A novel Mn(II) oxalato-bridged 2D coordination polymer: synthesis, crystal structure, spectroscopic, thermal and magnetic properties

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Abstract. Besides the fact that direct synthesis of oxalate-based Mn(II) complexes did not succeed a lot due to the high insolubility of manganese oxalate ($\text{Mn}^{\text{II}}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$), a new 2D polymeric Mn(II) salt has been synthesized by slow evaporation at room temperature and its structure has been determined by single-crystal X-ray diffraction. The structure was solved by direct methods and refined to conventional agreement indices. The crystal structure is built from anionic, two-dimensional, honeycomb networks formed by the oxalate-bridged Mn(II) ions, interleaved by 2,6-diaminopyridinium cations that are entrapped between the layers. The interactions between adjacent layers result from the extended network of intermolecular hydrogen bonds created by the mentioned cations and water molecules. The complex has been fully characterized by single crystal X-ray diffraction, FT-IR and UV-Vis spectroscopy, Rietveld refinement, TGA-DSC analysis and magnetic susceptibility. The title compound exhibits antiferromagnetic coupling between Mn(II) centres.

Keywords. 2D coordination polymer; manganese; oxalate; magnetism.

1. Introduction

Coordination polymers (CPs) are of rising interest because of their fascinating topologies and dimensionality associated with both structural and functional versatility. Various attempts to build high-dimensional CPs with intriguing architectures were successful through the multitude of N-donor ligands such as 1,10-phenanthroline derivatives,¹ benzidine ligand² and dipyrityl-based ligand^{3,4} as well as O-donor ligands including *o*-phthalic acid⁵ and carboxylic acid,⁶ due to their excellent coordinating ability. And among this wide variety of ligands, the oxalate ion was proven to be one of the most useful ligand, and played a prominent role by conferring electronic,⁷ photochemical,⁸ magnetic⁹ and optical¹⁰ properties on those materials. Because, oxalate ion acts as a rigid bidentate ligand that can facilitate the formation of extended structures by bridging 3d metals.

The 2D honeycomb structure is the most common for the oxalate CP structures.^{11,12} It offers exciting opportunities in the fields of molecular magnetism. Accordingly, complexation of transition metals (as spin carrying centres) with the oxalate ions (as bridging units and mediator for magnetic spin interaction) creates a variety of molecular magnets¹³ with short-range and long-range magnetic ordering behaviour and arouse interest in the organic/inorganic chemistry community. In this field, significant research have been devoted to manganese oxalate complexes^{14–18} and to analysing the structural features and physical properties of the compounds as molecular magnets.^{19–21}

We have extended our investigations on transition metal oxalate complexes and herein report the synthesis, crystal structure, spectroscopic studies, thermal analysis, Rietveld refinement and magnetic measurements of a new 2D Mn(II) coordination polymer, aiming for valuable applications.

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2. Experimental

2.1 Materials and methods

High purity manganese(II) sulphate monohydrate (Sigma-Aldrich, Germany), oxalic acid dihydrate (Prolabo, France) and 2,6-diaminopyridine (Sigma-Aldrich, Germany) were used without purification.

Elemental analyses for carbon, nitrogen and hydrogen were performed on a Flash 2000 Organic Elemental Analyser, CHNS-O analyser by Thermo Scientific (Centre of Scientific Instrumentation of the University of Granada). The infrared spectrum was recorded in the range 4000–400 cm^{-1} on a Bruker Tensor 27 FT-IR spectrometer, while the UV–Vis spectrum of the title compound in aqueous solution was recorded in the range 200–800 nm using UV-1800-Shimadzu Scientific Instruments (Department of Inorganic Chemistry of the University of Granada). XRD powder pattern was obtained using a D2 Phaser Bruker diffractometer equipped with a Cu anticathode (Cu $K\alpha$ radiation $\lambda = 1.54056 \text{ \AA}$) at room temperature (Department of Inorganic Chemistry of the University of Granada). Thermogravimetric analysis was recorded in air using a Mettler-Toledo TGA/DSC1 Thermogravimetric Analyser in the range from 36 to 950 $^{\circ}\text{C}$ (Centre of Scientific Instrumentation of the University of Granada). Magnetic susceptibility measurements were performed on powdered polycrystalline sample using a Quantum Design MPMS 5XL SQUID magnetometer operating in the range of 2–300 K (Centre of Scientific Instrumentation of the University of Granada). Empiric correction for diamagnetism of $-308.78 \text{ emu mol}^{-1}$, estimated by the use of Pascal's constants,²² was made for all the constituent atoms.

2.2 Synthesis

Brownish prismatic crystals suitable for X-ray analysis were obtained from the solution after almost two weeks of slow evaporation. Under continuous stirring at 373 K, an aqueous solution (10 cm^3) of manganese(II) sulphate monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (1 mmol, 197.20 mg) was added dropwise to a water/acetone solution (10 cm^3) of oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (1 mmol, 126.50 mg). After 15 min of stirring, a solution of 2,6-diaminopyridine, $\text{C}_5\text{H}_7\text{N}_3$ (2 mmol, 218.20 mg) dissolved in water/acetone (30 cm^3) was added dropwise with continuous stirring to the mixture until $\text{pH} \approx 5$. The solution was filtered off and the filtrate was heated for further 3 h, then left at room temperature in a petri dish. The elemental analytical results for carbon, hydrogen and nitrogen are close to the calculated values. Calculated: C: 29.64, H: 3.42, N: 12.96%; Found C: 30.49, H: 4.01, N: 13.32%.

2.3 X-Ray crystallography

Suitable single crystal of the title compound was carefully selected under a polarizing microscope and glued to a glass fibre then mounted on an Enraf-Nonius CAD-4 diffractometer²³ equipped with monochromatic graphite Mo $K\alpha$

radiation ($\lambda = 0.71069$). Data were collected at room temperature. The unit cell parameters were determined based upon 25 reflections in the $2^{\circ} \leq \theta \leq 10^{\circ}$ range and they were refined using the least-squares method in the $10^{\circ} \leq \theta \leq 15^{\circ}$ range. The reflection intensities were collected up to $\theta = 27^{\circ}$ with two standard reflections for intensities and orientation control. The crystal structure was solved using direct methods using the SHELX-97²⁴ computer program included in the WinGX software package²⁵ and refined by full matrices least squares against F^2 using SHELXL-2014.²⁶

All non-hydrogen atoms were refined anisotropically. Water molecules' hydrogen atoms were located from the Fourier difference maps. The O–H bond lengths were restrained to a value of 0.85(1) $\text{\AA}$ and the H $\cdots$ H distances were restrained to a value of 1.387(1) $\text{\AA}$. Amine hydrogen atoms of 2,6-diaminopyridinium cations were positioned geometrically as riding atoms ($\text{N–H} = 0.86 \text{ \AA}$) using adequate HFIX instructions and refined with AFIX instructions while aromatic C–H and N–H hydrogen atoms were simply located from the Fourier difference maps. The empirical absorption corrections were based on a ψ -scan. The structural graphics were created with the DIAMOND program²⁷ and Mercury.²⁸ Crystal data and experimental details for **1** are contained in Table 1. Selected bond distances and angles are listed in Table S1 in Supplementary Information.

3. Results and Discussion

3.1 Description of the structure

Single crystal X-ray diffraction analysis revealed that the title compound, *catena*-[bis(2,6-diaminopyridinium) tris(μ_2 -oxalato)-dimanganese(II) trihydrate] (**1**), crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of a binuclear complex anion $[\text{Mn}_2(\text{C}_2\text{O}_4)_3]^{2-}$, two protonated 2,6-diaminopyridine cations $[\text{C}_5\text{H}_8\text{N}_3]^+$ and three uncoordinated water molecules. In the complex anion, two crystallographically independent Mn^{2+} atoms with similar coordination environments are confirmed as +2 charged by bond valence sums (sums 2.10 and 2.11).²⁹ Each Mn^{2+} has six-coordinate octahedral geometry with six oxygens from three different oxalates. The two manganese ions are linked through a planar oxalate group in the usual bis(bidentate) fashion, leading to a metal-metal separation of 5.647(2) $\text{\AA}$. A drawing of the asymmetric unit showing the labelling scheme is given in Figure 1.

The first manganese ion is more distorted than the second with $\text{ID}_d = 0.011\%$ and $\text{ID}_a = 0.221\%$ for Mn1 and $\text{ID}_d = 0.006\%$ and $\text{ID}_a = 0.218\%$ for Mn2. Polyhedral distance and angle distortions in both Mn1O_6 and Mn2O_6 units were calculated using those expressions

$$\text{ID}_d = \left[\sum_{i=1}^6 \frac{|d_i - d_m|}{6 \times d_m} \right] \quad (1)$$

Table 1. Crystal data refinement results of $\{(C_5H_8N_3)_2[Mn_2(C_2O_4)_3] \cdot 3H_2O\}_n$.

Formula	$(C_5H_8N_3)_2[Mn_2(C_2O_4)_3] \cdot 3H_2O$
Formula weight ($g\ mol^{-1}$)	648.27
Temperature (K)	298 (2)
Wavelength ($\text{\AA}$)	0.71069
Space group	$P2_1/n$
Unit cell dimensions	
a ($\text{\AA}$)	9.756 (3)
b ($\text{\AA}$)	16.743 (5)
c ($\text{\AA}$)	15.420 (1)
β ($^\circ$)	97.53 (5)
Cell volume ($\text{\AA}^3$)	2497.1 (11)
Z	4
Absorption coefficient (mm^{-1})	1.096
Crystal size (mm^3)	$0.41 \times 0.34 \times 0.2$
Crystal sharp; colour	prism; brown
Theta range for data collection ($^\circ$)	2.34–26.97
Limiting indices	$-12 \leq h \leq 1; -21 \leq k \leq 1; -19 \leq l \leq 19$
Absorption correction; $T_{min}; T_{max}$	psi-scan; 0.6461; 0.7351
Reflections collected	6626
Independent reflections	5437 [$R_{int} = 0.029$]
Observed reflections [$I > 2\sigma(I)$]	3204
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.042$; $wR(F^2) = 0.109$
Residuals ($e\text{\AA}^{-3}$)	0.49; -0.30
Goodness of fit (S)	1.02

Figure 1. The structural unit of **1**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level for non-H atoms.

and

$$ID_a = \left[\sum_{i=1}^{15} \frac{|a_i - a_m|}{15 \times a_m} \right] \quad (2)$$

where d_m is the average Mn–O distance and a_m is the average O–Mn–O angle.

In the asymmetric unit, oxalate ligands are planar, the root-mean-square deviation of terminal oxalate ions from their mean planes are 0.0375 and 0.0306 $\text{\AA}$ while the value for the bridging oxalate ion is 0.0090 $\text{\AA}$. The dihedral angle between terminal/bridging least-square planes is $77.42(9)^\circ$ and $80.83(9)^\circ$. C–C distances between 1.546(4) and 1.549(4) $\text{\AA}$ and C–O distances from 1.242(4) to 1.251(4) $\text{\AA}$ are in the typical range reported for 2D Mn^{II} oxalate compounds³⁰ and in good agreement with our previous work on 1D Mn^{II} oxalate compound. The mean deviations of the pyridine rings of the cations are of 0.0012 and 0.0067 $\text{\AA}$ from the mean planes. Amine groups of each cation are almost coplanar with the pyridine rings.

In the structure packing of the compound, Mn^{II} ions are connected each to three bridging oxalates, creating a honeycomb motif. Hence, the structure can be described as composed of infinite manganese-oxalate layers, perpendicular to the $\vec{c}$ axis (Figure 2(b)). The separation of the manganese atoms along the three mentioned oxalate bridges (5.628(1), 5.647(2) and 5.697(1) $\text{\AA}$) are in the range observed for other manganese-oxalato compounds^{31,32} and generate slightly irregular hexagonal channels.

Figure 2. Layered sector of the title compound: (a) [010] projection; and (b) [001] projection for anionic layers only.

The charged components are connected by an extensive hydrogen-bonding network. Yet, the honeycomb layers are held together by hydrogen bonds *via* the water molecules of crystallization and 2,6-diaminopyridinium cations, situated between the layers as depicted in Figure 2(a). In fact, 2,6-diaminopyridinium cations coordinate anionic layers and water molecules *via* N–H···O hydrogen bonds. As shown in Figure 3(a) and Figure 3(b), both amine and pyridine nitrogen atoms act as hydrogen-bond donors and establish strong hydrogen bonds towards different oxygen atoms of both $[\text{Mn}_2(\text{C}_2\text{O}_4)_3]^{2-}$ layers and water molecules. These act at the same time as hydrogen-bond donors *via* O–H···O hydrogen bonds involving their oxygen atoms and hold together three different anionic planes, enhancing the stability of the crystal as depicted in Figure 3(c). An additional stability of the structure is provided by $\pi - \pi$ interactions between the anti-parallel pyridine rings of 2,6-diaminopyridinium cations, with centroid-centroid distance of 3.667 Å (Figure S1 in Supplementary Information).

3.2 Infrared spectroscopy

With the molecular structure of **1** being established crystallographically, further evidence of complexation was obtained from the spectral data. Indeed, the IR spectrum of **1** (Figure S2 in Supplementary Information) shows characteristic vibrations of the bridging oxalato ligand. In fact, a strong band at 1602 cm^{-1} shifted to lower wavenumber due to the ligand deprotonation, which can be characteristic of $\nu_{\text{as}}(\text{C}-\text{O})$ asymmetric vibration of the oxalate. The peak at 1303 cm^{-1} can be attributed to symmetric vibrations $\nu_{\text{s}}(\text{C}-\text{O})$ while the peak at 781 cm^{-1} can be attributed to $\delta(\text{O}-\text{C}-\text{O})$ supports the oxalate presence in a bis-bidentate coordination mode.^{33,34}

3.3 Powder XRD analysis

The powder diffraction measurement was performed under Bragg–Brentano geometry in the 5°–50° range with step of 0.02°. Rietveld refinement was performed using the FullProf Suite program,³⁵ whereas pattern indexing was carried out by means of the auto-indexing program TREOR.³⁶ As depicted in Figure 4, the absence of additional peaks in the diffraction pattern and the linearity of the background confirmed the purity of the powder sample based on the fully consistent results with those obtained from the single crystal diffraction data.

3.4 UV–Vis absorption spectrum

The title compound has good solubility in distilled water. The UV–Vis absorption spectrum in distilled water (Figure 5) exhibits two absorption bands at 240 and 329 nm. The lower energy band can be considered as $\pi \rightarrow \pi^*$ transition of the aromatic rings, while the higher one can be attributed to LMCT transition. Failure to observe the manganese(II) d–d band may be due to the weakness of absorption.

3.5 Thermal analysis

In order to characterize the compound more fully in terms of thermal stability, its thermal behaviour was carried out for powder sample of **1** in air from 36 to 950 °C under a heating rate of 10 °C min^{−1} (Figure S3 in Supplementary Information). The weight loss in the range upto 90 °C corresponds to the removal of the three water molecules (observed, 7.2%; calculated, 8.3%). The result shows good agreement with the formula of the compound. A major thermogravimetric loss step of almost 49% of the compound mass, (calculated,

Figure 3. View of the hydrogen bonds formed by, (a) the first organic cation (green dashed lines), (b) the second organic cation (purple dashed lines) and (c) water molecules (turquoise dashed lines). [Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $-x+3/2, y-1/2, -z+1/2$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $-x+1, -y, -z+1$; (vi) $-x, -y, -z$; (vii) $x+1/2, -y-1/2, z+1/2$; (viii) $-x+1, -y, -z$.]

47%), was detected which may be due to loss of organic cations and liberation of CO. The next loss step of 13.2% (calculated, 12.9%) may be attributed to another liberation of CO. Thus, the final residue is the formation of the metal oxide Mn₂O₃ (observed, 23.6%; calculated, 24.3%).

3.6 Magnetic susceptibility measurements

The temperature dependence of χ_m and $\chi_m T$ (χ_m being the magnetic susceptibility for one Mn(II) ion) was examined in the temperature range of 2–300 K (Figure 6).

The magnetic susceptibility plot, χ_m vs T , shows a broad maximum indicating the presence of antiferromagnetic ordering with a Néel temperature (T_N) of 12 K. The inverse susceptibility plot, χ_m^{-1} vs T (plot not shown), shows linear behavior above 30 K, its thermal evolution follows the Curie–Weiss law with $C = 4.69$ emu mol $^{-1}$ K and $\theta = -13.44$ K. Due to the lack of an easy applicable model to fit the experimental data, the magnetic properties of the two-dimensional homometallic $\{[M_2(C_2O_4)_3]^{2-}\}_n$ layers were mostly derived from that Curie–Weiss expression. The negative Weiss constant value of $-29.8(7)$ K for Cu(II)³⁷, -53 K for Fe(II) and -92.1 K for Co(II)³⁸ have always suggested an antiferromagnetic interaction between the metal centers through the oxalato-bridge. For the Mn(II) homometallic 2D oxalate-bridged compounds, an almost identical behavior as our compound, was reported for the complex $[NH(C_2H_5)_3][Mn_2(C_2O_4)_3 \cdot (5H_2O)]$ ¹⁵ with a Weiss constant of -14.2 K.

The observed $\chi_m T$ values gradually decrease upon cooling. At room temperature, $\chi_m T$ shows the asymptotic limit of 4.36 emu mol $^{-1}$ K, slightly lower than the expected value for an “isolated” Mn $^{2+}$ ion (4.38 emu mol $^{-1}$ K). The effective magnetic moment per Mn(II) ion, determined from the equation $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$ is also around $5.91 \mu_B$ and in good agreement with the expected value.

Accordingly, and taking into account the two-dimensional character of the title compound, the geometry of the asymmetric unit of the compound and the slight difference in the Mn $\cdots$ Mn distances previously discussed, the experimental data of $\chi_m T$ were first fitted to the theoretical dimer model expression (eq. 3) based on Heisenberg Hamiltonian $H = -2J.S_1.S_2$.³⁹

$$\chi_m T = \frac{2N_A \mu^2 g^2 \times (1 - \rho)}{k} \times \frac{[55 + 30e^{-10J/kT} + 14e^{-18J/kT} + 5e^{-24J/kT} + e^{-28J/kT}]}{[11 + 9e^{-10J/kT} + 7e^{-18J/kT} + 5e^{-24J/kT} + 3e^{-28J/kT} + e^{-30J/kT}]} + \frac{N_A \mu^2 g^2 S(S+1)}{k} + N_\alpha T \quad (3)$$

Then, the dimeric Mn(II) unit is taken as an effective classical spin system and χ_m was fitted by using an infinite-chain model derived by Fisher^{40,41} with the corresponding theoretical expression (eq. 4a) and (eq. 4b).

$$\chi_m = \frac{N \mu^2 g^2}{3kT} \cdot \frac{1+u}{1-u} \quad (4a)$$

$$u = \coth \left[\frac{J'S(S+1)}{kT} \right] - \left[\frac{kT}{J'S(S+1)} \right] \quad (4b)$$

Figure 4. Rietveld refinement plot for compound **1** showing the observed, calculated and difference patterns. The Bragg reflections are indicated by vertical bars.

ρ is the fraction of paramagnetic impurity in the sample, N_α is the temperature independent paramagnetism and the other symbols have their usual meanings. The best fits shown in Figure 6 correspond to $g = 2.18$, $J = -1.75$ cm $^{-1}$, $\rho = 0.035$, $N_\alpha = -0.002$ and $J' = -2.14$ cm $^{-1}$ with $R^2 = 0.9998$ and 0.9994 , respectively.

As the 2D system was regarded magnetically as an isolated 1D chain with μ -oxalato bridges, the result was compared to both 1D and 2D mixed ligands homometallic units including $[Mn(\mu - ox)]_n$ chains, and shown in Table 2. The survey of J values for the Mn(II) chains shows that the obtained values in this study are within the expected range of -0.58 to -3 cm $^{-1}$. Many factors contribute to the variation of the magnetic coupling along the oxalate bridge such as the replacement of

oxygen by nitrogen atoms in the Mn(II) coordination polyhedron which allows more electron density to be involved in the orbital overlap between the metal and oxalate. In our case, the magnitudes of the antiferromagnetic interaction (-1.75 and -2.14 cm $^{-1}$) lie in the higher range for Mn(II) oxalate-bridged compounds despite the relatively long Mn $\cdots$ Mn distance ($5.697(1)$ Å) which is unexpected for the more electronegative MnO $_6$ coordination environment. Further quantum

Figure 5. UV-Vis absorption spectrum of compound **1** (Concentration, 5×10^{-3} M, path length, 1 cm).

Figure 6. Plots of the temperature dependence of χ_m (solid squares) and $\chi_m T$ (solid circles). The solid line represents the best-fit using the equations and parameters described in the text.

chemical calculations is required to determine the magnetic coupling between Mn(II) in the two-dimensional honeycomb oxalate-bridge anionic layers^{47,48} to confirm the experimental results.

4. Conclusions

In conclusion, a new 2D polymeric structure of manganese(II) ions bridged by oxalate ligands has been presented. The compound has been successfully synthesized by slow evaporation at room temperature and its structure has been fully characterized by single crystal XRD and FT-IR.

The *catena*-[bis(2,6-diaminopyridinium) tris(μ_2 -oxalato)-dimanganese(II) trihydrate] compound exhibits a supramolecular assembly of 3D network constructed by N–H $\cdots$ O and O–H $\cdots$ O hydrogen bonds and $\pi - \pi$ interactions between adjacent 2D $\{[\text{Mn}_2(\text{C}_2\text{O}_4)_3]^{2-}\}_n$ layers.

The purity of the polycrystalline powder was checked by a Rietveld refinement. The thermal behaviour was in full agreement with the structural data. The material may be magnetically comparable to other typical two-dimensional manganese(II) systems showing weak antiferromagnetic coupling between Mn(II) centres. Further experiments which aim to study optical band gap, thermal and magnetic behaviour of different 2D bimetallic Mn/3d-metal and mixed valence $\text{Mn}^{\text{II}} - \text{Mn}^{\text{III}}$ oxalate-bridged compounds are ongoing.

Supplementary Information (SI)

Crystallographic data and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1434416. Copies of this

Table 2. Magnetostructural data for similar homometallic oxalato-bridged Mn(II) chain-like complexes.

Compound	Chromophore	Ref	Mn $\cdots$ Mn distance ($\text{\AA}$)	J (cm^{-1})
$[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(\mu - bpm)]_n$	MnO_4N_2	42	5.61	– 3.0
$[\text{Mn}_2(\mu - (\text{C}_2\text{O}_4))_2(\mu - bpe)(bpe)_2]_n$	MnO_4N_2	32	5.54	– 2.16
$[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(btz)_2]_n$	MnO_4N_2	43	5.67	– 2.16*
$[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(bnz)_2]_n$	MnO_4N_2		5.70 and 5.73	– 2.12*
$[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(\text{H}_2\text{O})(7\text{H} - pur - \kappa\text{N}^9)]_n$	MnO_5N	44	5.60	– 1.99
$\{[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(\text{H}_2\text{O})_2] \cdot (7\text{H} - ade) \cdot (\text{H}_2\text{O})\}_n$	MnO_6		5.71	– 1.82
$[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(4atr)_2]_n$	MnO_4N_2	7	5.60	– 1.74
$[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(bpy)]_n$	MnO_4N_2	19	5.62	– 1.20
$\{[\text{Mn}(\mu - (\text{C}_2\text{O}_4))(\text{H}_2\text{O})_2]_3(\text{H}_2\text{O})\}_n$	MnO_6	45	5.71	– 1.07
$[\alpha - \text{Mn}(\mu - (\text{C}_2\text{O}_4))(\text{H}_2\text{O})_2]_n$	MnO_6	46	5.63	– 0.58*

bpm = 2,2'-bipyrimidine; *bpe* = bis(4-pyridyl)ethylene; *btz* = benzotriazole; *bnz* = benzimidazole; *pur* = purine; *ade* = adenine; *4atr* = 4-amine-1,2,4-triazole; *bpy* = 2,2'-bipyridine;

*Value reported as J/k_B (K) in the original paper and has been converted to J (cm^{-1})

information may be obtained free of charge from The Director, CCDC, 12 Union Road, CAMBRIDGE, CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). $\pi-\pi$ stacking in the structure of compound **1** (Figure S1), IR spectrum of compound **1** (Figure S2), TGA-DSC curve for compound **1** (Figure S3) and selected bond lengths (Å) and angles (°) for **1** (Table S1) are given in Supplementary Information, available at www.ias.ac.in/chemsci.

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