

Spin Frustration in High-Spin Triiron(III) Complexes: An Inelastic Neutron Scattering Study

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Abstract: Inelastic neutron scattering spectra in the range 20–200 cm⁻¹ are used to identify magnetic transitions in exchange-coupled oxo-centered triiron(III) complexes. It is concluded that the triangular cluster in the compound [Fe₃O(O₂CCD₃)₆(C₅D₅N)₃]NO₃ is adequately described as isosceles, i.e. with two of the three *J*-values equal, but that the clusters in K₅[Fe₃O(SO₄)₆(D₂O)₃].6D₂O and [Fe₃O(O₂CC(CD₃)₃)₆(DOCD₃)₃]Cl are scalene. The deviations of the clusters from equilateral symmetry are discussed in terms of a magnetic Jahn–Teller effect.

Oxo-centered trinuclear basic carboxylate complexes of transition metal ions of the structural type [M₃O(O₂CR)₆L₃] provide good models for the study of magnetic and electronic interactions between metal centers.¹ The metal–metal distances are sufficiently large to preclude metal–metal bonding, in the usual sense of the term, but there are weaker coupling effects between the metal centers which can affect the physical properties in important ways. For example, although the electronic spectra can be interpreted to a good approximation in terms of d–d and charge-transfer transitions of the individual metal ions, the interactions lead to enhancement of the intensity of normally spin-forbidden bands and to transitions and splittings due to exchange coupling.^{2–4} The predominant interactions are antiferromagnetic, and the simplest model is the Heisenberg–Dirac–van Vleck (HDVV) spin-only coupling scheme.⁵ When applied to a cluster of three ions placed in an equilateral triangle, it invariably predicts a ground state of degeneracy greater than 2, but the degeneracy is lifted if the symmetry of the triangle is reduced by any structural modification which makes at least one *J*-value different from the other two. The degeneracy is a direct consequence of the fact that in this particular molecular geometry, as also in certain others, it is impossible for all possible pairings of spins to be simultaneously antiferromagnetic, hence the name “spin frustration”. The electronic energy gained by splitting the ground state provides a driving force for distortion: it has been called the “Magnetic Jahn–Teller Effect”.⁶

The possibility of spin-driven distortion in complexes of this type was envisaged in the original work of Jahn and Teller,⁷

and it has been discussed at some length for the case of the tetrahedral Cu^{II}₄O cluster.^{8,9} In extended lattices, the mechanism is well established under the name of “magnetostriction” and it accounts for phase changes of magnetic metal oxide systems, e.g. FeO which changes from cubic to trigonal symmetry on cooling below the Néel temperature and CoO which changes from cubic to tetragonal.¹⁰

In this paper, we present new data on symmetry lowering in homonuclear paramagnetic complexes. The method of inelastic incoherent neutron scattering (IINS) is shown to be a direct, sensitive, and quantitative probe of the ground state splitting referred to above. We show that two triiron(III) complexes which were previously thought to be of trigonal symmetry are actually of lower symmetry (at the low temperatures used in this work). While we cannot yet prove that the symmetry lowering is driven only by internal electronic interactions, we believe that the evidence is now sufficient for the hypothesis to be taken seriously.

Experimental Section

Preparation of Complexes. Tris(perdeuteriopyridine)hexakis(*μ*-perdeuterioacetato)(*μ*₃-oxo)triiron(III)nitrate, [Fe₃O(O₂CCD₃)₆(C₅D₅N)₃]NO₃, was made by the method of Johnson *et al.*¹¹ To 7.4 g of CD₃CO₂D (0.116 mol) was added 11.3 mL of 40% aqueous NaOH (0.113 mol), slowly, with stirring and cooling, to give solid sodium perdeuterioacetate. On warming this redissolved, and 19.5 g of Fe(NO₃)₃·9H₂O, (0.048 mol) was added slowly with stirring. Initially, the ferric nitrate dissolved, but after 15 min, the mixture changed to a paste. Stirring was continued for 5 min, then 20 mL of absolute ethanol was added to form a solution. The mixture was filtered through a glass sinter and washed through with a further 5 mL of ethanol. Perdeuteriopyridine (5 mL) was added to the solution, and an olive green precipitate immediately formed. The mixture was cooled in an ice bath for 10 min and then filtered in air. The product was washed once with a little ethanol/pyridine-*d*₅ mixture (20:1) and then with a little diethyl ether. The product, an olive green powder, was dried at 50 °C for 5 min and then at room temperature in a desiccator over P₂O₅. Yield,

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10.35 g. Anal. Calcd for $\text{Fe}_3\text{C}_{27}\text{D}_{33}\text{N}_4\text{O}_{16}$: C, 37.28; N, 6.44; Fe, 19.26. Found: C, 37.10; N, 6.19; Fe, 19.47.

Tris(perdeuteriomethanol)hexakis(μ -perdeuteriopivalato)(μ_3 -oxo)-triiron(III) chloride, $[\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CD}_3)_3)_6(\text{DOCD}_3)_3]\text{Cl}$, was prepared as described elsewhere,¹² following the initial report of Blake and Frazer.¹³

Analysis for Iron. To an accurately weighed quantity of sample (ca. 0.05 g) in dilute HCl (1 M, 20 mL) was added 0.1 M SnCl_2 (in 1 M HCl), dropwise, with heating and stirring until the yellow color disappeared. After the solution had been allowed to cool to room temperature, 10 mL of saturated HgCl_2 solution was added to oxidize excess Sn(II) to Sn(IV), and the Fe(II) was titrated potentiometrically (using saturated calomel and platinum electrodes) against Ce(IV).

Spectra. Incoherent inelastic neutron scattering spectra were obtained on spectrometers IN4 and IN5 at the high flux reactor of the Institut Laue-Langevin (ILL), Grenoble, France, and on HET at the spallation neutron source (ISIS) at the Rutherford Appleton Laboratory (RAL), Chilton, U.K. Samples, finely powdered, were sealed into flat-plate aluminium cans, with thickness calculated such that about 10–13% of neutrons would be scattered by the sample.

Data treatment involved subtracting the spectrum of the empty sample container, correcting for sample shape and geometry, and calibrating the neutron detectors by measuring the scattering from metallic vanadium. Data reduction and curve fitting were performed using the standard programs INX and PROFIT at the ILL and GENIE at the RAL.

Theory

The HDVV Hamiltonian for coupling between three spin centers a, b, and c is given by⁵

$$H_{\text{ex}} = -2(J_{\text{ab}}\mathbf{S}_a \cdot \mathbf{S}_b + J_{\text{bc}}\mathbf{S}_b \cdot \mathbf{S}_c + J_{\text{ac}}\mathbf{S}_a \cdot \mathbf{S}_c) \quad (1)$$

where J_{ij} is the spin-only coupling constant between centers i and j . The metal ions are assumed to have strictly localized oxidation states and high-spin electron configurations; hence, for these high-spin d^5 metal ions in nearly octahedral coordination, the ground terms are 6A_1 and the orbital angular momentum is neglected. Three sets of solutions have been derived in which all three, or two, or none of the J -values are equal. We call them “equilateral”, “isosceles”, and “scalene”, respectively, since they can result from these three shapes of the M_3 triangle, though we stress that the metal–metal distances as such need not be the predominant factors determining the J -values.

In the equilateral case, the Hamiltonian simplifies to

$$H_{\text{ex}} = -2J(\mathbf{S}_b \cdot \mathbf{S}_c + \mathbf{S}_a \cdot \mathbf{S}_c + \mathbf{S}_a \cdot \mathbf{S}_b) \quad (2)$$

and when all three atomic spins are equal, $S_a = S_b = S_c$, the expression for eigenvalues of the energy for all spin states is⁵

$$E = -J[S(S+1) - 3S_a(S_a+1)] \quad (3)$$

where S is defined by $\mathbf{S} = \mathbf{S}_a + \mathbf{S}_b + \mathbf{S}_c$. In the isosceles case, taking atom c as the unique atom, we have

$$H_{\text{ex}} = -2J(\mathbf{S}_b \cdot \mathbf{S}_c + \mathbf{S}_a \cdot \mathbf{S}_c) - 2J_{\text{ab}}\mathbf{S}_a \cdot \mathbf{S}_b \quad (4)$$

which gives⁹

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$$\begin{aligned} E &= -J_{\text{ab}}[S_{\text{ab}}(S_{\text{ab}}+1) - 2S_a(S_a+1)] - J[S(S+1) - \\ &S_{\text{ab}}(S_{\text{ab}}+1) - S_a(S_a+1)] \\ &= -J[S(S+1) - 3S_a(S_a+1)] + \Delta J[S_{\text{ab}}(S_{\text{ab}}+1) - \\ &2S_a(S_a+1)] \quad (5) \end{aligned}$$

where $S_{\text{ab}} = S_a + S_b$ and $\Delta J = J - J_{\text{ab}}$.

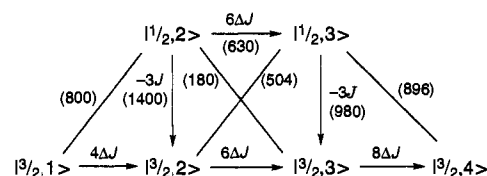
Formulas for scattering intensities have been given in detail in ref 14 and 15. The intrinsic transition probabilities I_0 depend on the quantum numbers for the ground and excited states;^{14,15} the variation with scattering angle 2θ is given by

$$I = I_0[\sin(QR)]/QR \quad (6)$$

$$Q^2 = k_0^2 + k_1^2 - 2k_0k_1 \cos 2\theta \quad (7)$$

where R is the iron–iron distance, Q is the momentum transferred, and \mathbf{k}_0 and \mathbf{k}_1 are the incident and scattered wave vectors. The main approximation involved is that, for the purpose of calculating the interference term in eq 6, the metal ion triangle can be considered as equilateral. The result is that, when J is negative and ΔJ is small, the lowest-lying eigenstates are as shown in Scheme 1, which gives the energy differences in the directions indicated by the arrows and the values of I_0 for each transition.

Scheme 1



In the scalene case it is convenient to introduce parameters $\langle J \rangle$, D , and Θ and define the three individual J -values as

$$J_{\text{ab}} = \langle J \rangle + D \cos \Theta \quad (8a)$$

$$J_{\text{bc}} = \langle J \rangle + D \cos(\Theta + 2\pi/3) \quad (8b)$$

$$J_{\text{ac}} = \langle J \rangle + D \cos(\Theta + 4\pi/3) \quad (8c)$$

The parameter $\langle J \rangle$ is the mean of the three pairwise coupling constants, and D , which we call the distortion parameter, measures the magnitude of the difference between nonequivalent sites, while Θ defines the “shape” of the triangle. Values $\Theta = 0$, 120° , and 240° correspond to isosceles cases with unique atoms c, a, and b, respectively, and with one J -value less negative than the other two in each case; the values $\Theta = 60^\circ$, 180° , and 300° correspond to isosceles cases with unique atoms b, c, and a and one J -value more negative than the other two. Jones *et al.* have shown¹⁶ that there are always two eigenvalues with $S = 1/2$ with energies independent of Θ and four eigenvalues with $S = 3/2$ whose energies vary periodically with Θ . Hence, provided that D is not too large, the energies are given by expressions of the form $(a + b \cos 3\Theta)$, where a and b are chosen so as to give the correct expressions in the isosceles cases. The intermediate quantum numbers S_{ab} (or S_{bc} or S_{ca}) are valid only in the appropriate isosceles cases, but discrete electronic transitions are predicted in all cases, with energies $E(i)$ and transition probabilities $I_0(i)$ as follows:

(16) Jones, D. M.; Sams, J. R.; Thompson, R. C. *J. Chem. Phys.* **1984**, *81*, 440.

$$E(1) = 9D \quad (9a)$$

$$E(2) = -3\langle J \rangle - 9D - \frac{3}{2}D \cos 3\Theta \quad (9b)$$

$$E(3) = -3\langle J \rangle + \frac{3}{2}D \cos 3\Theta \quad (9c)$$

$$E(4) = -3\langle J \rangle + 9D + \frac{3}{2}D \cos 3\Theta \quad (9d)$$

$$E(5) = -3\langle J \rangle + 18D - \frac{3}{2}D \cos 3\Theta \quad (9e)$$

$$I_0(1) = 9 \quad (10a)$$

$$I_0(2) = 12.1 - (\pm)0.685 \cos 3\Theta \quad (10b)$$

$$I_0(3) = 17 \pm 3 \cos 3\Theta \quad (10c)$$

$$I_0(4) = 4.9 \pm 2.3 \cos 3\Theta \quad (10d)$$

$$I_0(5) \approx 0 \quad (10e)$$

Results

The IINS spectrum of $[\text{Fe}_3\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3]\text{NO}_3$ at 4.3 K is shown in Figure 1. A Gaussian fit yields four bands of equal width, two of them overlapping. All are of magnetic origin as seen from the angular dependence of the scattered intensity (Figure 1, inset), while the high-angle data are dominated by a phonon background of different, overlapping bands. Data at 10 K (not shown) were very similar to those of the 4.3 K spectra, which confirms that all four magnetic transitions originate from the same ground state. The energies are quite different from those expected for transitions in an equilateral triangular system. As shown by eq 3, these would be $-3J$, $-5J$, $-7J$, etc., up to $-15J$. However, an excellent fit is obtained by using two intramolecular exchange coupling constants $J = -26.8$ and $J_{ab} = -32.9 \text{ cm}^{-1}$. This gives the ground state $|1/2, 2\rangle$ and leads to the assignments shown in Table 1. The relative intensities also agree well, as shown in the table.

The IINS spectrum of α -metavoltine, a mineral containing the cluster $[\text{Fe}_3\text{O}(\text{SO}_4)_6(\text{OH}_2)_3]^{5-}$, was reported in a pioneering study by Furrer and Güdel.¹⁷ Their data at $T = 10 \text{ K}$ are reproduced in Figure 2. Again four features are observed. The band at *ca.* 80 cm^{-1} is the most intense, and the previous

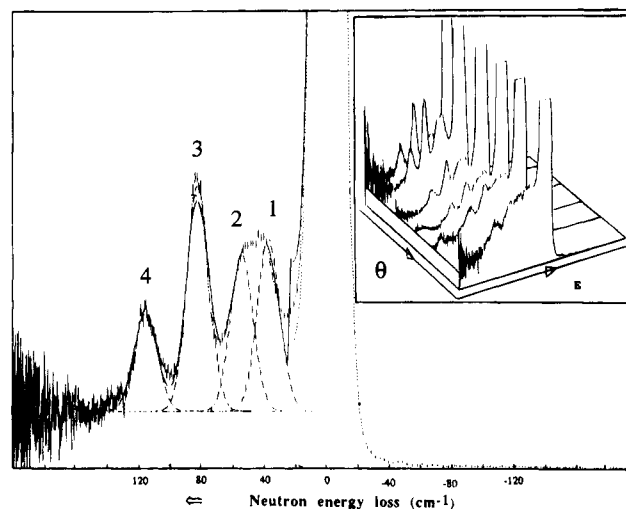


Figure 1. IINS spectrum of $[\text{Fe}_3\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3]\text{NO}_3$, measured on the spectrometer IN4: $T = 4.3 \text{ K}$; incident neutron energy = 28.76 meV ; average scattering angle, $2\Theta = 12.8^\circ$; fitted with Gaussians at energies of 37.2 , 54.5 , 82.5 , and 116.3 cm^{-1} . Inset: momentum-transfer dependence of the neutron energy loss spectra. Scattering angles (2Θ) are (from back to front) 4.50° , 12.75° , 30.38° , 46.13° , 60.75° , and 80.05° . Vertical scales: neutron counts/arbitrary units.

interpretation was that only this band was magnetic in origin, hence it was assigned to the $S = 1/2 \rightarrow 3/2$ transition for an equilateral system. The other bands were thought not to be magnetic, but as was noted at the time, the momentum-transfer dependence of the spectral features could not be investigated in any detail with the experimental facilities then available. The general similarity of this spectrum to the others reported here leads us to propose that all four inelastic bands may be of magnetic origin. Fitting to the isosceles model gives the assignments shown in Table 1.

An IINS spectrum of the iron(III) pivalate complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CD}_3)_3)_6(\text{CD}_3\text{OD})_3]\text{Cl}$ at $T = 5 \text{ K}$ is shown in Figure 3. From the angle dependence (inset) it can be seen that all of the sharp features are magnetic in origin, and this is confirmed by detailed fittings of intensity as a function of momentum transfer (see, for example, Figure 4). As the scattering angle increases, a phonon envelope grows in between 30 and 80 cm^{-1} . A spectrum at higher resolution on the

Table 1. Energies (cm^{-1}) and Intensities of Magnetic Transitions in IINS Spectra of Triiron Complexes, with Assignments using the Isosceles Model

assignment	band 1 $ 1/2, 2\rangle \rightarrow 1/2, 3\rangle$	band 2 $ 1/2, 2\rangle \rightarrow 3/2, 1\rangle$	band 3 $ 1/2, 2\rangle \rightarrow 3/2, 2\rangle$	band 4 $ 1/2, 2\rangle \rightarrow 3/2, 3\rangle$	rms	J	J_{ab}
$[\text{Fe}_3\text{O}(\text{OCCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{NO}_3)$							
E/cm^{-1} (obsd) ^a	37	55	82.5	116			
E/cm^{-1} (calcd) ^b	36.6	56.0	80.4	117.0	1.4	-26.8	-32.9
rel intens ^c (obsd) ^a	$\leq 0.7^g$	0.74	1.00	0.48			
rel intens ^c (calcd) ^b	0.67	0.97	1.00	0.48			
$\text{K}_5[\text{Fe}_3\text{O}(\text{SO}_4)_6(\text{OD}_2)_3](\text{D}_2\text{O})$							
E/cm^{-1} (obsd) ^d	29	58	79	101			
E/cm^{-1} (calcd) ^b	26.4	58.9	76.5	102.9	2	-25.5	-29.9
rel intens ^c (obsd) ^d	0.3	0.5	1.0	0.35			
rel intens ^c (calcd) ^b	0.6	0.9	1.0	0.5			
$[\text{Fe}_3\text{O}(\text{OCC}(\text{CD}_3)_3)_6(\text{CD}_3\text{OD})_3]\text{Cl}$							
E/cm^{-1} (obsd) ^e	19.7	88	100	113			
rel intens ^c (obsd) ^e	0.61	1.00	0.84	0.38			
rel intens ^c (calcd) ^b	0.39	1.00	0.92	0.34			
E/cm^{-1} (obsd) ^f	21	88	101	114			
rel intens ^c (obsd) ^f	0.58	0.96	1.00	0.28			
rel intens ^c (calcd) ^b	0.76	0.96	1.00	0.50			
E/cm^{-1} (calcd) ^b	25.0	88	99	116	3.1	-33.0	-35.8

^a $\pm 1 \text{ cm}^{-1}$. Instrument IN4 (Figure 1). ^b Calculated from the isosceles model (text, eqs 5–7). ^c Relative to the most intense peak in the spectrum. ^d *Ca.* $\pm 3 \text{ cm}^{-1}$; estimated from graphs in ref 24. ^e $\pm 1 \text{ cm}^{-1}$. Instrument IN4 (Figure 3). ^f $\pm 2 \text{ cm}^{-1}$. Instrument HET (Figure 5). ^g Upper limit only, due to possible contributions of phonon background and elastic scattering (see Figure 1).

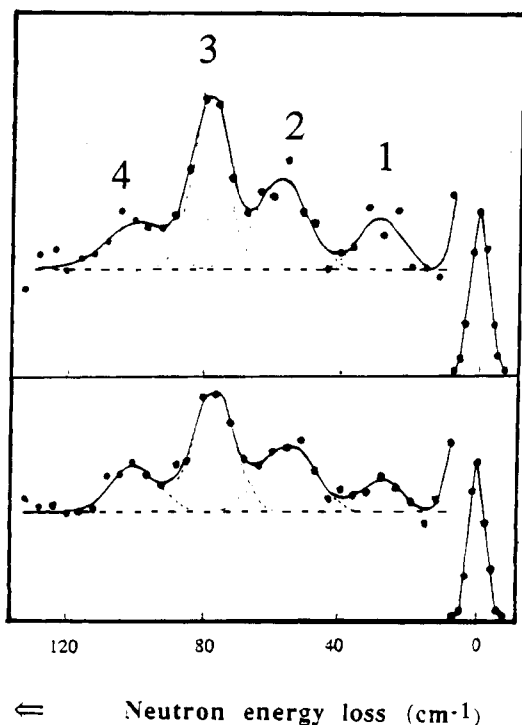


Figure 2. IINS spectra of α -metavoltine: $T = 10$ K; $Q = 1.3 \text{ \AA}^{-1}$ (above) and 1.8 \AA^{-1} (below). Redrawn from ref 17. The elastic peak at the right of each spectrum is plotted on a $\times 40$ scale. Vertical scale: neutron counts/arbitrary units.

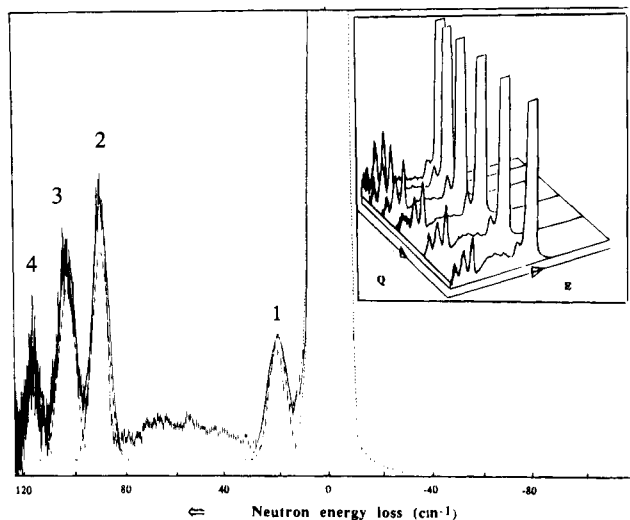


Figure 3. Neutron energy loss IINS spectrum of $[\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CD}_3)_3)_6(\text{DOCD}_3)_3]\text{Cl}$ measured on the spectrometer IN4: $T = 5$ K; incident neutron energy = 17 meV; average scattering angle, $2\Theta = 10.01^\circ$. Inset: angle dependence of the magnetic scattering. Scattering angles (2Θ) are (from back to front) 6.35° , 10.01° , 16.13° , 25.18° , 37.75° , and 47.30° . Vertical scales: neutron counts/arbitrary units.

instrument IN5 confirmed that the band at 19.7 cm^{-1} is the lowest-energy transition for this compound. A further spectrum, obtained with higher incident energy, on the instrument HET, is shown in Figure 4. It confirms that the peak at 114 cm^{-1} is genuine and also reproduces the other magnetic peaks. The peaks at ca. 186 cm^{-1} are assumed to be of vibrational origin, in view of the relatively high momentum transfer involved at this energy. Comparing Figures 3 and 5, the relative intensities appear different, but the differences are due to differences in momentum transfer and are consistent with the function plotted in Figure 4.

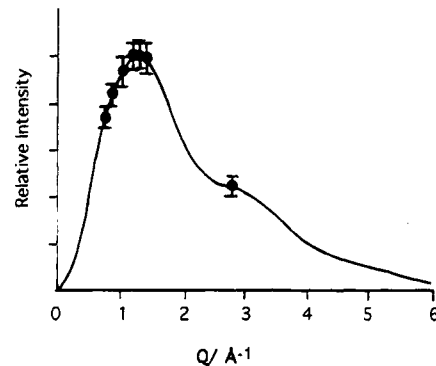


Figure 4. Momentum-transfer dependence of intensity of band 2 in the IINS spectrum of $[\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CD}_3)_3)_6(\text{DOCD}_3)_3]\text{Cl}$ (Figure 2). Data and calculated curve are normalized to the same maximum value.

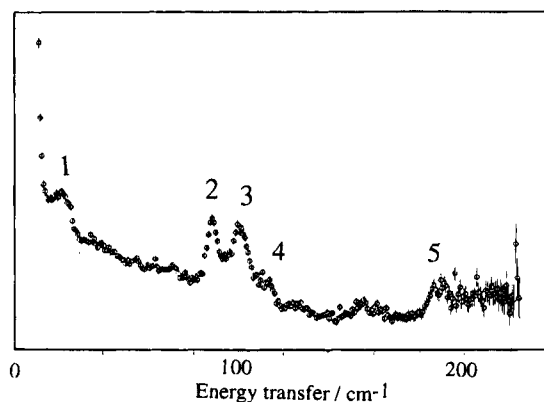


Figure 5. Neutron energy loss IINS spectrum of $[\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CD}_3)_3)_6(\text{DOCD}_3)_3]\text{Cl}$ measured on the HET: $T = 15$ K; incident neutron energy = 30.35 meV; average scattering angle, $2\Theta = 19^\circ$. Vertical scale: neutron counts/arbitrary units.

Discussion

The results of constrained fitting of all the data to the isosceles coupling scheme are shown in Table 1. Parameters J and J_{ab} were determined by least-squares fitting of the energies of the four peaks of each spectrum to the formulas shown in Scheme 1. The root mean square deviations of the energies are listed. In the case of the acetate-bridged complex, agreement is within experimental error. The same can be said of the sulphate-bridged compound except that the statistical errors are obviously greater, but for the pivalate-bridged compound, the agreement is less satisfactory.

More significant than the least-squares fitting, there is an obvious trend in the appearance of the spectra of the three materials. According to the energy calculations above, the relative spacings of the three ($S = 1/2 \rightarrow 3/2$) bands in each spectrum give a direct measure of the shape of the triangle. For an isosceles model, the ratio $[E(4) - E(3)]:[E(3) - E(2)]$ is 1:2 or 2:1; for an extreme scalene model, with three J -values different and separated by equal amounts, the ratio is 1:1. In terms of our angular "shape coordinate", the extreme scalene case is defined by $\Theta = 30^\circ$. Best-fitted values of the three general parameters (J), D , and Θ for all three complexes are listed in Table 2. It is clear that the isosceles model with $\Theta = 60^\circ$ is a reasonable description of the acetate-bridged complex, while a scalene model with Θ close to 30° is probably better for the sulphate-bridged and strongly favored for the pivalate-

Table 2. Magnetic Transitions in IINS Spectra of Triiron Complexes, Fitted to the Scalene Model

band energies/cm ⁻¹ ^a				$\langle J \rangle^b$	D^c	D^d	Θ^e	J_{ij}^f		
$E(1)$	$E(2)$	$E(3)$	$E(4)$							
37	55	82.5	116	[Fe ₃ O(OOCCD ₃) ₆ (C ₅ D ₅ N) ₃](NO ₃) -28.2	3.7	4.2	41°	-25.1	-27.4	-32.1
27	57	77	101	K ₃ [Fe ₃ O(SO ₄) ₆ (OD ₂) ₃](D ₂ O) -26.3	2.7	3.0	33°	-23.7	-26.1	-29.0
19.7	88	100	113	[Fe ₃ O(OOCC(CD ₃) ₃) ₆ (CD ₃ OD) ₃]Cl -33.5	1.4	2.2	27°	-31.5	-33.6	-35.3

^a Table 1. ^b $\langle J \rangle = -(E(2) + E(4))/6$. ^c $D = (E_4 - E_3)/9$. ^d $D = E(1)/9$. ^e Calculated using $\cos 3\Theta = 3(2E(3) - E(2) - E(4))/(E(4) - E(3))$. ^f (i, j) = (a, b, c); see text, eqs 8.

bridged complex. Independently of Θ , there are differences in values of the distortion parameter D , in the sequence [Fe₃O(O₂-CCD₃)₆(C₅D₅N)₃]⁺ > [Fe₃O(SO₄)₆(D₂O)₃]⁵⁻ > [Fe₃O(O₂CC(CD₃)₃)₆(DOCD₃)₃]⁺. We take it that the best values of D are those calculated directly from the energy of the lowest transition, i.e. using $D = E(1)/9$. The same trend is seen when D is calculated from the spread of the three values $E(2)$, $E(3)$, and $E(4)$, though the actual values are somewhat smaller.

The exchange parameters $\langle J \rangle$ and D are in line with results from previous bulk magnetic susceptibility studies on iron(III) complexes of this type, in which the data were constrained to the isosceles coupling scheme.¹ The fact that $\langle J \rangle$ values for acetate-, pivalate- and sulphate-bridged complexes are similar adds further evidence that the main exchange pathway is via the central oxide ion.⁴ In the isoelectronic heteronuclear system [Fe₂Mn(O₂CCD₃)₆(C₅D₅N)₃](C₅D₅N), the value of the Fe^{III}-Fe^{III} coupling constant, $J_{ab} = -58.6$ cm⁻¹, is about twice the value of that found in the triiron(III) systems while the value of the Fe^{III}-Mn^{II} coupling constant is about half.¹⁴ As the electronic configurations are the same, this reflects the influence of effective nuclear charge of the metal ions, with consequent changes in metal-ligand bond lengths and covalency.

The most significant result is that the degeneracy of the $S = 1/2$ ground state is lifted for all of the compounds measured. In the sulphate-bridged¹⁸ and pivalate-bridged¹³ compounds, the site symmetry at the center of the triangle is 3-fold at room temperature, but in view of the data presented here, this must now be regarded as an apparent symmetry caused by spatial and/or temporal averaging throughout the crystal. So far only room-temperature structures are available in either case, and the possibility that phase changes occur on going down to the temperatures of the present experiments is still to be considered. In the case of the sulphate-bridged material, the room-temperature structure involves a good deal of disorder of noncoordinated water molecules;¹⁸ but the pivalate-bridged compound is much less disordered, and indeed, Blake and Frazer pointed this out, remarking that for that reason it was a promising material for magnetic studies.¹³ Our data indicate that, at low temperature, the pivalate complex molecules are the least distorted of the ones we have studied.

We are now in a position to estimate, roughly, the extent of geometrical distortion in these triangular complexes by comparing the energy splittings of the electronic ground state with data obtained earlier from vibrational spectra. The basic argument is due to Murao.⁶ We emphasise again that, although we have used the geometrical terms "equilateral", "isosceles", and "scalene", to describe the coupling, it is not necessary to assume that the triangle of metal atoms as such is distorted. An alternative is that the triangle remains close to equilateral but the central oxygen is displaced from the center. This is expected

if, as noted above, the principal coupling mechanism is superexchange via the central oxygen. In studies of magneto-structural correlations, in various types of anion-bridged, antiferromagnetically coupled complexes, different authors have proposed that J is controlled mainly by the direct internuclear distance,¹⁹ by the distance along the shortest exchange pathway,²⁰ or by the metal-oxygen-metal bond angle.²¹ It makes little difference to the present discussion, and for simplicity, we will use as a first approximation to the structure of the Fe₃O core unit an equilateral triangle with the central oxygen displaced away from the 3-fold axis. In the IR spectra of these complexes, with the approximation of D_{3h} symmetry, we have assigned the in-plane asymmetric stretch of this unit to a frequency $\nu_{as} = 600$ cm⁻¹, and we have shown by isotopic substitution experiments that it is a fairly pure vibration of the oxygen atom.²² The force constant for this normal mode can therefore be calculated simply as $k_{as} = 4\pi^2\nu_{as}^2M_O$, where M_O is the mass of the oxygen, i.e. $k_{as} = 3.34$ N m⁻¹. To estimate the displacement distance x , we argue that the elastic energy U expended in displacing the oxygen is balanced by the electronic energy gained by splitting the ground state wave function and that this is given by the neutron scattering spectra as one-half the energy E_1 of the lowest magnetic transition. In the case of the compound [Fe₃O(O₂CCD₃)₆(C₅D₅N)₃]NO₃, this is $E_1/2 = 37.2/2 = 18.6$ cm⁻¹. Taking $U = 1/2kx^2$, we obtain $x = 0.013$ Å. Such a displacement could be measured by X-ray diffraction methods, provided a suitable compound can be found in which the displacement is not obscured by disorder. The amplitude A_{as} of the zero-point vibration of the oxygen can also be calculated, again in the approximation of D_{3h} symmetry, as $A_{as} = (h\nu_{as}/k_{as})^{1/2} = 0.054$ Å. This is much greater than the estimated value of x , but that does not preclude the proposed structural measurement, which would of course have to be done at low temperature.

Also consistent with the scalene model is an activated dynamic model in which the molecule switches among three potential energy minima of equal depth, characterized by the three permutations of J -values, or an *activationless* model in which every possible combination of J -values is equally favored but subject to constant values of $\langle J \rangle$ and D .¹⁶ If the crystallographic site symmetry is not 3-fold, these statements require modification. For the activated model, in a non-3-fold site, the potential wells will be of unequal depth.²³ For the activationless model, in a non-3-fold site, the probability density of the nuclear

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configuration will be higher at some points in the appropriate coordinate space than at others. But when the central cluster is embedded in a ligand environment which is large, compressible, and itself close to 3-fold symmetry, it may be effectively shielded from the crystal lattice potential. Of all the materials studied here, the pivalato complex comes closest to this condition. The displacement of the central oxygen, calculated as above, is 0.0098 Å. Such a small value, in relation to the amplitude of vibration, is consistent with a dynamic model.

The data presented in this work add further evidence for the view that antiferromagnetically exchange-coupled systems can

be subject to a structural distortion that is intrinsic to the system: the so-called magnetic Jahn–Teller effect.

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