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Crystal Structure And Magnetic Properties Of An One-Dimension Heptacoordinated Manganese Helical Chain Polymer Using Fumaratoligand As Bridging Spacer


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ABSTRACT

An infinite helical chain coordination polymer $[Mn_2(\text{fumarate})(\text{bipy})_2(\text{H}_2\text{O})_2]_m$ (**1**) (bipy = 2,2'-bipyridine) have been prepared and characterized by means of X-ray analysis and magnetic measurements. The heptacoordinated manganese(II) ion displays a distorted pentagonal bipyramidal configuration by virtue of two nitrogen atoms from 2,2'-bipyridine, four oxygen atoms from two different fumarate ligands, and one oxygen atom of a coordinated water molecule. Each manganese center is bridged by bis-bidentate fumarate ligands to yield infinite helical chains structure along b axis. The magnetic data for **1** has been analysed and interpreted in terms of Heisenberg chain model corrected by a mean molecular field. The fitting parameters obtained for J, g and zJ' are -0.57, 1.99, and -0.08, respectively, indicating the existence of weak antiferromagnetic intrachain and interchain interactions. The long-distance magnetic interactions through bridging fumaratoligands is discussed. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Heptacoordinated manganese(II);
One-dimension helical Chain Polymer;
Bridging fumaratoligand;
Long-distance magnetic interaction.

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INTRODUCTION

In the past decade molecular-based magnetic materials with paramagnetic metal ions, where bridging ligands act as a superexchange pathway between the metal centers, have been widely studied both experimentally and theoretically^[1,2]. Understanding the magnetic interactions between paramagnetic metal ions and bridging ligand is of major interest in this field. The key to the fabrication of such magnetic materials is the selection of appropriate bridging ligands capable of mediating magnetic interaction and coordination geometries of metal ions. Previous reports have revealed that dicarboxylic acids are good candidates as bridging ligands and frequently used as magnetic superexchange pathways between the metal ions, due to their versatile carboxylate-bridging coordination modes capable of transmitting magnetic coupling interactions to different degrees^[3,4].

As an unsaturated dicarboxylate anions, fumarate can interlink metal atoms to form the coordination polymers with different framework structures^[5-8] owing to its versatile coordination modes (SCHEME 1). In the course of our study on the molecular-based magnetic complexes, we pay special attention to the one-dimensional (1D) magnetic systems which are preferable for development of the suitable theoretical models required for better interpretation of the magnetic properties of extended coordination polymers. Recently we used the first principle method and quantum transfer matrix renormalization group method to study the magnetic properties of an one-dimensional fumarate-bridged Cu(II) chain-like polymer^[9,10]. In this Cu(II) coordination polymer^[5a], the fumarate ligand acts as a monoatomic bridging mode to form a short Cu-O-Cu magnetic superexchange pathway. Our analysis of spin magnetic moments along the fumarate ligand shows that the coupling between the carbon atoms is also ferromagnetic. Considering intrachain ferromagnetic and the weak interchain antiferromagnetic interaction, we proposed a two-leg spin ladder model to well describe the magnetic behavior of the copper(I) complex. In this report we obtained a rare binuclear heptacoordinated manganese(II) complex with an one-dimension helical chain, $[\text{Mn}_2(\text{u-C}_4\text{H}_2\text{O}_4)(\text{bipy})_2(\text{H}_2\text{O})_2]$, to further investigate the magnetic properties and the magnetostructural correction between fumarate and

metal atoms.

EXPERIMENTAL

Materials and general methods

All chemicals were of reagent grade and were used as received. Elemental analyses were performed with a Vario EL III CHNOS elemental analyzer. IR spectra were recorded on a Perkin-Elmer system FT-IR 2000 spectrophotometer in the form of KBr pellets. The magnetic measurement was carried out on a polycrystalline sample with a quantum design MPMS-7 SQUID magnetometer in a field of 1T diamagnetic corrections were made with pascal's constants for all constituent atoms.

Synthesis

Manganese fumarate was prepared in situ at 0°C by mixing disodium fumarate(1mmol) and manganese (II) chloride dihydrate(1mmol), dissolving in 20ml distilled water. After stirring the mixture for 1 hour, a methanolic solution(10ml) of 2,2'-bipyridine (1mmol) was slowly added with continuous stirring. The reaction mixture was filtered out and the filtrate was kept in the refrigerator. The pale yellow crystals suitable for X-ray diffraction analysis were obtained after a week. Aanal.Calcd: C,48.95; H-3.5; N-8.2.Found: C,48.4; H-3.26; N-8.08. IR: $\nu(\text{COO}^-)$, 1580.75, 1389.37 cm^{-1} ; $\nu(\text{O-H})$ 3354.82 cm^{-1}

X-ray crystallography

A suitable single crystal of the complex with the dimensions of 0.60×0.40×0.20 mm was carefully selected and glued to thin glass fibers with epoxy resin. Data for the complex was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The unit cell parameter and orientation matrix were determined by least-squares refinements with the setting angles from 1.75° to 25° and 2.13° to 26.00° Cell parameters were retrieved using SMART software and refined with SMART on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. The structures was solved by direct methods and refined by full-matrix least-squares methods on F² using the SHELXS-97 and SHELXL-97 programs^[11,12]. All non-hydrogen

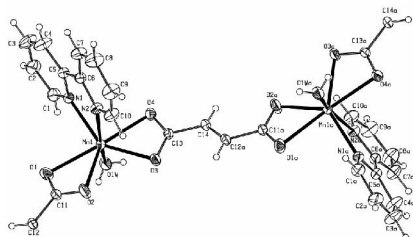


Figure 1 : ORTEP and atom labeling diagram for $[\text{Mn}_2(\text{fumarate})(\text{bipy})_2(\text{H}_2\text{O})_2]_m$

atomic positions were located in difference fourier maps and refined anisotropically. The corresponding crystallographic and refinement data were listed in TABLE 1. Selected bond lengths and angles of the complex were included in TABLE 2.

Structure description

The title complex is a one-dimension helical polymeric chain made up of dinuclear $\text{Mn}_2(\text{u-C}_4\text{H}_2\text{O}_4)(\text{bipy})_2(\text{H}_2\text{O})_2$ units linked together by fumarate bridging ligands (Figures 1 and 2). One of the independent structure units is shown in figure 1. together with the atom-numbering scheme.

As shown in figure 1, each Mn atom is hepta-coordinated which is different from other two reported fumarate-Mn complexes^[7]. Each manganese atoms in the title complex have a distorted pentagonal bipyramid coordination environment, being coordinated by two nitrogen atoms from 2,2'-bipyridine,

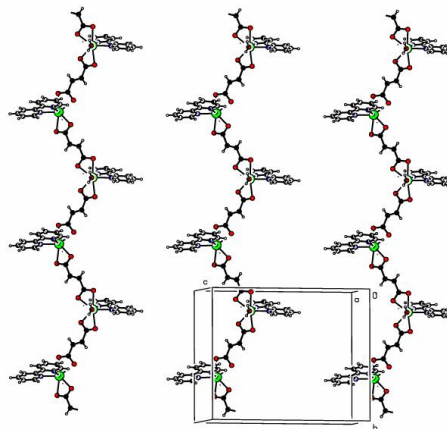


Figure 2: The extended 1D helical chain structure in $[\text{Mn}_2(\text{fumarate})(\text{bipy})_2(\text{H}_2\text{O})_2]_m$

four oxygen atoms from two different fumarate ligands, and one oxygen atom of a coordinated water molecule. The four oxygen donors O(1), O(2), O(3), O(4) and N(1) atoms defined an approximate equatorial plane and the manganese center is 0.042 Å out of this plane. The four Mn–O bond distances are different from each other to some extent (TABLE 2), with that to O2 being particularly short (2.2471(14) Å). Unexpectedly, the shortest bond distance is that to the coordinated water molecule (Mn1–O1w 2.1686(15) Å). The carboxyl oxygen atoms O1, O2 chelate to central manganese with an O(1)–Mn(1)–O(2) bond angle of 55.62(5)°, while O3, O4 of the other carboxyl group bind another manganese center with an O(1)–Mn(1)–O(2) bond angle of 56.38(4)°. The two bond angles in the equatorial plane deviate from 72° because they are restricted by the four-membered chelate rings. The Mn–N average distance is 2.2734 Å in normal range, while the all carbon and nitrogen atoms of the bipy ligand are coplanar with deviations from the mean plane not greater than ±0.06 Å.

In the title complex, the two carboxylate groups of fumarate ligands have the same coordination mode, which serves as a bidentate ligand to coordinate a manganese center. Seen from Figure 2, the manganese centers are bridged by bis-bidentate fumarate ligands., which yield infinite helical chains structure along b axis. The helical chain is decorated by 2,2'-bpy terminal ligands alternatively at the two sides and the 2,2'-bipy planes on the same side are absolutely parallel one another. The intrachain

TABLE 1 : Crystal Data and Structure refinement for complex 1

Chemical formula	$\text{C}_{28}\text{H}_{24}\text{Mn}_2\text{N}_4\text{O}_{10}$	Formula weight	686.39
temp (K)	293(2)	Wavelength(Å)	0.71073 Å
Crystal system	Orthorhombic,	Space group	Pbca
a[Å]	9.1142(6)	Scan range(°)	2.07 to 26.99
b[Å]	16.0007(10)	D_{calc} [g/cm ³]	1.586
c[Å]	19.7168(12)	R1, wR2	0.0335,
		(I > 2 σ(I))	0.0807
β(°)	90	R1, wR2 (all data)	0.0378, 0.0833
V [Å ³]	2875.4(3)	GOF	1.078
Z	4	Parameters	207

$$^a R = \frac{\sum |F_o|^2 - |F_c|^2|}{\sum |F_o|^2} \quad ^b R_w = \left[\frac{\sum \{w(F_o^2 - F_c^2)^2\}}{\sum \{w(F_o^2)\}} \right]^{1/2}$$

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TABLE 2 : Selected bond lengths (Å°) and bond angles (°) for complex 1

Bond distances(Å°)			
Mn(1) –O(1)	2.3868(15)	Mn(1) –O(2)	2.2471(14)
Mn(1) –O(3)	2.3041(12)	Mn(1) –O(4)	2.3280(13)
Mn(1) –O(1W)	2.1686(15)	Mn(1) –N(1)	2.2629(15)
Mn(1) –N(2)	2.2839(15)		
Bond angles(°)			
O(1) –Mn(1) –O(2)	55.62(5)	O(1) –Mn(1) –O(3)	135.69(5)
O(1) –Mn(1) –O(4)	159.71(6)	O(1) –Mn(1) –N(1)	82.57(5)
O(1) –Mn(1) –N(2)	107.53(6)	O(1) –Mn(1) –O(1W)	80.07(6)
O(2) –Mn(1) –N(1)	128.87(5)	O(2) –Mn(1) –N(2)	92.43(6)
O(2) –Mn(1) –O(3)	83.29(5)	O(2) –Mn(1) –O(4)	139.66(5)
O(2) –Mn(1) –O(1W)	104.74(6)	O(3) –Mn(1) –O(4)	56.38(4)
O(3) –Mn(1) –N(1)	141.42(5)	O(3) –Mn(1) –N(2)	88.19(5)
O(3) –Mn(1) –O(1W)	97.29(6)	O(4) –Mn(1) –N(1)	89.18(5)
O(4) –Mn(1) –N(2)	87.21(6)	O(4) –Mn(1) –(1W)	82.07(6)
N(1) –Mn(1) –N(2)	71.82(5)	N(1) –Mn(1) –O(1W)	94.06(6)
N(2) –Mn(1) –O(1W)	162.44(6)	C(13) –O(3) –Mn(1)	91.50(10)
C(13) –O(4) –Mn(1)	90.59(10)	C(11) –O(1) –n(1)	88.49(11)
C(11) –O(2) –Mn(1)	94.65(11)		

Mn...Mn separation is 9.056 Å°, while the shortest interchain Mn...Mn distance is 5.860 Å°. These helical chains are further extended by O-H...O hydrogen bonds into a two-dimensional network. The hydrogen-bonding parameters are listed in TABLE 2. The coordination mode of the fumarato group is to some extent similar to those previously reported for Mn(fumarate)(H₂O)₂(phen)^[7a], [Mn(fumarate)(H₂O)(4,4'-bipy)]_n·0.5(4,4'-bipy)^[7b]. However, the extension of the basic unit and the packing style are different from those related complexes.

So far, most of structurally characterized Mn(II) complexes are a six-coordinate octahedral geometry while complexes with coordination numbers exceeding six are limited. As far as the butane dicarboxylic acid, the maleato bipyridine manganese coordination polymer is the only one based on a hepta-coordinated manganese center to the best of our knowledge^[13]. In this report, the hepta-coordinated manganese bridged with fumarate ligand is another example.

Magnetic properties

The temperature dependence of the magnetic susceptibility for 1 was investigated in the tempera-

ture range 2-300K under a magnetic field of 2000oe. The variation of the reciprocal of $\gamma_M T$ and χ_M versus T for compound 1 is presented in figure 3 and figure 4. The room-temperature value of $\gamma_M T$ (4.325 cm³ K mol⁻¹) is slightly lower than the spin-only value for the Mn(II) ion ($S = 5/2$ $\gamma_M T = 4.38$ cm³ K mol⁻¹). Upon cooling, the value decreases continuously down to 3.785 cm³ K mol⁻¹ at 2K, indicating an overall antiferromagnetic coupling interaction between the metal atoms. According to the X-ray crystal structure determination, complex 1 is a homogeneous chain of Mn(II) with fumarate bridging. The gradual decrease in $\zeta_M T$ value with decreasing temperature reveals existence of antiferromagnetic interaction within the chain.

According to a classical Heisenberg model^[14] for a linear chain of the large spin Mn^{II} ion, the temperature dependence of the magnetic susceptibility data can be simulated by the following equation :

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2S(S+1)}{3kT} \frac{1+u}{1-u} \quad (1)$$

where g is the Lande's constant for $S = 5/2$ spin units, β is the Bohr magneton constant, N is Avogadro's

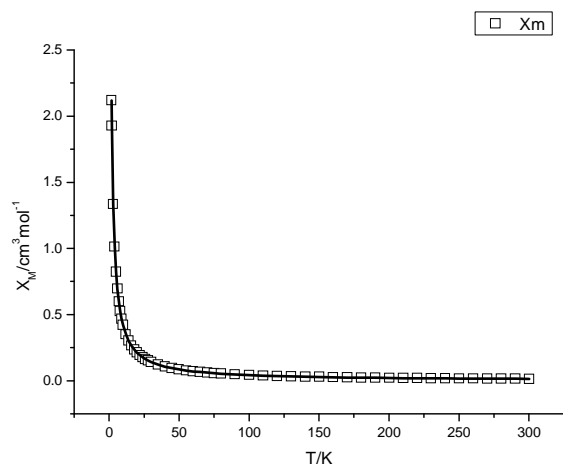


Figure 3: The plot of χ_m vs temperature of complex 1, The solid line represents best fit of data according to eq 1 and eq 2

number and $u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$ The exchange

Hamiltonian is written as $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ With consideration of the actual nature of the complex, a mean molecular field approximation term^[15] zJ' was added to describe the inter-chains spin-spin interactions. Thus the expression for the magnetic susceptibility becomes: $\chi_M = \chi_{\text{chain}} / [1 - (2zj' / Ng^2\beta^2) \chi_{\text{chain}}]$

The best fitting parameters obtained from this simulation are $g = 1.99$, $J = -0.58 \text{ cm}^{-1}$, $zj'/k = -0.08 \text{ cm}^{-1}$ with the agreement factor $R = \sum[(\chi_{M_{\text{obs}}} - \chi_{M_{\text{calc}}})^2] / \sum[(\chi_{M_{\text{obs}}})^2] = 3.49 \times 10^{-5}$.

Although the interchain distance is shorter (5.860 \AA), the absence of effective superexchange pathway and the steric effects cause the smaller value of zj' . Obviously, the weakly magnetic exchange interaction through fumarate bridging ligand is owing to the large intramolecular Mn...Mn separation (9.056 \AA). This weak long-distance magnetic interaction is consistent with another reported coordination complex using fumaratoligand as bridging spacer^[3c, 5b]. Previous reports have shown two paramagnetic centers could interact through extended bridging ligands, even if these centers were relatively far away from each other^[16]. According to our theoretical calculations^[9], the sign along the fumarate anion shows that the coupling between the carbon atoms is antiferromagnetic owing to the spin polarization within the π orbital of the fumarate groups. It is also seen from our experimental results that the spin polarization within the π orbital of the fumarate groups is the

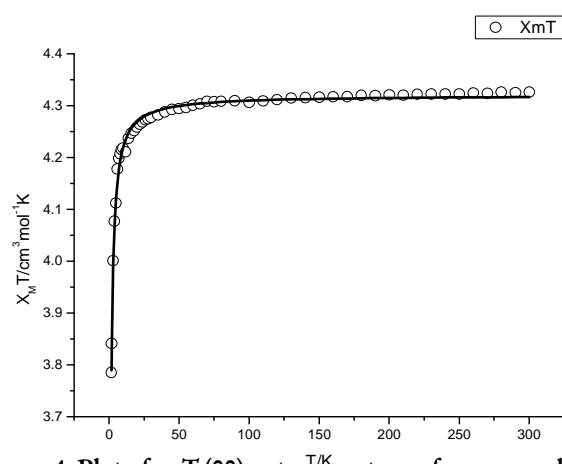


Figure 4: Plot of $\chi_m T$ (00) vs temperature of compound 1, The solid line represents best fit of data

leading factors attributing to the weak long-distance magnetic interaction. Recently we have designed and obtained a binuclear copper(II) complex using fumaratoligand as bridging spacer to further investigate the long-distance magnetic interactions through the bridging fumaratoligand. The weak antiferromagnetic interactions were also observed, suggesting the presence of the intramolecular interaction in bridging fumaratoligand magnetic system.

In conclusion, we obtained a rare heptacoordinated manganese(II) coordination polymer using fumaratoligand as bridging spacer. In this complex, each manganese centers are bridged by bis-bidentate fumarate ligands to yield infinite helical chains structure. The magnetic analysis revealed that the weak antiferromagnetic interactions are mainly intrachain interaction through the long-distance bridging fumaratoligands. Here we provide a new example of the long-distance magnetic interaction through the bridging fumaratoligand. It is worth noting that the bridging fumaratoligand can provide superexchange passway between paramagnetic centers owing to its spin polarization within the π orbitals. So the fumaratoligand, under certain conditions, is an appropriate bridging unit to design magnetic systems with expected properties.

IR analysis

The IR spectrum of the title complex clearly show both the presence of the fumarate ion and its coordination mode. The existence of two strong absorptions at 1580 cm^{-1} and 1389 cm^{-1} corresponds to asymmetric and symmetrical stretching vibrations, $\nu_{\text{as}}(\text{COO})$

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(1580.75 cm^{-1}) and $\nu(\text{CO}_2)$ (1389.37 cm^{-1}), of the coordinated carboxylato groups. These two bands are separated by ca. 191.38 cm^{-1} , suggesting a bidentate coordination mode for both carboxylato groups^[17,18]. This is in accordance with the result of X-ray diffraction analysis. In addition, the characteristic bands due to the $\nu(\text{O-H})$ stretching of the coordinated water molecules(3354.82) is also seen.

Supplementary materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC-272891. These data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; E-mail: eposit@ccdc.cam.ac.uk).

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