

POLYNUCLEAR ACETYLACETONATODIMETHOXYIRON(III)

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Abstract

The complex $[\text{Fe}(\text{acac})(\text{OMe})_2]$ was prepared. The temperature dependence of the magnetic susceptibility indicates that the complex is an antiferromagnet and that it may be binuclear.

Polynuclear alkoxy bridged compounds of trivalent iron are known to be antiferromagnetic. Antiferromagnetic trimeric alkoxides, trimeric and tetrameric halo alkoxides have been described.¹ Antiferromagnetic, probably tetrameric, complexes of the general formula $\text{FeL}(\text{OMe})_2$, where L is carboxylate and which appear to involve trigonal prismatic iron(III) have been also reported.²

Recently Wu *et al.*³ reported the bright yellow acetylacetonatodimethoxyiron(III), $[\text{Fe}(\text{acac})(\text{OMe})_2]$, which they prepared according to Emmert *et al.*⁴ by the oxygenation of a methanolic solution of $[\text{Fe}(\text{acac})_2(\text{py})_2]$ and also by treating a methanolic solution of $[\text{Fe}(\text{acac})_3]$ with methoxide ion. Wu *et al.* suggested that the compound is a polymer as it is insoluble in polar organic solvents and chars without melting. They did not report elementary analyses, the magnetic moment, or electronic spectra. Three infrared bands are quoted: 332s, 1050s, and 1450 cm^{-1} .

In this work $[\text{Fe}(\text{acac})(\text{OMe})_2]$ was prepared according to the method employed previously by us to prepare the carboxylatodimethoxyiron(III) complexes² using piperidine to remove chloride and protons as piperidinium chloride. The complex is a bright yellow powder. It decomposes without melting at about 235°C and is insoluble in boiling methanol, chloroform, acetone, carbon tetrachloride, benzene, and toluene. In the infrared spectra appear the three bands reported by Wu *et al.* (see Experimental). The magnetic moment at room temperature of 4.33 B.M. is well below the 5.9 B.M. expected for high-spin iron(III). With falling temperature the moment drops to 2.28 B.M. at the boiling point of liquid nitrogen. The reciprocal of the susceptibility passes through a minimum about 170 K (Fig. 1, Table 1). The magnetic behaviour

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¹ Kakos, G. A., and Winter, G., *Aust. J. Chem.*, 1969, **22**, 97.

² Kokot, E., Mockler, G. M., and Sefton, G. L., Abstracts, R.A.C.I. Divn Coord. Metal-Organic Chem., 4th Conf., Sydney and Camden, May 1972, C-3.

³ Wu, Chin-Hua, S., Rossman, G. R., Gray, H. B., Hammond, G. S., and Schugar, H. J., *Inorg. Chem.*, 1972, **11**, 990.

⁴ Emmert, B., and Seebode, W., *Ber. dt. chem. Ges.*, 1938, **71**, 242.

indicates that the compound is an antiferromagnet. The best fit theoretical susceptibilities for $g = 2.0$ were obtained from equation (1) for two⁵ and equation (2) for an infinite chain⁶ of iron(III) atoms coupled antiferromagnetically with J values of

TABLE 1
MAGNETIC DATA AT VARIOUS TEMPERATURES
 $-10^6\Delta = 90$

T (K)	$10^6\chi_A$	μ (B.M.)	T (K)	$10^6\chi_A$	μ (B.M.)	T (K)	$10^6\chi_A$	μ (B.M.)
77.5	8294	2.28	150.0	8709	3.25	250.0	8406	4.12
85.3	8382	2.40	173.8	8740	3.50	279.7	8239	4.31
97.0	8418	2.57	200.0	8744	3.75	300.0	8009	4.40
110.0	8559	2.76	206.5	8689	3.80	330.0	7769	4.55
125.0	8525	2.93	230.0	8518	3.97	350.0	7583	4.63

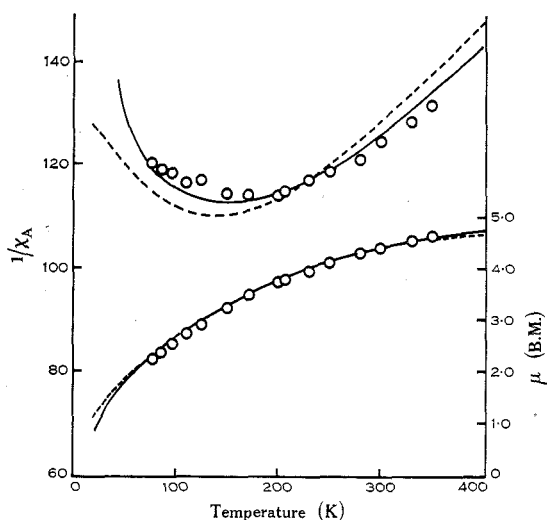


Fig. 1.—Reciprocal magnetic susceptibility ($1/\chi_A$) and magnetic moment (μ).
○ Experimental values;
full line calculated from equation (1);
broken line calculated from equation (2).

-18.3 and -11.5 cm^{-1} respectively (Fig. 1). The dimer model gives the better fit of the two.

$$\chi_A = (3K/T)[(55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28})/(11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30})] \quad (1)$$

where $x = \exp(J/k_B T)$ and $K = Ng^2\beta^2/3k_B$

$$\chi_A = [Ng^2\beta^2 S(S+1)/3k_B T] \cdot (1+\mu)/(1-\mu) \quad (2)$$

where $\mu = \coth[2JS(S+1)/k_B T] - k_B T/[2JS(S+1)]$ and $S = 5/2$.

A good fit on the dimer model requires $g = 2.05$, $J = -19.5 \text{ cm}^{-1}$; and for the chain model $g = 2.17$, $J = -14.0 \text{ cm}^{-1}$. It was not possible to fit calculated susceptibilities on the basis of trimeric^{1,7} or tetrameric¹ models.

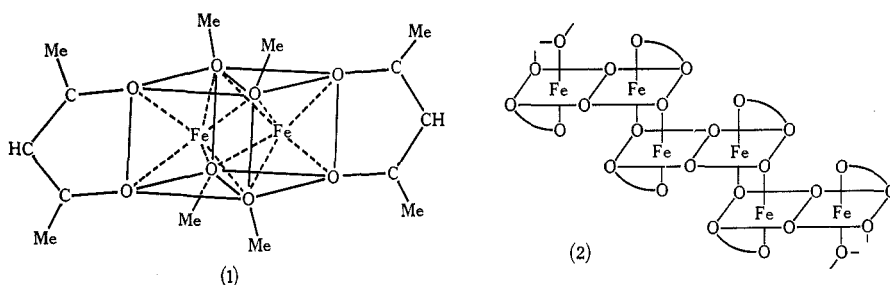
⁵ Earnshaw, A., and Lewis, J., *J. chem. Soc.*, 1961, 396.

⁶ Smith, T., and Friedberg, F. A., *Phys. Rev.*, 1968, **176**, 660.

⁷ Adams, R. W., Barraclough, C. G., Martin, R. L., and Winter, G., *Inorg. Chem.*, 1966, **5**, 346.

In the infrared spectrum only a single band at 1052 cm^{-1} appears in the C–O region (see Experimental). The presence of only one C–O stretching band points to the methoxide groups occupying equivalent sites. The frequency of 1052 cm^{-1} for the C–O stretch falls in the region $1030\text{--}1080\text{ cm}^{-1}$ observed for methoxide groups bridging two iron(III) atoms.^{1,3}

On the basis of the magnetic behaviour and the presence of a single C–O stretching band two structures may be written (1) and (2). The better fit of equation (1) favours the binuclear structure (1).



In the electronic reflectance spectrum two broad bands of low intensity are present at *c.* 10500 and 16600 cm^{-1} . Higher energy bands were not observed due to the presence of a strong charge transfer band in the high energy region (above 20000 cm^{-1}) of the spectrum.

Experimental

Preparation of Acetylacetonatodimethoxyiron(III)

Piperidine (0.15 mol) was added to a solution of acetylacetone (0.05 mol) in dry methanol. To the filtered solution was added a filtered solution of anhydrous iron(III) chloride (0.05 mol) in dry methanol (100 ml). The stoppered flask was shaken for 1 hr. The product was collected by centrifuging, dispersed in dry methanol, and again centrifuged. This was repeated until all chloride was removed. Excess solvent was removed under nitrogen by heating at 100°C for 18 hr (Found: C, 38.3; H, 5.9; Fe, 25.7. Calc. for $\text{C}_7\text{H}_{13}\text{FeO}_4$: C, 38.7; H, 6.0; Fe, 25.8%).

Physical Measurements

Magnetic measurements were carried out as described previously.⁸ The infrared spectrum in KBr was recorded with a Jasco DS 4039 infrared spectrophotometer. The electronic reflectance spectrum was obtained using a Zeiss PQM II spectrophotometer fitted with an RA-3 reflectance attachment.

Infrared Spectrum

$332, 429\text{m}, 450\text{m}(\text{sh}), 528, 550, 656, 669, 765, 926, 1020\text{m}, 1052\text{s}, 1184, 1269\text{m}, 1360\text{m}(\text{sh}), 1382\text{s}, 1440(\text{br}), 1525\text{s}, 1590\text{s}\text{ cm}^{-1}$.

⁸ Kokot, E., and Ryder, G. A., *Aust. J. Chem.*, 1971, **24**, 649.