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Synthesis, Magnetic Properties and EPR of μ-Oxalato-tetrakis(acetylacetonato)diiron(III)

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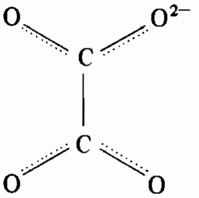
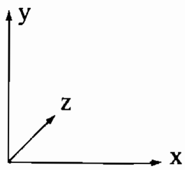
In the frame of our work on the interaction between transition metal ions through extended bridging ligands, we have shown that the tetradentate ligand μ-oxalato shown hereunder





was particularly able to propagate the electronic effects when the xy-type exchange pathway was operative. The large antiferromagnetic coupling generally observed is due to the strong overlap between the xy-type magnetic orbitals centered on the metal ions, and is delocalized towards the oxygen atoms of the oxalato bridge [1, 2]. Such a situation occurs in the linear chain $Cu(C_2O_4)\cdot 1/3H_2O$ [1], and in Ni(II) and Cu(II) binuclear species [3, 4]. To the best of our knowledge, the efficiency of the oxalato ligand to couple two high-spin iron(III) ions had not yet been put into evidence. In this letter, we describe the synthesis, the magnetic properties and the EPR spectrum of the molecular compound $(acac)_2Fe(C_2O_4)Fe(acac)_2\cdot ½H_2O$, noted *1* with acac = acetylacetonato.

The synthesis is carried out according to the scheme:

$$2Fe(acac)_3 + Fe^{3+} \rightleftarrows 3Fe(acac)_2^+$$

$$2Fe(acac)_2^+ + C_2O_4^{2-} \rightarrow 1$$

1 was obtained as a dark red polycrystalline solid by slow evaporation of a methanol solution containing 1.0 mmol of $Fe(acac)_3$, 050 mmol of $Fe(NO_3)_3\cdot 9H_2O$ and 0.75 mmol of $(C_5H_{12}N)_2C_2O_4\cdot 2H_2O$. $Fe(acac)_3$ was prepared as described [5] and the piperidinium oxalato dihydrate was isolated from piperidine and oxalic acid in dimethylformamide. *Anal.* Calcd.: C, 43.66; H, 4.79; Fe, 18.47. Found: C, 43.65; H, 4.78; Fe, 18.2.

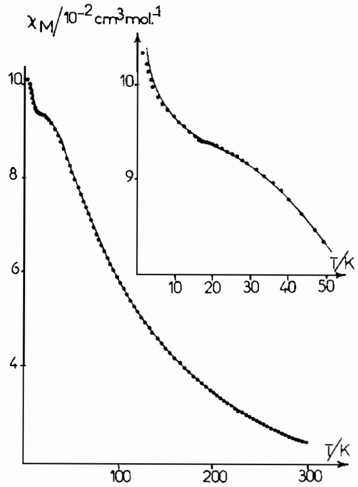
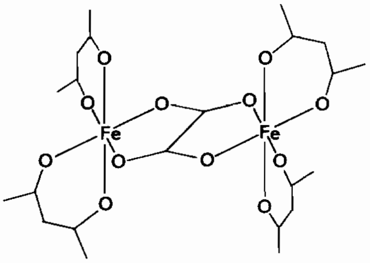


Fig. 1. Experimental (●) and theoretical (——) temperature dependences of the molar magnetic susceptibility of *1*.

The infrared spectrum of *1* exhibits in addition to the bands of the $acac^-$ ligand, the ν_{C-O} stretching vibration at 1675 cm^{-1} and the ν_{O-C-O} bending vibration at 805 cm^{-1} characteristic of the oxalato bridging ligand. It follows that the molecular structure of *1* is that shown hereunder, with two Fe(III) ions in octahedral surroundings of oxygen atoms, separated by more than 5 Å [4, 6, 7]:



The molar magnetic susceptibility χ_M *versus* temperature T plot for *1* is shown in Fig. 1, in the range $2 < T/K < 300$. When cooling down, χ_M increases much slower than expected from a Curie law, reaches a plateau around 20 K with $\chi_M = 9.28 \times 10^{-2}$ cm^3 mol^{-1}, then increases again. This behaviour is characteristic of an intramolecular antiferromagnetic coupling between two high-spin Fe(III) ions, with a very small amount ρ of uncoupled impurity. Assuming a C_{2v} site symmetry for the metal ions and a D_{2h} molecular symmetry, the interaction between two $^6A_1$ iron(III) single-ion ground states leads to

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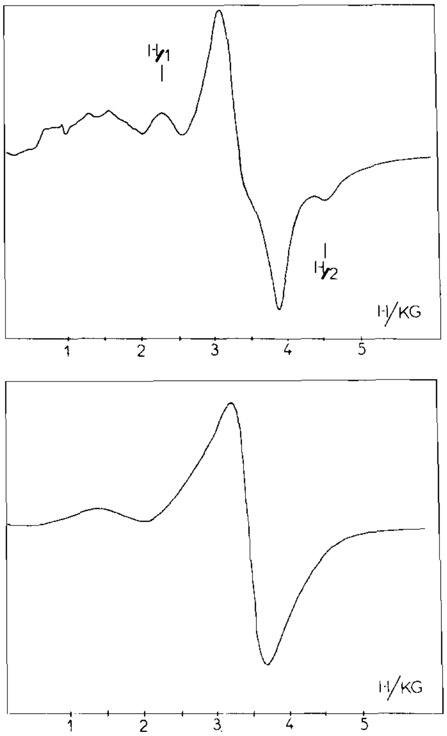

Fig. 2. X-band EPR spectra at 20 K of *1*. Top: spectrum of a solution in a 1/1 toluene–chloroform mixture. Bottom: spectrum of the powder solid.

^1A_g + $^3B_{1u}$ + ^5A_g + $^7B_{1u}$ + ^9A_g + $^{11}B_{1u}$ molecular states, the spin degeneracy of each term being eventually removed by the Zero Field Splitting. To determine the magnitude of the interaction in *1* from the magnetic data, we expressed the observed susceptibility χ_M as

$$\chi_M = \chi^D (1 - \rho) + \chi^I \rho$$

χ^D is the actual susceptibility of *1* and χ^I the susceptibility of the impurity. We assumed that the impurity was a monomeric high-spin iron(III) compound of the same molecular weight as *1*, with a magnetic susceptibility obeying the Curie law $\chi^I = 35\ N\beta^2g^2/12\ kT$. In a first calculation, we described the interaction by the $\mathcal{H} = -J\hat{S}_1 \cdot \hat{S}_2$ Hamiltonian, *i.e.* we considered that the relative energies of the molecular states followed the Landee interval rule, J being the ^1A_g – $^3B_{1u}$ energy gap. χ^D is then given by:

$$\chi^D = \frac{2N\beta^2g^2}{kT}\,\frac{x + 5x^3 + 14x^6 + 30x^{10} + 55x^{15}}{1 + 3x + 5x^3 + 7x^6 + 9x^{10} + 11x^{15}}$$

with

$$x = \exp(J/kT)$$

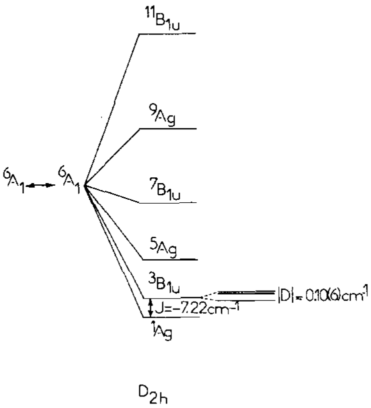

Fig. 3. Low lying states in *1* (see text).

J, the g factor and ρ determined by least squares fitting are found as:

$$J = -7.22\ \mathrm{cm}^{-1}$$

$$g = 1.99$$

$$\rho = 0.051$$

The agreement factor defined by $\Sigma(\chi_M^{obs} - \chi_M^{calc})^2/\Sigma(\chi_M^{obs})^2$ is then 2.3×10^{-5}, which is a very low value. In a second calculation, we introduced a biquadratic term $j(\hat{S}_1 \cdot \hat{S}_2)^2$ in the exchange Hamiltonian. This did not improve the fitting, owing to the excellent theory–experiment agreement derived from the simple HDVV Hamiltonian.

The X-band EPR spectra at 20 K of the powder solid and of the solution in a 1/1 toluene–chloroform mixture are shown in Fig. 2. These spectra are unchanged in the temperature range 4–80 K*. Since the ^5A_g state and the states of higher spin multiplicity are essentially not populated at 4 K, all the features visible in the spectra of Fig. 2 are associated to the first excited $^3B_{1u}$ state. Between 2000 and 5000 G the solution spectrum is typical of the $\Delta M_S = \pm 1$ transitions in a triplet state, with an axial Zero Field Splitting and an isotropic g-tensor. From the two peaks at 2238 and 4511 G corresponding to the resonant fields $H_{\parallel 1}$ and $H_{\parallel 2}$ when the applied magnetic field is parallel to the axis of the D tensor, one easily determines g = 2.00(3) and the Zero Field Splitting parameter |D| = 0.10(6) cm^{-1} [8]. Below 2000 G, the solution spectrum exhibits many weak features which may be assigned to the $\Delta M_S = \pm 2$ forbidden transitions. The

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*Except for the appearance below 10 K of a small feature at g = 4.3, most likely belonging to the uncoupled iron(III) impurity already detected in magnetism.

powder spectrum is poorly resolved. It only shows a large signal centered at g = 2.00 between 2000 and 5000 G which is clearly the envelope of all the $\Delta M_S = \pm 1$ transitions, and a small signal at low field, which is the envelope of the features detected in the solution spectrum below 2000 G.

From the magnetic and EPR investigations, we obtained a relatively accurate description of the relative energies and the nature of the low lying states in *1*. These results are summarized in Fig. 3.

In a forthcoming paper, we aim at rationalizing the results concerning the interaction through oxalato type bridging ligands. We restrict ourselves here to emphasize the magntidue of the coupling between two Fe(III) ions separated by more than 5 Å. This interaction is of the same order of magnitude as that occurring in di-μ-hydroxo Fe(III) dimers with a Fe–Fe separation of about 3 Å [9].

Experimental

The magnetic measurements were carried out on two samples weighing about 5 mg with a previously described Faraday type magnetometer [2]. The applied magnetic field was about 0.2 T. The independence of the susceptibility against the magnetic field was checked at both room temperature and 4.2 K. The diamagnetism was estimated as -167×10^{-6} cm^3 mol^{-1}. The EPR study was carried out with a Bruker ER 200 D spectrometer. A listing of the magnetic data may be obtained on request from the authors.

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