

A sheet structured MOF magnet: Poly[(1,10-phenanthroline)tetrakis(imidazolato)diiron(II)]



Tim Storr^{a,b,*}, John R. Thompson^b, Brian O. Patrick^a, William M. Reiff^{c,*}, Alan Storr^{a,*}, Robert C. Thompson^{a,*}

^a Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

^b Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

^c Department of Chemistry, Northeastern University, Boston, MA 02115, USA

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ABSTRACT

We report the synthesis and structural and magnetic characterization of poly[(1,10-phenanthroline)tetrakis(imidazolato)diiron(II)], $[\text{Fe}_2(\text{imid})_4(\text{phen})]_x$, **1**. The extended structure of **1** is that of a metal organic framework (MOF) involving double layer sheets (bilayers) of alternating tetrahedral and octahedral irons singly bridged by imidazolate ligands. The octahedral iron centers are each additionally coordinated by phenanthroline ligands. Mössbauer spectroscopy confirms the presence of octahedral and tetrahedral metal centers. A combination of DC susceptibility, ZFCM and Mossbauer studies reveals a magnetic phase transition to long-range order at ~ 7 K in **1**. Magnetic hysteresis is observed at low temperatures, with coercive fields of approximately 360 and 650 G and remnant magnetizations of approximately 450 and $720 \text{ cm}^3 \text{ G mol}^{-1}$ at 5 and 2.5 K respectively.

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1. Introduction

Molecule-based magnets have been the subject of intense research over the last several decades [1–8]. These materials undergo long-range ferromagnetic order below some critical temperature (T_c), and materials within this class include complex metal cyanides [9,10], organometallic systems [10,11], and organic compounds [12–14]. A focus of our research [15–20], and others [21–23], includes coordination polymers of paramagnetic first-row transition metals incorporating bridging 1,3-diazolate ligands. In our own work, we have documented examples of 1D, 2D and 3D extended lattice imidazolates which exhibit low temperature ferromagnetic ordering. $\text{Fe}(1\text{-Me-2-S-imid})_2 \cdot 0.5\text{Cp}_2\text{Fe}$ [17,24] (where 1-Me-2-S-imid = 1-methyl 2-thioimidazolate, and Cp = cyclopentadienyl), has a novel 1D extended chain structure incorporating alternating FeN_4 and FeS_4 tetrahedra. Examples with extended 3D lattice structures are $\text{Fe}_3(\text{imid})_6(\text{Himid})_2$ [19], $\text{Fe}(4\text{-abimid})_2$ [18], and $\text{Fe}(2\text{-meimid})_2 \cdot 0.13\text{Cp}_2\text{Fe}$ [20], (where imid = imidazolate, 4-abimid = 4-azabenzimidazolate, and 2-meimid = 2-methylimidazolate). Finally, $\text{Fe}_2(\text{imid})_4(\text{bipy})$ **2**

(where bipy = 2,2'-bipyridine) provides a 2D lattice structure example of these magnetic materials [15].

Diazine ligands have been used frequently in coordination polymers for applications in sensing [25], optical and electronic materials [26], and molecular magnetism [27–29]. By incorporating the diazine ligand, 2,2'-bipyridine, into the iron(II) imidazolate structure we were able to cap some of the iron centers and in the process obtain the extended 2D lattice structure exhibited in **2** [15]. Further studies on **2** show that the material magnetically orders with $T_c \sim 6.5$ K and, in addition, undergoes two hysteretic structural and spin-state transitions starting at 151 and 133 K on cooling from room temperature [16]. This remarkable behavior prompted the synthesis and study, reported here, of the 1,10-phenanthroline analogue, $[\text{Fe}_2(\text{imid})_4(\text{phen})]_x$, **1**. In this study we fully characterize the extended structure of **1**, and the magnetic ordering at low temperature.

2. Experimental

2.1. Synthesis

Ferrocene (0.30 g, 1.6 mmol), imidazole (0.2 g, 2.9 mmol) and anhydrous 1,10-phenanthroline (0.15 g, 0.8 mmol) were placed in a Carius tube under a dry dinitrogen atmosphere, which was sealed under vacuum. The tube was heated at 130 °C for 4 days, then

* Corresponding authors.

E-mail addresses: tim_storr@sfu.ca (T. Storr), w.reiff@neu.edu (W.M. Reiff), storr@chem.ubc.ca (A. Storr), thompson@chem.ubc.ca (R.C. Thompson).

opened under a dry dinitrogen atmosphere. Following extraction of excess starting materials with acetonitrile and xylene solvents, the product was isolated as dark blue/brown moisture sensitive crystals suitable for X-ray crystallographic analysis. Yield ~40%. *Anal. Calc.* for $C_{24}H_{20}Fe_2N_{10}$: C, 51.5; H, 3.6; N, 25.0. *Found*: C, 51.8; H, 3.7; N, 25.3%.

2.2. Physical measurements

Thermal gravimetric analysis (TGA) was done over the temperature range 35 °C to 800 °C using a TA Instruments TA 2000 system with a TGA 51 unit. Powdered samples (~10 mg) were heated in a stream of dinitrogen at a rate of 10 °C min⁻¹.

Table 1
Selected crystallographic data for **1**.

Chemical formula	$C_{24}H_{20}Fe_2N_{10}$
Formula mass	560.20
Crystal system	monoclinic
<i>a</i> (Å)	9.2363(9)
<i>b</i> (Å)	26.665(3)
<i>c</i> (Å)	10.3514(12)
α (°)	90.00
β (°)	107.041(4)
γ (°)	90.00
Unit cell volume (Å ³)	2437.5(4)
<i>T</i> (K)	173(1)
Space group	<i>P</i> 21/ <i>c</i>
No. of formula units per unit cell, <i>Z</i>	4
Radiation type	Mo $K\alpha$
Absorption coefficient, μ (mm ⁻¹)	1.225
No. of reflections measured	31343
No. of independent reflections	5805
<i>R</i> _{int}	0.0590
Final <i>R</i> ₁ values (<i>I</i> > 2 σ (<i>I</i>))	0.0355
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.0715
Final <i>R</i> ₁ values (all data)	0.0600
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0767
Goodness of fit (GOF) on <i>F</i> ²	1.052

DC Magnetic susceptibility measurements were made on powdered samples utilizing a Quantum Design (MPMS) SQUID magnetometer. The sample holder and details regarding the use of the equipment have been described elsewhere [30]. Magnetic susceptibilities were corrected for the background signal of the sample holder and for diamagnetic susceptibilities of all atoms ($-142 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$). DC susceptibilities were measured from 2 K to 300 K at 10 000 and 500 G. Field-cooled, zero-field-cooled, and remnant DC magnetization measurements were made at an applied field of 50 G and are reported over the temperature range 2–25 K. Magnetic hysteresis was examined by cycling the applied field between +55 000 and –55 000 G at 2.5 and 5 K. The data are reported on a per mole metal basis.

The Mössbauer spectra of powdered samples were determined using a conventional constant acceleration spectrometer operated in multi-channel scaling mode. The gamma ray source (Du Pont-Merck Co.) consisted of 51.5 mCi of Co^{57} in a rhodium metal matrix that was maintained at ambient temperature. The spectrometer was calibrated using a 6-micron thick natural abundance iron foil. Isomer shifts are reported relative to the center of the magnetic hyperfine pattern of the latter foil taken as zero velocity. The line widths of the inner-most pair of $\Delta M_I = \pm 1$ transitions of the latter Zeeman pattern were reproducibly determined to be 0.214 mm/s. Sample temperature variation was achieved using a standard exchange gas liquid helium cryostat (Cryo Industries of America, Inc.) with temperature measurement and control based on silicon diode thermometry in conjunction with a 10 micro ampere excitation source (Lakeshore Cryotronics, Inc). Spectra were fit to unconstrained Lorentzians using the program Fityk [31].

X-ray crystallographic studies were performed on a crystal of $C_{24}H_{20}Fe_2N_{10}$ mounted on a glass fibre. All measurements were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo $K\alpha$ radiation and the structure was solved with SIR-97 [32]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined and crystal data information is included in Table 1. Diagrams were prepared using ORTEP-3 [33].

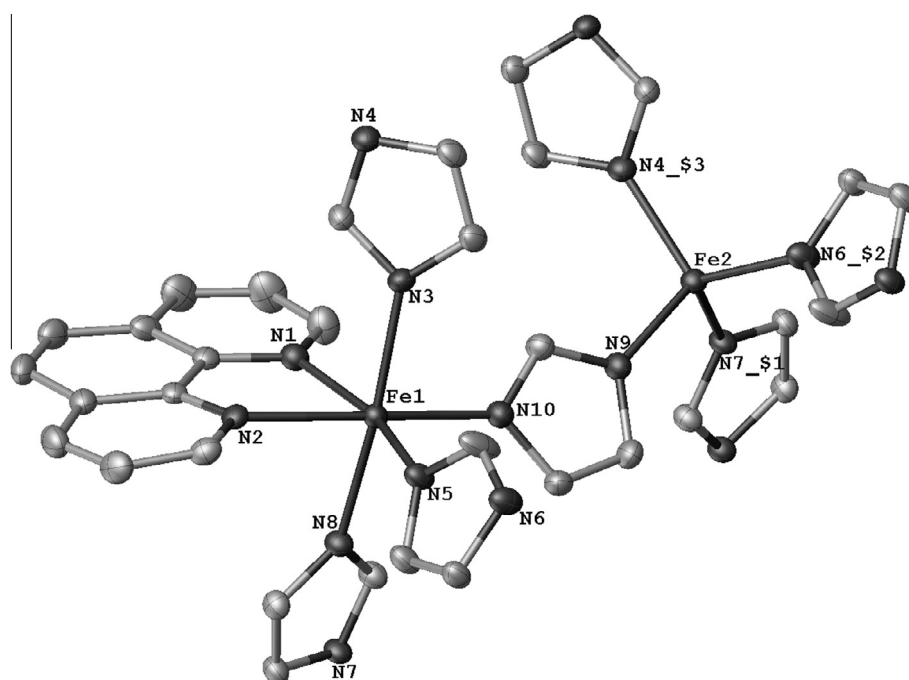


Fig. 1. ORTEP plot of **1** (50% probability) excluding hydrogen atoms showing the octahedral and tetrahedral Fe sites in the extended structure. Carbon atoms in grey

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