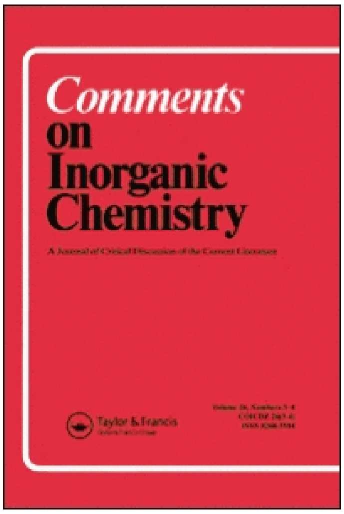

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High Nuclearity Spin Clusters: A New Dimension in Magnetism?

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High Nuclearity Spin Clusters: A New Dimension in Magnetism?

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Some key concepts which are needed in order to investigate the magnetic properties of high nuclearity spin clusters, HNSC, are reviewed. Particular mention is made of spin frustration, superparamagnetism, and of the problems associated with the calculation of the spin levels and of the magnetic susceptibility of the clusters. Spin frustration is described with a simple example of a trinuclear iron(III) complex. Superparamagnetism is introduced and an experimental case when it can be observed in an HNSC is discussed. An Irreducible Tensor Operator approach to the calculation of the spin levels and of the magnetic susceptibility is advocated and discussed in the form of a sample calculation on hexanuclear iron(III) clusters.

Key Words: *spin frustration, superparamagnetism, high nuclearity spin clusters, magnetic exchange*

INTRODUCTION

High nuclearity spin clusters consist of large molecular aggregates of magnetic centers and are referred to in the literature as HNSC. The analogy with high nuclearity metal clusters should be obvious.

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The expression "spin clusters" is used so as to include systems containing not only clusters of transition metal ions[1-31] but also organic radicals[32-40] and organic radicals coupled to transition metal ions.[41-44] The interest in these compounds is rapidly increasing, for many different reasons, one of which is that they can be used as models to investigate the mechanisms of biomineralization.[45,46] In this area there is a particular focus on clusters of iron and manganese. Since these ions are magnetic, the understanding of the magnetic properties is a fundamental part of the understanding of the correlation between structure and properties. A second reason is that more and more complex systems are currently synthesized as the result of increasing interest in supramolecular chemistry,[47-50] and the interest of chemists in general is shifting towards larger and larger molecular assemblies.[49,50]

Another important aspect of these clusters is that as they grow larger and larger they achieve dimensions which are intermediate between those of isolated ions and of bulk magnets, i.e., they enter the mesoscopic dimensions,[51,52] which are currently under active investigation in several areas of solid state physics.[53-63] In fact, it is expected that several new phenomena and properties will be observed in this range of dimensions, and already some exciting results have been reported.[62-66]

There are many groups working on these materials, and the novelty of these systems has imposed the acquisition of many new concepts, some of which are not well known to chemists. However, it cannot be expected that synthetic efforts alone can be completely successful, unless the magnetic properties of these materials can be adequately understood. We wish to focus here on some of the problems that can be encountered when investigating the magnetic properties of HNSC, and provide some indications on how to solve them.

The first problem, which has already been met for relatively small clusters, is that of calculating thermodynamic properties, of which magnetic susceptibility is traditionally the first for the characterization of new materials. One of the purposes of this paper is to show how it may be possible to perform rigorous calculations of the magnetic properties of relatively large clusters within the isotropic spin Hamiltonian approach and show the results of some sample calculations on model clusters.

When more than two spins interact, it may happen that a given spin is under the influence of conflicting interactions, which may show up as spin frustration. We will make some brief comments on the nature of spin frustration and compare its use in clusters with that in extended systems, for which it was originally suggested.[67]

Finally the third problem which will be touched upon is that of collective magnetism and when it starts to become apparent in large clusters. Chemistry up till now has been much more involved with paramagnetism, where each magnetic center is essentially uncorrelated with any others. Passing from paramagnetism to bulk magnetism is not just a simple matter of adding more spins together because ferromagnetism[68] is by definition a non-additive behavior, and collective properties become of paramount importance. This area has been largely investigated in recent years under the heading of organic (molecular) ferromagnetism.[68] When a ferromagnet is split into smaller pieces there is a certain particle size where its behavior in a magnetic field is like that of a paramagnet but with very high magnetization. This behavior is referred to as superparamagnetism.[69] When does superparamagnetism or other bulk properties begin and what are the important factors giving rise to this property in these systems, in which we can imagine the cluster as being assembled from interacting magnetic ions added one by one? This is a question which will only be answered by further investigation into the magnetic behavior of these types of compounds.

SPIN FRUSTRATION

Spin frustration was originally introduced by Toulouse[67] in the frame of the interactions in continuous lattices. As he stated, "the content of frustration is that topological constraints prevent neighboring spins from adopting a configuration with every bond energy minimized." The simplest case in which spin frustration arises is when three spins are antiferromagnetically coupled with each other. It is apparent that there is no way that each spin can be antiparallel to the other two. The term frustration is mutated from psychology, where it originated from the presence of attractions and repulsions between the members of a group, and indeed spin frustration originates from conflicting magnetic interactions.

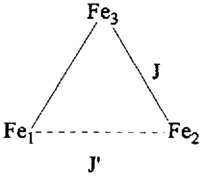
Spin frustration can be observed also in closed polygons containing odd numbers of centers, and in those containing even numbers, but also possessing next-nearest-neighbor interactions.

The main result of spin frustration is that hand waving arguments completely lose their validity and the identification of the ground state of the system cannot be made on the basis of simple considerations of preferred up and down arrangements of the spins.

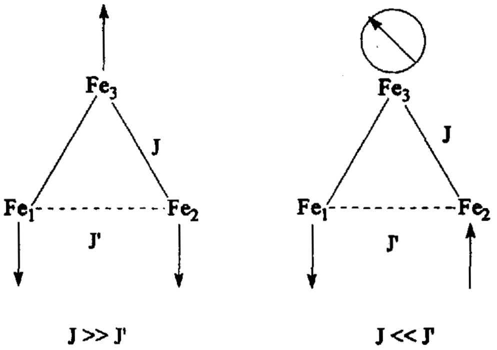
It is perhaps useful to resort to an example in order to clarify the above considerations. We will focus on a cluster of three $S = 5/2$ spins, which can represent a tri-nuclear high spin iron(III) complex.[70] Assuming isosceles geometry according to Scheme I the energies of the states are analytically calculated as:

$$E(S, S_{12}) = J'/2[S_{12}(S_{12} + 1) - 35/2] + J/2[S(S + 1) - S_{12}(S_{12} + 1) - 35/4]. \quad (1)$$

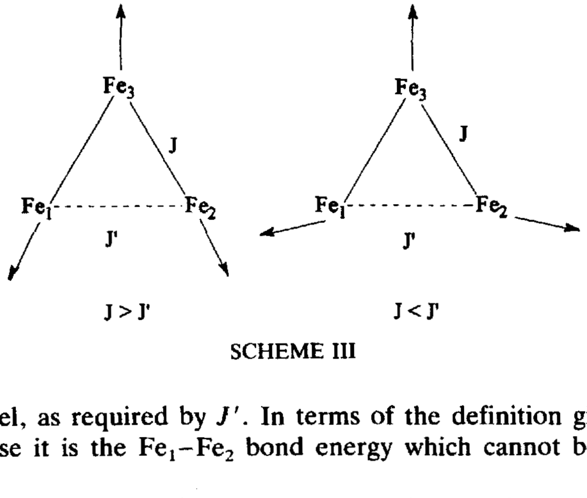
A ground state in which $S = 5/2$ can be obtained in two ways, both of which are depicted in Scheme II. In the case of $J >> J'$ the ground state is easily understood on the basis of up and down spin arrangements. In case of $J << J'$ the competing Fe_1–Fe_3 and Fe_2–Fe_3 interactions seem to almost decouple Fe_3 from the rest of the cluster so that it behaves like a paramagnet in the sense that it is uncorrelated to the other spin centers. In the case $J >> J'$ the strong antiferromagnetic interactions between Fe_3 and Fe_1 and Fe_3 and Fe_2 determine that it will be the Fe_1–Fe_2 interaction which will be frustrated. Hence the preferred orientation of these two spins is such that they are parallel to each other, rather than an-



SCHEME I



SCHEME II



SCHEME III

tiparallel, as required by J'. In terms of the definition given by Toulouse it is the Fe$_1$–Fe$_2$ bond energy which cannot be minimized.

Two possible ways in which a $S = 3/2$ ground state can be obtained are depicted in Scheme III. In these diagrams the spins are treated as vectors and the total spin is the vector sum of the three. For the sake of simplicity the quantized nature of the spins is ignored, since for the purposes of a qualitative understanding of these systems this is not important. The angles α between the spins on Fe$_1$ and Fe$_2$ are 74° and 157°, respectively. Finally the two possible $S = 1/2$ ground states can be represented also by Scheme III but with different orientation angles α of 106° and 132°, respectively. It is worth noting that when $J = J'$ the two $S = 1/2$ ground states have the same energy.

The energy levels of the low energy states given for varying values of the J/J' ratio are shown in Fig. 1. This figure readily shows that all the ground states with S ranging from 5/2 to 1/2 can be stabilized. In particular either for J/J' lower than 0.3 or larger than 2 an $S = 5/2$ is the ground state, while as J/J' approaches unity the competition between magnetic interactions within the triangle increases and eventually results in a completely frustrated system for the case where ($J/J' = 1$) in which a doubly degenerate $S = 1/2$ spin state is the ground state.

Therefore the result of spin frustration in the triangle is that of giving rise to many different ground states for different values of the competing interactions, in such a way that qualitative predictions are rather difficult to make in all but the simplest cases.

Since triangular arrangements like this are frequently observed in HNSC it is often impossible to make any reasonable guess as to the nature of the ground state. Therefore, qualitative rationalization of the magnetic properties of HNSC is often impossible and quantitative calculations are a necessity. These are often very

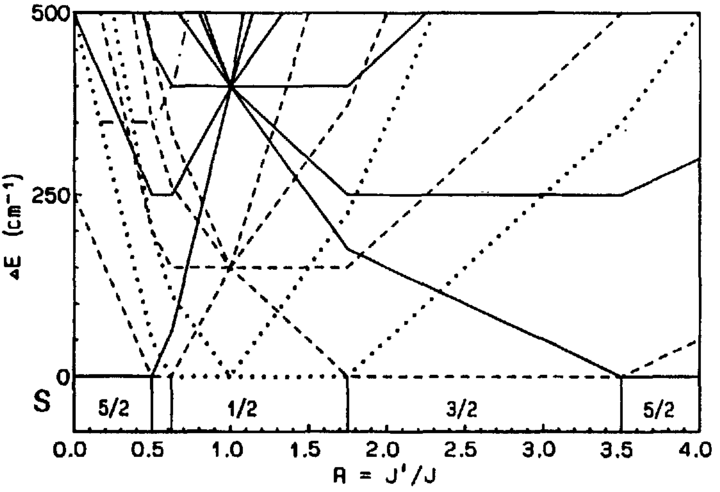


FIGURE 1 Energies of the spin state of a trinuclear iron(III) cluster with isosceles geometry as a function of the $R = J'/J$ ratio.

difficult to perform, but we will show in a following section how it is now possible to tackle the problem efficiently.

SUPERPARAMAGNETISM

Superparamagnetism is the limit behavior of ferro (ferri) magnetic particles, when they become so small that thermal energy can easily reverse their magnetization. In the absence of an external field, the net magnetization is zero (like in a paramagnet), while in a field a preferred orientation with the magnetization parallel to the external field will be observed, resulting in a large ("super") susceptibility. In a static experiment the magnetization will increase linearly with the applied field following a Brillouin function like a paramagnet with infinite (classic) spin.

A dynamic measurement provides much important additional information. In fact, if the susceptibility is measured with an oscillating field, for instance in an ac susceptibility experiment,[66] in a Mössbauer,[71-75] EPR[66,75] or NMR[75] spectrum, the response of the particles depends on the frequency of the oscillating field. In fact the magnetization must follow the time fluctuation of the field, reversing its orientation. In order to do this it must overcome a barrier, because orienting at right angles from the field requires an additional energy, as sketched in Fig. 2. The magnetization is characterized by a relaxation time τ, corresponding to the time needed to reverse its sign. If $\tau << \tau_e$ (τ_e is the characteristic time of the performed experiment) the response will be in phase and only the real component of the susceptibility will be observed. If on the other hand $\tau >> \tau_e$, then on the time scale of the experiment the magnetization will not be able to follow the oscillation of the field, and an out-of-phase response of the susceptibility will be observed. The transition from the static to the dynamic behavior will occur when thermal energy becomes of the same order as the barrier. The corresponding temperature is indicated as blocking temperature, T_B. This is, by definition, frequency dependent.

The techniques which are more often used to detect dynamic aspects of superparamagnetism are ac susceptibility[66] and Mössbauer spectroscopy.[45,46,71-75] τ_e for the former is ca. 10^{-2} s, for the latter 10^{-8} s. Therefore the blocking temperatures must be

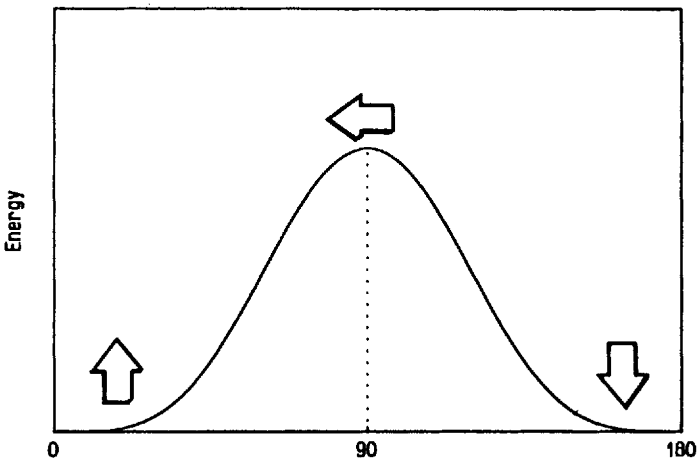


FIGURE 2 Energy barrier between opposite orientation of magnetization in an oscillating field.

very different for the two techniques. In fact the relaxation rate of the magnetization is expected to follow a law of the type:

$$\tau^{-1} = \tau_0^{-1} \exp(-E_a/kT). \tag{2}$$

The activation energy depends linearly on the volume of the particle; therefore relatively small variations in the volume of the particle correspond to dramatic variations in the relaxation rate. In particular the smaller the volume, the faster the relaxation rate. This means that the blocking temperature becomes lower when the particle becomes smaller.

Although superparamagnetism was originally observed for ferromagnetic particles, antiferromagnetic particles may also show similar behavior, because internal fields are present. In general Mössbauer spectroscopy has been the technique for the investigation of these particles.

Reducing the dimensions of the particles, one passes from superparamagnetic to simple paramagnetic behavior. The question is how the transition from the former to the latter regime occurs. This is precisely one of the problems which is currently being debated.

Superparamagnetic behavior must be characterized by large magnetizations (of the sublattices in the case of antiferromagnets) and large anisotropy barriers. The latter are necessary in order to observe a blocking temperature. However, the observation of a blocking temperature, especially for fast techniques like Mössbauer spectroscopy, is *not* a proof of superparamagnetic behavior, because even a simple paramagnet may show a blocking temperature in the presence of a large zero field splitting.

To our knowledge the molecular compound with the best evidence of superparamagnetic behavior analogous to that observed in small particles, is provided by $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)] \cdot 2CH_3COOH \cdot 4H_2O$,[66] the structure of which is sketched in Fig. 3. This compound, which has tetragonal symmetry, has been shown to possess a $S = 10$ ground state and zero field splitting of $D \sim -0.5\ \mathrm{cm}^{-1}$. The negative sign of D indicates that the ground state is $M_S = \pm 10$ and the value indicates the first excited levels, $M_S = \pm 9$, are ca. $10\ \mathrm{cm}^{-1}$ above the ground state. At sufficiently low temperatures the ground state can be treated as an effective $S = 1/2$ spin, whith very anisotropic g values: $g_{\|} = 40$, $g_{\perp} = 0$! This means that crystal field effects (ZFS) determine a large magnetic anisotropy even in zero field, exactly like in a ferromagnetic particle. This means that at low temperatures the magnetization

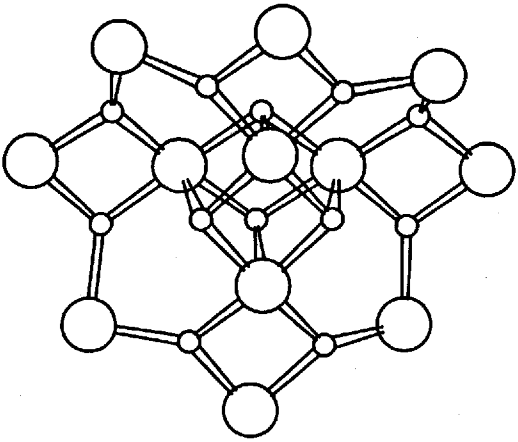


FIGURE 3 Structure of the core of the $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)] \cdot 2CH_3COOH \cdot 4H_2O$ cluster.

will not follow the oscillatory field in an ac experiment, and relaxation effects will be observed. This has indeed been observed below 10 K, where the out-of-phase component of the ac susceptibility becomes different from zero and goes through a maximum. The position of the maximum is frequently dependent, ruling out the presence of a magnetic phase transition. The relaxation times are of the order of 10^{-2} s in this range of temperatures. Preliminary measurements at 3 K[76] show hysteresis effects with features which are not those typical of three-dimensional materials. There is the possibility that this behavior is associated with molecular properties, a unique property so far observed.

CALCULATION OF THE SPIN LEVELS OF HNSC

The usual procedure for calculating the magnetic susceptibility of a cluster is that of calculating the energy levels of the spin Hamiltonian

$$\mathcal{H} = \Sigma_{i<k} J_{ik} \mathbf{S}_i \cdot \mathbf{S}_k \tag{3}$$

where the sum is extended to all the pairs of interacting spins. There are another three equivalent expressions for (3), with the coupling constant J substituted by $-J$, $2J$, or $-2J$. Unfortunately we do not see any possibility for researchers in this area to agree on a unique form for (3). An important property of (3), however expressed, is that it gives matrix elements different from zero only between states with the same total spin S. Therefore the problem of calculating $(2S_i + 1)^n$ levels, appropriate to a cluster comprising nS_i spins, is drastically reduced. For instance, in the case of four $S = 5/2$ the 1,296 × 1,296 matrix is split into eleven blocks, corresponding to $S = 10, 9, 8, 7, 6, 5, 4, 3, 2, 1$, and 0. The dimensions of the corresponding matrices are $n_s = 1, 3, 6, 10, 15, 21, 24, 21, 15, 6$, respectively. However, the reduction of the matrices can be done only at the expense of some mathematical labour, because it is necessary to write down the functions explicitly. This can be done in a standard way using Clebsch–Gordan coefficients.[77] The functions are written as linear combinations of state functions providing the M_i values on each center i of the cluster. Therefore each state function comprises n numbers. Since the number of state functions to be collected in the linear combinations is very large, this approach becomes rapidly impossible to use in terms of computer memory storage. For instance, in the above example for $S = 0$ a given total spin eigenfunction will be in principle a linear combination of 146 states.

Recently, we suggested a method which uses Irreducible Tensor Operators (ITO),[78] in order to simplify the problem. The ITO's are used in order to exploit the total spin symmetry as deeply as possible. Of course some involved mathematical elaboration is needed, but the results largely justify the effort. We do not enter into any detail here but suggest that the interested reader should address the original literature.[79,80] It is sufficient to say that the total spin functions are no longer written explicitly, but only indicated by the individual and intermediate spins which are obtained by the pairwise combination of the individual spins. In the example outlined above, a given $S = 0$ state is specified by four numbers rather than by the $146 \times 4 = 584$ numbers required by the usual approach. The other advantage of the ITO approach is that the matrix elements are easily calculated with a standard procedure very well suited for implementation on a computer. In this way it has become possible to calculate the energy levels of HNSC, and from these the magnetic susceptibility. The largest clusters we have calculated so far are $n = 15$ for $S_i = 1/2$ and $n = 8$ for $S = 5/2$. In the latter case we had to introduce explicitly point group symmetry to reduce the matrices to acceptable dimensions.[81]

In order to show the validity of the model we want to report here some sample calculations on Fe_6 clusters comprising six high spin iron(III) ions. Some compounds of this kind have already appeared in the literature,[2,82,83] but no quantitative interpretation has yet appeared, due to the complex nature of the system for the standard approaches. The geometry of the compounds can be schematized as far as exchange interactions are concerned as shown in Fig. 4.

Six $S = 5/2$ spins give rise to states with total spin ranging from $S = 15$ to $S = 0$, with the number of states with given total spin values shown in Table I. As is apparent from this table, the dimensions of the matrices involved in the calculation of the spin Hamiltonian are not prohibitive, and with a RISC workstation a

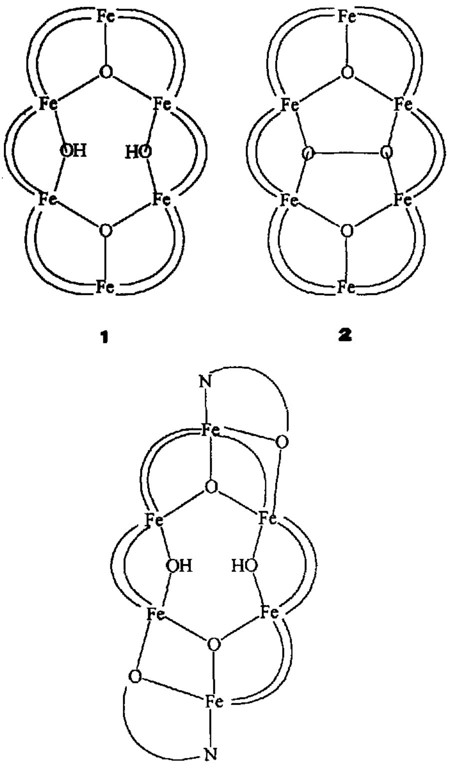


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FIGURE 4 Schemes of the structures of the hexanuclear iron(III) clusters.

single calculation takes several minutes. We feel, however, that this case is well suited to appreciate the advantages of our approach.

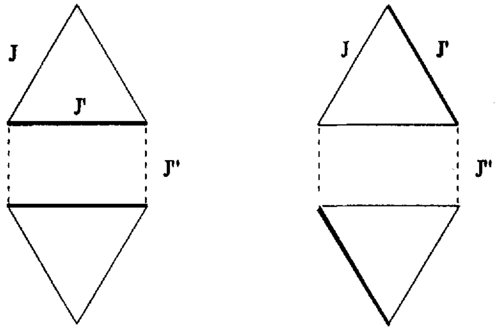
As far as the magnetic interactions are concerned, clusters **1**–**3** can be considered as made up by two $[Fe_3O]^{7+}$ unit exchange coupled either through μ-hydroxo bridges or through a peroxo bridge.

The two isosceles triangles can be coupled in the two different ways depicted in Scheme IV, which correspond to completely different magnetic behavior. According to a and inversion center and

TABLE I

Dimensions of the total spin matrices for six $S = 5/2$ spins

S	n_S	S	n_S
15	1	7	405
14	5	6	505
13	15	5	581
12	35	4	609
11	70	3	575
10	126	2	475
9	204	1	315
8	300	0	111



(a) (b)

SCHEME IV

a mirror plane are present while in **b** an inversion center is still present but the mirror symmetry is absent.

It is interesting to see if the concepts described above, regarding the nature of the ground state of the triangular fragments, can be exploited to predict the nature of the ground state of the cluster. This should be possible because the interactions between the two triangles have no frustration effects, which are operative only within the triangles.

In case **a** the two sites of one triangle, which have a nearest-neighbor on the other triangle, are identical. Therefore, the antiferromagnetic interaction J'' will orient nearest-neighbors antiparallel to each other and $S = 0$ must be the ground state for every value of R and J'' (as long as all the exchange interactions are assumed to be antiferromagnetic).

Case **b** is much richer in perspective, because in this case the sites in the central portion of the cluster have different relationships with the ions at the apex of each triangle, and the antiferromagnetic coupling will result in ground states with $S \neq 0$. Several different ground states can be expected, depending on the values of the R ratio. A pictorial example for the case of a large R is shown in Fig. 5.

These qualitative considerations are borne out by quantitative calculations, which also provide the temperature dependence of the magnetic susceptibility. In fact, if we use the interaction scheme **a**, the observed ground state is always $S = 0$ irrespective of the value of the three coupling constants, but marked differences are reflected in the magnetic behavior depending on the J/J' ratio. In Fig. 6 we report the calculated χT product vs. T, and in Fig. 7 the χ vs. T plot for different values of the J/J' ratio. In these calculations we used a fixed value of the coupling constants J' and J'' of 100 and 10 cm^{-1}, respectively, and varied J from 0 to 300 cm^{-1}. For $J = 0$ the ground state of the system corresponds to two uncorrelated $S = 5/2$ and the χT value decrease from the high temperature value to the expected value of 8.75 emu mol^{-1} K. When J is different from zero, three distinct regimes of magnetic behavior can be recognized depending on the value of J. When $J < J'$ the χT product slowly decreases from high temperature to about 20 K and then abruptly drops to zero. When J approaches J' the χT product decreases almost linearly with temperatures, while for $J > J'$ it decreases monotonically from a high temperature value which is larger for larger J values. It must be pointed out that using the reported values of the coupling constants, even when

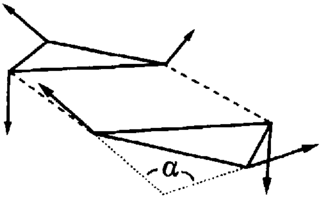


FIGURE 5 A possible spin configuration for $R > 1.5$.

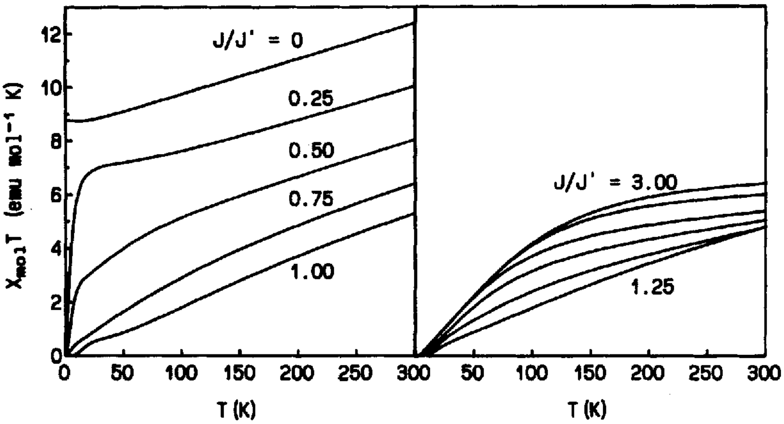


FIGURE 6 Calculated χT vs. T product for type **a** clusters.

$J = 0$, the high temperature value does not correspond to that of six uncorrelated iron(III) (26.25 emu mol^{-1} K). The three magnetic regimes are even more apparent if one looks at the χ vs. T plots (see Fig. 7). In the cases in which $J < J'$, χ goes through a sharp maximum at very low temperature ($kT/J' = 0.03$ for $J = 25$ cm^{-1}), while for $J > J'$ the maximum is broader, has a lower value and corresponds to higher temperatures ($kT/J' = 0.3$ K for $J = 200$ cm^{-1}). Noticeable is the fact that for the $J/J' = 1$ case the χ vs. T plot presents two distinct maxima: a very broad one at ca. $kT/J' = 1.1$ and a sharper one at $kT/J' = 0.2$. To our knowledge this behavior has not yet been observed.

If the two isosceles triangles are coupled as in **b** all the total spin states ranging from 5 to 0 can be the ground state depending on the J/J' ratio. In Fig. 8 is reported a spin phase diagram for type **b** clusters in which are shown the total spin values of the different ground states obtained for different values of the J/J' ratio and of the J'' constant. From this plot it is apparent that either for low or high values of the J/J' ratio high spin ground states are stabilized; for $J/J' \geq 2$ we observe an $S = 5$ ground state irrespective of the value of J''. In general the S value of the ground state is not very sensitive to the J'' value, apart from the portion of the diagram corresponding to $J/J' < 0.5$ where the pattern is rather complex. As already stated in the treatment of the triangular unit, when

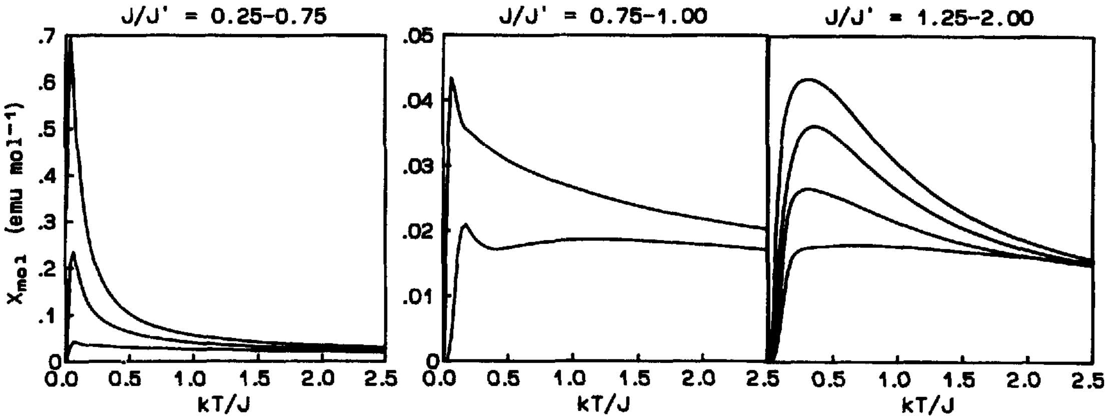


FIGURE 7 Calculated susceptibility for type a clusters.

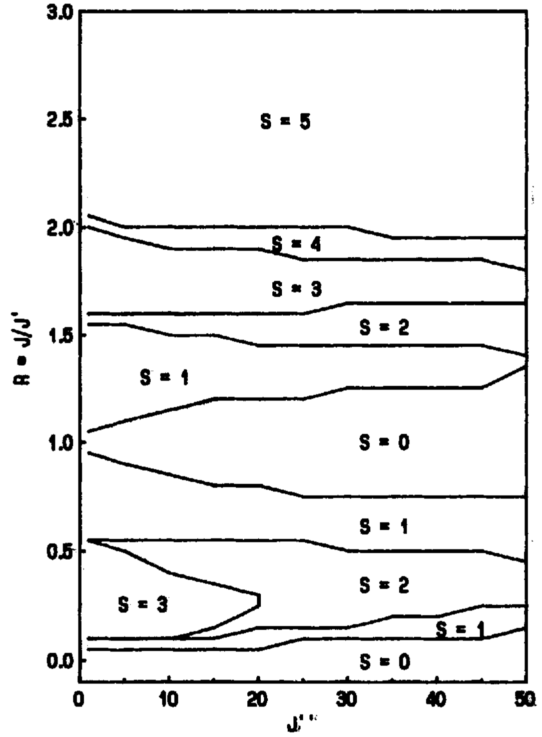


FIGURE 8 Spin phase diagram for a type **b** hexanuclear cluster (see text).

J/J' approaches unity the competition between interactions within the triangular units increases, and in the condition which corresponds to two coupled equilateral triangles, i.e., for $J/J' = 1$, a completely frustrated system with $S = 0$ ground state is realized. The calculated χT product for (II) type clusters with different values of J/J' and $J'' = 10$ are reported in Fig. 9.

It is worthwhile to point out that both the type **a** and **b** clusters have been experimentally observed. In fact type **a** corresponds to clusters **1**[82] and **2**[83]; cluster **3**[2] instead shows a magnetic behavior which is in agreement with an $S = 5$ ground state which can be realized for the type **b** interaction scheme with a J/J' ratio larger than 2 (see Fig. 7).

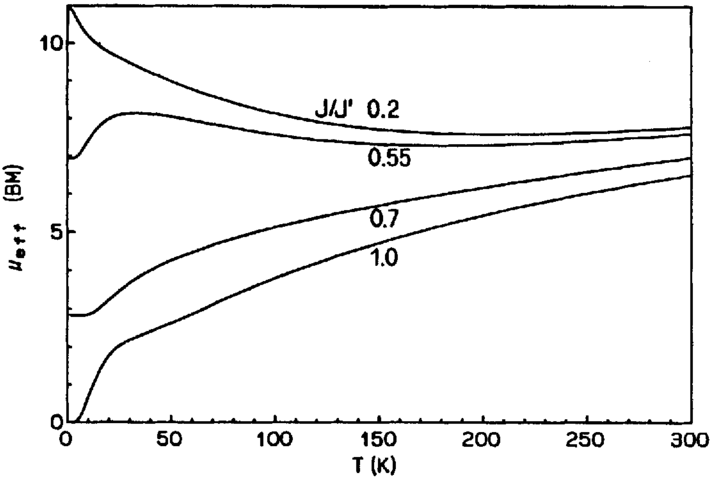


FIGURE 9 Calculated χT vs. T product for type **b** clusters.

CONCLUSIONS

The magnetic properties of HNSC are just beginning to be investigated, due to the increasing number of clusters recently reported. However, despite many complications associated with the large number of interacting spins there is ample evidence that many interesting properties are going to be observed, and there is no doubt that useful magneto structural correlations will be established in the near future.

Several problems will have to be overcome, however, before really large clusters can be tackled. For instance, efficient procedures must be developed for the calculation of the energy levels and thermodynamic properties. Our ITO method complimented by the use of point group symmetry can cope with clusters of only moderate size, and although efficient, cannot be extended to larger compounds without computing facilities with extremely large memory. Finally it must be recalled that up till now, only isotropic spin Hamiltonians have been used, but anisotropic components in the exchange interactions may well be required.[80] In this case a whole new set of problems may well need to be overcome.

From the experimental point of view, it will be necessary to employ many different techniques in order to have as much information as possible. In many cases, it will be necessary to measure both the static and ac susceptibilities at very low temperatures, considerably lower than 4.2 K. Magnetization studies at very high fields[84] will also be required, and variable frequency EPR investigations will also be very important. In particular we feel that new spectrometers which use an infrared laser,[85,86] in place of the usual microwave generator, will prove to be of fundamental importance in identifying the nature of the ground state and low lying levels, especially those which can be stabilized by an external field.

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