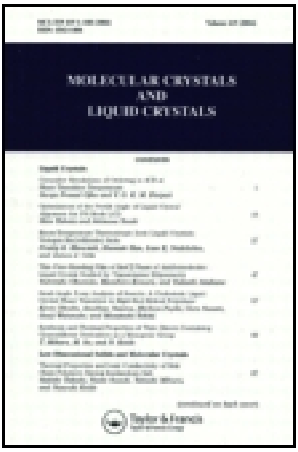

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Magnetism of High Nuclearity Spin Cluster

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MAGNETISM OF HIGH NUCLEARITY SPIN CLUSTER

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Abstract

The magnetic properties of clusters containing large but finite number of exchange coupled paramagnetic metal ions (high nuclearity spin clusters) are reviewed. Some polyoxovanadates and iron(III) clusters allow us to present the current theoretical and experimental approaches to this central area in the chemical research and materials science.

INTRODUCTION.

Synthetic efforts in many different directions have recently produced a large number of polynuclear metal complexes containing large, but finite numbers of paramagnetic centers.[1-9] On one side these efforts have been justified by the goal of mimicking the large iron clusters which are found in ferritin[10], the iron storage protein of mammalians and bacteria, and by the possibility of understanding the biomineralization process of magnetite, which occurs for instance in magneto-tactic bacteria.[11] Beautiful clusters have been reported containing six[4,12], eight[7], ten[2], up to nineteen[1] iron ions, whose magnetic properties start to be investigated.[13]

Manganese containing clusters have been synthesized with the aim of mimicking the properties of the active centers of bacterial photosystem II[14], and systems containing up to twelve manganese ions have been reported.[3]

All these new materials provide exciting perspectives for the investigation of the magnetic properties. In fact although the properties of simple paramagnetic materials on one hand and bulk magnetic materials on the other hand are well understood, the intermediate area of magnetic particles which are large but cannot be considered as infinitely large, is an essentially unexplored one. These large particles may be expected to show new properties, where quantum effects coexist with bulk behavior. For instance very recently it has been reported[15] that nanoscale particles of γ-Fe_2O_3, the well known material used for magnetic coating in audio and video recording tape, are optically transparent, while the bulk material is opaque as most of the currently used magnetic materials.

On the other side we have discovered[16] that manganese clusters show unusual relaxation effects in an alternating magnetic field usually observed only in bulk particles[11,17] which is typical of superparamagnetic or spin glass behavior.

We like to call the large clusters reported so far high nuclearity spin clusters HNSC, by analogy with the high nuclearity metal clusters which have been intensively investigated in the last twenty years as models of the behavior of bulk metals.[18,19] We feel that the detailed investigation of their magnetic properties, together with the development of suitable models of their behavior will open many new possibilities for the understanding of the magnetic properties of bulk materials, and also for the exploitation of new properties.

It must be made clear from the outset, however, that the quantitative interpretation of the magnetic properties of HNSC is made difficult by the fact that the number of spin levels increases dramatically with the number of interacting spins, and the fact that translational symmetry is not present as in the infinite assemblies of spins encountered in bulk materials does not allow the simplifications which are possible for the latter class of materials. We have recently developed an efficient formalism for the calculation of the spin levels of HNSC which exploits total spin and point group symmetry, which makes relatively large clusters tractable.[20]

We wish to review here a few HNSC which we have investigated in the last few years, with the aim to show how their magnetic properties can be quantitatively interpreted, and how they can be used as models for the behavior of bulk materials. In particular we will focus on vanadium clusters and on iron clusters, as representation examples. Other interesting clusters are reported by D.N. Hendrickson in these same proceedings.

VANADIUM CLUSTERS

Polyoxometallates have long been known, and their properties actively investigated for a broad spectrum of different interests, ranging from catalysis to antiretroviral activity.[8] Although some paramagnetic centers may be present in them , up to very recently no cluster containing large numbers of magnetic ions have been reported. Matters have drastically changed since Müller et al. reported an extended series of polyoxovanadates containing both vanadium(IV) and vanadium(V).[9,21-30] Other groups reported similar compounds later.[31,32]

Vanadium(IV) clusters are very interesting, because they contain metal centers with one unpaired electron which can be coupled in several different ways according to the cluster topology. Clusters containing up to 18 oxovanadium(IV) ions are now available.[25] They are very good testing grounds for existing theories of exchange coupling, because the S= 1/2 spins are the least demanding in terms of computational requirements. However there is also a limitation, because the relative simplicity of the magnetic interactions involving S= 1/2 spins in general result in a simple antiferromagnetic behavior.

Matters may become more interesting in the numerous clusters in which vanadium(IV) and vanadium(V) are present at the same time. In some cases vanadium(IV) and vanadium(V) sites are clearly localized[23], as shown by the X-ray crystal structure. In some other cases the bond distances are intermediate between those of vanadium(IV) and vanadium(V) and it can be assumed that, at room temperature and on the time scale of the X-ray diffraction experiment, the valencies are delocalized. The actual determination of the oxidation state of the vanadium ions is by no means trivial. The most commonly used procedure uses the so called bond-valence summations,[33] s, which are defined by the relationship:

$$s = \Sigma_R(R/R_0)^{-N}$$

where R_0 and N are empirical constants which are tabulated, and R is the observed bond length. The summation is extended to all the atoms around the vanadium ion. Ideally the value of s should correspond to either 4 or 5 in clusters containing localized vanadium(IV) and vanadium(V), respectively. Since the computed value of s depends on R_0 and N, and these in turn depend on the charge on the metal ion, two different calculations must be performed each time. In the localized case one must be close to either 4 or 5, while in the delocalized case intermediate values are calculated with both sets of parameters.

Another complication associated with the assignment of the number of vanadium(IV) and vanadium(V) ions lies in the determination of the charge on the cluster. All the clusters are negatively charged and in general the number of cations is easily determined. However sometimes disorder makes the determination of their number not so obvious as it might seem. Further, quite often variable number of protons are present on the oxide ions of the clusters, and this provides an additional complication in order to determine the charge globally present on the vanadium ions.

So far we have investigated the magnetic properties of $K_6[V_{15}As_6O_{42}(H_2O)].8H_2O$, V_{15}, and $(NH_4)_6[V_{14}As_8O_{42}(SO_3)]$, V_{14},[34] which comprise fifteen and fourteen vanadium(IV) ions, respectively, $K_6[H_3KV_{12}As_3O_{39}(AsO_4)].8H_2O$, $V_{3+1/12}$,[35] which has three localized and one delocalized vanadium(IV), $[V_{12}As_8O_{40}(HCO_2)]^{3-}$, $V_{4+2/12}$, and $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ $V_{4+4/12}$,[36] which comprise four localized, and two and four delocalized vanadium(IV) respectively. One interesting feature of these compounds is that they can trap ions or molecules within the molecular cage, as shown in Figure 1 for V_{15}. In this case the trapped molecule is a water molecule, which in the formula is indicated in parenthesis. The role of these trapped molecules is not only a passive one, but rather they have been found to influence the shape of the cluster anion which is formed.[27]

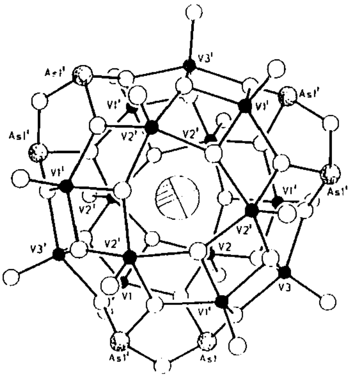

FIGURE 1. Crystal structure of V_{15}.

The structures of these compounds are interesting on their own, being essentially dtermined by the oxygen atoms. Vanadium(IV) ions are always in the oxovanadium(IV) form, and the four oxygen atoms connected to V=O are bridging between two or three vanadium atoms. In this way different polygons are defined which often form a quasi spherical anion. In general tetragons, hexagons, and octagons are defined, which are differently connected. The way the vanadium(IV) ions are bridged by oxygen atoms is very important, because it determines the extent of the magnetic coupling between the metal ions.

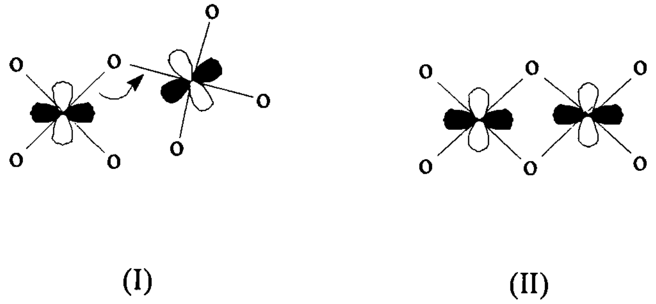

FIGURE 2. Magnetic orbital of V(IV) in μ-oxo bridged (I) and bis μ-oxo bridged (II) moieties.

The magnetic orbital on vanadium(IV) is essentially d_{xy} in nature, with the lobes bisecting the O-V-O angles. For single μ_2-oxo bridge the xy orbitals are expected to interact antiferromagnetically for V-O-V angles not far from 180° which are usually observed, as sketched in Figure 2. It is assumed that that the mechanism is essentially determined by superexchange through the oxygen atoms. The effectiveness of the oxygen in transmitting the exchange interaction depends on the number of atoms to which the oxygen atoms are connected. So a μ_2-oxo group is more efficient than a μ_2-hydroxo group.[34]

The other common geometry which is encountered is that of bis-μ-oxo bridges as sketched in Figure 2. In this case the distance between the two vanadium ions is much shorter than in the previous case, reaching 29 pm. Under these conditions a strong antiferromagnetic coupling is expected. These qualitative conclusions are borne out also by Extended Hückel calculations.[34] A more thorough approach using Xα-SW methods is currently underway.[37]

Unfortunately the work of modellization of the exchange interactions which has been so extensively carried out for copper(II) dinuclear complexes is almost totally absent for oxovanadium(IV) complexes. In a di-μ-hydroxo bridged complex J was found to be 354 cm^{-1},[38,39] while a similar di-μ-oxo bridged complex was practically diamagnetic at room temperature.[40]

The structure of V_{15} is shown in Figure 1. The fifteen vanadium atoms can be grouped in two external hexagons and a middle triangle. The six vanadium atoms in the hexagons are bridged by two μ_3-oxo and by a μ_3-oxo and a μ-arseniato group, respectively. The corresponding vanadium-vanadium distances are 287 and 305 pm respectively. A similar μ-oxo, μ-arseniato double bridge is present also between a vanadium of the hexagons and one of the triangle, with a metal-metal distance of 302 pm. The magnetic properties of V_{15} indicate that antiferromagnetic interactions between

the spins dominate. Below 100 K the effective magnetic moment stabilizes to the value expected for three uncoupled spins, while below 20 K it rapidly decreases.
Complementary single crystal EPR spectra show that the spins responsible of the magnetism in the range 10-100 K are localized in the middle triangle. Therefore it must be concluded that the coupling within the hexagons is so effective to completely couple the spins in the two external layers.

A quantitative fit of the temperature dependence of the magnetic data was performed using two different approaches. In the first one it was assumed that the energy levels are largely determined by the configurations arising fromt the strong coupling within the hexagons. All the other coupling constants were successively introduced with a perturbative treatment. In the second approach the energy levels were directly calculated using the ITO approach briefly outlined in the previous section. The two approaches were found to yield practically superimposable fits, which required a value of J= 550 cm^{-1} for the coupling constant corresponding to the vavadium-vanadium distance of 287 pm. All the other constants are smaller.

It is interesting to notice that the fact that the three vanadium ions in the triangle are essentially uncoupled down to ca. 15 K is not due to vanishingly small coupling constants, but rather to the spin topology of the clusters which determine spin frustration effects. Due to this peculiarity the cluster can be regarded as a model of a metal multilayer systems, with the external hexagons mimicking two antiferromagnetic layers sandwiching a paramagnetic layer.[41]

The structure of V_{14} is shown in Figure 3. The spin topology in this case is completely different from that of V_{15}, as evidenced also by the magnetic data. In fact the temperature dependence of the effective magnetic moment initially decreases on decreasing temperature like in V_{15}; below 200 K and down to 80 K it stabilizes to a plateau corresponding to six uncoupled spins, then increases to a maximum at ca 15 K, and below it decreases again rapidly.

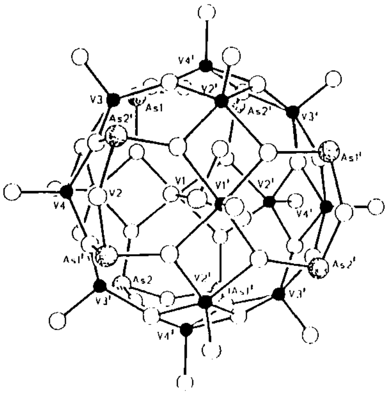

FIGURE 3. Crystal structure of V_{14}.

In V_{14} the vanadium atoms can be outlined as shown in Figure 3, with an equatorial octagon connected by two handles of three atoms respectively. The bridges connecting the V_3 and V_4 atoms are very similar to those corresponding to the strongest exchange interaction in V_{15}, the metal-metal distance, 281 pm, being even shorter. In the quantitative fitting of the magnetic data it was assumed that this strong coupling constant is responsible of the initial coupling of the spins leaving six of them uncoupled in the intermediate range of temperatures. Along these lines it was possible to satisfactorily fit the temperature dependence of the effective magnetic moment with both a perturbative and a full matrix approach. The value of the strongest coupling constant is 500 cm^{-1} in good agreement with the value calculated in V_{15}.

The quantitative fit of the magnetic data also explained the surprising presence of a maximum at 15 K in the temperature dependence of the effective magnetic moment. This in fact is not due to the presence of ferromagnetic coupling constants, because all of them were found to be antiferromagnetic in nature. Therefore the increase in the effective magnetic moment in the 100-15 K range of temperature is due to incipient ferrimagnetic behavior, like that observed in magnetite and maghemite for instance.

In the presence of delocalized spins matters become immediately much more difficult. In fact, as already said it is not easy to decide if the spins are totally/partially localized on the ground of X ray structural data alone. Further, even if convincing evidence can be reached at room temperature, it is not granted that the same conditions hold at low temperature. In fact, vibronic coupling can support total delocalization at room temperature and induce localization at low temperature. Finally, no really good method has been reported to describe the energy levels for delocalized systems. In fact these are generally expressed using parametric approaches which rapidly become dramatically overparametrized in the presence of numerous delocalized centers.

In order to make these considerations clear it may be useful to resort to an example, which has also some connection with real systems. Consider a square with four vanadium ions at the vertices, and see what happens when one or two of them are vanadium(IV) respectively. We will assume that the valence is completely delocalized.

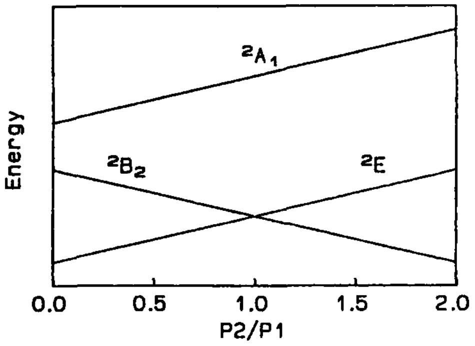

FIGURE 4. Energy levels for a square of three V(V) and one completely delocalized V(IV) as a function of the ratio between the two electron transfer parameter $r=P_2/P_1$

In the case of one delocalized vanadium(IV), two parameters, P_1 and P_2 are needed,[42] describing the electron transfer between neighboring and distant sites respectively. The corresponding levels are as shown in Figure 4 as a function of the $P_2/P_1 = r$ ratio. For positive P_1 $^2B_1$ is the ground state for r< 1, while ^2E become lowest in energy for r> 1. The symmetry notation we use is that of C_{4v} symmetry.

On passing to two vanadium(IV) centers the number of parameters dramatically increases. In fact beyond the electron transfer parameters P_1 and P_2 one must include the corresponding Coulomb repulsion parameters K_1 and K_2, and also two-electron transfer processes, of which there are at least four. Finally the Heisenberg exchange must also be included. If it is assumed that the Coulomb repulsion parameters are the most important, they stabilize the states where the two unpaired electrons are opposite along the diagonal of the square, d-states, over the states in which they are along the same side of the square, n-states. A detailed discussion of the relative importance of the parameters is absolutely beyond the interest of this article. However the important conclusion which is reached is that strong delocalization always favors the state where the two electrons are antiferromagnetically coupled. This result is completely different from that observed in in mixed valence systems where both the valence states are magnetic, where delocalization favors the parallel alignment of the spins. The latter effect is called double exchange, and it has recently received large attention in connection with the magnetic properties of iron sulfur proteins.

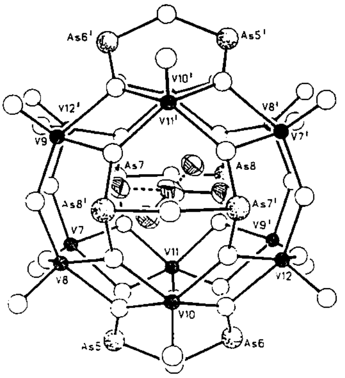

FIGURE 5. Crystal structure of the $[V_{12}As_8O_{40}(HCO_2)]^{n-}$ (n=3,5) anion present in the $V_{4+2/12}$ and $V_{4+4/12}$ clusters.

The $V_{4+2/12}$ and $V_{4+4/12}$ clusters are practical realizations[36] of the above abstract example. These anions have the practically identical structures depicted in Figure 5. The twelve vanadium ions can be grouped in three squares, with the central one comprising four vanadium(IV), and the two external ones, related by an inversion center, containing 1 or 2 completely delocalized vanadium(IV) ions, respectively. The magnetic properties of the two compounds are rather different from each other. The effective magnetic moment at room temperature of $V_{4+4/12}$ corresponds to four uncorrelated spins, while that of $V_{4+2/12}$ indicates six uncoupled spins. Since the former differs from the latter for containing two more delocalized vanadium(IV) ions, the differences in the magnetic properties must be determined by these additional electrons. This is in agreement with the theoretical treatment outlined above, which suggests a strong antiferromagnetic coupling for two electrons delocalized in a square. Therefore we suggest that in $V_{4+4/12}$ only the unpaired electrons which are localized in the internal squares are magnetically active at room temperature, while in $V_{4+2/12}$ both the localized and the delocalized electrons are magnetically active.

The temperature dependence of the magnetic moment of $V_{4+4/12}$ is monotonic, in agreement with a coupling within the vanadium(IV) ions in the square of 10 cm^{-1}. The temperature dependence of the effective magnetic moment in $V_{4+2/12}$ is more puzzling, passing through a maximum at ca. 25 K, and then decreasing. We could reach a seemingly satisfactory fit of the magnetic data, but only introducing a ferromagnetic coupling constant between the localized and delocalized vanadium(IV) centers. Whether this is real, or the result of the assumptions intrinsic to the model of delocalization is not clear to us at the moment.

Finally the EPR spectra of these compounds must be considered. The spectra of $V_{4+2/12}$ at 9 GHz are rather obvious, with one exchange narrowed line at the g value corresponding to the average of the g values of the individual tensors of the vanadium(IV) ions in the cluster. The spectra recorded at 255 GHz at low temperature on the other hand correspond to an S= 2 state. We assume that the high field of the latter experiment stabilize the S=2 state.

The EPR spectra of $V_{4+4/12}$ at X-band frequency at low temperature are typical of a triplet, while those at 295 GHZ are averaged. In this case the strong field determines the admixing of several spin levels. Therefore in a qualitative way the EPR spectra at low and high field provide an image of a complex pattern of levels close to the ground state.

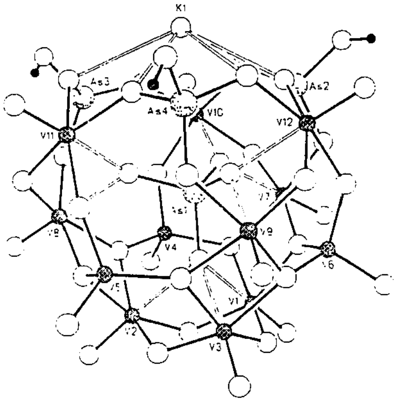

FIGURE 6. Crystal structure of $V_{3+1/12}$.

A last relatively simple example is provided by $V_{3+1/12}$, which has three localized vanadium(IV), plus an additional one which is delocalized over three sites.[35] The residual six centers are localized vanadium(V). The structure of $V_{3+1/12}$ is shown in Figure 6. The localized vanadium(IV) are V10, V11, and V12, while the fourth vanadium(IV) is delocalized over the V1, V2, and V3 sites. Given the relative simplicity of this structure it can be expected that the magnetic data should provide a confirmation to the above assignment of the nature of the metal ions performed on the basis of structural data alone. In fact the effective magnetic moment at room temperature corresponds to the value expected for four uncoupled spins. This agrees with the structural data, which show that the V10, V11, and V12 vanadium(IV) ions are bridged by long arseniato bridges, which are not expected to be very effective in transmitting the exchange interaction between the paramagnetic centers. Further their distance from the delocalized vanadium(IV) is long, so that this interaction must be even smaller. These expectations are borne out by the temperature dependence of the effective magnetic moment, which decreases on decreasing temperature, and reaches a plateau at ca. 20 K, corresponding to the presence of two uncoupled spins. The data could be quantitatively fit with a model which requires a coupling constant J= 63 cm^{-1}.

The conclusions which can be reached from the analysis of the magnetic properties of this limited series of vanadium clusters are the following:

i) large spin clusters can mimick the properties of bulk materials. Although the interactions between vanadium(IV) ions have been found generally to be antiferromagnetic in nature, in some range of temperature limited spin frustration effects can be observed.

ii) despite the complex nature of the spin levels of these materials, the temperature dependence of the effective magnetic moments often provides some useful hint which helps in reconstructing their gross features. Horizontal segments of the χT vs. T plots may reveal the number of unpaired electrons present in a given range of temperatures.

iii) some indications about the relative strengths of exchange interactions of the various bridges which are present in these materials begin to emerge, allowing for useful magneto-structural correlations.

iv) the magnetic properties of materials with delocalization effects are much more difficult to predict than the localized ones. Hard work is needed in this area before the energy levels can be adequately described with some effective hamiltonian. Also, antiferromagnetic interactions seem to dominate, so that we have not found any real indication of the possibility of stabilizing high spins in these materials.

IRON CLUSTERS

Given the limitations associated with the S= 1/2 spins, it is instructive to move to S= 5/2 which correspond to the highest value which can be found in transition metal ions. Iron(III) is a very important example in this area, due to the large number of large clusters which have been recently reported.[1-7,12] In fact many efforts have been performed in order to synthesize large iron clusters which allow a better understanding of the biomineralization of iron and mimick the properties of ferritin.[10,11] Clusters containing up to 19 iron(III) ions have been reported,[1] and in some cases it has been reported that incipient superparamagnetic behavior was observed.[1,11]

Here we want to give our contribution to the area reporting the results of some sample calculation on some model Fe_6 clusters[43], and on the magnetic properties of an Fe_8 cluster. Several Fe_6 clusters have been reported[12,44,45] with the spin topology shown in Figure 7. The three iron(III) ions are bridged by a μ_3-oxo group, and the two triangles are bridged by either two μ_2-hydroxo or by one peroxo group. These compounds have been reported to have either an S= 0 [44,45] or an S= 5 [12] ground state. It is beyond the purpose of the present article to quantitatively fit the experimental temperature dependence of the effective magnetic moments of the real compounds. We will only outline how it is possible to delimit the range of values of the parameters which allow to have either one or the other ground state.

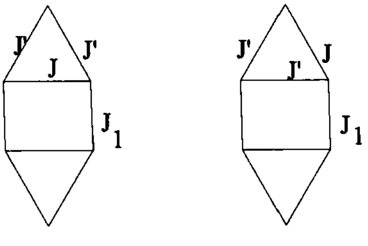

FIGURE 7. Spin topologies for two Fe_6 clusters. In both cases a center of symmetry is assumed for the cluster.

A simple look at the spin topology of the clusters shows that large spin frustration effects must be associated with the two triangles within which antiferromagnetic couplings must be expected. In fact the nature of the ground state within the triangle depends on the J/J' ratio, r. When r=1, i.e. for an equilateral triangle, the ground state is a degenerate pair of S= 1/2 states. For r different from one the two S= 1/2 levels split. For r> 1.8 the ground state becomes S= 3/2, while for r> 3.5 an S= 5/2 becomes lowest in energy. It is apparent that when two such triangles are considered together many different ground states can be obtained, depending on the relative values of the coupling constants. In the real systems[12,44,45] which are the background of our calculation, the J_1 coupling constant is smaller than the others. Sample calculations were performed by keeping J' fixed, J_1= J'/8, and letting J vary between J'/5 and J.

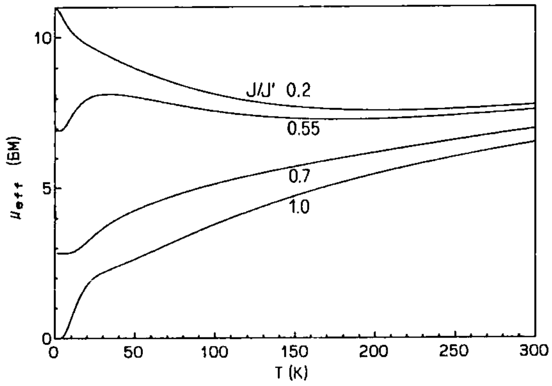

FIGURE 8. Calculated effective magnetic moment of Fe_6 clusters for different values of the J/J' ratio.

The situation is particularly simple for the case on the left of Figure 7, because the ground state is always S= 0, independent of all the parameters. The case on the right of Figure 7 is much more interesting, because many different ground states can be stabilized. The ground state is calculated to be S= 5 for J/J'= 0.2. The corresponding effective magnetic moment goes through a broad minimum, as shown in Figure 8.

When J/J'= 0.55 the ground state becomes S= 3, and the temperature dependence of the effective magnetic moment is rather complex, passing through a minimum and a maximum before stabilizing at the value expected for S= 3. For J/J' = 0.7 the ground state is S= 1, while for J/J'= 1 the ground state is S= 0.

From these calculations we conclude that indeed it is possible to stabilize different ground states for these clusters, in agreement with the experimental finding of both S= 0 and the S= 5 ground states.

The largest iron cluster for which detailed calculations have been possible up to now is Fe_8 cluster originally reported by Wieghardt et al.[7] The eight iron ions are bridged by both oxo and hydroxo groups. The connection between the iron ions and the corresponding J_i parameters are shown in Figure 9. The presence of eight iron ions makes the calculation of the spin levels extremely cumbersome, because the total degeneracy of the spin manifold is 1,679,616. It was necessary to implement methods which fully exploit the total spin and point group symmetry in order to arrive at tractable matrices, and also in this case it is necessary to diagonalize 81 matrices, the largest of which is 4170x4170.[13]

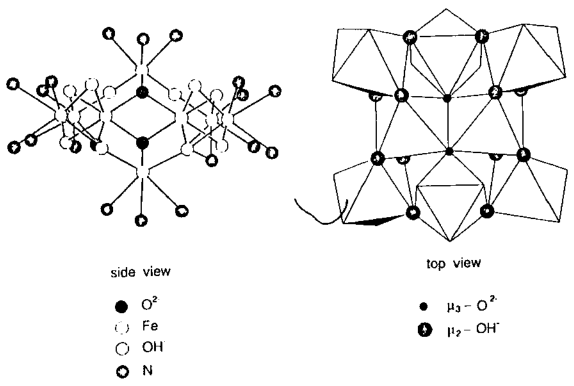

FIGURE 9. Crystal structure of Fe_8

The effective magnetic moment of Fe_8 increases on decreasing temperature, goes through a maximum correponding to a value intermediate between an S= 10 and an S= 9 ground state, and then decreases slightly. Magnetization data agree with a ground S= 9 state, even if they do not completely rule out the possibility of an S= 10 state. As it is apparent from Figure 9 that also in this case there are several different triangles in the spin topology, which determine spin frustration effects, and eventually justify the large spin in the low lying states.

Although we developed a rather efficient computer program[13,20] it was not really possible to fit the experimental data, but we found a range of values of the parameters which produce calculated temperature dependence of the effective magnetic moment which satisfactorily reproduce the experimental data. The values of the parameters which we used compare reasonably well with those usually reported for smaller iron clusters.

In order to provide an idea of the difficulties in the calculation of the spin levels of these clusters we show in Figure 10 the calculated densities of spin states for Fe_8. It is apparent that the levels in this cluster begin to merge in bands, like in infinite assemblies of metal ions. However it is interesting to notice that we did not observe any anomalous magnetic relaxation effect in the ac susceptibility measurement of Fe_8, contrary to Mn_{12}, where we observed frequency dependent out-of-phase susceptibility in the range of 10 K.[16] We assume that the difference in the behavior of the two compounds is associated with the large magnetic anisotropy of the latter, which has no counter-part in the former.

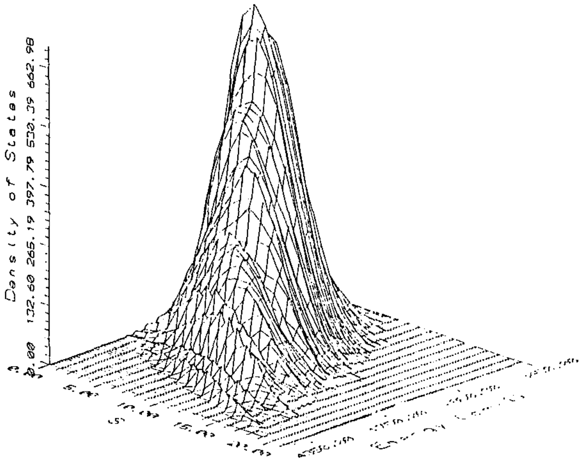

FIGURE 10. Calculated density of spin state for Fe_8.

CONCLUSIONS

The magnetic investigation of HNSC is still at the beginning and already interesting behaviors being to emerge. In particular it is becoming clear that many low lying levels are very close to each other in energy and either one or the other can be stabilized by relatively minor perturbations in the geometry of the clusters, or by external magnetic fields. This could provide opportunities to develop new magnetic field sensors in perspective. Also the optical properties of these materials deserve investigation, with the perspective of developing magneto-optical devices.

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