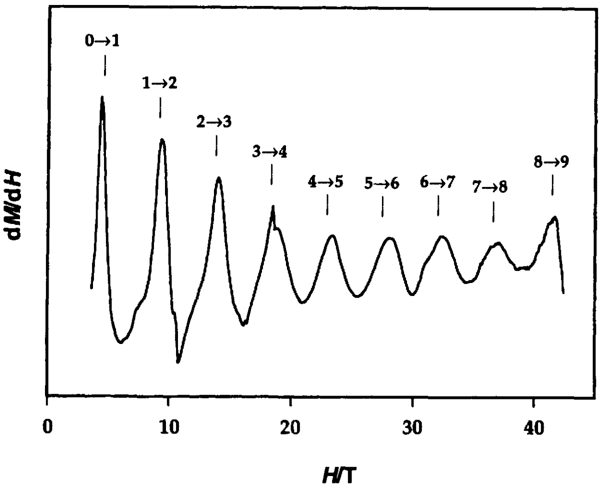


Figure 15 Differential magnetization, dM/dH for $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$ measured in a pulsed field The crossover at 0 65 K between the S, $(S+1)$ spin states is noted above each maximum

5.4 Fe_{17} and Fe_{19} Clusters

The magnetic susceptibility of $[Fe_{17}+Fe_{19}]$ has a temperature dependence[15] which is very similar to that of $[Fe_8]$ Actually if the susceptibilities per iron ion are reported for the two compounds they are seen to be practically identical Therefore it can be concluded that $Fe_{17}+Fe_{19}$ are ferrimagnetic clusters The low-temperature magnetization shows that the ground states of one of the clusters cannot be smaller than 33/2 This is the largest ground spin state so far observed in magnetic clusters

The EPR spectra of $[Fe_{17}+Fe_{19}]$ recorded at room temperature show one very broad signal centred at $g = 2$ At low temperature the spectrum becomes anisotropic, with $g_{\perp} \approx 3$ This behaviour is analogous to that observed in low-dimensional magnetic materials,[36] in which internal fields determine a shift in the g values No anomaly could be observed in the Mossbauer spectra, which show usual paramagnetic behaviour down to 3 2 K

6 Conclusions

Iron-oxo clusters are a very important class of materials First of all they provide some insight into the mechanisms of formation of inorganic cores which are observed in iron biomineralization The structure of the clusters seems to be dominated at an early stage by the tendency of the oxygen atoms to define close-packed structures, even when they are bound to the organic part of the ligands The synthetic strategies developed so far are still rather naive and more work is needed in this area in order to learn how to grow larger clusters, to control their structures

From the magnetic point of view the reported clusters provide large variability, within the general scheme of antiferromagnetic exchange interactions The cyclic $[Fe_6$ ring$]$ and $[Fe_{10}]$ clusters are excellent models of the magnetic behaviour of one-dimensional antiferromagnetic materials, and they have provided for the first time a detailed knowledge of the energies of the excited states More ring structures would be desirable, in order to clarify some points which remain unclear, such as the detailed behaviour of the susceptibility observed at low temperature, below the maximum

The quantitative treatment of the magnetic properties requires drastic improvements, introducing explicitly zero-field splitting effects also However some encouraging successes have been obtained, which suggest that the whole matter is not hopeless

All the clusters we have reported here, except $[Fe_6$ octahedra$]$, have essentially planar arrangements of the iron ions, and they can be considered as models of one- and two-dimensional magnetic materials It will be necessary also to investigate in more detail the magnetic properties of systems which have pseudo three-dimensional arrangements of the iron ions in order to model the properties of three-dimensional magnets

The reported data clearly show that the magnetic properties of the clusters slowly evolve toward bulk magnetic behaviour on increasing the number of ions The observation of superparamagnetic-like behaviour is associated with the development of the magnetic anisotropy of the clusters The requirements which so far emerge in order to give rise to such behaviour are those of having a large ground spin state with a magnetic anisotropy characterized by the presence of one easy axis, *i e* an Ising type anisotropy More clusters are needed in order to confirm this view, making clear which are the conditions determining such type of anisotropy

7 References

1 W Schneider, *Chimia*, 1988, **42**, 9
2 *Biomineralization Chemical and Biochemical Perspectives*, ed S Mann, J Webb and R J P Williams, VCH, New York, 1988
3 D Gatteschi, *Adv Mater*, 1994, **6**, 635
4 K L Taft, G C Papaefthymiou and S J Lippard, *Science*, 1993, **259**, 1302
5 D D Awschalom, D P DiVincenzo and J F Smyth, *Science*, 1992, **258**, 414, S Gider, D D Awschalom, T Douglas, S Mann and M Chaparala, *Science*, 1995, **268**, 77
6 R Sessoli, D Gatteschi, A Caneschi and M A Novak, *Nature*, 1993, **365**, 141
7 A J Leggett, *Phys Rev B*, 1984, **30**, 120
8 P Politi, A Rettori, F Hartmann Boutron and J Villain, *Phys Rev Lett* , 1995, **75**, 537
9 A Muller, E Krickemeyer, S Dillinger, H Bogge, A Proust, W Plass and R Rohlfing, *Naturwissenschaften*, 1993, **80**, 843
10 W Micklitz, V McKee, R L Rardin, L E Pence, G C Papaefthymiou, S G Bott and S J Lippard, *J Am Chem Soc* , 1994, **116**, 8061, S M Gorun, G C Papaefthymiou, R B Frankel and S J Lippard, *J Am Chem Soc* , 1987, **109**, 3337
11 H L Tsai, H J Eppley, N de Vries, K Folting, G Christou and D N Hendrickson, *J Chem Soc Chem Commun* , 1994, 1745
12 K Hegetschweiler, H Schmalle, H M Streit and W Schneider, *Inorg Chem* , 1990, **29**, 3625, K Hegetschweiler, H Schmalle, H M Streit, V Gramlich, H U Hund and I Erni, *Inorg Chem* , 1992, **31**, 1299
13 R D Cannon and R P White, *Progr Inorg Chem* , 1988, **36**, 195
14 K L Taft, C D Delfs, G C Papaefthymiou, S Foner, D Gatteschi and S J Lippard, *J Am Chem Soc* , 1994, **116**, 823
15 A K Powell, S L Heath, D Gatteschi, L Pardi, R Sessoli, G Spina, F Del Giallo and F Pieralli, *J Am Chem Soc* 1995, **117**, 2491
16 A Caneschi, A Cornia and S J Lippard, *Angew Chem Int Ed Engl* , 1995, **34**, 467
17 A Caneschi, A Cornia, A C Fabretti, D Gatteschi and W Malavasi, *Inorg Chem* 1995, **34**, 4660, A Caneschi, A Cornia, A C Fabretti and D Gatteschi, *Angew Chem* , 1995, **34**, 2716
18 C A Christmas, H L Tsai, L Pardi, J M Kesselman, P K Gantzel, R K Chadha, D Gatteschi, D F Harvey and D N Hendrickson, *J Am Chem Soc* , 1993, **115**, 12483
19 N V Gerbeleu, A S Batsanov, G A Timko, Y T Struchkov, K M Indrichan and G A Popovich, *Dokl Akad Nauk SSSR*, 1987, **293**, 122
20 W Micklitz and S J Lippard, *Inorg Chem* 1988, **27**, 3067, W Micklitz, S G Bott, J G Bentsen and S J Lippard, *J Am Chem Soc* , 1989, **111**, 372
21 J K McCusker, C A Christmas, P M Hagen, R K, Chadha, D F Harvey and D N Hendrickson, *J Am Chem Soc* , 1991, **113**, 6114, V S Nair and K S Hagen, *Inorg Chem* 1992, **31**, 4048
22 C J Harding, R K Henderson and A K Powell, *Angew Chem Int Ed Engl* , 1993, **32**, 570
23 K Wieghardt, K Pohl, I Jibril and G Huttner, *Angew Chem Int Ed Engl* , 1984, **23**, 77
24 J K McCusker, J B Vincent, E A Schmitt, M L Mino, K Shin, D K Coggin, P M Hagen, J C Huffman, G Christou and D N Hendrickson, *J Am Chem Soc* 1991, **113**, 3012
25 K Bleaney and K D Bowers, *Proc Roy Soc* 1952, **A214**, 451
26 D Gatteschi and L Pardi, *Gazz Chim It* , 1993, **123**, 231
27 S M Gorun and S J Lippard, *Inorg Chem* , 1991, **30**, 1625
28 D M Jr Kurtz, *Chem Rev* 1990, **90**, 585
29 A H Morrish, *The Physical Principles of Magnetism*, Wiley, New York, 1966
30 J Vannimenous and G Toulouse, *J Phys C Solid State Phys* , 1977, **10**, L537
31 C D Delfs, D Gatteschi and L Pardi, *Comments Inorg Chem* , 1993 **15**, 27
32 A Cornia, D Gatteschi and K Hegetschweiler *Inorg Chem* , 1994, **33** 1559

33 K Kambe, *J Phys Soc Jpn* , 1950, **5**, 48

34 C D Delfs, D Gatteschi, L Pardi, R Sessoli, K Wieghardt and D Hanke, *Inorg Chem* . 1993, **32**, 3099, A L Barra, P Debrunner, D Gatteschi, C E Schulz and R Sessoli, submitted for publication

35 D Gatteschi, A Caneschi, L Pardi and R Sessoli, *Science*, 1994, **265**, 1054

36 D Gatteschi and R Sessoli, *Magn Reson Rev* , 1990, **15**, 1