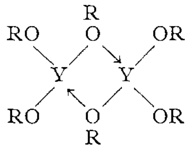
dence of the formation of oxy–alkoxy polymers of the type suggested for zirconium alkoxides.[14] The isopropoxides of Y, Dy, and Yb react rapidly with water vapor in the air. As the size of the R group increases, the compounds are more stable (particularly alkoxides of C_5H_{11} and larger derivatives).

The X-ray spectrum of yttrium isopropoxide gave a powder pattern with broad, overlapping lines. Adequate resolution was achieved using a special collimator,[15] a copper target, and very long exposure times. Small crystals of purified yttrium isopropoxide were analyzed by infrared, nuclear magnetic resonance, and combustion analysis with no substantial impurities or second phase found. These crystals were ground and loaded into capillaries in an inert atmosphere. No oxide phase was found in the results, and it is believed that no other second phase was present considering prior chemical analysis. The lines are given in Table III. The pattern has not yet been indexed; however, several transition metal isopropoxides have been reported to have a monoclinic structure.[16]

The molecular weight determination of yttrium isopropoxide indicated that it exists as a dimer. A probable structure would be[2]



The infrared spectra of Yb and Dy isopropoxide suggest structures identical with that of the Y compound.

Table III

$Y(OC_3H_7)_3$ X-Ray Diffraction Powder Line Data (Cu Kα Radiation)

I/I_0	d, A	I/I_0	d, A
30	11.2	5	4.33
100	10.79	10	3.63
100	9.81	5	3.58
5	9.03	5	3.46
5	8.27	10	3.20
30	7.70	30	3.00
20	6.57	10	2.853
10	6.03	5	2.768
10	5.40	5	2.723
10	5.01	5	2.176

Molecular weights for yttrium 3-methyl-2-butoxide and yttrium 2-pentoxide averaged out between a monomer and dimer at 1.5 and 1.7, respectively. The lowered tendency for intermolecular association correlates with the increased branching of these compounds and higher volatility compared with the isopropoxide.[17]

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(14) W. B. Blumenthal, *Ind. Eng. Chem.*, **55**, 51 (1963).

(15) The offset collimator, developed by R. L. Prickett, had a 0.015-in. diameter collimator offset of 0.020 in.

(16) S. A. Iman and B. R. Rao, *Naturwissenschaften*, **50**, 517 (1963).

(17) This paper was presented in part at the 147th National Meeting of the American Chemical Society, Inorganic Division, Philadelphia, Pa., April 10, 1964.

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Magnetism, Electronic Spectra, and Structure of Transition Metal Alkoxides. III. Spin–Spin Coupling in Trinuclear Fe_3 Systems[1]

By R. W. ADAMS, C. G. BARRACLOUGH, R. L. MARTIN, and G. WINTER[2]

Received October 20, 1965

The anomalous temperature dependence of the magnetic susceptibility of trimeric *n*-alkoxides of tervalent iron, $[Fe_3(OR)_9]$, is interpreted in terms of cooperative spin coupling between the three iron atoms which constitute the Fe_3 core of a model involving FeO_4 tetrahedra sharing corners to give the point group symmetry D_{3h}. The magnitude of the isotropic coupling constant J in the spin–spin Hamiltonian $\mathcal{H} = -2J\hat{S}_i\cdot\hat{S}_j$ is estimated from the $\chi_M(T)$ data to be $J = -10$ cm^{-1}, and this value is compared with those observed for some related polynuclear systems.

Introduction

The trimeric *n*-alkoxides of tervalent iron[1] provide a favorable new class of polynuclear compound with which to test current concepts of metal–metal interaction.

The effective magnetic moments of $Fe_3(OCH_3)_9$, $Fe_3(OC_2H_5)_9$, and $Fe_3(OC_4H_9)_9$ fall in the range 4.4–4.5 BM at room temperature and are strongly dependent on temperature. The three compounds follow a Curie–Weiss law with θ values between -170 and $-200°$, and the inclusion of these values gives corrected moments of 5.5–5.9 BM, which are then independent of temperature. Dissolution of the iron(III) alkoxides in benzene at room temperature does not simplify this anomalous behavior, the effective magnetic moments remaining at 4.2–4.4 BM and being independent of solute concentration. This provides good evidence that the magnetic anomaly is intramolecular in its origin and that the molecular species in benzene is the one also present in the pure liquid *n*-butoxide and the crystalline methoxide and ethoxide. Cryoscopy in

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(1) Part II of this series: R. W. Adams, R. L. Martin, and G. Winter, *Australian J. Chem.*, in press.

(2) Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia.

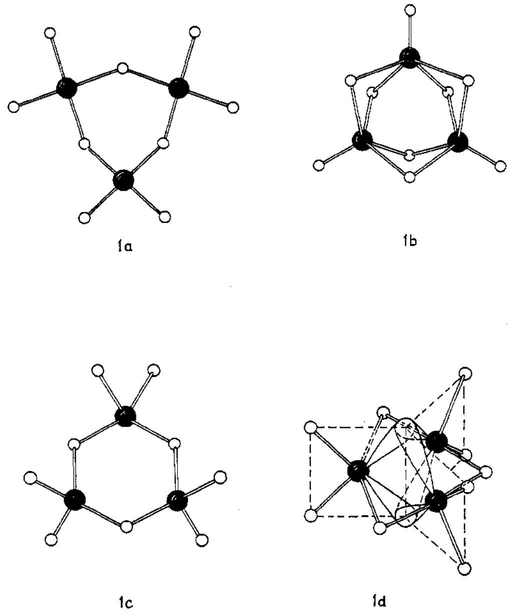

Figure 1.—Possible structures for trimeric iron(III) *n*-alkoxides, $[Fe_3(OR)_9]$.

benzene establishes the trimeric nature of the three alkoxides, although the detailed stereochemistry of the $[Fe_3(OR)_9]$ remains unknown.

In the present paper, the magnetic data are compared in detail with the Heisenberg–Dirac–Van Vleck model[3] for cooperative spin coupling between metal atoms. Since a symmetrical stereochemical environment based on a linear arrangement of the three iron atoms is incompatible with the stoichiometry $[Fe_3(OR)_9]$, we favor here an Fe_3 core consisting of an equilateral triangle of iron atoms. The most symmetrical formulation would involve three FeO_4 tetrahedra sharing corners to give a trimer with the point group symmetry D_{3h} as shown in Figure 1c.

Theoretical Model for Spin Coupling in Fe_3 Clusters

In considering the anomalous magnetic behavior of the iron(III) alkoxides, we follow the procedure used so effectively by Kambe[4] to account for the anomalous behavior of Welo's[5,6] trinuclear basic acetates of tervalent iron, which can now be safely formulated[7,8] as $[Fe_3O(CH_3COO)_6]^+$. It is assumed that three iron atoms are arranged at the corners of an equilateral triangle, each being in a $^6A_1$ ground state with no orbital angular momentum. Intermolecular interactions are assumed to be negligible and only spin–spin interactions between the three iron atoms of spin $S = {}^5/_2$ are considered. Van Vleck[3] has shown the spin coupling can be included in the total Hamiltonian for the system by assuming an isotropic interaction between the *i*th and *j*th iron atoms of the form

$$\hat{\mathcal{H}}_{ij} = -2J_{ij}(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)$$

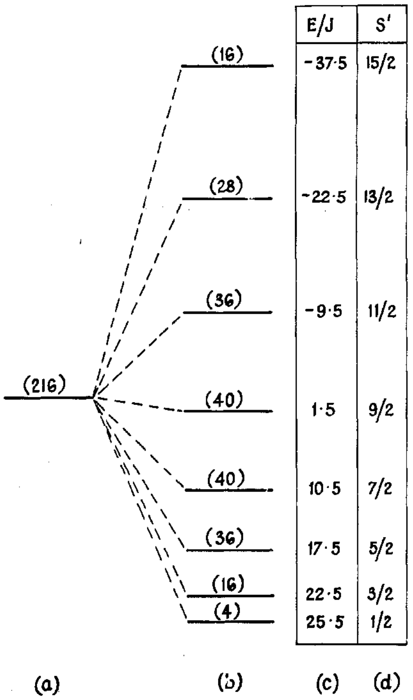

Figure 2.—Energy level scheme for a trio of weakly interacting iron atoms: (a) total spin degeneracy of ground state, (b) effect of spin–spin interaction of the form $-2J\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$, (c) spin–spin energy ($E/J$), (d) values of S'.

where J_{ij} denotes the exchange coupling constant per electron and $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{S}}_j$ are the spin operators for the respective metal atoms. For a symmetrical trimer, $J_{12} = J_{23} = J_{31} = J$ and the interaction is simply written

$$\hat{\mathcal{H}} = -2J(\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_1)$$

where $-2J$ measures the difference in energy between the parallel and antiparallel positions of two electron spins. The eigenvalues of this Hamiltonian are readily obtained by making use of the vector model, and the calculated energies are of the form

$$E(S') = -J[S'(S' + 1) - 3S(S + 1)]$$

The 216-fold spin degeneracy of the Fe_3 cluster is partially lifted by spin–spin interaction to give eight spin levels (*cf.* Figure 2), each being specified by the spin quantum number S' which can take the values $^1/_2$, $^3/_2$, ... $^{15}/_2$. The term $3S(S + 1)$ is constant with $S = {}^5/_2$ and may be ignored if the level $S' = {}^1/_2$ is taken as the ground state of zero energy. The manifold of eight spin states shown in Table I then describes the system.

TABLE I

SPIN LEVELS (S') FOR Fe_3 CLUSTER WITH $S = {}^5/_2$

S'	Energy, $E(S')$	Multiplicity of state divided by $(2S' + 1)$
$^{15}/_2$	$-63J$	1
$^{13}/_2$	$-48J$	2
$^{11}/_2$	$-35J$	3
$^9/_2$	$-24J$	4
$^7/_2$	$-15J$	5
$^5/_2$	$-8J$	6
$^3/_2$	$-3J$	4
$^1/_2$	0	2

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(3) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Chapter XII, Oxford University Press, London, 1932.

(4) K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

(5) L. A. Welo, *Phys. Rev.*, **32**, 320 (1928).

(6) L. A. Welo, *Phil Mag.*, [7] **6**, 48 (1928).

(7) L. E. Orgel, *Nature*, **187**, 504 (1960).

(8) B. N. Figgis and G. B. Robertson, *ibid.*, **205**, 695 (1965).

When the iron alkoxides are subjected to an external homogeneous magnetic field **H** (along the Z axis), the spin degeneracy of each S' level is lifted to give ($2S' + 1$) sublevels. The Hamiltonian operator for the Fe_3 cluster becomes

$$\hat{\mathcal{H}} = -2J \sum_{i<j} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - g\beta \hat{S}'_Z H_Z$$

where $\hat{S}'_Z$ is the operator for the Z component of total spin. The first-order Zeeman terms $M_{S'} g\beta H$ must be added to the energy of the zero-field levels, with $M_{S'}$ taking the values $S', S' - 1 \ldots\ldots -S' + 1, -S'$. The eigenvalues then are

$$E(S', M_{S'}) = -J[S'(S' + 1) - 3S(S + 1)] - g\beta M_{S'} H$$

The variation with temperature of the molar susceptibility of the trimer is then readily derived from application of Van Vleck's formula

$$\chi_M = \frac{N \sum\limits_{S', M_{S'}} \left\{ \dfrac{\omega(S')[E^{(1)}{}_{S',M_{S'}}]^2}{kT} \right\} \exp \dfrac{[-E^{(0)}{}_{S'}]}{kT}}{\sum\limits_{S'} \omega(S') g_{S'} \exp \dfrac{[-E^{(0)}{}_{S'}]}{kT}}$$

where $E^{(0)}{}_{S'}$ denotes the energy of each spin level under zero magnetic field and $E^{(1)}{}_{S',M_{S'}}$ is the coefficient of the first-order Zeeman displacements of the levels assuming an expansion of the form

$$E_{S',M_{S'}} = E^{(0)}{}_{S'} + E^{(1)}{}_{S',M_{S'}} H + E^{(2)}{}_{S',M_{S'}} H^2 + \ldots\ldots\ldots$$

The magnetic field removes the spin degeneracy $g_{S'}$ of each S' level which, however, may occur $\omega(S')$ times as given in column 3 of Table I. If the summation is restricted to terms in the first order of magnetic field strength, the total susceptibility per mole of trimer is given by

$$\chi_M = \frac{N\beta^2}{3kT} \frac{3g^2}{4} \times \left\{ \frac{1 + 20\exp(-3x) + 105\exp(-8x) + 210\exp(-15x) + 330\exp(-24x) + 429\exp(-35x) + 455\exp(-48x) + 340\exp(-63x)}{1 + 4\exp(-3x) + 9\exp(-8x) + 10\exp(-15x) + 10\exp(-24x) + 9\exp(-35x) + 7\exp(-48x) + 4\exp(-63x)} \right\}$$

where the parameter $x = -J/kT$. The magnetic moment squared (μ_{eff}^2) is simply $3g^2/4$ multiplied by the quantity enclosed in parentheses.

The general features of the magnetic behavior to be expected for the spin-coupled Fe_3 model are as follows: The experimental $\mu_{eff}(T)$ curves show that, in the iron alkoxides, the ground state is that corresponding to the minimum value of S', *i.e.*, the sign of J is negative. As $kT/|J|$ approaches zero, only the lowest spin level $S' = 1/2$, is appreciably occupied and the $\chi_M^{-1}(T)$ curve in this region will have a limiting slope corresponding to $\mu_{eff}^2 = 1$ (BM)^2 per Fe_3 cluster. On the other hand, the effects of spin coupling become negligible for very large values of $kT/|J|$, since all levels become populated according to their statistical weights so that the limiting slope of the $\chi_M^{-1}(T)$ curve will correspond to $\mu_{eff}^2 = 105$ (BM)^2 per Fe_3 cluster. In this region, the equation for the susceptibility reduces to

$$\chi_M = \frac{N\beta^2}{3kT} \frac{3g^2}{4} \left\{ \frac{35}{1 + \dfrac{35x}{3} \ldots\ldots} \right\}$$

The Weiss temperature, θ, which is determined by the intercept on the T axis of the high temperature asymptote to the $\chi_M^{-1}(T)$ curve will give a useful measure of J since

$$\theta = \frac{35}{3} \frac{J}{k}$$

At intermediate temperatures, there will be a gradual transition between these two limiting conditions, and in particular the $\chi_M^{-1}(T)$ curves should pass through both maximum and minimum values $T_{max} = 0.88|J|/k$ and $T_{min} = 2.35|J|/k$. Such maxima and minima in $\chi_M^{-1}(T)$ curves have been observed[9,10] experimentally for trinuclear $[Cr_3O(CH_3CO_2)_6Cl \cdot 9H_2O$ and for mononuclear iron(III) dithiocarbamates in which $^6A_1$ and $^2T_2$ states are in thermal equilibrium.[11]

Structure and Magnetism of Iron(III) *n*-Alkoxides

The magnetic properties of iron(III) *n*-alkoxides conform well with the expectations of the spin-coupled model. Both the sign and magnitude of the iron–iron exchange interaction are established by comparing the experimental magnetic moments with the $\mu_{eff}(T)$ curve calculated for $J = -15k$ (see Figure 3). The free electron spin value, $g = 2.0$, is used here since the iron atoms are taken to be in $^6A_1$ states, and contributions from orbital angular momentum are likely to be extremely small. A plot of the reduced reciprocal susceptibility (expressed as $-N\beta^2/\chi_M J$) against the reduced temperature (expressed as $kT/|J|$) provides a more sensitive test of the theory (see Figure 4). The experimental data for the three alkoxides vary linearly with temperature between 90 and 300°K as required by the model for the values of $kT/|J|$ larger than about 5. However, an extension of the measurements to much lower temperatures is now required to confirm the expectations of a maximum and minimum in the $\chi_M^{-1}(T)$ curves and the limiting slope corresponding to $\mu_{eff}^2 = 1$ (BM)^2.

In spite of precautions taken during the preparation

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[9] J. Wucher and H. M. Gijsman, *Physica*, **20**, 361 (1954).

[10] H. M. Gijsman, T. Karantassis, and J. Wucher, *ibid.*, **20**, 367 (1954).

[11] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, (London), **A280**, 235 (1964).

TABLE II

θ AND J VALUES FOR Fe_3 AND Cr_3 CLUSTERS

Compound	θ, °K	J		$k\theta/J$		Ref
		°K	cm^{-1}	Calcd.	Obsd.	
$Fe_3(OCH_3)_9$	−198	−15	−10	11.7	11.7	This work
$Fe_3(OC_2H_5)_9$	−190	−15	−10	11.7	11.9	This work
$Fe_3(OC_4H_9)_9$	−168	−15	−10	11.7	12.0	This work
$[Fe_3O(CH_3CO_2)_6]NO_3\cdot 7H_2O$	−577	−39	−27	11.7	14.8	4, 5, 6
$[Fe_3O(ClCH_2CO_2)_6]NO_3\cdot 6.5H_2O$	−593	−41	−29	11.7	14.5	4, 5, 6
$[Cr_3O(CH_3CO_2)_6]Cl\cdot 9H_2O$	−131	−15	−10	5.0	8.7	9
$[Cr_3O(ClCH_2CO_2)_6]Cl\cdot 9H_2O$	−93	−14	−10	5.0	6.6	4, 5, 6
$[Cr_3O(ClCH_2CO_2)_6]I\cdot 3NH_3$	−116	−17	−12	5.0	6.8	4, 5, 6

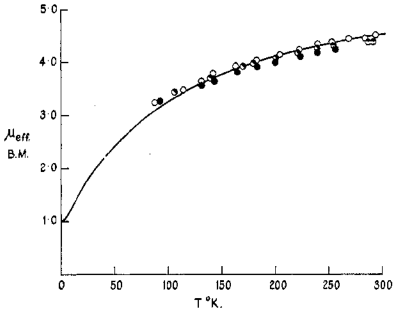

Figure 3.—Temperature dependence of magnetic moment (expressed per Fe atom) of iron(III) alkoxides, $[Fe_3(OR)_9]$: ○, R = CH_3; ◑, R = C_2H_5; ●, R = n-C_4H_9. Full curve calculated for $J = -15k$.

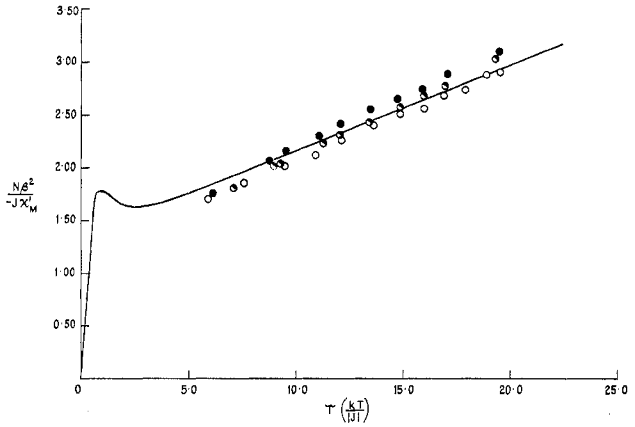

Figure 4.—Dependence of the reduced reciprocal susceptibility ($N\beta^2/-J\chi_M$) on the reduced temperature ($\tau = kT/|J|$) of iron(III) alkoxides, $[Fe_3(OR)_9]$: ○, R = CH_3; ◑, R = C_2H_5; ●, R = n-C_4H_9. Full curve calculated for $J = -15k$.

and subsequent handling of these compounds, their extreme reactivity makes contamination by traces of hydrolysis products always a possibility. In a previous paper[1] we have demonstrated that deliberate hydrolysis of iron(III) alkoxides progressively increases the slope of $\chi_M{}^{-1}(T)$ curves and leads to lower values of θ and hence to magnetic moments which are diminished below 5.92 BM when calculated according to the Curie–Weiss law. Thus we suspect that our magnetic data for the ethoxide and n-butoxide are slightly less reliable than those for the methoxide and that the observed experimental scatter probably does not reflect real differences in the magnitude of J with changes of the alkyl substituent. For these reasons and those approximations which are implicit in the spin-coupled model,[12] we are disinclined to consider an elaboration of the spin Hamiltonian in the form

$$\mathcal{H} = -2[J_0(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_3\cdot\hat{S}_1) + (J_0 + J_1)\hat{S}_2\cdot\hat{S}_3]$$

even though a closer fit to the experimental might thereby be achieved.

The experimental[9,10,13–15] and theoretical[4,16–18] investigations of Welo's trinuclear complexes of iron(III) and chromium(III) have occupied a pivotal position in the development of the spin-coupling model for isolated clusters. Accordingly, it is of particular interest to compare the magnitude of the present spin–spin interaction constants with the values available for his compounds (see Table II).

The magnitude of the spin–spin interaction constant for iron(III) alkoxides is about one-third as large as that of the basic iron(III) acetates but similar to that of the basic chromium(III) acetates. From the Heisenberg–Dirac–Van Vleck model, it follows that the Curie–Weiss temperature, θ, is given by

$$\theta = \frac{2S(S+1)}{3k}\sum_k Z_k J_k$$

where S is the spin per metal atom of the cluster and Z_k the number of kth nearest neighbors of a given atom. For the compounds listed in Table II, $Z_k = 2$ and $S = {}^5/_2$ (Fe) and ${}^3/_2$ (Cr), giving theoretical ratios of $k\theta/J = {}^{35}/_3$ (Fe) and 5 (Cr), respectively. The agreement between experimental and calculated values is reassuring evidence both for the applicability of the model and the assumption of a molecular structure based on a triangular central core of iron atoms. The experimental values of $k\theta/J$ will always tend to be slightly too high because of the difficulty of making susceptibility measurements in a region of temperature sufficiently high for the spin levels to be populated according to their statistical weights.

A striking feature which emerges from these data is that a spin–spin interaction constant of a rather small magnitude is quite sufficient to produce distinct anomalies in the magnetic behavior of iron(III) alkoxides at room temperature. Thus the present value of $J = -15k$ may be compared with the much larger value of

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[12] J. S. Smart, "Magnetism," Vol. III, G., T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1965, p. 63.

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[16] A. Abragam, J. Horowitz, and J. Yvon, *J. Phys. Radium*, **13**, 489 (1952)

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[18] J. T. Schriempf and S. A. Friedberg, *J. Chem. Phys.*, **40**, 296 (1964).

$J = -108k$ for the copper(II) acetate dimer[19] which, however, displays quite similar anomalies at room temperature. This situation derives from the difference in over-all width of the manifold of spin levels which is $-63J$ for the iron(III) alkoxides but only $-2J$ for copper(II) acetate.

Structure and Bonding in Iron Alkoxides

Cryoscopy and ebulliometry establish the trimeric stoichiometry of the iron(III) *n*-alkoxides. The anomalous temperature dependence of their paramagnetism conforms reasonably well to the above model based on spin–spin coupling between iron atoms in the Fe_3 core of each $Fe_3(OR)_9$ entity. The magnitude of the intramolecular exchange integral J in the spin–spin Hamiltonian $\hat{\mathcal{H}} = -2J\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j$ is extremely small and negative ($J = -15°$K). It remains to comment briefly on the possible stereochemistry and bonding in the trimeric species and on the factors which may determine the magnitude of the spin interaction.

The iron atoms of the Fe_3 core can form either a linear or a triangular (isosceles or equilateral) arrangement. However, the stoichiometry $Fe_3(OR)_9$ restricts the symmetrical condensation of iron–oxygen polyhedra to the equilateral arrangement of iron atoms, *i.e.*, D_{3h} appears likely to be the most appropriate point group.

The least likely arrangement in D_{3h} is that based on three FeO_4 squares which share corners (1a). No examples of a square-coplanar stereochemistry for tervalent iron are established, and ligands of high electronegativity like oxygen are known to favor a tetrahedral geometry as in the $FeCl_4^-$ anion. Furthermore, the paramagnetism exhibited by the iron alkoxides is consistent with a spin quantum number of $S = {}^5/_2$; $S = {}^3/_2$ is to be expected for a low-spin square-coordinated complex, although examples of high-spin complexes with this geometry have been claimed.[20,21]

If two, rather than one, OR groups bridge pairs of iron atoms, the environment about each iron atom becomes square-pyramidal with edge sharing of the basal planes (1b). The spin states $S = {}^5/_2$ and $S = {}^3/_2$ are both possible, although it is significant that two complexes with this geometry are both characterized by $S = {}^3/_2$, namely, [Fe(phthalocyanine)Cl][22] and $[Fe(S_2CN(C_2H_5)_2)Cl]$.[23]

Each iron atom can achieve a preferred coordination state with oxygen if three FeO_4 tetrahedra are linked through corners to give the cyclic structure (1c) which involves a single OR bridge between pairs of iron atoms. Alternatively, if the six equatorial terminal OR groups of structure 1a are rotated through 90° into semiaxial positions, and the Fe–O–Fe angles are simultaneously closed to about 90°, a closely related structure (1d) is obtained. This structure may be described in terms of three $[FeO_4\square_2]$ octahedra sharing a single common edge with the two opposed apical vacant positions (designated here by the symbolism, □) being the regions of maximum overlap for two three-center Fe–Fe bonds formed from six lobes of $d_\gamma{}^2sp^3$ hybrid orbital centered on the three iron atoms.

The iron–iron spin interaction is so weak (the total spread of energies of the manifold of spin levels for the ground state is only 945°K, *i.e.*, 630 cm^{-1}) that the direct overlap of nonbonding 3d orbitals must be extremely small. Under these conditions, a molecular orbital approach in terms of metal–metal bonding becomes a poor approximation and is unlikely to provide a realistic description of the observed spin coupling. However, it is perhaps relevant to note that both the 2s and 2p orbitals of the three bridging OR groups belong to irreducible representations $(a_1' + e')$, $(a_2'' + e'')$ in the point group D_{3h} and so can interact with combinations of 3d orbitals of corresponding symmetry centered on the Fe_3 core. Thus while the observed spin coupling is likely to arise from weak direct interactions between the three iron atoms, it may be further reinforced through a superexchange mechanism operating *via* the bridging OR groups.

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[22] J. S. Griffith, *Discussions Faraday Soc.*, **26,** 81 (1958).

[23] B. F. Hoskins, R. L. Martin, and A. H. White, unpublished work.