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Magnetic Exchange Coupling in the $\mathrm{Fe^{III}}_6(\mu_6\text{-O})$ Core: A Hint to the Magnetic Properties of Higher-Nuclearity Spin Clusters

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Introduction

Iron oxo clusters are currently actively investigated for many different reasons, ranging from the elucidation of the mechanism of iron biomineralization[1] to the search for nanoscale magnetic materials.[2] In these compounds various kinds of μ-oxo bridges are present. μ_2-Oxo[3–6] and μ_3-oxo[6,7] bridges are relatively well-known, μ_4-oxo[6,8,9] bridges have been reported in a few instances, and μ_6-oxo bridges were practically unknown until recently.

It has been reported that a new class of polyiron compounds containing 12 iron(II,III) atoms per cluster may be obtained by slow reaction of iron(II) salts with dioxygen in strongly basic methanol solutions. Single-crystal X-ray diffraction studies on the complexes $[\mathrm{Fe^{III}}_4\mathrm{Fe^{II}}_8(\mathrm{O})_2(\mathrm{OCH_3})_{18}(\mathrm{O_2CCH_3})_6(\mathrm{CH_3OH})_{4.67}]$ (**1**) and $\mathrm{Li_2}[\mathrm{Fe^{III}}_2\mathrm{Fe^{II}}_{10}(\mathrm{O})_2(\mathrm{OCH_3})_{14}(\mathrm{O_2CCH_3})_{10}(\mathrm{CH_3OH})_2]$ (**2**) revealed that these compounds are good structural models of the ferritin core;[10] the arrangement of the oxygen atoms from the methoxide, methanol, and acetate ligands and of the two central μ_6-oxide ions reproduces a fragment of a cubic lattice whose octahedral holes are occupied by the iron atoms. A compound with the same overall structure but containing peripheral chloroacetate and chloride ligands has been recently synthesized.[11] As the μ_6-oxo bridges in these complexes may play a central role in the exchange phenomena, it was considered of interest to investigate the magnetic properties of the isolated $\mathrm{Fe^{II,III}}_6(\mu_6\text{-O})$ unit. Though no hexanuclear mixed-valence complex with a central μ_6-oxo bridge has yet been synthesized, one of us reported the synthesis and X-ray structure of the two compounds $\mathrm{Fe^{III}}_6\mathrm{O(THME)}_6[\mathrm{N(CH_3)_4}]_2\cdot 4\mathrm{CH_3OH}$ (**3**) (where THME is the trianion of 1,1,1-tris(hydroxymethyl)ethane)[12] and $\mathrm{Na_2Fe^{III}}_6\mathrm{O(OCH_3)}_{18}\cdot 6\mathrm{CH_3OH}$ (**4**),[13] both containing the $\mathrm{Fe^{III}}_6(\mu_6\text{-O})$ core. These are in principle the simplest compounds which may be investigated containing the μ_6-oxo bridge. We want to present here the results of magnetic susceptibility measurements on compounds **3** and **4**.

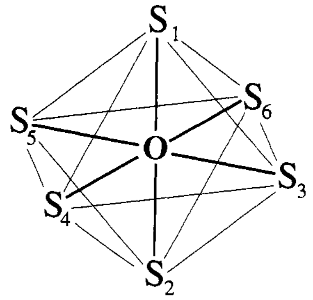

Figure 1. Schematic view of the spin–spin magnetic interactions in compounds **3** and **4** assuming an idealized O_h symmetry. Bold lines represent *trans*-interactions.

Experimental Section

Preparation of the Samples. Complexes **3** and **4** were synthesized according to published procedures.[12,13] Due to the extreme air-sensitivity of the compounds, special precautions were used during the preparation and handling of the samples.

Microcrystalline samples of **3** and **4** (samples I and II, respectively) were separated from their mother liquors by filtration under argon, immediately wrapped in a thin paraffin foil, and weighed (3.5 and 132.9 mg, respectively). An additional microcrystalline sample of **4** (sample III) was filtered out and directly embedded in liquid paraffin. The EPR measurements were performed on compound **4** only, and the sample was prepared with the latter technique.

Instrumentation and Physical Measurements. Magnetic susceptibilities of microcrystalline samples were measured by using a Métronique Ingénièrie MS03 SQUID magnetometer in the temperature ranges 2.2–280, 4.9–130, and 2.2–280 K for samples I–III, in applied fields of 2, 1, and 0.5 T, respectively. In order to reduce any possible decomposition of the samples, all measurements were performed by first cooling the sample to the lowest temperature. The contribution of the sample holder and of the amount of liquid paraffin employed in connection with sample III was determined separately in the same temperature range and field. Diamagnetic corrections were estimated from Pascal's constants.

EPR spectra of microcrystalline samples were obtained with a Varian E9 spectrometer operating at X-band frequency, equipped with an Oxford Instruments ESR9 liquid-helium continuous-flow cryostat, in the temperature range 4.2–298 K.

Least-Squares Calculations. All calculations were performed on a Convex 220 computer using the E04FCF-NAG Fortran Library minimization routine. $\mathrm{SSQ} = \sum_i[(\chi^{\mathrm{obs}}_i - \chi^{\mathrm{calc}}_i)/\chi^{\mathrm{obs}}_i]^2$ was minimized in the least-squares cycles; in the text we report the parameter $R = \mathrm{SSQ}/(n - p)$, where n is the number of experimental data points and p is the number of parameters allowed to vary in the minimization routine.

Results and Discussion

The results of X-ray diffraction studies point to crystallographically imposed C_i and C_2 symmetry for the $\mathrm{Fe_6}(\mu_6\text{-O})$ core of compounds **3** and **4**, respectively.[12,13] Bond distances and angles, however, suggest that a model with O_h symmetry may give a fairly good description of the magnetic exchange interactions in these clusters. O_h symmetry leads to only two topologically distinct types of exchange interactions (Figure 1). The first involves *trans*-iron atoms and is mediated by the μ_6-oxo bridge only; the second involves *cis*-iron atoms and is mediated both by the central μ_6-oxo bridge *and* the peripheral oxygen donors from the alkoxo ligands. This exchange-coupling scheme results in the following

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(1) (a) Lippard, S. J. *Chem. Br.* **1986**, *22*, 222. (b) Hagen, K. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1010.
(2) Papaefthymiou, G. C. *Phys. Rev. B* **1992**, *46*, 10366.
(3) (a) Jameson, D. L.; Xie, C.-L.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 740. (b) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1. (c) Drüeke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Bominaar, E. L.; Sawaryn, A.; Winkler, H.; Trautwein, A. X. *Inorg. Chem.* **1989**, *28*, 4477.
(4) Kurtz, D. M., Jr. *Chem. Rev.* **1990**, *90*, 585 and references cited therein.
(5) Snyder, B. S.; Patterson, G. S.; Abrahamson, A. J.; Holm, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 5214 and references cited therein.
(6) Micklitz, W.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6856.
(7) (a) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195. (b) Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77. (c) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149. (d) Heath, S. L.; Powell, A. K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 191.
(8) Hagen, K. S.; Nair, V. S. *Inorg. Chem.*, in press.
(9) Nair, V. S.; Hagen, K. S. *Inorg. Chem.* **1992**, *31*, 4048.
(10) Taft, K. L.; Papaefthymiou, G. C.; Lippard, S. J. *Science* **1993**, *259*, 1302 and references cited therein.
(11) Caneschi, A.; Taft, K. L.; Lippard, S. J. Private communication.
(12) Hegetschweiler, K.; Schmalle, H. W.; Streit, H. M.; Schneider, W. *Inorg. Chem.* **1990**, *29*, 3625.
(13) Hegetschweiler, K.; Schmalle, H. W.; Streit, H. M.; Gramlich, V.; Hund, H. U.; Erni, I. *Inorg. Chem.* **1992**, *31*, 1299.

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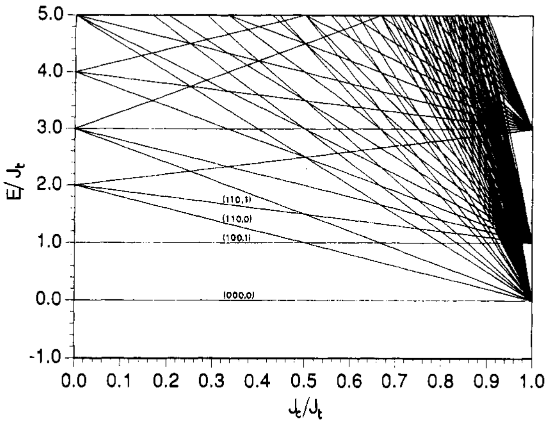

Figure 2. Plot of the reduced eigenvalues of Hamiltonian (2) as functions of the parameter J_c/J_t for J_c, $J_t > 0$. For the labeling of the states, see text.

spin-only Heisenberg Hamiltonian:

$$\mathbf{H} = J_t(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_3\cdot\mathbf{S}_5 + \mathbf{S}_4\cdot\mathbf{S}_6) + J_c(\mathbf{S}_1\cdot\mathbf{S}_3 + \mathbf{S}_1\cdot\mathbf{S}_4 + \mathbf{S}_1\cdot\mathbf{S}_5 + \mathbf{S}_1\cdot\mathbf{S}_6 + \mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_2\cdot\mathbf{S}_4 + \mathbf{S}_2\cdot\mathbf{S}_5 + \mathbf{S}_2\cdot\mathbf{S}_6 + \mathbf{S}_3\cdot\mathbf{S}_4 + \mathbf{S}_3\cdot\mathbf{S}_6 + \mathbf{S}_4\cdot\mathbf{S}_5 + \mathbf{S}_5\cdot\mathbf{S}_6) \quad (1)$$

where J_t and J_c are the *trans* and *cis* exchange-coupling constants, respectively, and $S_i = {}^5/_2$. Although it would now be possible to calculate the eigenvalues of Hamiltonian (1) using an irreducible tensor operator approach,[14] in the present high-symmetry case the Kambe[15] vector-coupling approach leads to the energy levels in analytical form. When the following intermediate coupling spin operators are defined

$$\mathbf{S}_{12} = \mathbf{S}_1 + \mathbf{S}_2 \qquad \mathbf{S}_{35} = \mathbf{S}_3 + \mathbf{S}_5 \qquad \mathbf{S}_{46} = \mathbf{S}_4 + \mathbf{S}_6$$

the total spin operator becomes

$$\mathbf{S} = \mathbf{S}_{12} + \mathbf{S}_{35} + \mathbf{S}_{46}$$

and the Hamiltonian (1) may be easily rewritten as

$$\mathbf{H} = (J_c/2)\mathbf{S}^2 + [(J_t - J_c)/2](\mathbf{S}_{12}^2 + \mathbf{S}_{35}^2 + \mathbf{S}_{46}^2) \quad (2)$$

As a substantially antiferromagnetic exchange coupling between the iron atoms is expected, the dependence of the reduced eigenvalues of Hamiltonian (2), E/J_t, on the parameter J_c/J_t for J_c, $J_t > 0$ may be significant and is shown in Figure 2. Selected eigenvalues are labeled $(S_{12}S_{35}S_{46},S)$ so that $S_{12} \geq S_{35} \geq S_{46}$. The levels which differ only for a permutation of the intermediate spin quantum numbers are degenerate with these.

The ground state is the singlet (000,0) arising from the complete *trans*-coupling of the spin vectors ($S_{12} = S_{35} = S_{46} = 0$). The first excited state is the singlet (110,0) for $0.5 < J_c/J_t < 1.0$ and the triplet (100,1) for $0 < J_c/J_t < 0.5$. The latter is also the lowest lying multiplet with $S \neq 0$ for any J_c/J_t value in the J_c, J_t range considered. In fact, for J_c/J_t approaching to 1.0 all the singlets converge to $E/J_t = 0$, all the triplets to $E/J_t = 1$, all the quintets to $E/J_t = 3$, etc., since in the limit $J_c = J_t$ the energies depend only on the total spin S and not on the intermediate spins.

The variable-temperature EPR spectra performed on compound **4** confirm the diamagnetic nature of the ground state. A broad isotropic signal at $g \cong 2$ is observed at room temperature (peak-to-peak line width ≅ 1000 G). Upon cooling, the signal intensity gradually decreases, and at liquid-helium temperature, only weak resonances, which have been attributed to a monomeric iron(III) impurity, appear at $g \cong 2$, $g \cong 4$, and $g \cong 10$.

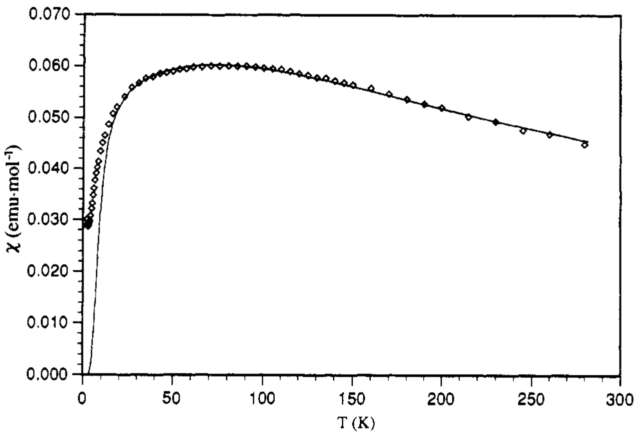

Figure 3. Temperature dependence of the magnetic susceptibility of compound **3** (sample I). The solid line represents the calculated susceptibility with $J_t = 21.2$ cm^{-1}, $J_c = 9.9$ cm^{-1}, and $g = 2.0$.

A plot of the measured magnetic susceptibility of compound **3** (sample I) as a function of temperature is reported in Figure 3. The least-squares fitting of the theoretical susceptibility, derived from Hamiltonian (2) and the Van Vleck equation,[16] to the experimental data yields $J_t = 21.0(5)$ cm^{-1} and $J_c = 9.0(9)$ cm^{-1}. The fit has been truncated below 20 K, as the model is unable to reproduce the low-temperature behavior of the susceptibility. The introduction of a correction for the presence of a small amount of a magnetically dilute monomeric iron(III) impurity does not lead to a significant improvement of the low-temperature fit. The uncertainties in the J_t and J_c values arise mainly from the small variations in the best-fit parameters on application of different constraints to the g factor. The solid line in Figure 3 represents the calculated susceptibility with $J_t = 21.2$ cm^{-1}, $J_c = 9.9$ cm^{-1}, and $g = 2.0$ ($R = 3.0 \times 10^{-5}$).

Very similar considerations apply to compound **4**. The experimental magnetic susceptibility data on sample II were taken in the temperature range 4.9–130 K, as this was judged sufficient to get accurate estimates of the exchange-coupling constants while limiting the sample decomposition. The possibility of obtaining a reasonable fit depends critically on the truncation of the data set below 20 K ($J_t = 17.3(1)$, $J_c = 9.2(1)$ cm^{-1}, $R = 2.4 \times 10^{-5}$ with g fixed at 2.0). Despite the very similar geometry of the $\mathrm{Fe^{III}}_6(\mu_6\text{-O})$ core in compounds **3** and **4**,[12,13] the temperature and the height of the maxima in the χ *vs* T curves obtained for samples I and II are significantly different. To reduce the possible influence of the extreme air-sensitivity of compound **4**, a set of susceptibility measurements in the temperature range 2.2–280 K with the sample embedded in liquid paraffin was considered worthwhile. As an accurate weighing of the sample was impossible, a scale factor has been refined in the least-squares fitting routine, which yields $J_t = 21.3(1)$ and $J_c = 8.9(1)$ cm^{-1} ($R = 7.8 \times 10^{-6}$). Again, the data points below 20 K must be excluded from the least-squares calculations.

While the temperature of the maximum of the calculated χ *vs* T curves depends mainly on J_t, which can be then determined quite precisely, the susceptibility at the maximum is related to both the J_t and the J_c values. Since the effect of a small variation of J_c on the susceptibility curve may be roughly counterbalanced by a suitable variation of an overall scale factor, the best-fit J_c value may be influenced by uncertainties in the sample weight, by the presence of diamagnetic impurities, etc. Nevertheless, the least-squares calculations yield J_t and J_c values lying in a reasonably narrow interval ($J_t = 19(2)$ cm^{-1}, $J_c = 9(1)$ cm^{-1}), which may be considered adequate for our purposes.

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(14) Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

(15) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48.

(16) Carlin, R. L. Magnetochemistry; Springer: New York, 1986; p 21.

(17) (a) Norman, R. E.; Holz, R. C.; Ménage, S.; O'Connor, C. J.; Zhang, J. H.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 4629. (b) Bossek, U.; Weyhermüller, T.; Wieghardt, K.; Bonvoisin, J.; Girerd, J. J. *J. Chem. Soc., Chem. Commun.* **1989**, 633.

In the case of interacting iron(II,III) spins, the search for convincing, theoretically-supported correlations between the magnetic exchange-coupling constants and the geometrical features of the metal–metal bridge has proved to be particularly difficult. However, it has been shown that in several oxo-bridged iron(III) compounds an approximate inverse exponential relationship holds empirically between the coupling distance and the coupling constant.[18] Furthermore, it is widely accepted that in iron(III) μ_2-oxo dimers the extent of antiferromagnetic exchange coupling between the metal centers is almost insensitive to the Fe–O–Fe angle, a result which has been connected to the large number of different exchange pathways available.[4,17]

From X-ray structural data it may be seen that in the series $Fe_2(\mu_2\text{-}O)_{linear}$ (a),[4] $Fe_4(\mu_4\text{-}O)_{planar}$ (b),[8] and $Fe_6(\mu_6\text{-}O)_{octahedral}$ (c)[12,13] the Fe–O average bond distances increase in the order a < b < c. As fragments with linear Fe–O–Fe geometry are present in all these compounds, while the coordination number of the central oxygen atom increases from 2 to 6, a comparison between the J values found for the three classes of compounds should be instructive. In non-heme μ_2-oxo monobridged diferric complexes with a linear or nearly-linear oxo bridge (170° < Fe–O–Fe ≤ 180°) Fe–O bond distances of 1.78(1) Å and J values close to 200 cm^{-1} are quite typical.[4] The evaluation of J_t and J_c in compounds containing a planar $Fe_4(\mu_4\text{-}O)$ unit[8] has not yet been possible, because the $Fe_4(\mu_4\text{-}O)$ moiety is almost invariably part of much more complicated architectures.[6,8,9] The results of our magnetic studies on compounds **3** and **4** clearly show that a very weak coupling between the metal centers occurs within the $Fe_6(\mu_6\text{-}O)$ unit (J_t = 19(2) cm^{-1}, J_c = 9(1) cm^{-1}). When comparison is made with class a compounds, it appears that an increase of the average Fe–O distance from 1.78(1) to 2.25(1) Å leads to a reduction of 1 order of magnitude of the J value through a linear Fe–O–Fe fragment.[4] Interestingly, the above mentioned empirical relationship between the coupling distance and the coupling constant found in oxo-bridged iron(III) compounds[18] predicts a much lower J value (≃1 cm^{-1}) when the present average Fe–O(oxo) bond distance is introduced.

The smaller value of J_c as compared to J_t indicates that the relative contribution of ferromagnetic superexchange pathways mediated by the central μ_6-oxo bridge increases significantly as the Fe–O–Fe angle is reduced from 180 to 90° *and/or* that the oxygen atoms from the peripheral alkoxo ligands may provide significant additional ferromagnetic pathways. The latter possibility seems unlikely, as bis(μ-OR) bridges in structurally characterized diferric complexes invariably mediate antiferromagnetic interactions with J values in the range 10–40 cm^{-1} when the bridging geometry is similar to that observed in **3** and **4**.[5]

The discrepancy between the calculated and the observed temperature dependence of the magnetic susceptibility of both compounds **3** and **4** at T < 20 K is possibly connected to the presence of unexpected impurities in the samples *and/or* to an inadequacy of the strong-exchange O_h model which is implicit in (1). Subtle electronic features of the interacting metal centers, such as zero-field splitting contributions, or intercluster interactions may become relevant in the low-temperature region due to the low value of the exchange energies.

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[18] (a) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1991**, *30*, 1625.
(b) Turowski, P. N.; Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 681.