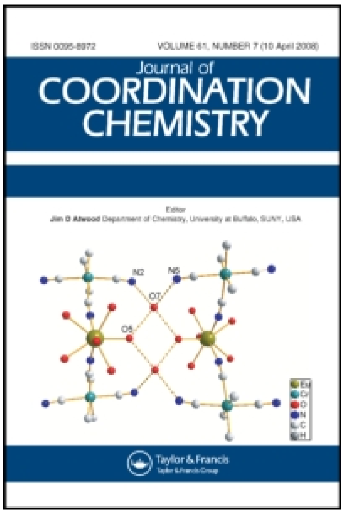

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A substitution product generated from a Mn- <i>p</i> -ferrocenylbenzoate precursor: synthesis, crystal structure and properties

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A substitution product generated from a Mn-*p*-ferrocenylbenzoate precursor: synthesis, crystal structure and properties

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A one-dimensional linear chain polymer $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(DMF)_2]\}_n$ (**1**) was obtained by substitution from a precursor polymer $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(H_2O)_2](H_2O)\}_n$ (**P1**), in which the terminal coordinated H_2O molecules are substituted by DMF, while the bridging aqua molecules are intact, so product **1** and precursor **P1** are isomorphous. Polymer **1** behaves as a 1D Heisenberg Mn(II) chain with weak intrachain antiferromagnetic interaction between the local high-spin Mn(II) ions; the exchange coupling parameters $J = -5.00\,cm^{-1}$ are larger than most of the reported di-Mn(II) complexes containing μ_2-aqua and μ_2-carboxylato units and some one-dimensional Mn(II) carboxylic polymers.

Keywords: Ferrocenylbenzoate polymer; Substitution reaction; Magnetic property

1. Introduction

Design and construction of transition-metal supramolecular structures with potential applications in catalysis, electrical conductivities, luminescent, nonlinear optical, porous materials and magnetism have attracted much interest [1–4]. The versatility of organic building blocks and diversity of coordinate units have led to a wide array of functional organic–inorganic hybrid materials [5–7], such as 4,4′-bpy and its analogues, polycarboxylates, pyridinecarboxylates and dicyanamide, etc. Ferrocenyl carboxylate as the derivative of carboxylate recently has become a building block with unique features and multiconnecting ability [8]. We are particularly interested in exploring the function-structural correlations of complexes with important topologies.

Ferrocenyl carboxylate as a functional group in metal-organic frameworks has provided a route to new functional materials. Many such complexes have been reported [8]; nearly all are prepared by the direct method. In constructing a predefined structure, utilizing precursor complexes as building blocks is one way [9]. Precursor complexes possess specific geometries, helpful in construction of a desired structure [10]. Precursor complexes need to contain facile leaving groups or coordinatively

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unsaturated metal ions. The self-assembly of these precursor complexes with appropriate solvent, adjuvant ligands, metal ions, etc. by substitution or addition reactions can result in new products, which may possess some properties of precursor complexes [11].

In order to explore the reaction ability of precursor complexes which contain facile leaving groups, we use Mn–*p*-ferrocenylbenzoate (*p*-$HOOCC_6H_4Fc$ $Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) polymer $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(H_2O)_2](H_2O)\}_n$ (**P1**) [8c] as a precursor, containing facile leaving groups (terminal coordinated H_2O molecules). Through addition of DMF, an isomorphous polymer $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(DMF)_2]\}_n$ (**1**) is obtained. The magnetic properties for **1** are discussed.

2. Experimental

2.1. *General*

All chemicals were of reagent grade obtained from commercial sources and used without further purification; *p*-ferrocenylbenzoic acid and its sodium salt were prepared according to a literature method [12]. **P1** was prepared according to reference [8c].

2.2. *Preparation of* $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(DMF)_2]\}_n$ *(1)*

Single crystals of $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(H_2O)_2](H_2O)\}_n$ (**P1**) were dissolved in 2 ml DMF and 6 ml CH_3OH was added as diffusion solvent. The mixture was kept at room temperature in the dark. About three weeks later, good quality red crystals were obtained. Yield: 46%. Anal. Calcd for $C_{40}H_{42}O_7N_2Fe_2Mn$: C, 57.92; H, 5.10. Found: C, 57.83; H, 5.19. IR (cm^{-1}, KBr): 3422s, 3091m, 1604s, 1534s, 1403s, 1180m, 1105m, 1006m, 819m, 789m, 708m, 476m.

2.3. *Physical measurements*

C, H and N analyses were carried out on a Carlo-Erba 1106 elemental analyzer. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region.

Temperature-dependent magnetic susceptibility measurements on a powdered solid sample were carried out on a SQUID magnetometer (MPMS Quantum Design) over the temperature range 300–5 K. The magnetic field applied was 500G. The observed susceptibility data were corrected for underlying diamagnetism by using Pascal's constants [13].

2.4. *X-ray crystallography*

Crystal data collection and refinement parameters for **1** are given in table 1. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with

Table 1. Crystallographic data for **1**.

Formula	$C_{40}H_{42}Fe_2MnN_2O_7$
Fw	829.40
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	46.439(9)
b (Å)	9.785(2)
c (Å)	8.2233(16)
α (°)	90
β (°)	91.32(3)
γ (°)	90
V (Å^3)	3735.9(13)
D_c (Mg m^{-3})	1.475
Z	4
μ (mm^{-1})	1.151
Reflections collected/unique	5412/3055 $R(\text{int}) = 0.0714$
Data/restraints/parameters	3055/0/242
$F(000)$	1716
R_1^a	0.0525
WR_2	0.1676
GOF on F^2	1.071
$\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ (e Å^{-3})	0.590 and −0.532

$R_1^a = \sum \| F_o| - |F_c\| / \sum |F_o| \cdot wR = \{\sum[w(F_o^2 - F_c 2)^2 / \sum[w(F_o^2)^2]]^{1/2}\}$.

Table 2. Selected bond lengths (Å) and angles (deg) for **1**.

Mn1–O1	2.092(3)	Mn1–O3	2.198(4)
Mn1–O(4)#1	2.285(2)		
O1–Mn1–O1#1	180.00(6)	O1–Mn1–O4	87.85(9)
O1–Mn1–O3	90.99(16)	O1#1–Mn1–O3	89.01(16)
O1–Mn1–O4#1	92.16(10)	O3#1–Mn1–O4	94.52(14)
O3#1–Mn1–O3	180.0(19)	O4#1–Mn1–O4	180.0(2)
O3–Mn1–O4	85.48(14)		

Symmetry transformations used to generate equivalent atoms: For **1**: #1 $-x$, $-y+1$, $-z+1$; #2 $-x$, y, $-z+3/2$.

graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A red prismatic single crystal of **1** was selected and mounted on a glass fiber. The data were collected at 291(2) K and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using the *SHELXL-97* crystallographic software package [14]. Selected bond lengths and angles are tabulated in table 2.

3. Results and discussion

3.1. *Preparation of polymer 1*

Polymer $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(H_2O)_2](H_2O)\}_n$ (**P1**) contains terminal coordinated H_2O molecules as facile leaving groups. Dissolving single crystals of **P1** in DMF gave good quality single crystals of **1**. As expected, the terminal H_2O molecules in **P1** are replaced by DMF. Since the bonds between H_2O and Mn(II) in **P1** are weak, the H_2O molecules are labile and readily substituted by DMF; DMF molecules do not displace the bridging aqua molecules in **P1**, so the framework is unchanged.

Polymer **1** is stable in air, insoluble in common solvents such as CH_3OH, CH_2Cl_2, C_2H_5OH, and CH_3CN and slightly soluble in polar solvents such as DMSO and DMF.

3.2. *Crystal structure of $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(DMF)_2]\}_n$ (1)*

Polymers **1** and **P1** are isomorphous; **1** also crystallizes in the space group C2/c. X-ray diffraction analysis reveals that the Mn(II) ions are bridged by μ_2-H_2O molecules forming one-dimensional linear chains (figure 1). The coordination geometry around

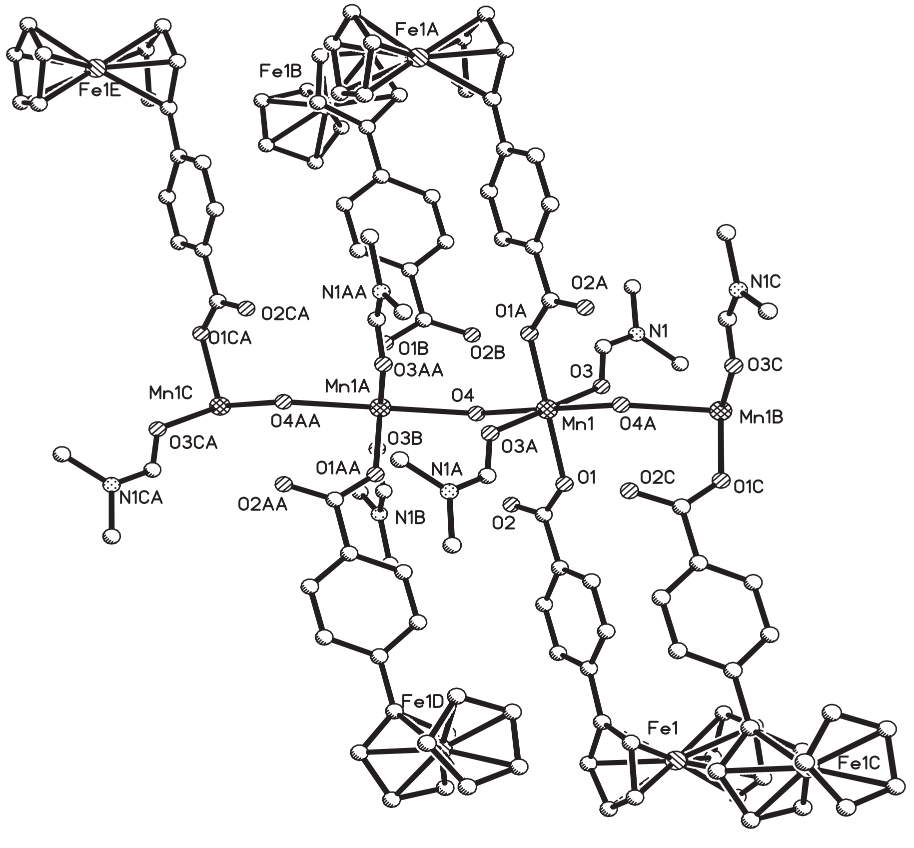

Figure 1. ORTEP drawing with atom labeling scheme of the one-dimensional chain polymer $\{[Mn(OOCC_6H_4Fc)_2(\mu_2\text{-}OH_2)(DMF)_2]\}_n$ (**1**). (Hydrogen atoms and solvent molecules are omitted for clarity).

Mn1 is a slightly distorted octahedron. The Mn(II) ions are coordinated by six O atoms from two terminal monodentate $FcC_6H_4COO^-$ units (O1, O1A), two DMF molecules (O3, O3A), and two bridging μ_2-H_2O molecules (O4, O4A). The equatorial plane, O1, O1A, O3 and O3A, is an ideal plane in which O1–Mn1–O1A and O3–Mn1–O3A bond angles are 180°, the axial angle O4–Mn1–O4A also is 180°, and the other bond angles around the center Mn(II) ion range from 85.48(14) to 94.52(14)°. The Mn1–O1 bond distance is nearly equal to that of $Mn–O_{(FcC6H4COO-)}$ in **P1**; the Mn1–O3 bond distance (2.198(4) Å) is much longer than the corresponding Mn–O(H_2O) distance in **P1**. The bridging Mn1–O4 (2.285(2) Å) distance is a little shorter than that of the corresponding Mn–O bond (2.311(3) Å) in **P1**, and still a little longer than the corresponding Mn–O distances of some (μ_2-aqua)-(μ_2-carboxylato)-bridged manganese polymers: $[Mn_2(NTC)(H_2O)_2]_n$ (NTC = 1,4,5,8-naphthalenetetracarboxylate anion) (Mn–O distance is 2.2204(14) Å) [15], as well as $[Mn_2(\mu_2\text{-}OH_2)(\mu_2\text{-}OAc)_2(Bzim)_4(OAc)_2]$ (Bzim = benzimidazole) (2.227(2) Å) and $[Mn_2(\mu_2\text{-}OH_2)(\mu_2\text{-}OAc)_2(Im)_4(OAc)_2]$ (Im = imidazole) (2.246(2) Å) [16]. The 1-D···Mn···O···Mn···O···chain is not strictly linear, but displays some twist with Mn1–O4–Mn1A 128.2°, bigger than that of **P1** (124.2°) and $[Mn_2(NTC)(H_2O)_2]_n$ (109.24°) [15].

The intra-chain Mn···Mn distance is 4.112 Å, a little longer than that of **P1** (4.085 Å), but still significantly shorter than that of $[Mn(\mu_2\text{-}OOCC_6H_4Fc)_2(phen)]_n$ (phen = phenanthroline) (Mn···Mn distance = 4.817 Å) [8c]. It is also longer than the Mn···Mn distances in some other (μ_2-aqua)bis(μ_2-carboxylato) di-Mn(II) complexes, such as $[Mn_2(NTC)(H_2O)_2]_n$ (3.635 Å) [15], $[Mn_2(H_2O)(piv)_4(Me_2bpy)_2]$ (3.5950(9) Å) (piv = pivalate), and $[Mn_2(H_2O)(OAc)_4(tmeda)_2]$ (tmeda = N,N,N′,N′-tetramethylenediamine) (3.621(2) Å) [17]. The inter-chain Mn···Mn distance is 9.827 Å. The spatial configuration and steric effect of the ferrocene group make all the ferrocene moieties parallel, alternatively, with each other along the chains. The well-separated infinite chains are parallel with each other and packed along *a* (figure 2).

Addition of DMF only resulted in the substitution of the terminal coordinated aqua molecules in **P1**, and the Mn(II) ions are still connected by the μ_2-aqua bridge retaining the framework.

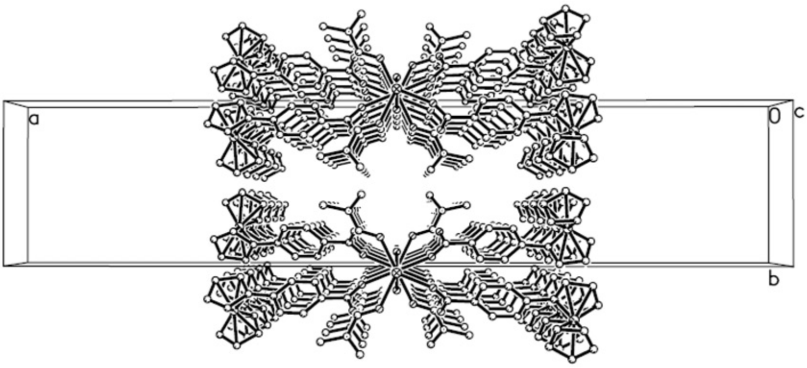

Figure 2. The solid state structure of **1**.

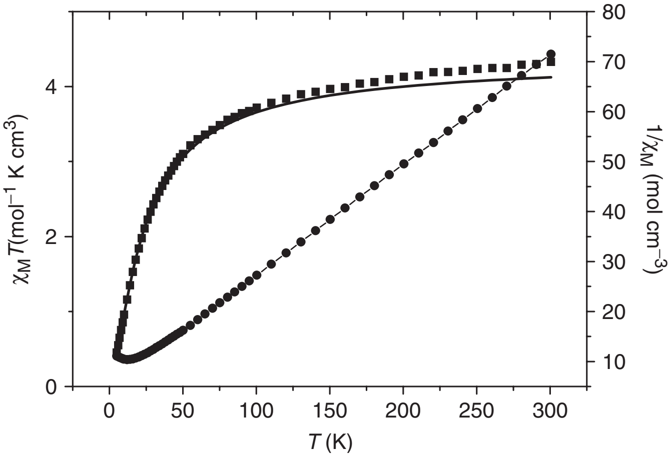

Figure 3. The temperature dependence of the product of the molar magnetic susceptibility of **1** over the temperature range 300–5 K at 500 G; the experimental data are plotted as the thermal variation of the reciprocal susceptibility $\chi_M{}^{-1}$.

3.3. *Magnetic property*

The magnetic susceptibility of **1** was measured in the 5–300 K temperature range and shown as $\chi_M{}^{-1}$ and $\chi_M T$ *versus* T plots in figure 3.

The $\chi_M T$ value at room temperature (4.32 cm^3 K mol^{-1}) is close to the expected value of an uncoupled Mn(II) ($g = 2.0$, $\chi_M T = 4.38$ cm^3 K mol^{-1}), continuously decreasing upon cooling to 0.452 cm^3 K mol^{-1} at 5 K. This indicates an antiferromagnetic interaction between Mn(II) ions for **1**. The inverse susceptibility plot is a linear function of temperature (figure 3) with data closely following a Cure–Weiss law $\chi_M = C/(T - \theta)$ with $C = 4.69$ and $\theta = -31.11$ K. The negative value of θ confirm the antiferromagnetic exchange between Mn(II) ions. The close approximation between the experimental moment of **1** (5.8μ_B) and the theoretical spin-only value for $S = 5/2$ ($\mu_{eff} = 5.9\mu_B$) suggests that the polymer contains largely isolated spins.

Mn(II) has a large quantum spin number ($S = 5/2$) and a small spin anisotropy due to negligible spin-orbit coupling, so the data can be analyzed assuming a classical isotropic Heisenberg pairwise interaction between Mn(II) ions in a linear chain.

We fitted the data of **1** using the analytical expression derived by Fisher for an infinite chain model ($H = -2J\sum_{i=1}^{n} S_i \cdot S_{i-1}$) of classical spin scaled to $S = 5/2$ (equation (1)) [18].

$$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT} \times \frac{(1+u)}{(1-u)} \tag{1}$$

where

$$u = \coth\frac{|J|S(S+1)}{kT} - \frac{kT}{|J|S(S+1)}.$$

The best least-squares fits of the experimental data of $J = -5.00\,\mathrm{cm}^{-1}$ and $g = 2.00$ with agreement factor $R = 2.68 \times 10^{-3}$ indicates antiferromagnetic exchange interactions between Mn(II) ions in **1**.

The magnetic exchange pathway between Mn(II) ions in **1** is also supported by the μ_2-aqua bridge forming a Mn $\cdots$ O $\cdots$ Mn pathway, similar to **P1**. The magnetic exchange parameter of **1** is a little weaker than that of **P1** ($J = -5.20\,\mathrm{cm}^{-1}$). This may be due to the small structural differences affecting the Mn–O bond lengths and Mn–O–Mn bond angles. In **1** the Mn1–O4–Mn1A (128.2°) angle is bigger than that of **P1** (124.2°), resulting in a longer intra-chain Mn$\cdots$Mn distance (4.112 Å for **1**) than for **P1** (4.085 Å). The magnetic exchange parameter J is larger than that of another Mn-*p*-ferrocenylbenzoate polymer, $[\mathrm{Mn}(\mu_2\text{-OOCC}_6\mathrm{H}_4\mathrm{Fc})_2(\mathrm{phen})]_n$ (phen = phenanthroline) ($J = -3.25\,\mathrm{cm}^{-1}$), and much stronger than some carboxylate bridged dinuclear-Mn(II) complexes [16,17,19] containing μ_2-aqua and μ_2-carboxylato bridges and one-dimensional Mn(II) carboxylic polymers [15,20,21]. Shorter Mn $\cdots$ Mn distances bridged by oxygen provide stronger antiferromagnetic exchange interaction than for carboxylato bridge $[|J_{(\mu\text{-O})}| > |J_{(\mu\text{-OCO})}|]$ [22]. The magnetic exchange pathways have a great influence on the intensity of the magnetism.

Supplementary materials

The CCDC number is 662539. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 12 23 33 6033 or E-mail: deposit@ccdc.cam.ac.uk).

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