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Azide-bridged manganese(III) one-dimensional chain: synthesis, structure, and magnetic study

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A new end-to-end azide-bridged one-dimensional coordination polymer, $[\text{Mn}^{\text{III}}(\text{L})(\mu_{1,3}\text{-N}_3)]_n$ (**1**) (where L represents the dianionic form of the neutral tetradentate Schiff base H_2L obtained by 1 : 2 condensation of ethane-1,2-diamine, and 5-chloro-2-hydroxyacetophenone in methanol), has been synthesized and characterized by elemental analyses, IR spectroscopy, single-crystal X-ray diffraction, and variable temperature magnetic study. X-ray crystal structure determination of **1** reveals that a chain system with the repeating unit $[\text{Mn}^{\text{III}}(\text{L})(\mu_{1,3}\text{-N}_3)]_n$ bridged by $\mu_{1,3}$ azide. Each manganese(III) is a distorted octahedral geometry. Variable-temperature magnetic study (between 2 and 300 K) suggests a moderate antiferromagnetic interaction in this complex, similar to other studies reported.

Keywords: Manganese(III); Chain; Azide-bridged; Crystal structure; Magnetic study

1. Introduction

Molecule-based magnetic materials with exotic properties like single-molecule magnets [1–5] and single-chain magnets [6–8] have been studied for their potential applications in magnetic devices. To synthesize the aforementioned molecular magnetic systems, it is necessary to select appropriate bridging ligands that can hold paramagnetic centers closely together and communicate effective magnetic exchange coupling between them. It is desirable to use ligands with short paths such as oxide, cyanide, carboxylate, or azide [9–12]. Azide acts as a bridge in diverse binding modes and many structures with azide have been reported using paramagnetic transition-metal ions such as Mn^{2+} , Mn^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , etc. and magnetic properties relying on the metal contents have also been evaluated

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[13–23]. From the magnetic view-point, Co^{2+} and Mn^{3+} have similarities, because both ions show strong magnetic anisotropy to give exotic magnetic characteristics such as spin-canting, metamagnetism, slow magnetic relaxation, and long range order [24–27]. Schiff-base complexes of Mn^{3+} are of particular interest because Mn^{3+} , whose oxidation state is stabilized in the N_2O_2 environment of tetradentate Schiff bases, allows for significant magnetic anisotropy in association with typical Jahn–Teller distortion [28]. The use of the Schiff base in equatorial coordination makes two axial sites available for azide. Accordingly, self-assembly of the Mn^{III} Schiff base with azide led to dinuclear entities [29–32] and frequently constrained one-dimensional (1-D) chains [20, 29, 33–37]. Polynuclear Mn (III) species also play an important role in catalytic and biological fields, especially in the oxygen evolving compound of photosystem II [38, 39].

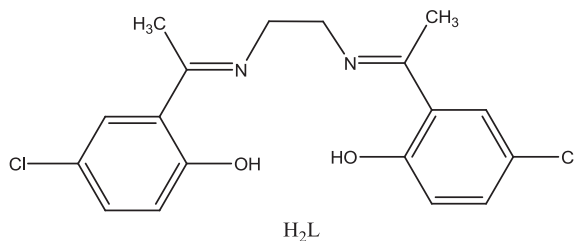
Three new Mn(III) 1-D coordination polymers have been reported with tetradentate Schiff bases [37]. The crystal systems differ according to the Schiff bases used and each manganese has Jahn–Teller distortion. Magnetic measurements show the presence of apparent spin canting. Two complexes exhibit a field-induced metamagnetic transition from an antiferromagnetic state to a weak ferromagnetic phase, whereas another complex shows a field-induced, two-step magnetic phase transition. In another study, Bhowmik *et al.* reported an end-to-end azide-bridged Mn(III) 1-D chain in which Mn(III) has a six-coordinate, pseudo-octahedral geometry, and the deprotonated di - Schiff base constituted the equatorial plane and axial positions is occupied by two azides [36]. Magnetic characterization shows that the $\mu_{1,3}$ -bridging azide mainly transmits an antiferromagnetic interaction which is very similar to earlier reported cases [20, 33–35].

Here, we extend the examples of polymeric Mn(III) azido complexes containing Schiff base as a blocking co-ligand, reporting the synthesis, X-ray crystal structure, and magnetic study of a 1-D polymer, $[\text{Mn}^{\text{III}}(\text{L})(\mu_{1,3}\text{-N}_3)]_n$ (**1**); L represents the dianionic form of the neutral tetradentate Schiff base H_2L (see scheme 1) prepared by 1:2 condensation of ethane-1,2-diamine and 5-chloro-2-hydroxyacetophenone.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were commercially available and used as received without purification. IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Perkin–Elmer Spectrum RXI FTIR Spectrometer. Elemental analyses were carried out using a



Scheme 1. Schematic representation of the neutral H_2L .

Heraeus CHN-O-Rapid elemental analyzer. Variable-temperature magnetic susceptibility measurements were carried out on a microcrystalline sample from 2 to 300 K using a Quantum Design MPMS SQUID susceptometer operating under a magnetic field of 0.1 T. Diamagnetic corrections for the complexes were estimated from Pascal's constants.

2.2. Preparation of $[Mn^{III}(L)(\mu_{1,3}-N_3)]_n$ (**1**)

Caution! Since azide compounds of metal ions are potentially explosive, only small amount of the material should be prepared and handled with care.

To a solution of 5-chloro-2-hydroxyacetophenone (0.340 g, 2 mmol) in 20 mL of methanol, ethane-1,2-diamine (0.06 g, 1 mmol) was added and the resulting mixture was heated under reflux for 4 h. A methanolic solution (10 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.724 g, 2 mmol) was added to this solution. The reaction mixture was refluxed for 2 h. An aqueous solution of NaN_3 (0.26 g, 4 mmol) was then added and stirred for 1.5 h. The resulting solution was then filtered. After 2 weeks, black needle crystals of **1** were formed with a 70% yield. Anal. Calc. for $C_{18}H_{16}Cl_2MnN_5O_2$: C, 46.8; H, 3.4; N, 15.2. Found: C, 47.0; H, 3.5; N, 15.6%.

2.3. Crystal structure determination of **1**

Crystal data for **1** are given in table 1. Bond distances and angles for **1** are given in table 2. Four thousand and twenty-four – total independent data for **1** were collected on a STOE IPDS 2T device with a STOE detector equipped with graphite monochromated Mo K_α radiation ($\lambda=0.71073$ Å). Data collection was carried out using a STOE detector and for

Table 1. Summary of crystal data and refinement details of **1**.

Empirical formula	$C_{18}H_{16}Cl_2MnN_5O_2$
Formula weight	460.20
Crystal dimension (mm)	$0.30 \times 0.17 \times 0.05$
Crystal system	Orthorhombic
Space group	P c a 21
a (Å)	13.3469(5)
b (Å)	12.8284(7)
c (Å)	11.4068(5)
α (°), β (°), γ (°)	90.00
V (Å ³)	1953.07(16)
Z	4
Temperature (K)	193(2)
D_{calc} (g cm ⁻³)	1.565
μ (mm ⁻¹)	0.974
$F(0\ 0\ 0)$	936
θ (°)	2.83–29.67
Total data	4714
Unique data	3588
R	0.0427
R_w	0.1126
Goodness-of-fit on F^2 , S	1.039
R_{int}	0.0846
$\Delta\rho_{max}$ (e Å ⁻³)	0.296
$\Delta\rho_{min}$ (e Å ⁻³)	-0.484

$$w = 1/[\sqrt{s^2 \wedge (Fo^{\wedge 2})^{\wedge 2} + (0.0564P)^{\wedge 2} + 0.2207P}], \text{ where } P = (Fo^{\wedge 2} + 2Fc^{\wedge 2})/3'$$

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Mn1–O2	1.862(3)	O1–Mn1–O2	92.0(1)
Mn1–N1	1.990(3)	O1–Mn1–N1	91.4(1)
Mn1–N2	2.003(3)	O1–Mn1–N2	176.2(1)
Mn1–N3	2.336(3)	O1–Mn1–N3	94.2(1)
Mn1–N5	2.258(3)	O1–Mn1–N5	93.4(1)
C11–C4	1.752(4)	O2–Mn1–N1	176.6(1)
C12–C14	1.741(4)	O2–Mn1–N2	91.6(1)
O1–C1	1.324(5)	O2–Mn1–N3	91.5(1)
O2–C17	1.317(5)	O2–Mn1–N5	93.1(1)
N1–C7	1.296(5)	N1–Mn1–N2	85.1(1)
N1–C8	1.482(4)	N1–Mn1–N3	88.9(1)
N2–C9	1.479(4)	N1–Mn1–N5	86.0(1)
N2–C11	1.289(5)	N2–Mn1–N3	84.4(1)
N3–N4	1.178(5)	N2–Mn1–N5	87.7(1)
N4–N5	1.189(5)	N3–Mn1–N5	170.9(1)
N5–Mn1	2.258(3)	Mn1–O1–C1	128.1(2)
C1–C2	1.411(6)	Mn1–O2–C17	127.4(2)
C1–C6	1.412(6)	Mn1–N1–C7	128.1(2)
C2–H2	0.950(4)	Mn1–N1–C8	110.2(2)
C2–C3	1.380(5)	C7–N1–C8	120.4(3)
C3–H3	0.950(4)	Mn1–N2–C9	109.8(2)
C3–C4	1.374(6)	Mn1–N2–C11	127.7(2)
C4–C5	1.383(6)	C9–N2–C11	121.3(3)
C5–H5	0.950(4)	Mn1–N3–N4	110.2(2)
C5–C6	1.404(5)	N3–N4–N5	178.1(4)
C6–C7	1.473(6)	N4–N5–Mn1	122.2(3)

data reduction, STOE X-AREA software package was used. The structure was solved by SIR 97 [40]. Structure refinement was also performed by full-matrix least squares based on F^2 with SHELXL-97 [41]. All non-hydrogen atoms were refined anisotropically. The C-bound hydrogens were constrained to ideal geometry and included in the refinement in the riding model approximation. Data for molecular geometry, intermolecular interactions, and figures were produced using Platon-2009 [42] and ORTEP 3.2 [43].

3. Results and discussion

3.1. Synthesis and IR spectroscopy

H₂L was prepared by 1:2 condensation of ethane-1,2-diamine with 5-chloro-2-hydroxyacetophenone in methanol. The ligand was not isolated separately but the yellow methanolic solution obtained by the condensation was used in the present work. This ligand was previously reported in the preparation of base adducts of cobalt(II) and nickel(II) chelates with some Schiff bases using 2,2'-bipyridine and 1,10-phenanthroline [44]. The dianionic form of the ligand is a N₂O₂ donor in the reported complexes. The yellow methanolic solution – reacted with manganese(II) perchlorate hexahydrate and sodium azide in methanol-water mixture with refluxing to prepare the 1-D chain **1**. Mn(III) – is six coordinate by N₂O₂ donor, L²⁻ and two bridging azides. Related Schiff bases, viz. 5-OCH₃ salen or 5-F salen, form azide bridged polynuclear compounds under cold condition [34]. Another interesting feature of this ligand is that all other ligands reported were with the salicylaldehyde analogue, our ligand with o-hydroxy acetophenone analogue.

In IR spectra of **1**, the distinct band at 1589 cm^{-1} is due to azomethine (C=N) of the Schiff base. The asymmetric stretch of the azide (ν_{as}) is at 2032 cm^{-1} , attributed to the presence of an end-to-end azide bridge [45].

3.2. Description of the structure

Single-crystal X-ray analysis reveals that **1** consists of a chain system with the repeating unit $[\text{Mn}^{\text{III}}(\text{L})(\mu_{1,3}\text{-N}_3)]_n$ bridged by μ -1,3 azide (figure 1). There is only one crystallographically independent Mn(III) in a distorted octahedral geometry, which is coordinated by N_2O_2 donors from one Schiff base in the equatorial mode and two N_3^- ions in the axial positions (figure 2). Each azide functions as a *trans*- $\mu_{1,3}$ bridge to link monomeric $[\text{Mn}^{\text{III}}(\text{L})]^+$ units into a 1-D zigzag chain along the crystallographic *c* axis. In the equatorial plane, the Mn(1)–O(1), Mn(1)–O(2), Mn(1)–N(1), and Mn(1)–N(2) bond lengths are 1.866(2), 1.862(3), 1.990(3), and 2.003(3) Å, respectively, which are close to those in other Mn(III)-salen compounds [29, 33, 34]. As expected, the bond lengths in the axial position of Mn(1)–N(3) and Mn(1)–N(5A) [2.336(3) and 2.258(3) Å] are elongated due to Jahn–Teller distortion of the high-spin d^4 metal [14, 28]. The bond angles of Mn(1)–N(3)–N(4) and Mn(1)–N(5A)–N(4A) are $110.2(2)$ and $122.2(3)^\circ$, respectively. Deviations of the coordinating atoms in the basal plane, O(1), O(2), N(1), and N(2), from the least-square mean planes are 0.348, 0.348, 0.331, and 0.331 Å, respectively, and that of Mn(III) from the same plane is 0.877 Å. For N_3^- , N(3)–N(4) and N(4)–N(5A) have almost the same bond lengths [1.178(5) and 1.189(5) Å] and the N(3)–N(4)–N(5A) bond angle is $178.1(4)^\circ$, close to 180° . The manganese–manganese repeating distance is 5.825 Å along the chain.

3.3. Magnetic properties

The magnetic response of **1** was recorded from 2 to 300 K under a 0.1 T field. The resulting $\chi_{\text{M}}T$ vs. *T* plot is depicted in figure 3. At 300 K, the $\chi_{\text{M}}T$ is $2.47\text{ cm}^3\text{ mol}^{-1}\text{ K}$,

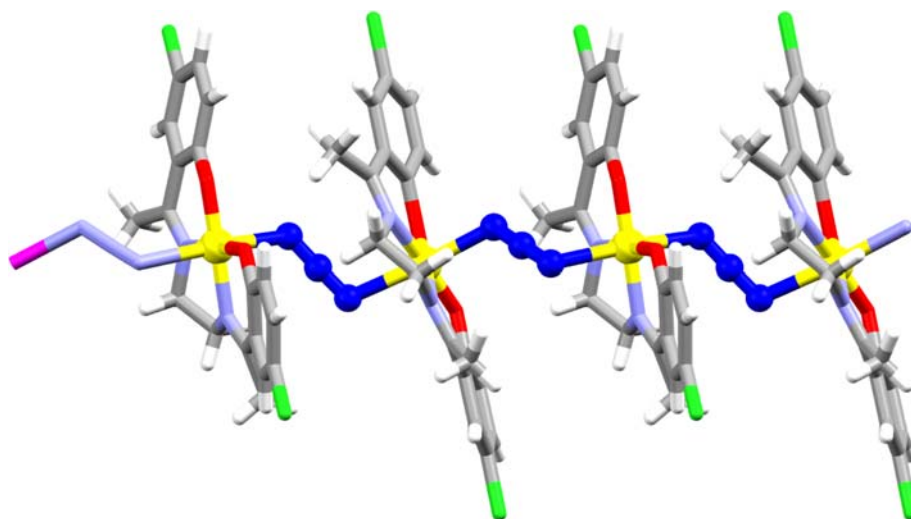


Figure 1. View of 1-D zigzag chain of **1**.

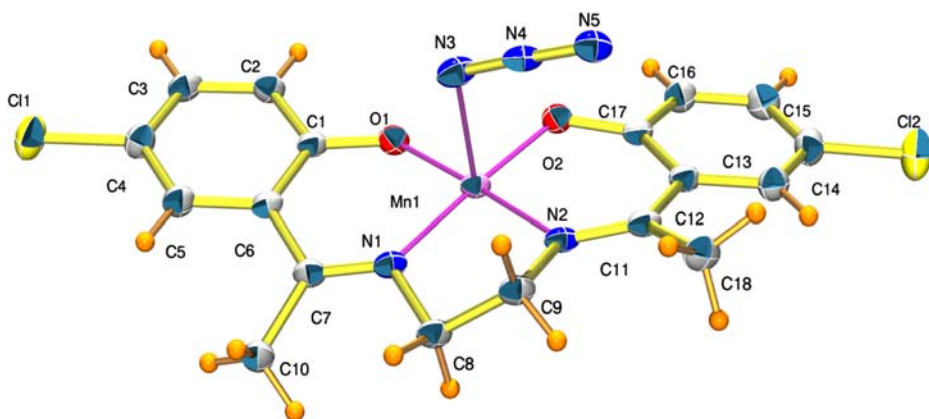


Figure 2. ORTEP diagram (30% ellipsoidal probability) with atom numbering scheme.

appreciably lower than the expected value for a well-isolated $S=2$ spin ($3.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), indicating the presence of antiferromagnetic interactions. Upon cooling, this value gradually decreases to $0.16 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, corroborating this assumption. At lower temperatures, this decrease is more pronounced, probably due to zero-field splitting (zfs) and/or Zeeman contributions of paramagnetic impurities. Due to this contribution, and to the zfs contributions of Mn^{III} in **1**, theoretical studies were carried out over the 300–20 K regime.

Interchain interactions were disregarded and the Hamiltonian considered was:

$$\hat{H} = -2J \sum_i \hat{S}_i \hat{S}_{i+1}$$

The $\chi_{\text{M}}T$ versus T data were fitted according to Fisher's model assuming classical spins [46], considering a paramagnetic impurity fraction ρ . The equation used was:

$$\chi = (1 - \rho) \frac{Ng^2 \beta^2 S(S+1)}{3k_B T} \frac{1 + u(K)}{1 - u(K)} + \rho \frac{Ng^2 \beta^2}{3kT} S(S+1) \quad (1)$$

where $u(K) = \coth K - 1/K$ and $K = \frac{4JS(S+1)}{k_B T}$.

Substituting with $S = S_i = S_{i+1} = 2$, the best-fit parameters were: $J = -7.8(1) \text{ cm}^{-1}$, $g = 1.95(1)$, and $\rho = 8.6(1)\%$ ($R = 7.1 \times 10^{-6}$).

Manganese(III) 1-D systems with Schiff bases as coligands and with single $\mu_{1,3}$ -azido bridge reported are summarized in table 3. In these systems, the Jahn–Teller axis of the Mn(III) ions is located in the azido bridge direction, with one electron in the d_{z^2} orbital; the $d_{x^2-y^2}$ orbital remains empty pointing to the capping ligand.

Escuer *et al.* [47] analyzed the effects of the structural parameters for Mn(II) end-to-end azido-bridged systems, with respect to their magnetic interactions, concluding that the exchange couplings are always antiferromagnetic, being the result of two types of contributions: σ (through the d_{z^2} orbital) and π (through the d_{xy} and d_{yz} orbital). The exchange coupling constant depends on three structural parameters: the Mn–N distance (d), the Mn–N₁–N₂ angle (α), and the Mn–N₁–N₃–Mn torsion angle (τ). In this way,

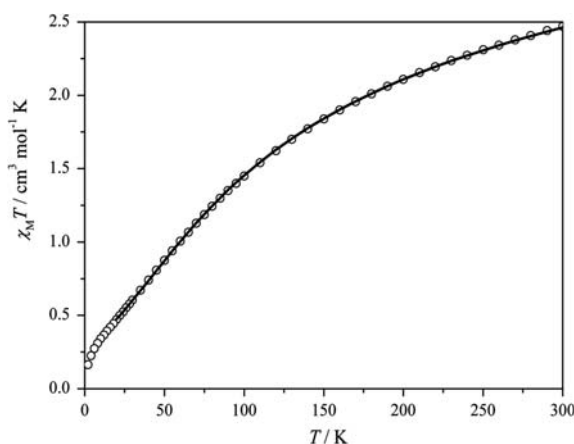


Figure 3. $\chi_M T$ vs. T data for **1** and best-fit curve according to the model described in the text.

Table 3. Selected structural and magnetic parameters for 1-D manganese compounds with $\mu_{1,3}$ -azido bridge ($H = -J \sum_{ij} S_i S_j$); $\alpha = \text{Mn-N-N}$ angles; $\tau = \text{Mn-N}_1\text{-N}_3\text{-Mn}$ torsion angle.

	d (Mn-N)/Å	α /°	τ /°	J/cm^{-1}	Ref.
[Mn(5-Fsalen)(N ₃) _n]	2.31	116.6	110.6	-8.8	[34]
[Mn(5-Meosalen)(N ₃) _n]	2.31	118.4	104.7	-6.0	[34]
[Mn(salen)(N ₃) _n]	2.31	116.5	109.8	-5.2	[33]
[Mn(5-Brsalen)(N ₃) _n]	2.20	119.3	106.5	-6.5	[29]
[Mn(salpn)(N ₃) _n]	2.34	127.6	126.8	-6.2	[20, 35]
[Mn(L)(N ₃) _n (1)	2.33	110.2	115.5	-7.8	Our study

Salen = tetradentate Schiff base obtained from the condensation of salicylaldehyde with ethane-1,2-diamine. Salpn = tetradentate Schiff base obtained from the condensation of salicylaldehyde with propane-1,3-diamine.

systems with short Mn-N distances, α angles close to 110°, and τ torsion angles similar to 0° (or 180°) should show the most antiferromagnetic interactions.

The exchange coupling of our compound, in agreement with every compound reported in previous work (see table 3), shows antiferromagnetic behavior. However, comparing the three factors mentioned above, it is not possible to establish any direct magneto-structural correlations with the strength of the exchange coupling. It appears that these factors are very much relevant and the first two are the deciding factors to control the strength of the exchange coupling for these types of complexes [34, 37]. Therefore, it may be concluded that **1** shows similar Mn-N distance found for this type of Mn(III) system (see table 3), α angles close to 110°, and as a result, moderate antiferromagnetic behavior.

4. Conclusion

A new Mn^{III}-Schiff base complex has been synthesized and characterized structurally, showing that azide bridges successive Mn(III)-Schiff base units into a 1-D coordination polymeric chain. Low-temperature magnetic measurements of the system reveal that $\mu_{1,3}$ -bridging azides mediate antiferromagnetic interaction among the Mn^{III} centers. The

strength of antiferromagnetic interaction in this system is moderate and compares well with other structurally identical azido-bridged Mn^{III} chain systems. Preparation of the present complex enriches the azide-based magneto chemistry, but also indicates that other closely related magnetic systems can be designed by varying the Schiff base as well as the transition metal.

Supplementary material

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication CCDC No. 883775. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/conts/retrieving.html>).

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