

A one-dimensional azido-bridged manganese(III) complex with bidentate Schiff base: Crystal structure and magnetic properties

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Abstract

The synthesis, structural characterization, and magnetic behavior of a novel one-dimensional azido-bridged manganese(III) complex of formula $[\text{Mn}(\text{L})_2\text{N}_3]$ (**1**) is reported, where HL is the bidentate Schiff base obtained from the condensation of salicylaldehyde with 4-methoxy aniline. Complex **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 11.743(4)$ Å, $b = 24.986(9)$ Å, $c = 13.081(5)$ Å, $\beta = 95.387(7)^\circ$ and $Z = 2$. The complex is of one-dimensional chain structure with single end-to-end azido bridges and the manganese(III) ion has an elongated octahedral geometry. Magnetic studies show that the weak antiferromagnetic interaction is mediated by the single end-to-end azido bridge with the exchange parameter $J = -5.84 \text{ cm}^{-1}$.

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1. Introduction

The coordination chemistry of manganese compounds has been of considerable interest [1,2]. These complexes are significant not only for their redox active role in several biochemical processes [3,4], but also for the diversity of their magnetic properties [5,6]. In this context, the Mn(III) complexes have received intense attention in recent years owing to their important roles in the area of molecular magnetism. For instance, the first single-molecule magnet (SMM) is a Mn_{12} complex [7–9] and the first bimetallic single-chain magnet (SCM) is a compound based on Mn(III) tetradenate Schiff base complex [10]. On the other hand, azide is the most versatile ligand in terms of being an efficient magnetic coupler and constructing diverse structural topologies [11]. Normally, the azide ligand mediates antiferromagnetic interaction when it bridges in an end-to-end (EE) mode and ferromagnetic interaction in an end-on (EO) mode, but an increasing number of exceptions have

been observed recently [12–15]. To date, a large number of azide-bridged manganese(II) complexes with various structures have been prepared and magnetically characterized for the understanding of the interaction between magnetic centers and for the development of new molecule-based magnetic materials [11,16–20]. However, to the best of our knowledge, the azido-bridged manganese(III) complexes are very rare and only few examples have been reported [21–27]. Herein we report the synthesis, crystal structure, and magnetic properties of a novel one-dimensional azido-bridged manganese(III) complex $[\text{Mn}(\text{L})_2\text{N}_3]$ (**1**), where HL is the bidentate Schiff base obtained from the condensation of salicylaldehyde with 4-methoxy aniline.

2. Experimental

2.1. General

All reagents and chemicals were purchased from commercial sources and used as received. Elemental analyses for C, H and N were carried out with a Perkin-Elmer 240 elemental analyzer. The infrared spectrum was taken on a Bruker Tensor 27 Fourier transform infrared

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spectroscopy in the 4000–400 cm^{-1} regions, using KBr pellets. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using $\text{CuK}\alpha$ radiation. Variable temperature magnetic susceptibilities on polycrystalline samples were measured on a SQUID magnetometer. The experimental susceptibilities were corrected for the sample holder and the diamagnetism contributions estimated from Pascal's constants.

2.2. Preparation of $[\text{Mn}(\text{L})_2\text{N}_3]$ (**1**)

A mixture of salicylaldehyde (0.244 g, 2 mmol) and 4-methoxy aniline (0.246 g, 2 mmol) in 10 mL of methanol was refluxed for 2 h to obtain a yellow solution of the Schiff base, and then added a solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.36 g, 1.0 mmol) in 20 mL methanol, followed by the addition of solid NaN_3 (0.19 g, 3 mmol). The resulted solution was refluxed for 1.5 h. The filtrate was left to stand for 3 weeks at room temperature. The dark brown crystals were collected (yield 65%). Anal. found (%): C, 61.59; H, 4.78; N, 12.30. Calcd. for $\text{C}_{28}\text{H}_{24}\text{MnN}_5\text{O}_4$: C, 61.20; H, 4.40; N, 12.74. IR (KBr): 2063 (s) cm^{-1} ($\nu_{\text{as}}(\text{N}_3)$), 1608 (s) cm^{-1} ($\nu(\text{C}=\text{N})$).

2.3. Crystallographic data collection and structure determination

Single crystal of the complex **1** was mounted on a Bruker Smart 1000 diffractometer with a CCD area detector and a graphite monochromated $\text{MoK}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$). Data collection was performed at room temperature. Empirical absorption corrections by SADABS were carried out [28]. The structure was solved by direct methods using the SHELXS-97 program [29] and refined with SHELXL 97 [30] by full matrix least-squares

Table 1
Summary of crystallographic data for complex **1**

Empirical formula	$\text{C}_{28}\text{H}_{24}\text{MnN}_5\text{O}_4$
Formula weight	1648.39
T (K)	294(2)
Crystal system	Monoclinic
space group	$P2_1/n$
a (\AA)	11.743(4)
b (\AA)	24.986(9)
c (\AA)	13.081(5)
α (deg)	90
β (deg)	95.387(7)
γ (deg)	90
V (\AA^3)	3821(2)
Z	2
μ (cm^{-1})	0.563
$F(000)$	1704
Data/restraints/parameters	7731/0/520
Reflections collected/unique	21433/7731
Final R indices [$I > 2\sigma$]	$R_1 = 0.0507$, $wR_2 = 0.0807$
R indices (all data)	$R_1 = 0.1433$, $wR_2 = 0.1009$
Largest difference in peak and hole (e \AA^{-3})	0.398 and -0.447
Goodness-of-fit on F^2	1.003

Table 2
Selected bond lengths (\AA) and angles (deg) for complex **1**

Bond lengths			
Mn(1)–O(2)	1.851(2)	Mn(1)–N(2)	2.221(3)
Mn(1)–N(1)	2.058(3)	Mn(2)–N(4)	2.290(3)
Mn(2)–O(6)#2	1.839(2)	Mn(2)–O(4)	1.853(2)
Mn(2)–N(8)#2	2.057(3)	Mn(2)–N(5)	2.087(3)
Mn(2)–N(6)	2.267(3)		
Bond angles			
O(2)#1–Mn(1)–O(2)	179.999(1)	O(2)#1–Mn(1)–N(1)	89.80(11)
O(2)–Mn(1)–N(1)	90.20(11)	O(2)#1–Mn(1)–N(1)#1	90.20(11)
O(2)–Mn(1)–N(1)#1	89.80(11)	N(1)–Mn(1)–N(1)#1	179.997(2)
O(2)#1–Mn(1)–N(2)#1	90.93(11)	O(2)–Mn(1)–N(2)#1	89.07(11)
N(1)–Mn(1)–N(2)#1	85.26(12)	N(1)#1–Mn(1)–N(2)#1	94.74(12)
O(2)#1–Mn(1)–N(2)	89.07(11)	O(2)–Mn(1)–N(2)	90.93(11)
N(1)–Mn(1)–N(2)	94.74(12)	N(1)#1–Mn(1)–N(2)	85.27(12)
N(2)–N(3)–N(4)	177.8(4)	N(3)–N(2)–Mn(1)	140.1(3)
O(6)#2–Mn(2)–O(4)	177.44(11)	O(6)#2–Mn(2)–N(8)#2	88.90(11)
O(4)–Mn(2)–N(8)#2	88.88(11)	O(6)#2–Mn(2)–N(5)	91.82(11)
O(4)–Mn(2)–N(5)	90.22(10)	N(8)#2–Mn(2)–N(5)	172.99(10)
O(6)#2–Mn(2)–N(6)	91.61(11)	O(4)–Mn(2)–N(6)	89.94(11)
N(8)#2–Mn(2)–N(6)	97.37(11)	N(5)–Mn(2)–N(6)	89.57(11)
O(6)#2–Mn(2)–N(4)	87.73(11)	O(4)–Mn(2)–N(4)	90.90(11)
N(8)#2–Mn(2)–N(4)	87.47(11)	N(5)–Mn(2)–N(4)	85.59(11)
N(6)–Mn(2)–N(4)	175.10(12)	N(6)–N(7)–N(6)#2	179.997(2)
N(3)–N(4)–Mn(2)	123.5(3)	N(7)–N(6)–Mn(2)	138.6(2)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z+2$; #2: $-x+2, -y+1, -z+1$.

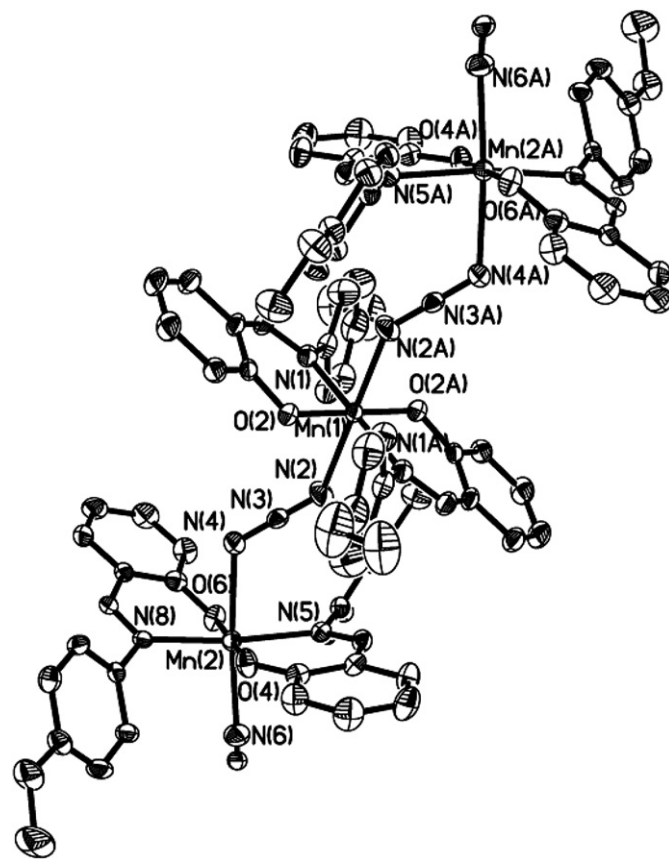


Fig. 1. An ORTEP drawing of $[\text{Mn}(\text{L})_2\text{N}_3]$ with atom-labeling and 30% thermal ellipsoids.

method on F^2 . All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. Crystallographic data are summarized in Table 1, selected bond distances and bond angles are given in Table 2.

3. Results and discussion

3.1. Crystal structure of **1**

The X-ray structure analysis of complex **1** reveals an azido-bridged Mn(III) chain as shown in Figs. 1 and 2. Two crystallographically independent Mn(III) ions lie in slightly distorted octahedral geometry in which the metal ion binds to two Schiff base ligands in the equatorial mode and two azide ligands in the axial positions and the Mn(1) is located at the inversion center. Each azide ligand functions as a $trans-\mu_{1,3}$ bridge to link monomeric $[\text{Mn}(\text{L})_2]^+$ units into a 1D chain. In the equatorial N_2O_2 plane, the average Mn–N and Mn–O bond lengths are 2.067(3) and 1.848(2) Å, respectively. As expected for octahedral Mn(III) ions, the Jahn–Teller distortion leads to elongated Mn–N_{azide} bond distances, which vary from 2.221(3) to 2.290(3) Å. The coordination of azide bridge is

symmetrical for Mn(1): Mn(1)–N(2)–N(3) is $140.1(3)^\circ$, while that is asymmetrical for Mn(2): Mn(2)–N(4)–N(3) is $123.5(3)^\circ$ and Mn(2)–N(6)–N(7) is $138.6(2)^\circ$. The shortest intrachain Mn–Mn distance is 6.212 Å.

3.2. Magnetic properties

The temperature dependence of magnetic susceptibility of complex **1** was measured from 2.0 to 300 K in an applied magnetic field of 2 kOe using polycrystalline sample. Powder X-ray diffraction of complex **1** and the simulated PXRD pattern calculated from the single-crystal data are identical (Fig. 3). The magnetic susceptibility χ_M and effective magnetic moment μ_{eff} versus T plots are shown in Fig. 4. The μ_{eff} value of $4.48 \mu_B$ at 300 K is slightly smaller than that expected for non-interacting Mn(III) ($S = 2$, $4.90 \mu_B$). As the temperature is lowered, the μ_{eff} value decreases smoothly to $0.49 \mu_B$ at 2.0 K. The χ_M values show

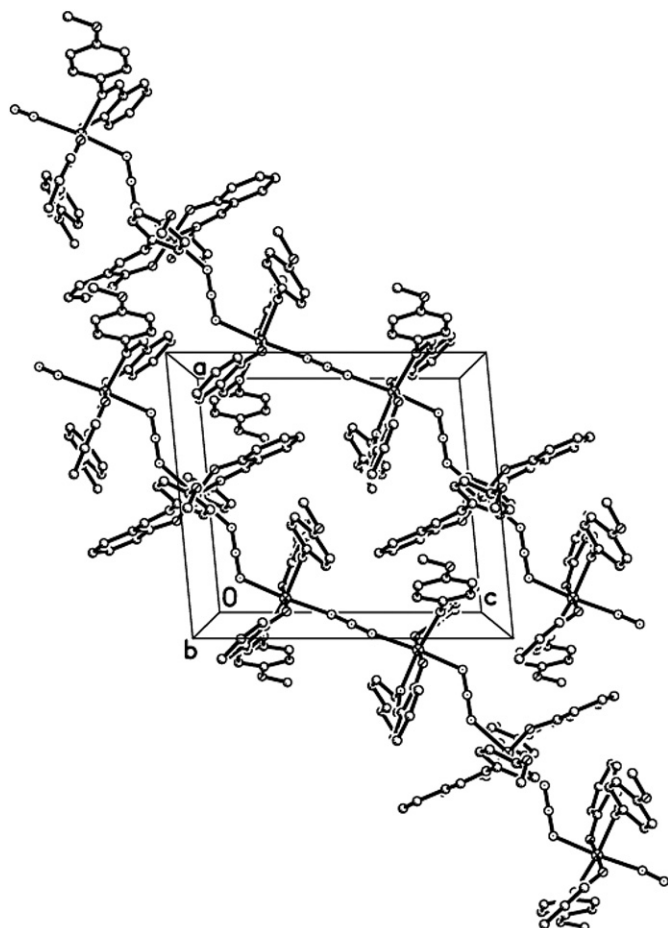


Fig. 2. View of the chains of $[\text{Mn}(\text{L})_2\text{N}_3]$ in the unit cell.

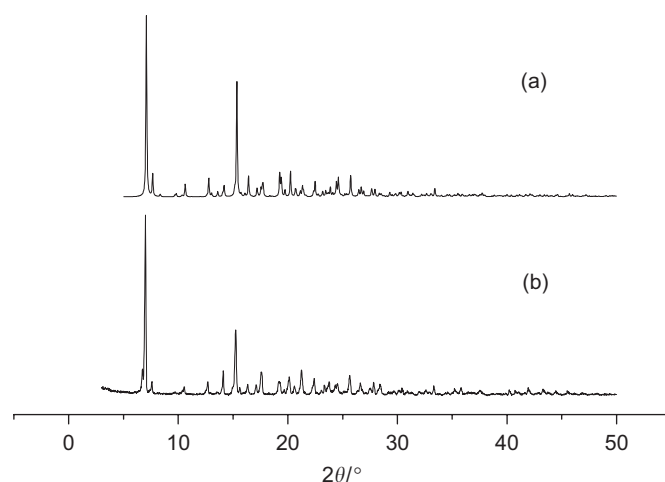


Fig. 3. PXRD patterns for $[\text{Mn}(\text{L})_2\text{N}_3]$: (a) the simulated PXRD pattern calculated from the single-crystal structure and (b) taken at room temperature.

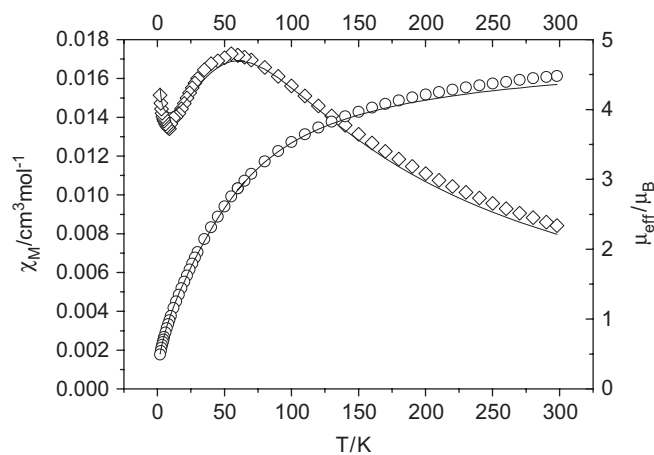


Fig. 4. Plots of χ_M (\square) and μ_{eff} (\circ) versus T for $[\text{Mn}(\text{L})_2\text{N}_3]$. The solid line corresponds to the best theoretical fits.

Table 3
Selected structural and magnetic parameters for reported 1D Mn(III) complexes bridged by $\mu_{1,3}$ -azido

Complex	Mn–N _{azido} (Å)	Mn–N–N (deg)	J (cm ⁻¹)	Reference
[Mn(salpn)N ₃]	2.331(4), 2.348(4) (2.339) ^a	137.8(3), 137.5(2) (127.5) ^a	-4.03	[23,24]
[Mn(acac) ₂ N ₃]	2.245(2)	131.3(2)	-5.3	[21]
[Mn(salen)N ₃]	2.280(2), 2.334(2) (2.307) ^a	118.42(16), 114.64(16) (116.53) ^a	-5.19(8)	[25]
[Mn(5-Brsalen)N ₃]	2.341(3), 2.299(3) (2.320) ^a	119.3(4)	-6.5	[27]
[Mn(L) ₂ N ₃]	2.221(3), 2.290(3), 2.267(3) (2.260) ^a	140.1(3), 123.5(3), 138.6(2) (134.1) ^a	-5.84	This work

salpn: dianion of *N,N'*-bis(salicylidene)-1,3-diaminopropane; acac: acetylacetonate anion; salen: dianion of *N,N'*-bis(salicylidene)-1,3-diaminoethane; 5-Brsalen: dianion of *N,N'*-bis(5-bromosalicylidene)-1,3-diaminoethane.

^aAverage value.

a broad maximum around ca. 55 K, which indicates that an antiferromagnetic interaction takes place between manganese(III) ions. Meanwhile, the rising of χ_M at low temperature is due primarily to the presence of a small amount of paramagnetic impurities. It should be noted that a sharp increase in susceptibility at low temperature is observed in [Mn(salpn)N₃] [23,24], [Mn(acen)₂N₃] [22] and [Mn(acac)₂N₃] [21]. This can be attributed to the result of spin canting which arises from the zero-field splitting of Mn(III) [21]. However, this does not occur with complex **1** since no any small peak is observed in the curve of μ_{eff} versus T at low temperature. According to the crystal structure, the magnetic data can be analyzed using the expression for antiferromagnetic one-dimensional $S = 2$ chain given by Hiller et al. [31]. Considering the magnetic behavior at low temperature, the paramagnetic impurities ρ and the mean-field approximation (zJ) were introduced [32].

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{kT} \frac{A + Bx^2}{1 + Cx + Dx^3} (1 - \rho) + \frac{Ng^2\beta^2 S(S + 1)}{3kT} \rho,$$

$$\chi_M = \frac{\chi_{\text{chain}}}{1 - \chi_{\text{chain}}(zJ'/Ng^2\beta^2)},$$

where $A = 2.000$, $B = 71.938$, $C = 10.482$, $D = 955.56$ and $x = |J|/kT$.

The best fit gives $J = -5.84 \text{ cm}^{-1}$, $g = 2.02$, $zJ' = -0.76 \text{ cm}^{-1}$, $\rho = 0.13\%$ and $R = 8.66 \times 10^{-4}$ (R value is defined as $\sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \sum[(\chi_M)_{\text{obs}}]^2$). The fitting results show that there exists weak antiferromagnetic interaction between Mn(III) ions. In order to compare the results of the present complex with other reported 1D Mn(III) complexes bridged by azide in $\mu_{1,3}$ mode, the relevant magneto-structural data of these complexes are listed in Table 3. It can be seen that the magnitude of magnetic coupling between Mn(III) ion is mainly related to the distance of Mn–N(azido). The longer the bond Mn–N is, the weaker the magnetic exchange coupling is. There almost is no correlation between the magnetic coupling and Mn–N–N angle. For $\mu_{1,3}$ -azido-bridged Mn(III) complexes, due to Jahn–Teller distortion, the only magnetic orbital that can make a significant contribution to the magnetic coupling should be the d_{z^2} orbital of Mn(III) ion [33] and the axial ligand, azide, will provide mainly a σ -type superexchange pathway. The longer axial bonds are, the

smaller the overlap of magnetic orbitals is, and this results in weaker antiferromagnetic coupling.

3.3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 635289. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

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