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An ambient temperature-stable organometallic ferromagnet

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Abstract. The magnetic properties of an ambient temperature-stable organometallic ferromagnet are reported. The compound exhibits a saturation magnetization $M_s = 26.4 \text{ emu g}^{-1}$ at room temperature ($H = 50 \text{ kOe}$). A magnetic hysteresis loop was observed with residual magnetization $M_r = 5 \pm 1 \text{ emu g}^{-1}$, and coercive force $H_c = 180 \pm 5 \text{ Oe}$ at room temperature. Acid treatment, ESR and Mössbauer spectroscopy show that the iron ions should play no essential role in the ferromagnetism of the sample. Probably the ferromagnetism was due to organic free radicals.

1. Introduction

The systematic study of low-dimensional organic donor (D)–acceptor (A) charge-transfer complexes with a segregated-stack crystal structure has led to great advances in highly conducting organic metals. However, studies on the magnetic properties of the charge-transfer complex have been limited since, unlike many inorganic transition metals, most of the organic materials are diamagnetic or weakly paramagnetic. Current research (Cowan and Wiygul 1989, Jerome 1982) on the syntheses of magnetic organic materials is aimed towards development of organic ferromagnets. Recently, Chakraborty *et al* (1988, 1989) synthesized a quasi-one-dimensional (quasi-1D) charge-transfer salt of $(\text{DMeFe})^+(\text{TCNE})^-$, consisting of stacks of alternate donors (DMeFe) and acceptors (TCNE). Magnetization, neutron diffraction, Mössbauer and specific heat results show that the system becomes a ferromagnet below 4.8 K. This is the first confirmed low-temperature ferromagnetic organometallic material. Poly(pyridilenemethideneniloliron) was said to be a ferromagnetic compound by Lions and Martin (1957). This polymer and its derivative was carefully reprepared and its unusual magnetic properties have been reinvestigated by Nishide *et al* (1989). Mössbauer spectroscopy and x-ray diffractometry on the polymers indicated that the unusual magnetic properties are caused by the slight amount of ferromagnetic iron oxide formed in the polymers.

Recently, we synthesized firstly an ambient temperature-stable, highly ferromagnetic oligomer with the chemical composition of $\text{Cu}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ (Zhao *et al* 1990a, b). The compound exhibits a saturation magnetization $M_s = 16.9 \text{ emu g}^{-1}$ and a

coercive force $H_c = 278$ Oe at room temperature ($H = 50$ kOe). Here, we report further Mössbauer, ESR and magnetic measurements on a compound of nominal composition $\text{Cd}_2\text{Fe}_2\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_4$; its chemical composition may be denoted as $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$.

2. Synthesis of the organometallic ferromagnet

All operations were carried out under pre-purified nitrogen using Schienk tube techniques. Methylene chloride was distilled from calcium hydride under nitrogen prior to use; *p*-phenylenediamine was purified by recrystallization from water, followed by vacuum sublimation (melting point 140–141 °C). Reagent grade *n*-amyl alcohol and hydrated cadmium acetate were obtained from commercial sources, 1,1'-diacetylferrocene was prepared by modification of the method given in the literature (Rosenbium and Woodward 1958) (recrystallization from acetone; melting point, 125–126 °C).

A solution of *p*-phenylenediamine (0.54 g; 5 mmol) in 50 ml of *n*-amyl alcohol was dropwise added to a stirred solution of 1,1'-diacetylferrocene (1.35 g; 5 mmol) in 100 ml of *n*-amyl alcohol under nitrogen. The solution mixture was refluxed gently for 6 h; following this period, a solution of $\text{Cd}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1.24 g; 5 mmol) in 50 ml of *n*-amyl alcohol was added to the solution above, and the mixture was refluxed continuously for 3 h. A black powder separated out from the solution during the reaction. The precipitate was collected by filtration, washed with hot ethanol and hot water and dried for 4h at 100 °C in vacuum. The chemical composition of the nominal compound, $\text{Cd}_2\text{Fe}_2\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_4$, may be denoted by formula $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ (see Zhao *et al* (1990a, b)). Because single-crystal samples were not prepared, the crystal structure of this compound needs further investigation.

3. Magnetization measurements

The magnetizations were measured in a computer-controlled vibrating-sample magnetometer (model 155) at the Magnetic Measurement Laboratory, Institute of Physics, China Science Academy, Beijing.

Figures 1 and 2 display the field dependences of magnetization per gram mass for the sample FCD-3 at 1.5 K and 295 K, respectively. The plot of magnetization against the field strength saturates at about 10 kOe at 1.5 and 300 K, and magnetic hysteresis loops were observed with a residual magnetization $M_r = 5 \pm 1$ emu g^{-1} and a coercive force $H_c = 180 \pm 5$ Oe at 295 K, and $M_r = 12.05 \pm 1$ emu g^{-1} and $H_c = 500 \pm 5$ Oe at 1.5 K; this is the characteristic of a ferromagnet.

Figure 3 displays the temperature dependence of the saturation magnetization per gram mass for sample FCD-3 at 50 kOe. The curve obeys a linear relation $M_s = 43 - 0.055T$ in the temperature range 1.5–300 K, and $M_s(T = 0) \approx M_s(T = 1.5 \text{ K}) \approx 43$ emu g^{-1} . By use of the formula $M_s(0) = 5585n_B/m$ for the saturation magnetization per gram mass and using $m = 630.74$, we get $n_B = 4.85 \approx 5$.

4. ESR spectroscopy

For ESR measurements a Bruker ER-200D spectrometer was used. The ESR spectrum of sample FCD-3 was measured at 293 K and shows an axially symmetrical powder pattern

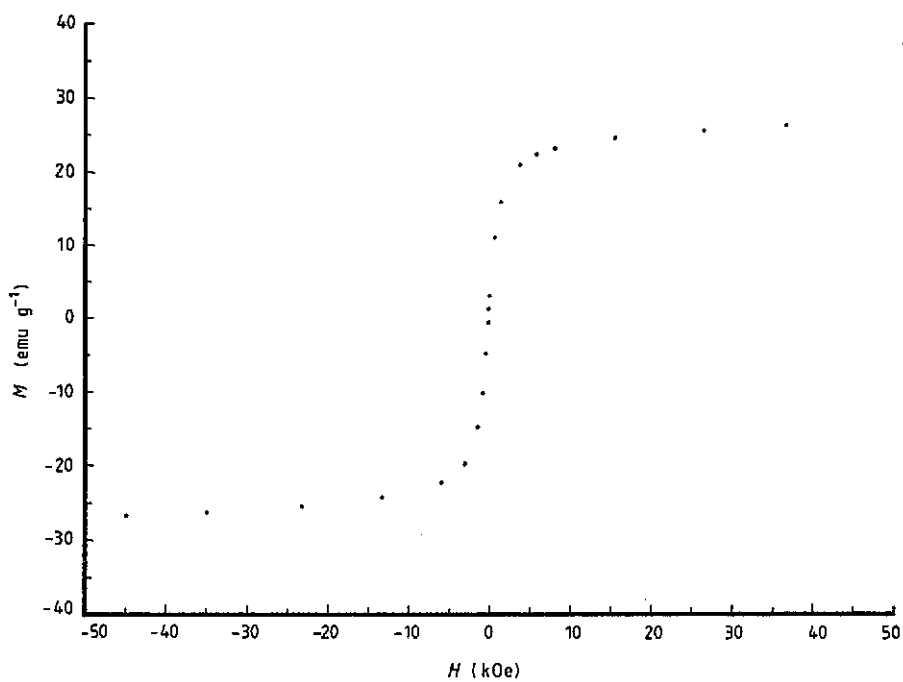


Figure 1. Magnetization per gram mass plotted as a function of applied field for the compound $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ ($T = 300$ K).

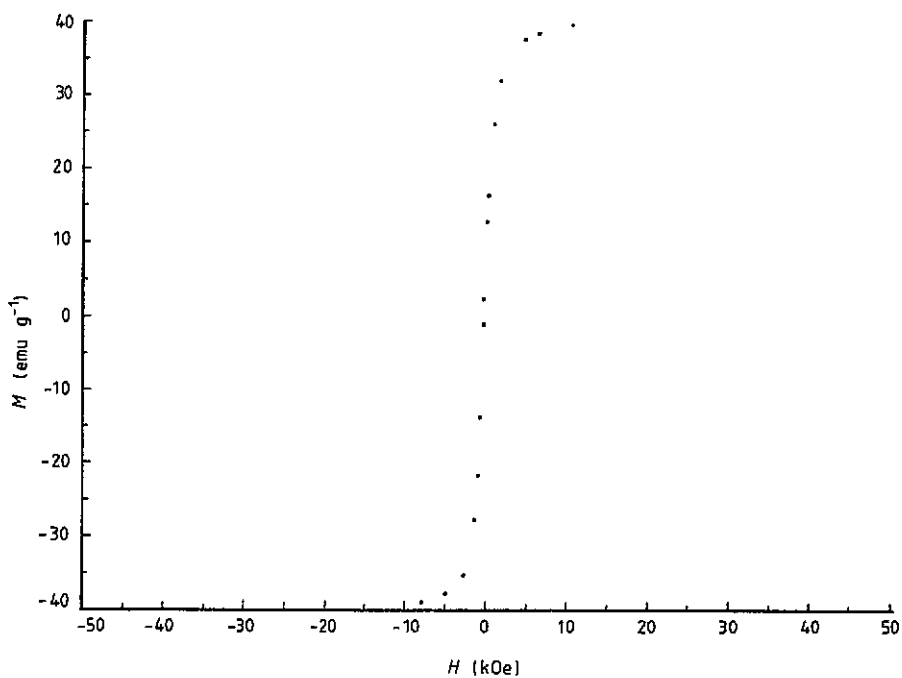


Figure 2. Magnetization per gram mass plotted as a function of applied field for the compound $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ ($T = 1.5$ K).

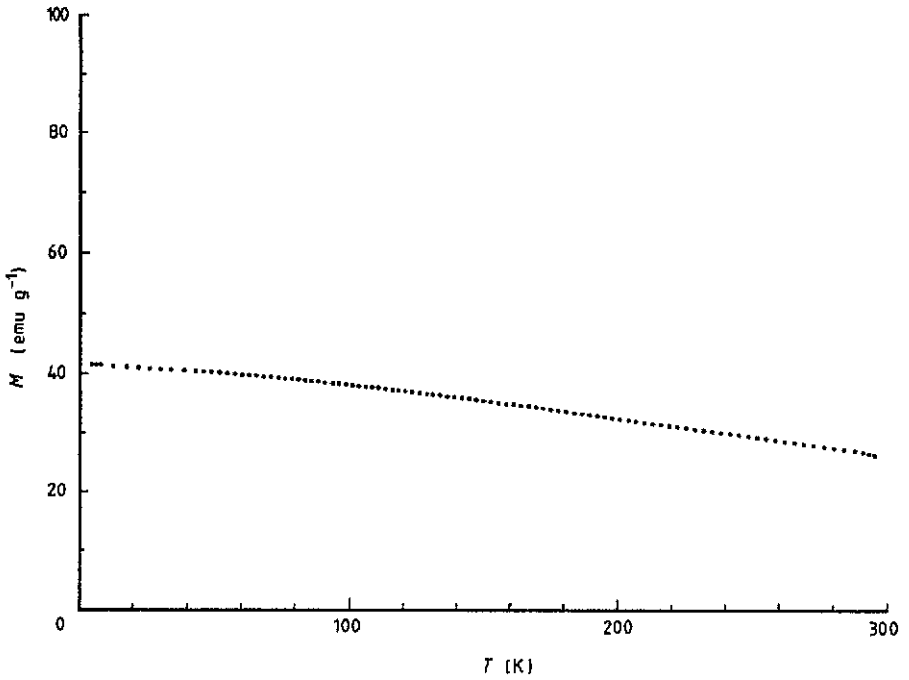


Figure 3. Saturation magnetization per gram mass plotted as a function of temperature for the compound $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ ($H = 50$ kOe).

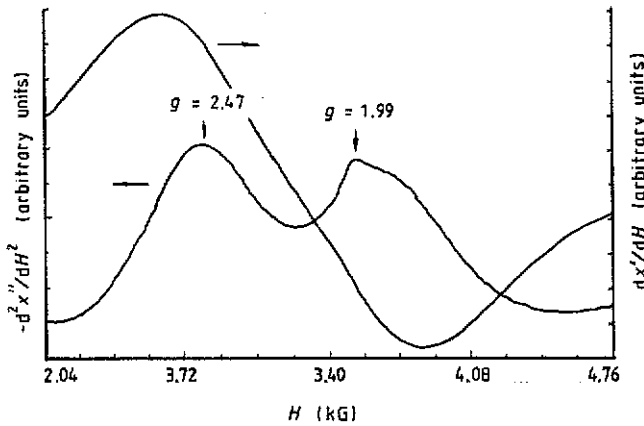


Figure 4. ESR spectrum of the compound $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ ($T = 293$ K; microwave frequency, 9603 MHz; microwave power, 50 dB, $2 \mu\text{W}$; gain, 4×10^2 ; field modulation, 100 kHz).

characterized by $g_{\parallel} = 2.47 \pm 0.005$ and $g_{\perp} = 1.99 \pm 0.005$ (figure 4). The very intense signal was attributed to the presence of a paramagnetic low spin Fe(III) with $s = \frac{1}{2}$, because the ferromagnetic compound without Cd ($\text{Fe}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$) also has a similar

intense signal characterized by $g_{\parallel} = 3.02 \pm 0.005$ and $g_{\perp} = 1.93 \pm 0.003$ at room temperature. It is certain that Fe exhibits a paramagnetic resonance peak instead of a ferromagnetic resonance peak. In fact, if Fe is in a ferromagnetic state, there must be a very broad peak covering the range 0–7 kOe (Ovchinnikov *et al* 1988); so the results show that, in the ferromagnet $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$, Fe ions are in a paramagnetic low-spin state instead of a ferromagnetic state. The ferromagnetism is not due to the iron ions, and this phenomenon is just the unusual behaviour of the new material. There is further evidence from Mössbauer measurement to verify this point in section 5. Since typical crystal-field splittings exceed 10^4 cm^{-1} , small distortions from D_{5d} symmetry could further split the levels. The approximate g -factor expressions are given by (Soon and McWilliams 1989)

$$g_{\parallel} = 2 + 4 \cos(2\alpha)$$

$$g_{\perp} = 2 \sin(2\alpha)$$

with

$$\tan(2\alpha) = \sigma/\xi$$

where ξ is the spin-orbit coupling constant for Fe^{3+} , and σ is the one-electron orbital energy splitting, which scales the distortion from D_{5d} symmetry.

Using $\cos(2\alpha) = 0.1175$, we obtain

$$g_{\parallel} = 2.47$$

$$g_{\perp} = 1.986.$$

Since two experimental g -factors can be fitted from a fitting parameter of α , it is correct that Fe is in an axially symmetric Fe(III) low-spin state. The g anisotropy $\Delta = g_{\parallel} - g_{\perp}$ of 0.48 is much smaller than the value of 3.08 found for both ferrocenium and decamethylferrocenium cations (Miller *et al* 1989).

In order to understand further the origin of ferromagnetism, an acid treatment was carried out at room temperature for 16 h. After acid treatment with HCl (0.02 N), the ferromagnetism is unchanged. This indicates that the ferromagnetism of this compound is not related to iron oxide which, if there is any, is dissolved by the HCl solution.

5. ^{57}Fe Mössbauer spectroscopy

The Mössbauer spectrum was measured with a computer-controlled spectrometer (model AME-50). The spectrum of sample FCD-3 at room temperature was computer fitted to a given number of Lorentzian lineshapes using the least-squares iterative procedure (figure 5). It contains a paramagnetic split pattern with $is = 0.28 \text{ mm s}^{-1}$, $\Gamma_{1/2} = 1.02 \text{ mm s}^{-1}$, $QS = 0.81 \text{ mm s}^{-1}$ and $H_{\perp} = 0$, which indicates that the Fe(III) ions were in a paramagnetic low-spin state rather than in the ferromagnetic high-spin state below the Curie temperature ($T_C > 500 \text{ K}$) and that the ferromagnetism of sample FCD-3 was not due to iron ions, because there is no Fe magnetic hyperfine six-line pattern in the range of experimental error. Contrary to this, there is an Fe six-line pattern for the ferromagnet $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ (Zhao *et al* 1990a, b). Probably the ferromagnetism in sample FCD-3 was due to five organic free radicals per unit because the Fe^{3+} and Cd^{2+} ions were in the paramagnetic and diamagnetic states, respectively, and $n_B \approx 5$ (see section 3), below the Curie temperature.

Table 1. Comparison between samples FCD-3 and FCU-3.

Nominal	Composition		M_s (emu g ⁻¹)	M_r (emu g ⁻¹)	H_c (Oe)	g-factor	Mössbauer parameters
	Nominal	Chemical					
[Cd ₂ Fe ₂ C ₃₆ H ₃₈ N ₄ O ₄]		Cd ₂ Fe ₂ C ₁₂ H ₁₀ N ₂ O ₇] _n	43 ± 0.5 (T = 1.5 K) 26.4 ± 0.5 (T = 295 K)	18 ± 1 (T = 1.5 K) 5 ± 1 (T = 295 K)	520 ± 5 (T = 1.5 K) 180 ± 5 (T = 295 K)	$g_1 = 2.47 \pm 0.005$ $g_2 = 1.99 \pm 0.005$ (T = 293 K)	$\delta = 0.28 \text{ mm s}^{-1}$ $\Delta E_q = 0.81 \text{ mm s}^{-1}$ $\Gamma_{1/2} = 1.02 \text{ mm s}^{-1}$ $H_1 = 0$ (T = 295 K) (Grain size, 2–5 μm)
[Cd ₂ Fe ₂ C ₃₆ H ₃₈ N ₄ O ₄]		[Cd ₂ Fe ₂ C ₁₂ H ₁₀ N ₂ O ₇] _n n = 3	20 ± 0.5 (T = 1.5 K) 17 ± 0.5 (T = 294 K)	11 ± 1 (T = 1.5 K) 7 ± 1 (T = 294 K)	576 ± 5 (T = 1.5 K) 278 ± 5 (T = 294 K)	$g_1 = 2.91 \pm 0.005$ $g_2 = 1.95 \pm 0.005$ (T = 293 K)	$\delta = 0.36 \text{ mm s}^{-1}$ $\Delta E_q = 0.02 \text{ mm s}^{-1}$ $\Gamma_{1/2} = 1.19 \text{ mm s}^{-1}$ $H_1 = 466 \text{ kOe}$ (T = 300 K) (Grain size, 2–5 μm)

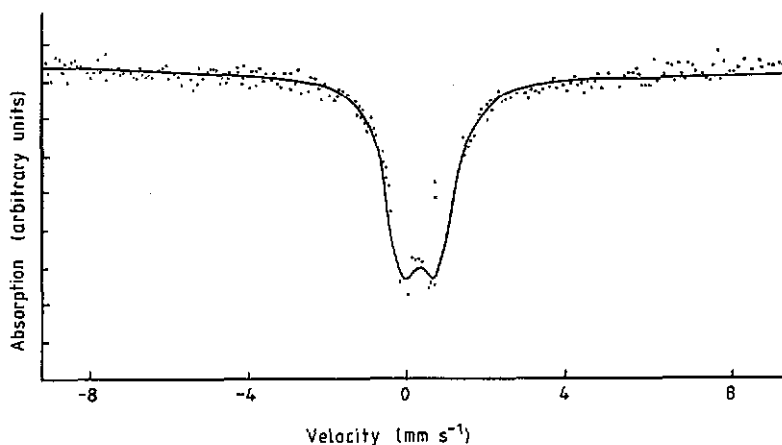


Figure 5. Mössbauer spectrum of the compound $\text{Cd}_2\text{Fe}_2\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_7$ ($T = 295$ K; grain size, 2–5 μm). The isomer shift δ is relative to the α -Fe film.

It must be indicated that the existing points do seem to show a doublet structure; the very large linewidth might conceivably be due to an Fe final-state magnetic hyperfine interaction but, because of the random and left–right asymmetry of the experimental points on the two sides of the paramagnetic peak, our attempt to fit a six-line magnetic hyperfine structure failed. So we concluded that the ferromagnetism is not due to the iron ions within the range of experimental error.

In summary, acid treatment, ESR and Mössbauer measurements show that the iron oxide and iron ions should play no essential role in the ferromagnetism of oligomer FCD-3. The main results were summarized in table 1.

Acknowledgments

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