Magnetic Properties of an Octanuclear Iron(III) Cation

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The magnetic properties of $\{[(tacn)_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]Br_7(H_2O)\}Br\cdot H_2O$, Fe_8, tacn = 1,4,7-triazacyclononane, a molecule comprising eight iron(III) ions bridged by oxo and hydroxo groups, are reported. The magnetic susceptibility, both dc and ac, and the magnetization indicate that at low-temperature spin levels with $8 < S < 10$ are populated. EPR confirms that levels of high spin multiplicity are populated at 4.2 K. For the first time an attempt is made to calculate the energy of the spin levels of such a large cluster within a spin Hamiltonian formalism. The 1 679 616 states originating from the coupling of eight $S = {}^5/_2$ spins are classified by using total spin and point group symmetry, and the Hamiltonian matrix is calculated using an irreducible tensor operator approach. In this way the susceptibility can be calculated, and satisfactory fits of the experimental magnetic susceptibility are achieved. The values of the required parameters compare well with those previously reported in analogous iron complexes.

Introduction

Polynuclear iron(III) complexes are the focus of very active research aiming at developing synthetic strategies to obtain larger and larger clusters.[1-9] One of the reasons for the interest in these types of materials is that of understanding the properties of ferritin, the iron storage protein of bacteria, plants, and animals, which can store up to 4500 iron atoms as octahedral iron(III) ions connected by oxo bridges.[10,11] One of the features of these large clusters is that of being superparamagnetic,[10,12] due to the dimensions which are intermediate between those of simple paramagnets and those of bulk materials, containing infinite assemblies of interacting centers. This gives an additional reason of interest for the synthesis of large iron and, in general, metal ion clusters, i.e. that of synthesizing magnetic materials of mesoscopic scale, where interesting new properties can be anticipated and where bulk behavior may coexist with paramagnetic properties.[13]

The interpretation of the magnetic properties of large metal ion clusters is hampered by the difficulties associated with the calculation of the thermally accessible energy levels and of the thermodynamic properties in systems which are too large to use the simple approaches required for the interpretation of di- and trinuclear clusters but do not afford the simplification associated with translational symmetry of infinite assemblies of spins. In fact up to now only clusters comprising four iron(III) ions[14] have been successfully tackled in the general case, even if treatments are available for particularly simple larger clusters.[15]

Very recently we have developed in Florence a fast and efficient procedure for the calculation of the spin levels of high-nuclearity spin clusters using irreducible tensor operators,[16] ITO, which we have successfully applied to Fe^{III}_6 clusters.[17]

This approach made it possible for the first time to attempt quantitative interpretation of the magnetic properties of high-nuclearity spin clusters: for instance satisfactory fits of the magnetic susceptibility of clusters containing 14 and 15 oxovanadium(IV) ions were obtained.[13]

Recently one of us reported a cluster containing eight high-spin iron(III) ions, of formula $\{[(tacn)_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]Br_7(H_2O)\}Br\cdot H_2O$, Fe_8, tacn = 1,4,7-triazacyclononane,[3] whose structure is sketched in Figure 1, but only preliminary magnetic data were reported. We felt that this compound might provide an ideal testing ground for the ITO method to calculate the magnetic susceptibility of large clusters, and we wish to report here its magnetic properties, together with a detailed interpretation based on the extensive use of symmetry in order to reduce the dimensions of matrices. We feel that this represents a case history which can be used as a general model for the interpretation of the magnetic properties of high-nuclearity spin clusters.

Experimental Section

The compound was prepared as previously described.[3] The static magnetic susceptibility of a powder sample was measured by using a Metronique Ingeniérie MS02 SQUID magnetometer. The ac susceptibility of a powder sample was measured on a laboratory-assembled susceptometer based on a mutual inductance bridge at the frequency of 100 Hz. Isothermal magnetization was measured up to 20 T using a Bitter magnet.[18]

Results

The temperature dependence of χT of Fe_8 in a field of 2 T is shown in Figure 2. At room temperature χT is 20.06 emu mol^{-1} K, much smaller than expected for eight uncoupled $S = {}^5/_2$ spins, and steadily increases on decreasing temperature, reaching a maximum corresponding to $\chi T = 45.8$ emu mol^{-1} K, at ca 25 K. Below 10 K χT rapidly decreases on decreasing temperature

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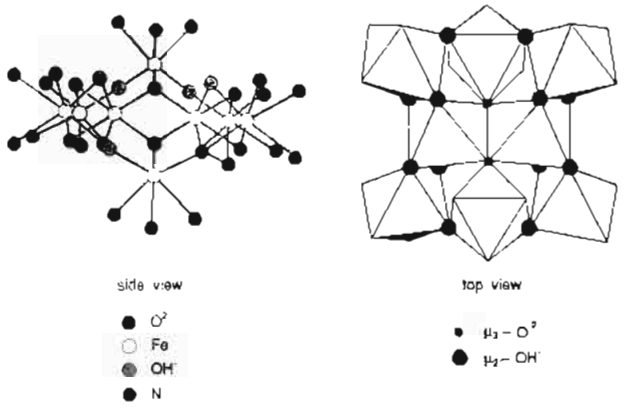

Figure 1. Molecular structure of $\{[(tacn)_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]Br_7(H_2O)\}Br\cdot H_2O$, Fe_8.

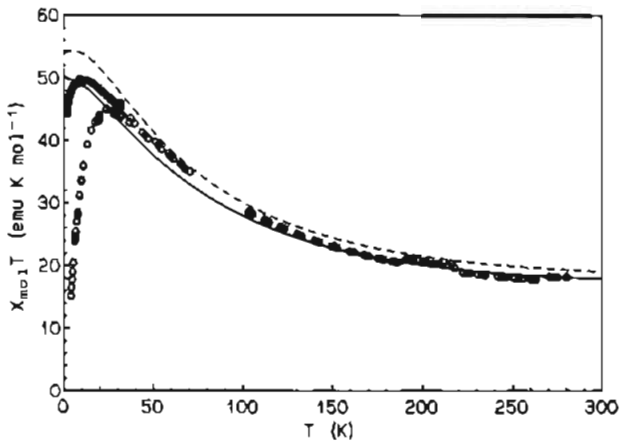

Figure 2. Magnetic Properties of Fe_8 in the form of χT product vs T: (○) $H = 2$ T; (●) $H \sim 0$. Curves represent calculated values of χT for (dashed) $J_1 = 20$, $J_2 = 120$, $J_3 = 15$, $J_4 = 35$ cm^{-1}, (solid) $J_1 = 102$, $J_2 = 120$, $J_3 = 15$, $J_4 = 35$ cm^{-1}.

reaching 15 emu mol^{-1} K at ca. 2 K. In order to rule out any effect associated with the presence of an external magnetic field, the measurements were performed also with an ac susceptometer without any applied field. The results drawn as filled circles in Figure 2 indicate that the maximum is higher for the zero-field measurement reaching 52 emu mol^{-1} K at 10 K and that the decrease at lower temperatures is much less marked reaching 45 emu mol^{-1} K at 4 K, suggesting that effects due to saturation affect the measurements at $H = 2$ T. It is interesting to note that no out of phase response was observed in this case in contrast with the results observed[19] in a Mn_{12} cluster, which also has a similar large χT value at low temperature.

In order to determine the field dependence of the magnetization, measurements were performed at 1.8 and 4.2 K, and the results are shown in Figure 3. The data points at the two temperatures are very close to each other, much closer than expected for an isolated spin multiplet. For both the temperatures and magnetization regularly increases with increasing field and saturates at the value of ca. 19 μ_B in a field of 10 T.

Polycrystalline powder EPR spectra of Fe_8 were recorded at X-band frequency in the range 4.2–300 K and are shown in Figure 4. At high temperature only a very broad featureless band is observed at $g \sim 2$. On cooling some structure starts to appear and eventually at 4.2 K at least seven relatively intense transitions are observed. Although they are not exactly equispatiated, they are separated by intervals of ca. 1000 G. Attempts were made also to record single-crystal spectra, but the obtained crystals were found to be too small to give detectable signals.

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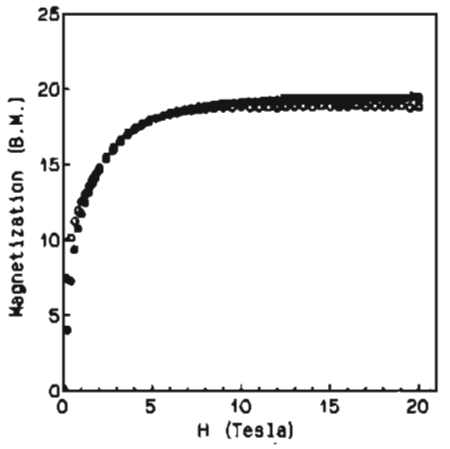

Figure 3. Magnetization curves for Fe_8: (●) $T = 4.2$ K; (○) $T = 1.8$ K.

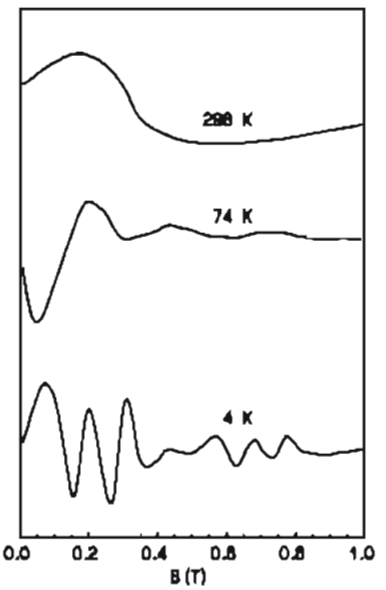

Figure 4. Polycrystalline powder X-band EPR spectra of Fe_8.

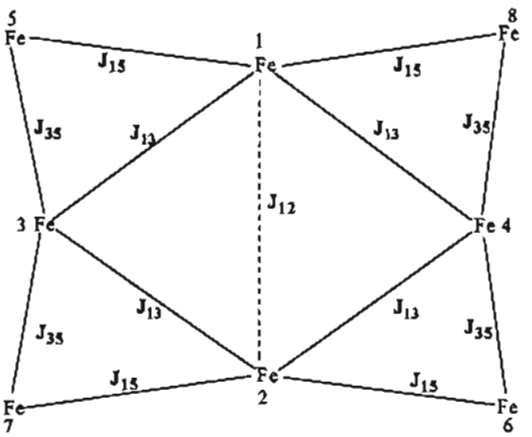

Figure 5. Scheme of the exchange pathways connecting iron(III) centers in Fe_8.

Discussion

Qualitative Aspects. The exchange pathways connecting the eight iron(III) ions can be schematized as shown in Figure 5. The four iron(III) ions connected by μ_3-oxo bridges have the now well-known "butterfly" configuration, which has been extensively discussed for both iron[14,20,21] and manganese[22,23] tetranuclear

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Table I. Group Theoretical Classification of Total Spin States for a Cluster of Four $S = {}^5/_2$ Spins

S	reprsentations in T_d	$D_2(S_A)$	$D_2(S_B)$
10	A_1	A	A
9	T_2	$B_1 + B_2 + B_3$	$A + B_2 + B_3$
8	$A_1 + E + T_2$	$3A + B_1 + B_2 + B_3$	$3A + B_1 + B_2 + B_3$
7	$A_1 + T_1 + 2T_2$	$A + 3B_1 + 3B_2 + 3B_3$	$3A + B_1 + 3B_2 + 3B_3$
6	$2A_1 + 2E + T_1 + 2T_2$	$6A + 3B_1 + 3B_2 + 3B_3$	$6A + 3B_1 + 3B_2 + 3B_3$
5	$A_1 + E + 2T_1 + 4T_2$	$3A + 6B_1 + 6B_2 + 6B_3$	$6A + 3B_1 + 6B_2 + 6B_3$
4	$2A_1 + A_2 + 3E + 2T_1 + 3T_2$	$9A + 5B_1 + 5B_2 + 5B_3$	$8A + 6B_1 + 5B_2 + 5B_3$
3	$A_1 + E + 3T_1 + 4T_2$	$3A + 7B_1 + 7B_2 + 7B_3$	$6A + 4B_1 + 7B_2 + 7B_3$
2	$2A_1 + 3E + A_2 + 2T_1 + 2T_2$	$9A + 4B_1 + 4B_2 + 4B_3$	$7A + 6B_1 + 4B_2 + 4B_3$
1	$2T_1 + 3T_2$	$5B_1 + 5B_2 + 5B_3$	$3A + 2B_1 + 5B_2 + 5B_3$
0	$A_1 + A_2 + 2E$	6A	$3A + 3B_1$

complexes. The butterfly is connected to four other iron ions through hydroxo bridges. J_1 corresponds to the exchange interaction transmitted along the body of the butterfly, J_2 to that transmitted between the body and the wings, J_3 to a di-μ_2-hydroxo, and J_4 to a single μ_2-hydroxo bridge. All these pathways are expected to be antiferromagnetic.[4,14,21] In the butterfly complexes J_1 has been found[14,20] in the range 18–25 cm^{-1} and J_2 in the range 90–120 cm^{-1},[14] and the hydroxo bridges have been observed[24] to correspond to interactions in the range 15–35 cm^{-1}.

Qualitative conclusions about the nature of the ground state are very difficult to draw, due to the presence of many triangles in the network of interactions, which provide frustration effects when the couplings are all antiferromagnetic as expected in this case. In fact, in a triangle a spin is subject to two conflicting opposite interactions, and as a result the most stable configuration of the spins does not correspond to alignment to either 0 to 180° but to a different angle which depends on the ratio of the conflicting coupling constants.

Particularly large frustration effects have been observed in the butterfly complexes containing manganese,[23] while for the analogous tetranuclear iron complexes the ground state has always been found to be diamagnetic.[14,20] This has been justified with a model where J_2 is much larger than J_1.[14]

A qualitative analysis of the temperature dependence of χT indicates the presence of antiferromagnetic couplings, because the high-temperature value is much smaller than expected for 8 uncoupled spins. The increase of χT on decreasing temperature indicates that below room temperature low-spin states are selectively depopulated. This is in agreement with frustration effects[4] and with previous findings in large spin clusters.[25] The value of the maximum in χT is intermediate between the values expected for a ground $S = 9$ (45 emu mol^{-1} K) and an $S = 10$ state (55 emu mol^{-1} K). This must be taken as an indication that at ca. 10 K levels with $S > 8$ are populated.

The saturation value of the magnetization of 19.5 μ_B at 4.2 K and 18.9 μ_B at 1.8 K agrees with an $S = 10$ ground state, even though the fact that the experimental curves at the two different temperatures are almost superimposable and do not follow a Brillouin function for a pure $S = 10$ state indicates that in this range of temperatures there is not one isolated spin multiplet populated. The best explanation is that a strong field stabilizes the $S = 10$ state, which is close in energy to an $S = 9$ state.

The decrease in χT below 5 K may be due to several different effects, such as the presence of low-lying states with $S < 8$, zero-field splitting, and/or intermolecular antiferromagnetic interactions. All these factors are expected to determine variations of the magnetization curves from simple Brillouin behavior.[26]

The presence of a state with a large spin which is thermally populated at 4.2 K is confirmed by the EPR spectra. Since at least four transitions spatiated by ca. 1000 G are observed at high fields, the spin state must be at least $S = 4$. The fact that the low-field transitions are more intense than the high-field ones indicates that the sign of D is negative.[27]

This is the maximum we are able to achieve from a qualitative analysis of the magnetic data. In order to proceed further it is necessary to have an idea of the nature of the low-lying levels. This will be discussed in the following section.

Model for the Calculations of the Spin Levels. The total degeneracy of the spin states of eight $S = {}^5/_2$ spins is 1 679 616, which can be grouped in total spin states S ranging from 0 to 20. In order to calculate the spin levels, and the magnetic susceptibility, we attempted to use the approach of irreducible tensor operators in order to take full advantage to the total spin symmetry.[16] However, this approach alone is not sufficient to produce tractable matrices for a cluster of this size. For instance the matrices corresponding to $S = 5$ and $S = 4$ have dimensions $n = 16\,576$ and 16 429, respectively.

In order to reduce the dimensions of the matrices to be diagonalized, we employed point group symmetry. Tsukerblatt et al.[28] showed that the best way to do that is to use permutation symmetry for the different spin sites of the cluster, because the spin Hamiltonian is symmetric relative to interchange of identical particles. For n identical particles the permutation group is π_n, which has $n!$ elements and a number of irreducible representations which can be obtained using the Young tableaux. For instance if we must consider four identical particles, the appropriate group is π_4, which has 24 elements, grouped in five classes corresponding to five irreducible representations of dimensions 1, 1, 2, 3, 3. This means that the highest degeneracy of the total spin levels for four identical particles is 3.

The π_4 group is isomorphous to the point group T_d, which is certainly more familiar to chemists, and the irreducible representations of π_4 correspond to the well-known representations A_1, A_2, E, T_1, and T_2 of T_d. Therefore it is convenient to use the latter to characterize the symmetry of the spin levels.

In order to assign the appropriate symmetry labels to the total spin functions of four identical particles, it is sufficient to investigate their behavior under the operations of the group T_d. For instance, for four $S = {}^5/_2$ the total spin function characterized by $S = 10$ and $M_s = 10$ corresponds to $|{}^5/_2\ {}^5/_2\ {}^5/_2\ {}^5/_2\rangle$, where the function is written with the $|m_1\ m_2\ m_3\ m_4\rangle$ components of the four $S = {}^5/_2$ spins on the individual centers. It is easy to verify that this function remains unaltered for any interchange of two particles; therefore, it is a basic for the totally symmetric irreducible representation of T_d (π_4). We may indicate this function as $^{21}A_1$. By writing explicitely the total spin functions, we can classify them as shown in Table I.

In Fe_8 there is no rigorous symmetry; however, the eight iron(III) ions are not far from D_2 symmetry as far as the exchange

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Table II. Symmetry Classification of the Total Spin States for Fe_8 in the D_2 Group

S	A	B_1	B_2	B_3	tot. deg
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

pathways are concerned, as shown in Figures 1 and 5. The eight atoms are divided into two subsets of four, namely 1, 2, 3, and 4 in one set and 5, 6, 7, and 8 in the other. The former couple gives $S_A = S_1 + S_2 + S_3 + S_4$, and the latter $S_B = S_5 + S_6 + S_7 + S_8$. The symmetry of each subset is also D_2; therefore, we can classify the states as shown in Table I. In order to take into account the fact that the point symmetry is D_2 and not T_d, we have just to use the correlation tables, taking into account the difference between the S_A and S_B subsets.

In order to classify the total spin states $S = S_A + S_B$ we have to write them down explicitely and look at their behavior in the group D_2. The overall classification schemes appropriate for Fe_8 is shown in Table II. Actually, since the two subsets of intermediate spin states $|S_A\ M_A\rangle$ and $|S_B\ M_B\rangle$ do not mix with each other, the irreducible representation Γ of $|S_A\ M_A\ \Gamma_A\ S_B\ M_B\ \Gamma_B\ S\ \Gamma\rangle$ is just given by the direct product $\Gamma_A \otimes \Gamma_B$. The validity of this approach has been checked on systems of eight $S = {}^3/_2$ spins, which are tractable without introducing point group symmetry.

By taking advantage of the symmetry, we find that the largest blocks are now 4170 × 4170 compared to 16 576 × 16 576 and computation time is also reduced since the number of matrix interactions ($J_{ij}S_1 \cdot S_2$) which need to be calculated is reduced by a factor of ${}^4/_{13}$ for each matrix element.

Calculation of the Spin Levels. Notwithstanding the simplifications so far introduced a full calculation for a given set of parameters requires roughly 70 h on our RISC 6000 computer. Therefore we could not afford a random calculation with large variations of the parameters in order to identify the ranges which could reproduce the experimental data. This simply would have been too time consuming. In order to overcome, this problem we made sample calculations in a system with eight $S = {}^3/_2$ spins. It was hoped that in this way it might be possible to find approximately the ratios between the J_i values which reproduce analogous magnetic behavior to the Fe_8 cluster, namely χT increasing on decreasing temperature, reaching a plateau at low temperature corresponding to a high-spin state. We use the correspondence $S = 10$ for Fe_8 with $S = 6$ for the cluster of eight $S = {}^3/_2$ spins; therefore, we looked for the conditions under which the ground state is larger than 4, and several high-spin states ($S > 4$) are close to it.

Following this procedure we found that, in order to meet these conditions, J_4 must be slightly larger than J_3, and $J_1 \approx J_2$. This marks a difference with the relative values of J_1 and J_2, which have been used[14,21] for butterfly iron complexes. However if we assume $J_1 \ll J_2$, as generally used[14,21] in those cases, a ground $S = 6$ state is strongly stabilized compared to all the others.

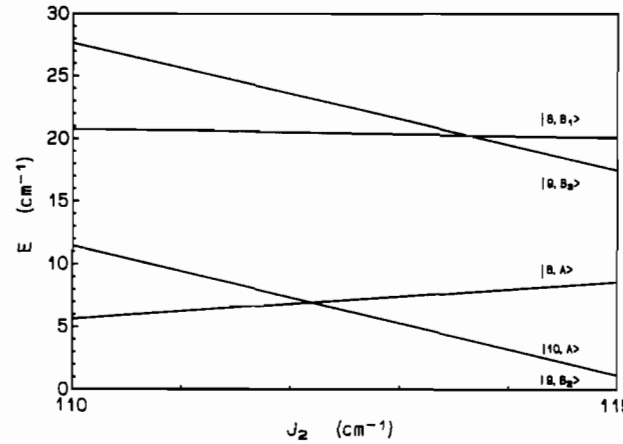

Figure 6. Energy of the lowest lying spin states as a function of J_2.

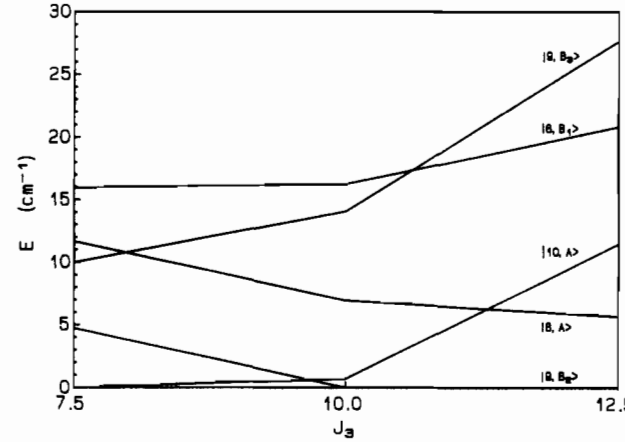

Figure 7. Energy of the lowest lying spin states as a function of J_3 ($J_4 = 2J_3$).

Given the structural similarity of the part of the Fe_8 cluster given by Fe's 1, 2, 3, and 4 to the butterfly complexes, an obvious starting point in fitting the experimental data was to use coupling constants similar to those found in the literature for the Fe_4O_2 butterfly complexes and typical values for the hydroxy bridges.[14,24] The χT vs T curve calculated with $J_1 = 20$ cm^{-1}, $J_2 = 120$ cm^{-1}, $J_3 = 15$ cm^{-1}, and $J_4 = 35$ cm^{-1} is given in Figure 2. All the known iron butterfly compounds have a very large difference between J_1 and J_2 which, in this compound, results in a $|10,A\rangle$ ground state and a $|9,B3\rangle$ first excited state more than 25 cm^{-1} higher in energy. This is reflected in Figure 2, where the χT curve goes to 55 emu K mol^{-1} at low temperature.

In order to determine the effect of changes in the coupling constants on the ground state and the low-lying energy levels, we have plotted the eigenvalues for a number of states against the coupling coefficients J_2 and J_3. Figure 6 shows how the eigenvalues of the lowest lying states depend on J_2. Increasing J_2 stabilizes the $|10,A\rangle$ and $|9,B_3\rangle$ states; a similar plot in which both J_1 and J_2 were varied but with $J_1 - J_2$) kept constant resulted in a set of nearly parallel lines. Hence the difference between J_1 and J_2 is the important parameter here. Therefore Figure 6 suggests that a large difference between J_1 and J_2 will result in an isolated $|10,A\rangle$ ground state, in accordance with the trends observed in the analogous $S = {}^3/_2$ calculations. In Figure 7 we give the energy levels of the low-lying states as a function of J_3, keeping $J_4 = 2J_3$. Increasing these parameters destabilizes the $|10,A\rangle$ state relative to the $|9,B_2\rangle$ and the $|8,B_1\rangle$ states.

Better agreement with the experimental data was obtained by increasing J_1 to 102 cm^{-1} at which point there are $|10,A\rangle$ and $|9,B2\rangle$ states separated by less than 0.5 cm^{-1} and well separated (20 cm^{-1}) from the other spin states. The agreement between the calculated curve and the experimental data, Figure 2, can be

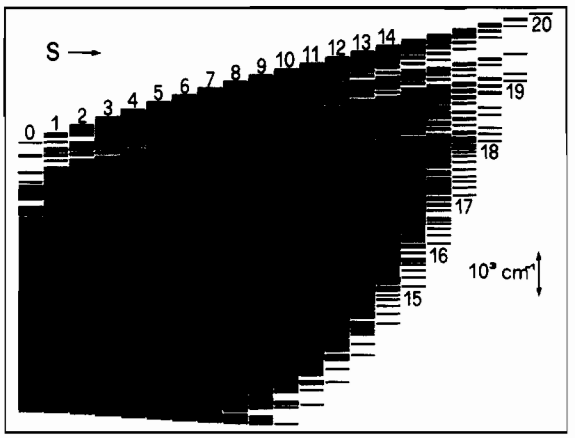

Figure 8. Calculated energy levels for Fe_8. $J_1 = 102$, $J_2 = 120$, $J_3 = 15$, and $J_4 = 35$ cm^{-1}.

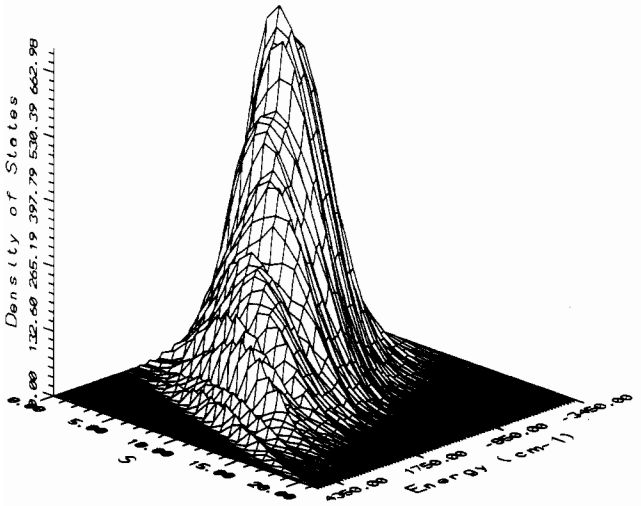

Figure 9. Calculated density of states for Fe_8. The parameters are the same as in Figure 8. The horizontal axes correspond to the total spin values S and to the energies.

considered satisfactory given the size of the calculation and the time required.[29]

The $S = 10$ spin state can be described by a predominant spin configuration in which the spins of the Fe_5, Fe_6, Fe_7, and Fe_8 are parallel to each other, while the spins of Fe_{1-4} are alternatively up and down. In fact the spins of Fe_3 and Fe_4 can be set up, and Fe_1 and Fe_2 down. The use of $J_4 > J_3$ determines the parallel alignment of the spins of the Fe_{5-8} ions.

The energies of the spin levels corresponding to the fit are shown in Figure 8. It is apparent that the large number of spin states contained within a maximum of 9000 cm^{-1} determines a *quasi-continuum* which corresponds to the structure expected for infinite assemblies of spins. Figure 8 also shows that the high-energy side of the bands is characterized by high-spin states, while close to the bottom only states with $S \leq 10$ are present. As a consequence, if the susceptibility could be measured in a sufficiently high range of temperature, χT would be seen to decrease initially, go through a minimum, and increase at lower temperature. Figure 9 shows the density of states in a three-dimensional plot from which it is clear that the maximum density is achieved for low-spin states and relatively low energies.

(29) In this range of J parameters we did not find any evidence of a ground state with $S < 9$ which could reproduce the experimental data.

In order to justify the apparently large difference between the J_1 value found for this compound and those given in the literature, we have compared the structural details of this compound with those of several other butterfly complexes.[14,20,21] The most consistent difference between the two sets of complexes lies in the Fe–O–Fe angles. For instance the Fe1–O–Fe3 angle is 128.5° and the Fe3–O–Fe2 angle is 127.7°, while the corresponding angles in the butterfly complexes are approximately 120 and 130°, respectively. The corresponding Fe–Fe distances also change with the larger the angle, the greater the distance. With this in mind we have performed some sample calculations on a butterfly complex in which the "wing-body" interactions were allowed to differ. In these calculations $J_{13} = J_{24} = 135$ cm^{-1} and J_{12} and $J_{14} = J_{23}$ were allowed to vary, the subscripts refer to the numbering scheme in Figure 5. The calculated susceptibility was compared to published values, and good fits could be obtained in which both J_{12} and J_{14} were of a magnitude similar to that of J_{13}. Hence the small difference between J_{13} and J_{14} was sufficient to allow J_{12} to have a much larger value. Although this model may be more appealing than that used by Hendrickson et al.[14] due to the closer magnetic structural correlation, it introduces a third parameter into a system which can already be well described by a two-parameter model. However, the two parameters which were varied, J_{12} and J_{14}, were found to be strongly correlated such that the difference between the two parameters is the better defined parameter. The large "body–body" interaction, J_{12}, found in these analyses is consistent with that which was found to reproduce the experimental data for the Fe_8 cluster.

Conclusions

In the field of iron clusters Fe_8 is the one with the highest spin in the ground state so far reported. The high-spin multiplicity is determined by the combined effects of antiferromagnetic coupling constants and the complex exchange topology of the cluster, which allows large spin frustration effects. In this respect Fe_8 is similar to the Mn_{12}[19,30] and $Mn_6(NITPh)_6$[25] complexes, which also have been reported to have high-spin multiplicities in the ground state as a result of antiferromagnetic coupling. Fe_8, like $Mn_6(NITPh)_6$, does not show any anomaly in the ac susceptibility like the one observed in Mn_{12}, where frequency-dependent relaxation effects were reported.[19] The main difference between the two types of compounds lies in the magnetic anisotropy, which is much larger in Mn_{12} compared to the other two. Therefore, it may be concluded that the superparamagnetic-like behavior of Mn_{12} must be associated with large magnetic anisotropy effects.

The other iron(III) clusters reported so far have been found generally to have low-spin ground states ($S = 0, {}^1/_2$), and only in some Fe_6 clusters spin frustration effects were found to yield a ground $S = 5$ state.[4] With the present compound the conditions which are required in order to have a high-spin ground state become better defined.

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