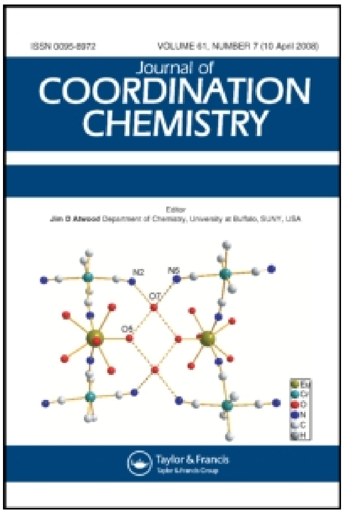

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# Synthesis, crystal structure and magnetism of [Mn(tfbdc)(MeOH)$_4$] (tfbdc = tetrafluoroterephthalate)

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# Synthesis, crystal structure and magnetism of $[Mn(tfbdc)(MeOH)_4]$ (tfbdc = tetrafluoroterephthalate)

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$[Mn(tfbdc)(MeOH)_4]$ was synthesized by reaction of tetrafluoroterephthalic acid with manganese(II) perchlorate hexahydrate in methanol. The complex was characterized by elemental analysis, IR spectra, magnetism, and X-ray single crystal structure analysis. This complex crystallizes in the monoclinic system with space group *C2/c*. Mn(II) has a distorted octahedral geometry coordinated by two oxygens from two tetrafluoroterephthalate (tfbdc) and four MeOH molecules. Each tfbdc ligand bridges two Mn(II) ions in end-to-end fashion, forming a zigzag chain. These chains are connected by hydrogen bonds, forming a 2-D supramolecular network. Magnetic susceptibility data from 300–1.8 K show that there is a weak antiferromagnetic exchange between Manganese(II) ions.

*Keywords*: Manganese(II); Coordination polymer; Tetrafluoroterephthalatic acid; Crystal structure; Magnetic property

## 1. Introduction

Metal carboxylates have diversity of binding modes of carboxylates, a wide range of structures and potential applications in separation, gas storage, heterogeneous catalysis, and molecule-based materials [1]. In particular, multibenzenecarboxylates are good building blocks in the design of metal–organic materials with desired topologies owing to their rich coordination modes. In spite of the rich coordination chemistry exhibited by 1,3-difluoroterephthalatic acid, 1,4-benzenedicarboxylic acid, bromobenzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid [2–13], studies on tetrafluoroterephthalatic acid ($H_2$tfbdc) are less reported. By carefully controlling the reaction conditions, we have found $H_2$tfbdc is also a versatile building block for construction of metal–organic complexes through complete or partial deprotonation of its carboxyl groups, and a series of interesting structures have been obtained [14–19]. With the aim of understanding the coordination chemistry of $H_2$tfbdc, we recently began to study

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assembly reactions of $H_2$tfbdc with metal ions *via* general solution synthetic methods [20]. In particular, we are interested in such reactions in the presence of auxiliary ligands. Considering the special bioactivity of manganese carboxylate complexes [21] along with their interesting magnetic properties, we focused our work on the Mn(II) and $H_2$tfbdc system. Herein we report a 1-D coordination polymer [Mn(tfbdc)(MeOH)$_4$], obtained from assembly of Mn(II) and $H_2$tfbdc in the presence of hexamethylenetetramine (hmt).

## 2. Experimental

### 2.1. *Material*

Tetrafluoroterephthalatic acid ($H_2$tfbdc), manganese(II) perchlorate hexahydrate, hmt, and solvents were of reagent grade without purification before use.

### 2.2. *Physical measurements*

Elemental analysis (C, H) was performed on a Perkin-Elmer 2400 Series II element analyzer. FTIR spectra were recorded on a Nicolet 460 spectrophotometer as KBr pellets. Variable-temperature magnetic susceptibilities were determined on a Quantum Design SQUID magnetometer with a 2000 Oe magnetic field from 1.8–300 K. Diamagnetic corrections were made using Pascal's constants.

### 2.3. *Synthesis of [Mn(tfbdc)(MeOH)$_4$]*

A 3 mL anhydrous methanol solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.0615 g, 0.17 mmol) was slowly added to a 5 mL anhydrous methanol solution containing $H_2$tfbdc (0.0405 g, 0.17 mmol) and hmt (0.0042 g, 0.03 mmol) to afford a colorless solution. Upon slow evaporation of the solvent at room temperature for 5 days, colorless block crystals were obtained. Anal. Calcd for $C_{12}H_{16}F_4MnO_8$ (%): C, 34.38; H, 3.85. Found: C, 34.30; H, 3.92. IR data (cm$^{-1}$, KBr pellet): 3285 cm$^{-1}$ (s, br), 2852(s), 2495(m), 2381(m), 1604(s), 1535(s), 1475(s), 1416(s), 1387(s), 1264(s), 1070(s), 995(s), 934(s), 866(s), 804(s), 775(s), 740(s), 708(s), 659(s), 627(s), 514(s), 478(s), 438(m).

### 2.4. *X-ray crystallography*

Single-crystal X-ray diffraction of the title complex was carried out with a Bruker Smart Apex CCD diffractometer at 296(2) K. Intensities of reflections were measured using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.071073$ nm) with the $\psi$–$\omega$ scan mode in the range $2.66^\circ < \theta < 27.62^\circ$. The structure was solved by direct methods using SHELXS-97 [22] and refined by full-matrix least-squares on $F^2$ with the SHELXS-97 program package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analyses are summarized in table 1; selected bond lengths (nm) and angles (°) are given in table 2, and hydrogen bond parameters are presented in table 3.

Table 1. Crystal structure parameters of the title complex.

| | |
|---|---|
| Formula | $C_{12}H_{16}F_4MnO_8$ |
| Formula weight | 419.19 |
| Color | Colorless |
| Crystal system | Monoclinic |
| Space group | $C2/c$ |
| Scan type | $\psi$–$\omega$ |
| Unit cell dimensions (nm, °) | |
| $a$ | 0.9164(3) |
| $b$ | 1.4082(5) |
| $c$ | 1.3641(4) |
| $\beta$ | 95.433(4) |
| $V(\mathrm{nm}^3)$ | 1.7524(10) |
| $Z$ | 4 |
| Temperature (K) | 296(2) |
| Calculated density ($\mathrm{g\,cm^{-3}}$) | 1.589 |
| $\mu$(Mo-K$\alpha$) ($\mathrm{mm^{-1}}$) | 0.829 |
| Limiting indices | $-11 \leq h$s11; $-17 \leq K \leq 18$; $-17 \leq l \leq 17$ |
| $F(000)$ | 852 |
| Crystal size ($\mathrm{mm}^3$) | $0.24 \times 0.22 \times 0.20$ |
| $\theta$ range for data collection (°) | 2.66 to 27.62 |
| A total reflections collected | 7282 |
| Independent reflections | 2025 ($R_{\mathrm{int}} = 0.0265$) |
| Observed reflections | 1638 |
| $\mu$(Mo-K$\alpha$) ($\mathrm{mm^{-1}}$) | 0.071073 |
| Goodness-of-fit on $F^2$ | 1.040 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0290, 0.0749 |
| $R_1$, $wR_2$ (all data) | 0.0412, 0.0818 |

Table 2. Selected bond lengths (nm) and angles (°) of the complex.

| | | | |
|---|---|---|---|
| Mn1–O2 | 0.21347(14) | Mn1–O4A | 0.21866(14) |
| Mn1–O4 | 0.21866(14) | Mn1–O2A | 0.21347(14) |
| Mn1–O3 | 0.21969(14) | Mn1–O3A | 0.21969(14) |
| O2–Mn1–O2A | 91.11(9) | O2–Mn1–O4A | 89.62(6) |
| O2A–Mn1–O4A | 176.01(5) | O2–Mn1–O4 | 176.01(5) |
| O2A–Mn1–O4 | 89.62(6) | O4A–Mn1–O4 | 89.93(8) |
| O2–Mn1–O3A | 91.15(5) | O2A–Mn1–O3A | 86.92(5) |
| O4A–Mn1–O3A | 89.14(6) | O4–Mn1–O3A | 92.81(6) |
| O2–Mn1–O3 | 86.92(5) | O2A–Mn1–O3 | 91.15(5) |
| O4A–Mn1–O3 | 92.81(6) | O4–Mn1–O3 | 89.14(6) |
| O3A–Mn1–O3 | 177.25(7) | | |

Symmetry code: A: $-x+1$, $y$, $-z+1/2$.

Table 3. Hydrogen bond distances and angles in the complex.

| D–H $\cdots$ A | D–H (nm) | H $\cdots$ A (nm) | D $\cdots$ A (nm) | D–H $\cdots$ A (°) |
|---|---|---|---|---|
| O4–H4A $\cdots$ O1$^{\mathrm{C}}$ | 0.0820 | 0.1880 | 0.2695(2) | 174.50 |
| O3–H3A $\cdots$ O1 | 0.0820 | 0.1910 | 0.2607(19) | 159.50 |

Symmetry code: C: $x$, $-y+1$, $z-1/2$.

## 3. Results and discussion

### 3.1. *Crystal structure description of [Mn(tfbdc)(MeOH)$_4$]*

Figure 1 represents the coordination polymeric zigzag chain with atom numbering. The tfbdc attached to Mn(II) atom is monodentate with end-to-end bridging of manganese centers. Four methanols are also coordinated to the metal. The coordination environment of each manganese(II) is distorted octahedral geometry, with equatorial positions with two tfbdc ligands [Mn1–O2A = 0.21347(14) nm and Mn1–O2 = 0.21347(14) nm] and two methanols [Mn1–O4A = 0.21866(14) nm and Mn1–O4 = 0.21866(14) nm]. Apical positions are occupied by O3, O3A of methanol [Mn1–O3 = 0.21969(14) nm and Mn1–O3A = 0.21969(14) nm]. The Mn–O bond distance of tfbdc is shorter than methanol. The bond angle of O3–Mn1–O3A (axial positions) is 177.25(7)°, indicating a distorted octahedral geometry. The distance between Mn1–Mn1A is 1.1553 nm. Each tfbdc bridges two Mn(II) ions in end-to-end fashion, forming a zigzag chain along the *b*-axis. This 1-D zigzag chain is quite similar to that of Mn($C_5NH_4$–2–$CH_2OH$)$_2$($C_6F_5CO_2$)$_2$ reported by Ito and Onaka [15]. Formation of hydrogen bonds between zigzag chains [O4–H4A ⋯ O1* = 0.2695(2) nm and O3–H3A ⋯ O1 = 0.2607(19) nm], as shown in figures 2 and 3, leads to a 2-D network. The shortest Mn(II) ⋯ Mn(II) distance between the closest neighbors in the same layer *via* hydrogen bonds is 0.6857 nm.

### 3.2. *Infrared spectrum*

The IR spectrum of [Mn(tfbdc)(MeOH)$_4$] shows a strong absorption band in the 3600–3000 cm$^{-1}$ region corresponding to $\nu$(OH) of coordinated methanol. The 2852 cm$^{-1}$ absorption is from $\nu$($CH_3$) of methanol. All carboxylic groups are deprotonated indicated by no absorption around 1730 cm$^{-1}$ for a protonated carboxylic group.

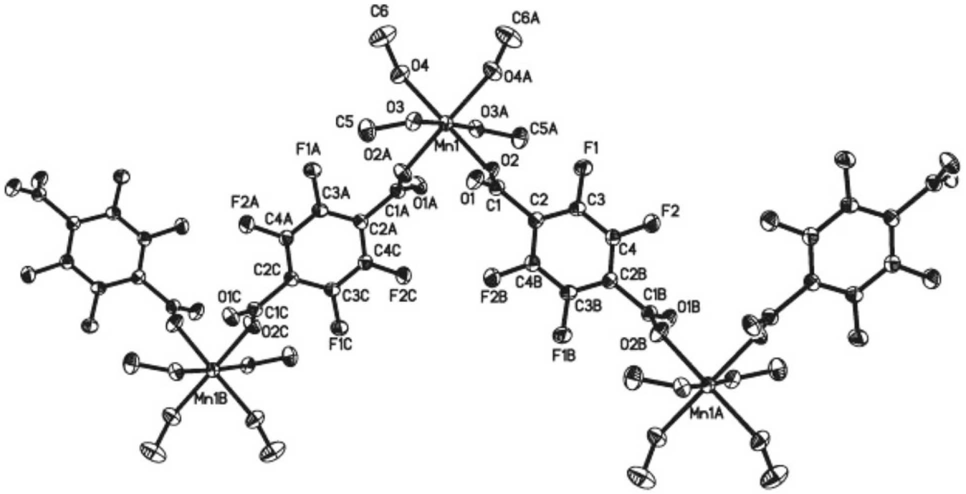

Figure 1. Molecular structure of the complex, with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity). Symmetry code: A: $-x+1$, $y$, $-z+1/2$; B: $-x+1/2$, $-y+3/2$, $-z+1$; C: $x$, $-y+1$, $z-1/2$.

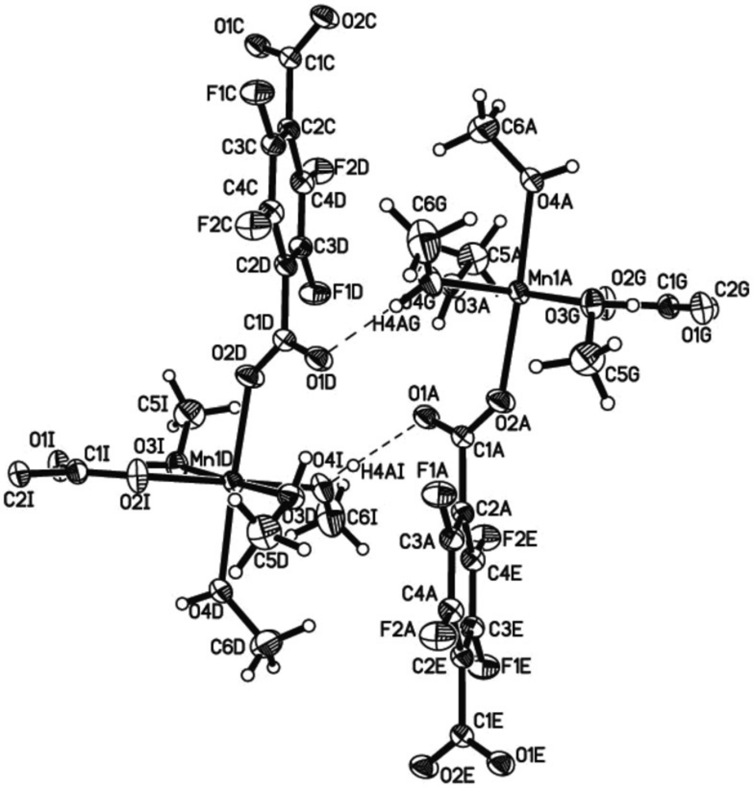

Figure 2. Structure of the complex indicating hydrogen bonds.

Strong peaks at 1604, 1416, and 1387 $\mathrm{cm}^{-1}$ are the $\nu_{\mathrm{as}}$(OCO) and $\nu_{\mathrm{s}}$(OCO) stretching modes of coordinated tfbdc, while strong absorption at *ca* 708 $\mathrm{cm}^{-1}$ is the $\delta$ (OCO) of tfbdc. The shifts of 217 $\mathrm{cm}^{-1}$ and 188 $\mathrm{cm}^{-1}$ between $\nu_{\mathrm{as}}$(OCO) and $\nu_{\mathrm{s}}$(OCO) indicate that the tfbdc ligands are monodentate and bridging mode [23, 24] as proved by the X-ray crystal structure analysis of $[\mathrm{Mn(tfbdc)(MeOH)_4}]$.

### 3.3. *Magnetic property*

Variable-temperature magnetic susceptibility measurements of a crystal sample were performed in the range of 300 K to 1.8 K with a Quantum Design SQUID magnetometer. Global antiferromagnetic behavior is evident from the magnetic measurements shown in figure 4. The variation of $1/\chi_{\mathrm{M}}$ with temperature follows the Curie–Weiss law. The corresponding Curie constant ($C$) and Weiss constant ($\theta$) are 2.08 $\mathrm{emu\,K\,mol^{-1}}$ and −5.872 K, respectively. The $\chi_{\mathrm{M}}$ value is 0.0119 $\mathrm{emu\,mol^{-1}}$ at 300 K. The $\chi_{\mathrm{M}}T$ product is 3.57 $\mathrm{emu\,K\,mol^{-1}}$ at 300 K, smaller than the value expected for spin-only Mn(II) (4.376 $\mathrm{emu\,mol^{-1}\,K}$ with $g = 2.0$). The $\chi_{\mathrm{M}}T$ value is almost invariable to 100 K (1.986 $\mathrm{emu\,mol^{-1}\,K}$) and gradually decreases from room temperature to 0.489 $\mathrm{emu\,mol^{-1}\,K}$ at 1.8 K. The shape of these curves is characteristic of weak antiferromagnetic interactions between the Mn(II) centers in the complex.

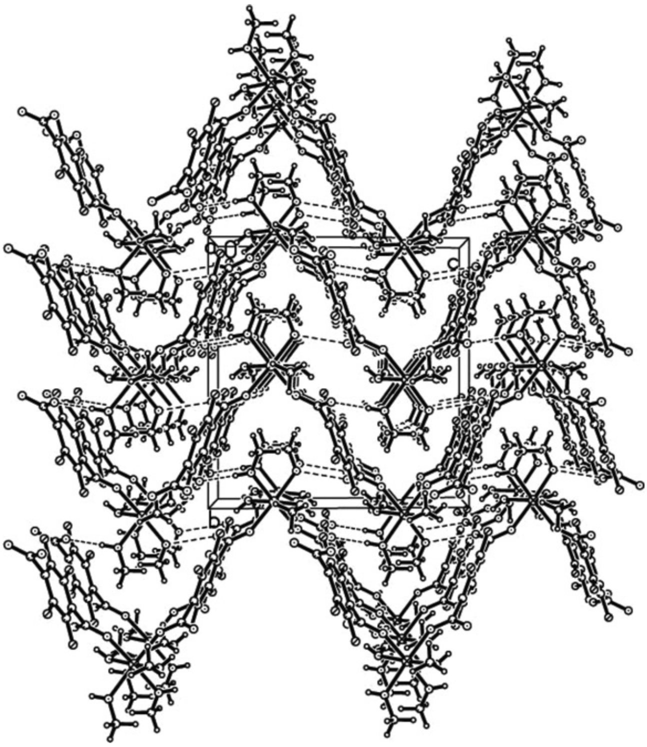

Figure 3. The molecular crystal cell packing of the complex viewed along the *a*-axis, dash lines indicate hydrogen bonds between the layers.

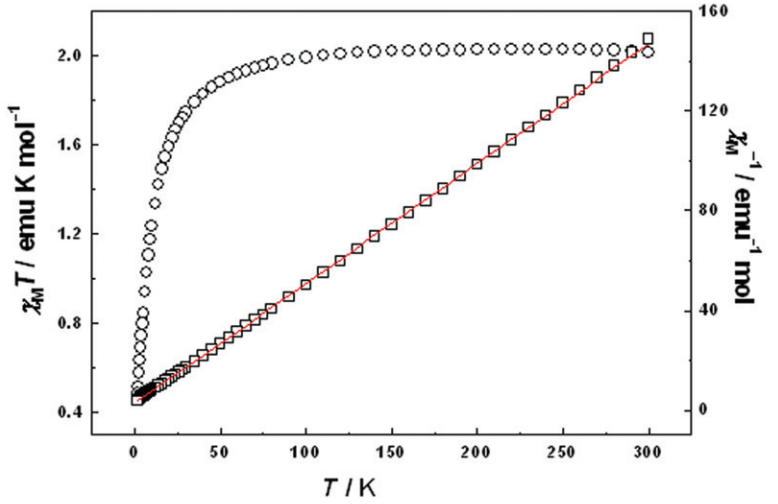

Figure 4. Temperature dependence of the reciprocal of molar magnetic susceptibility ($1/\chi_M$) (□) and $\chi_M T$ (○) for the title complex. The solid line (—) shows the best fit.

## 4. Conclusion

A 1-D zigzag chain coordination polymer [Mn(tfbdc)(MeOH)$_4$] was prepared via reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ with $H_2$tfbdc in the presence of hmt. Antiferromagnetic exchange exists between Mn(II) ions.

## Supplementary material

CCDC 670461 for [Mn(tfbdc)(MeOH)$_4$] contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internet) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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