



Catena- Poly [[2,2-bipyridine- $\kappa^2 N^1, N^{1'}$) Mn(II)]- μ -oxalato $\kappa^4 O^1, O^{1'}: O^2, O^{2'}$] a zigzag coordination polymer

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ABSTRACT

The new coordination polymer $[Mn(C_{12}H_{8}N_2O_4)]_n$ takes the form of one dimensional zigzag chain built of Mn(II) cations linked by oxalate dianions. The oxalate anion coordinated as a bridging tetradentate ligand with bidentate of coordination of individual oxygen atoms. The Mn(II) cation has a highly distorted octahedral geometry formed by four oxygen atoms from two bidentate oxalate anions and two nitrogen atoms from one chelating 2,2-bipyridine (bipy) ligand. The zigzag chain which run along the a-axis, further construct a three-dimensional metal-organic framework via π -stacking and C-H...O hydrogen bonds.

KEYWORDS : One dimension; Oxalate; Zigzag ;MnII; Bipyridine.

INTRODUCTION

The design and construction of metal-organic coordination polymer is an interesting research field due to the fascinating structural diversity of these compounds and to their potential applications in nonlinear optical and fluorescent materials^{1,2}, as well as several other different fields such as luminescence, catalysis, gas storage, molecular adsorption, magnetic materials, ion exchanges and zeolite-like materials³. Self-assembly of these complexes can be realized by selection of proper organic ligands and there is a lot of interest in the search for new bridging ligands, which could give desired properties to newly synthesized materials. In particular, new magnetic materials with intriguing structural features and magnetic properties have been recently reported^{4,7}. In the last decade dianionic oxalates have widely used to synthesize magnetic materials, due to its role as a short bis(chelating) ligand^{8,9}. On the other hand the auxiliary ligands containing nitrogen donors such as bipyridine have been extensively employed in

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materials, due to its role as a short bis(chelating) ligand. On the other hand the auxiliary ligands containing nitrogen donors such as bipyridine have been extensively employed in the construction of a wide variety architectures. Bipyridine display versatile coordination properties with metals forming well-known chelate structures. We know that the carboxylate group can act as a bridging ligand between adjacent metal centers in several modes such as syn-syn, syn-anti and anti-anti coordination modes. The oxalate ligand can act as a dicarboxylate anion and bridge two adjacent metal centers in an anti-anti mode.

EXPERIMENTAL

2.1 Synthesis

A mixture containing Mn(ClO₄)₂ · 6H₂O (60mg, 0.25mmol), CH₂(COOEt)₂ (63mg, 0.13mmol) and dipy (15mg, 0.10mmol) was dissolved in 20% ethanolic solution (12ml). The mixture was refluxed for

two hours, and then transferred to a small vial by filtration. The prismatic yellow crystals with suitable size for analysis appeared within two days. The complex is stable in air and insoluble in all common solvents.

2.2 Crystal structure determination and refinement of the title complex

Suitable yellow prismatic single crystals of the title complex were obtained by slow evaporation of the solvent at room temperature within two days. X-ray single-crystal diffraction were calculated on a Xcalibur, Onyx diffractometer at 120 K, Cu K α radiation ($\lambda = 1.54180$) was used and a multi-scan correction for absorption were used. The structure was solved by direct methods and refined on F² by full-matrix least-squares (SHELX97)¹⁰, and WingGX¹¹. Crystal data, data collection and structure refinement details are summarized in (Table 1). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated position as riding atoms (SIR92)¹² and refined isotropically. Additional material available from the Cambridge Crystallographic Data Center comprises thermal parameters and remaining bond distances and angles (CCDC No. 921255). These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data.

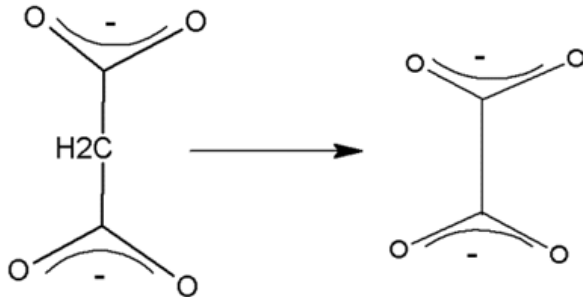
Table 1. Crystal data and structure refinement details for the complex

Empirical formula	C ₁₂ H ₈ MnN ₂ O ₄
Formula weight	299.14
Temperature	120 K
Wavelength	1.54180 Å
Crystal system	orthorhombic
Space group (No.)	Pna21
Unit cell parameters	
a = 9.7463(3) Å,	
b = 9.1446(3) Å,	
c = 13.7452(4) Å,	

Cell volume	1225.05(7)
\AA^3	
Z	4
ρ_c	1.622 g cm ⁻³
μ	8.896 mm ⁻¹
F(000)	604
Crystal size	0.2 × 0.1 × 0.1 mm ³
θ range for data collection	5.81 – 70.71 °
Index ranges	-8 ≤ h ≤
11, -10 ≤ k ≤ 7, -16 ≤ l ≤ 14	
Reflections collected	3107
Independent reflections	1800 [R(int) = 0.0517]
Data / restraints / parameters	1800 / 1 / 172
Goodness-of-fit on F ²	1.023
R indices	[I > 2 σ (I)] R1 = 0.0521,
wR2 = 0.1229	
R indices (all data)	R1 = 0.0685, wR2 =
0.1342 3.	

RESULTS AND DISCUSSION

A new one-dimensional coordination polymer with mixed bipy and oxalate ligands [Mn(bipy)(ox)]_n (1) scheme 1 was synthesized by refluxing a mixture of Mn(ClO₄)₂·3H₂O, malonate and bipy involving in situ formation of oxalate ligand. In this context the in situ formation of oxalate dianion from the reaction of malonate dianion, bipy and Mn(ClO₄)₂, bears some resemblance to the in situ formation of oxalate and pyrimidine-2-carboxylate reported by Jian-Yong et al.13, where 2-cyanopyrimidine and MnCl₂ were used as starting materials. The transformation of malonate dianion might proceed through a pathway similar to that reported by Jian-Yong, scheme 2. The asymmetric unit of (1) contains one Mn(II) atom, one oxalate dianion and one bipy ligand. Each Mn(II) atom is six coordinate in a highly distorted octahedral by four oxalate oxygen atoms from two different oxalate anions and two nitrogen atoms from one bipy ligand with Mn-N₂O₄ chromophore forming a (4+2) coordination polyhedron (Figure 1).



Scheme 1.

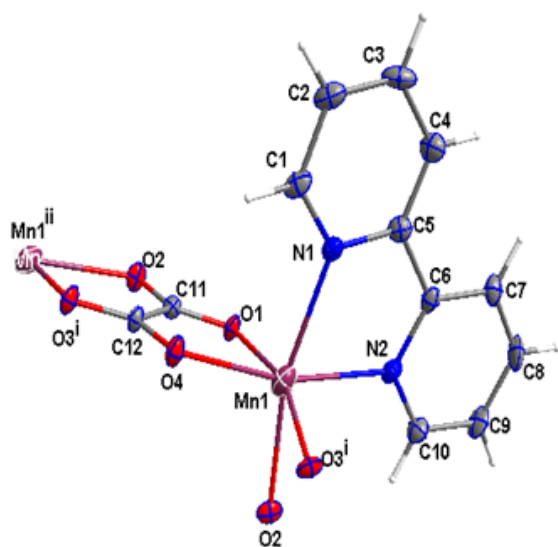


Fig.1. ORTEP view of the title complex. Symmetry codes: (i) $x+0.5, -y+0.5, z$; (ii) $x-0.5, -y+0.5, z$.

The two oxygen O (O₂, O₄) atoms from two different oxalate groups and two nitrogen N (N₁, N₂) atoms of the bipy ligand are coplanar and

define the equatorial plane of the octahedron (max deviation from the mean plane 0.162 (6) Å for N₁, Mn only 0.010 (1) Å apart from this plane), which is significantly distorted due to small bite angles 76.8 (2)°, 76.6 (2)° and 73.4(2)° of the oxalate groups and the bipy ligand respectively. Two oxygen O (O₁, O₃) atoms from two oxalate groups already involved in coordination to the equatorial plane occupy the axial positions of the octahedron. The Mn(II) center is coordinated by two different types of ligands, which both behave as chelating ligand (Mn-O = 2.155(5) Å, 2.178(5) Å, 2.157(5) Å, 2.169(5) Å for O₁, O₂, O₃, and O₄ and Mn-N = 2.251(6) Å and 2.39(6) Å for N₁ and N₂ respectively) (Table 2).

Table 2

Selected bond lengths (Å) and angles (°)

Bond lengths			
Mn1—O1	2.155(5)	Mn1—O3 ⁱ	2.155(5)
Mn1—O4	2.169(5)	Mn1—O2 ⁱ	2.178(5)
Mn1—N2	2.239(6)	Mn1—N1	2.251(6)
Bond angles			
O1—Mn1—O3 ⁱ	160.98 (16)	O1—Mn1—O4	76.83 (17)
O3 ⁱ —Mn1—O4	90.15 (18)	O1—Mn1—O2 ⁱ	92.09 (18)
O3 ⁱ —Mn1—O2 ⁱ	76.61 (17)	O4—Mn1—O2 ⁱ	100.87 (18)
O1—Mn1—N2	97.99 (19)	O3 ⁱ —Mn1—N2	97.9 (2)
O4—Mn1—N2	165.2 (2)	O2 ⁱ —Mn1—N2	93.1 (2)
O1—Mn1—N1	97.4 (2)	O3 ⁱ —Mn1—N1	97.2 (2)
O4—Mn1—N1	93.4 (2)	O2 ⁱ —Mn1—N1	164.4 (2)
N2—Mn1—N1	73.35 (19)		

Symmetry codes: (i) $x+1/2, -y+1/2, z$.

Each crystallographically unique Mn(II) atom is bridged by the oxalate anion into a zigzag chain (Figure 2) to generate a novel 1 D framework which develops along the a-axis. The oxalate ions uses its four oxygen atoms as bis(chelating) to link in an anti-anti mode two neighboring Mn centers [Mn...Mn = 5.623(1) Å which is shorter than the 5.732 Å Mn...Mn distance reported by Jian-Yong. The Mn-Mn-Mn angle across two oxalate anions is close to 120.12°. Each chain lies at 9.1446(3) Å from the chain translated of one period along the b axis.

The coordinated bipy units are parallel to each other and protrude towards opposite directions (the angle between the two mean plane is 2°), so that off-set π -stacking contacts, with inter-planar distance of 3.973(5) Å and 3.965(5) Å, respectively, and ring centroid-ring centroid distance of 4.219(7) Å, are established between the bipy units of adjacent chains (Figure 2).

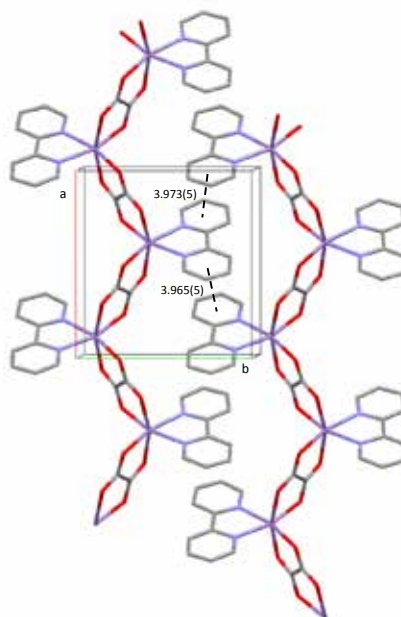


Fig.2. zigzag chain growing along the b axes; interplanar distances (Å), the π -stacking

Interactions.

As a result, a 2D network based on both coordination bonds and weak interactions is obtained. The crystal packing is then completed by the action of the two-fold screw axis running along the c axis, which repeats the 2D network, in a parallel plane lying 6.873(2) Å apart (Figure 3)

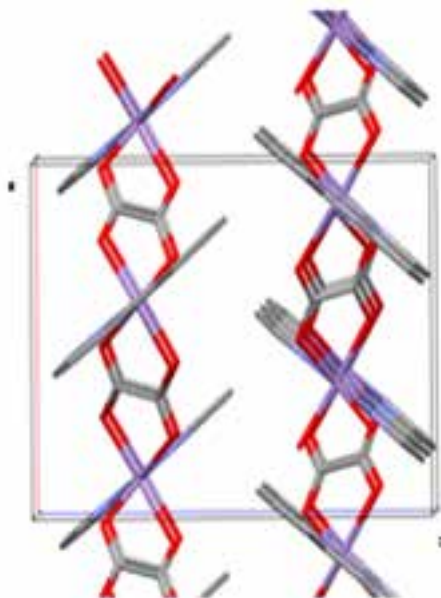


Fig.3. 2D networks repeated along the c-axis

Further analysis of the packing structure reveals that the parallel 2D networks interact throughout C-H—O hydrogen bonds (C9-H9—O4 = 2.390(5) Å, C9—O4 3.276(9) Å) which contribute to sustain the overall assembly of the title compound (Figure 4).

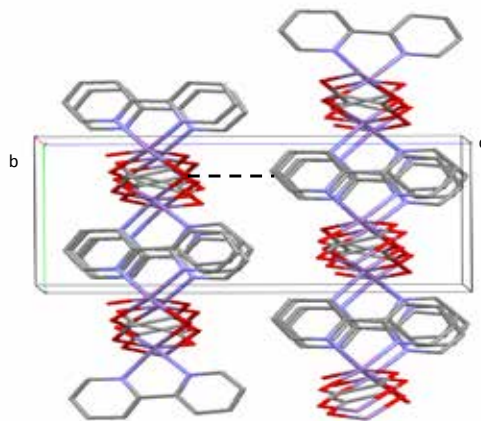


Fig.4. Top view of the 2D networks repeated along the c-axes and CH...O interactions.

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