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Synthesis and Crystal Structure of One-Dimensional Azide-Bridged Mn(III) Polymer [Mn($BrSal_2MePn$)($\mu_{1,3}$-N_3)]$_n$ ($BrSaI_2MePn$ = N,N'-Bis(salicylidene)-1,2-propanediamine)[1]

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Abstract—A new one-dimensional manganese(III) Schiff base complex [Mn($BrSal_2$MeĐn)($\mu_{1,3}$-N_3)]$_n$ (**I**) was synthesized by the reaction of $MnCl_2 \cdot 6H_2O$ with the Schiff base ligand H_2BrSal_2MeĐn condensed from 2,2-dimethylpropylenediamine with 5-bromosalicylaldehyde and was characterized by elemental analyses and FT-IR spectroscopy. The molecular structure of **I** has been determined from single-crystal X-ray diffraction analysis. In this structure, the Mn^{3+} ion is in a distorted octahedral geometry with an obvious Jahn–Teller effect, where the deprotonated tetradentate Schiff-base ligand $BrSal_2MePn^{2-}$ is bound in the equatorial plane and the N_3^- anions show $\mu_{1,3}$-bridging mode in the axial direction.

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INTRODUCTION

In recent years extensive studies have been focused on the chemistry of manganese(III) complexes with Schiff-base ligands because of their growing interest in the field of molecular magnetism [1], metalloenzymes [2], and inhibitors of xanthine oxidase [3] and in understanding their catalytic activities in many organic reactions [4]. These complexes have high-spin ground state and apparent magnetic anisotropy and are among the complexes acting as paramagnetic building blocks for constructing expanded structures with appealing magnetic properties [5].

One-dimensional manganese(III) Schiff base complexes are of particular interest in the field of molecular magnetism [6–11]. These complexes are generally found to exhibit both weak antiferromagnetic [6, 7] and ferromagnetic [8–11] interaction. To date, an increasing number of manganese(III) coordination polymers based on tetradentate Schiff base ligands bridged by conjugated small groups, such as cyano, oxalate, nitride, and azido, have been reported [6–11]. Among these short bridging ligands, in particular, the azide ion exhibits versatile bridging mode, such as $\mu_{1,1}$ [12], $\mu_{1,3}$ [13], and rarely $\mu_{1,1,3,3}$ [14]. However, to the best of our knowledge, the azido-bridged manganese(III) complexes are very rare and only few examples have been reported [6–11]. This study is part of our ongoing effort to synthesize and characterize an extensive series of manganese(III) complexes with the N_2O_2 Schiff-base ligand [15, 16].

Herein we report the synthesis and crystal structure a of new one-dimensional manganese(III) Schiff base complex [Mn($BrSal_2MePn$)($\mu_{1,3}$-N_3)]$_n$ (**I**).

EXPERIMENTAL

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR PerkinElmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer.

Synthesis of complex I. H_2BrSal_2MePn was prepared by the condensation of 2,2-dimethylpropylenediamine with 5-bromosalicylaldehyde following the literature methods [17]. The solid yellow Schiff base ligand [H_2BrSal_2MePn] (0.468 g, 1 mmol) was dissolved in a 1 : 1 methanol–acetone mixture (20 ml) with vigorous stirring. A methanolic solution (10 ml) of $MnCl_2 \cdot 2H_2O$ (0.322 g, 2 mmol) was added to the stirred solution of H_2BrSal_2MePn and was further stirred for 2 h at room temperature. An aqueous solution (5 ml) of sodium azide (0.65 g, 10 mmol) was slowly added dropwise to the above solution resulting in the precipitation of a small amount of a brown coloured solid that redissolved upon complete addition of the sodium azide solution. The resulting solution was stirred for 20 min at room temperature and filtered. The filtrate was left at room temperature (at 25°C). Dark brown single crystals of I suitable for X-ray analysis were obtained after several days by slow evaporation of

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solvents at room temperature, then collected by filtration, and dried in vacuo. The yield was 81%.

For $C_{38}H_{36}Br_4Mn_2N_{10}O_4$

anal. calcd., %:	C, 40.52;	H, 3.22;	N, 12.44.
Found, %:	C, 40.66;	H, 3.31;	N, 12.84.

IR (KBr; ν, cm^{-1}): 2869–2966 (C–H aliphatic and aromatic), 2048 s (N_3), 1619 s (C=N), 1455–1589 (C=C aromatic), 1290 s (C–O), 463 s (Co–N), 418 s (Co–O).

Caution! Although we did not experience any problem during the work, perchlorate- and azide-containing compounds being potentially explosive, such compounds should be used in small quantities and handled with great care.

X-ray structure determination. A single crystal of **I** was placed at the top of a glass fiber with silicone grease and mounted on an Xcalibur 2 CCD diffractometer (Oxford Diffraction) fitted with a graphite monochromated MoK_α radiation (λ = 0.71073 Å). Data were collected at 170 K. The structure was solved by direct methods and successive Fourier difference syntheses and was refined on F^2 by weighted anisotropic full-matrix least-squares methods [18]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were calculated and, therefore, included as isotropic fixed contributors to F_c. Data collection and data reduction were done with the CRYSALIS-CCD and CRYSALIS-RED programs [19]. All other calculations were performed with standard procedures (WINGX) [20]. Crystal data, structure refinement and collection parameters for **I** are listed in Table 1.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 810811; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and experimental details for complex **I**

Parameter	Value
Molecular weight	1126.29
Crystal system, space group	Monoclinic, $P2_1/c$
a, Å	12.6445(4)
b, Å	12.8920(5)
c, Å	12.4737(6)
β, deg	90.603(4)
V, Å^3	2033.26(14)
Z	2
ρ_{calcd}, g cm^{-3}	1.840
μ, mm^{-1}	4.61
F(000)	1112
Reflections measured	11698
$\theta_{min}/\theta_{max}$, deg	2.8/31.8
Reflections unique/R_{int}	5977/0.060
Reflections with $I > 2\sigma(I)$	2480
N_v	262
$R(F^2 > 2\sigma(F^2))$	0.039
$wR(F^2)$	0.077
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.83/–0.56
S	0.77
$(\Delta/\sigma)_{max}$	0.002
Index parameters	$-18 \le h \le 17$
	$-18 \le k \le 11$
	$-18 \le l \le 11$

$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

H_2BrSal_2MePn was prepared by the condensation of 2,2-dimethylpropylenediamine with 5-bromosalicylaldehyde following the literature methods [17]. The Schiff-base ligand H_2BrSal_2MePn is soluble in common solvents, such as $CHCl_3$ and CH_2Cl_2, while the respective Mn(III) complex is soluble in DMF and DMSO but insoluble in EtOH, MeOH, $CHCl_3$, and CH_2Cl_2. All compounds synthesized in this work are stable at room temperature in the solid state.

The IR spectra of the free ligand H_2BrSal_2MPn exhibit the characteristic band of the imine group (–C=N–) which appears at 1633 cm^{-1}. This band is shifted in the complexes toward lower frequencies because of the coordination of the nitrogen atom to the metal ion [6–11], and appears at 1619 cm^{-1} (**I**). The observed red shift of the –C=N– vibration with an addition coordination to the Mn atom can be attributed to the metal to ligand π-back bonding. In the infrared spectra of **I** the sharp band in a range of 2048 cm^{-1} that is absent in the spectrum of the pure ligand is assignable to the asymmetric stretching vibration of the N_3 moiety [6–11]. The phenolic C–O stretching is obtained at about 1290 cm^{-1} in **I** and 1278 cm^{-1} in the free ligand [21, 22]. The ligand coordination to the cobalt center is substantiated by prominent bands appeared at nearly 463 and 418 cm^{-1}, which can be attributed to ν(Co–N) and ν(Co–O), respectively [21, 22].

The molecular structure of complex **I**, including the atom-numbering schemes, is shown in Fig. 1, and selected bond lengths and angles are given in Table 2. Single-crystal X-ray analyses reveal that complex I consists of one-dimensional chains based on $[Mn(BrSal_2MePn)]^+$ subunits, and the manganese center has a distorted octahedral geometry, which is coordinated by the N_2O_2 donor atoms from one $BrSal_2MePn$ ligand in the equatorial plane and two nitrogen donor atoms from two $\mu_{1,3}$-azido ions in the axial direction [6–11]. Each azide ligand function as a trans $\mu_{1,3}$ bridge to link monomeric

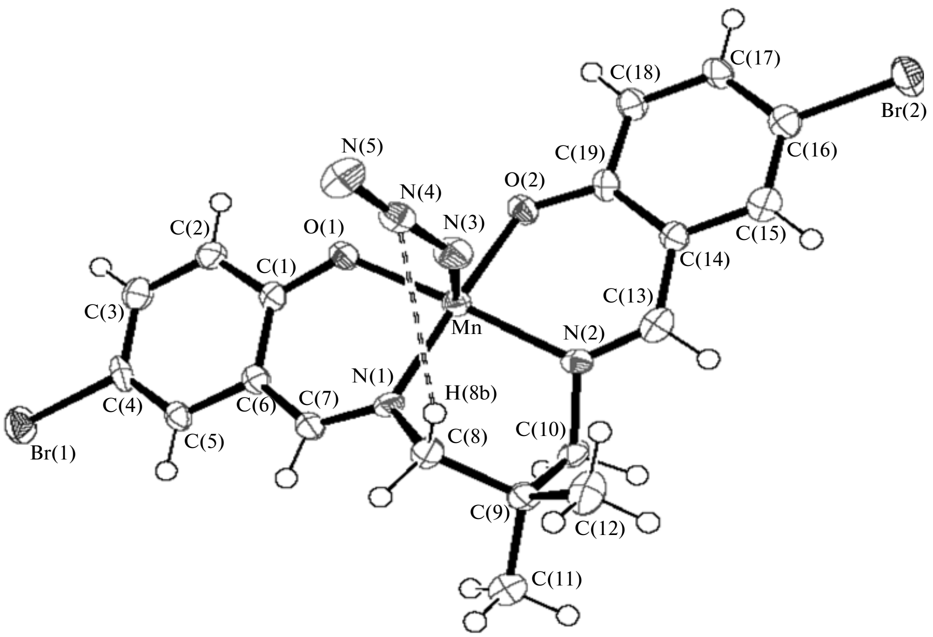

Fig. 1. Molecular structure of **I**, showing 50% probability displacement ellipsoids and atom numbering. Dashed lines indicate C–H···N hydrogen bond.

Fig. 2. View of the one-dimensional zigzag chain of **I**.

$[Mn(BrSal_2MePn)]^+$ units into a one-dimensional zigzag chain along the *x* axis (Fig. 2). The chain structure belongs to a modification of the type **I** azide chain based on the recent classification [23].

In the equatorial plane the bond lengths of Mn–N(1), Mn–N(2), Mn–O(1), and Mn–O(2) are 2.005(3), 2.013(3), 1.892(2), and 1.894(2) Å, respectively, which are close to those in other one-dimensional manganese(III) Schiff-base complexes [6–11]. The bond distances in the axial position of Mn–N(3) and Mn–N(5)^i are 2.266(3) and 2.284(3) Å, respectively, which are close to those in other one-dimensional manganese(III) Schiff-base complexes and are elongated to the Jahn–Teller distortion at the high-spin d^4 Mn(III) center [6–11]. In complex I, the equatorial atoms Mn, O(1), O(2), N(1), and N(2) are nearly coplanar and the two phenyl rings of 5-bromosalicylaldehyde lie in two different planes.

The equatorial angles of I are similar to those found in $[Mn(Salpn)(N_3)]$ [7, 8], $[Mn(Salen)(N_3)]$ [8], and $[Mn(X\text{-}Salen)(N_3)]$ [10, 11]. As for $\mu_{1,3}$-azido anions, the N(3)–N(4) and N(4)–N(5) bond distances have almost the some lengths (1.178(4) and 1.174(4) Å, respectively), and the N(3)N(4)N(5) bond angle is

Table 2. Selected bond distances and angles for **I***

Bond	d, Å	Bond	d, Å
N(1)–Mn	2.005(3)	N(5)–Mn^{i}	2.284(3)
O(1)–Mn	1.892(2)	N(2)–Mn	2.013(3)
N(3)–N(4)	1.178(4)	N(5)–N(4)	1.174(4)
C(10)–N(2)	1.479(4)	C13–N(2)	1.283(4)
C(7)–N(1)	1.281(4)	C(8)–N(1)	1.473(4)
C(4)–Br(1)	1.907(3)	C(16)–Br(2)	1.898(4)
C(1)–O(1)	1.327(4)	C(19)–O(2)	1.314(4)
N(3)–Mn	2.266(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)MnN(2)	88.17(11)	O(1)MnO(2)	92.06(10)
O(2)MnN(1)	176.41(11)	O(1)MnN(1)	90.51(10)
O(2)MnN(2)	89.48(11)	O(1)MnN(2)	174.86(11)
C(13)N(2)C(10)	118.8(3)	C(7)N(1)C(8)	118.4(3)
C(8)N(1)Mn	118.9(2)	C(7)N(1)Mn	122.3(2)
C(10)N(2)Mn	115.9(2)	C(13)N(2)Mn	125.1(2)
N(4)N(5)Mn^{i}	129.1(3)	N(4)N(3)Mn	138.8(3)
N(1)C(7)C(6)	126.7(3)	N(1)C(8)C(9)	115.5(3)
C(1)O(1)Mn	125.8(2)	C(19)O(2)Mn	128.9(2)
N(2)C(13)C(14)	126.3(3)	N(2)C(10)C(9)	115.0(3)
O(1)Mn)N(3)	96.31(11)	O(2)MnN(3)	91.58(11)
N(1)Mn)N(3)	85.64(11)	N(2)MnN(3)	88.55(11)
O(1)MnN(5)^{ii}	87.23(11)	O(2)MnN(5)^{ii}	92.26(11)
N(1)MnN(5)^{ii}	90.37(12)	N(2)MnN(5)^{ii}	87.80(11)
N(5)N(4)N(3)	177.1(4)	N(3)MnN(5)^{ii}	174.68(11)

* Symmetry codes: ^{i} x, $-y\ -1/2$, $z + 1/2$; ^{ii} x, $-y - 1/2$, $z - 1/2$.

177.1(4)°, which is close to 180° [6–11]. The distances between Mn···Mn^{i} is 6.246 Å, being a little longer than [Mn(F-Salen)(N_3)] (5.583 Å), [Mn(MeO-Salen)(N_3)] (5.592 Å) [10], [Mn(Salen)(N_3)] (5.56 Å) [8], while those are not sufficiently short for metal–metal bonding. The bond angles MnN(3)N(4) and Mn^{i}N(5)N(4) are 138.8(3)° and 129.1(3)°, respectively, indicating nonlinear Mn–N(3)–N(4)–N(5)–Mn^{i}, and are larger than [Mn(F-Salen)(N_3)] (114.7(2)° and 118.5(2) Å), [Mn(MeO-Salen)(N_3)] (120.3(2)° and 116.5(2)°) [10].

In complex **I**, there is non-classical intramolecular C–H···N hydrogen bond observed between aliphatic hydrogen atoms and one nitrogen atom of the azide ions C(8)–H(8b)···N(4) (3.750 Å and 134.137°) (Fig. 1).

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