A Novel Hydrogen-bonded Zigzag Chain Manganese(III) Complex: Synthesis, Crystal Structure and Magnetic Properties

Hulya Kara

Balikesir University, Faculty of Art and Sciences, Department of Physics, TR-10145 Balikesir, Turkey

Reprint requests to Dr. H. Kara. E-mail: hkara@balikesir.edu.tr

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The synthesis, crystal structure and magnetic properties of $[Mn(III)L(H_2O)_2]^+ClO_4^-$, **1** [L = *N*,*N*′-bis(rac-3,5-dichlorosalicylidenato)-1,2-diaminopropane] are reported. Single crystal X-ray diffraction studies showed the structure to consist of $[MnL(H_2O)_2]^+$ octahedra, with *trans*-coordinated water molecules, which are linked into infinite helices by hydrogen bonds. The distorted octahedral manganese(III) centre contains an $N_2O_2O'_2$ coordination sphere made up of the Schiff base ligand in the equatorial plane. In the axial direction, an elongation of the *trans* Mn–O_{water} bonds to 2.165(2) and 2.187(2) Å is observed. Such elongations are typical of d^4 systems but in this case may also be attributed to the poorer donor power of the water molecules.

Key words: Crystal Structures, Manganese(III) Complex, Schiff Base Ligand, Hydrogen Bond, Supramolecular Chemistry

Introduction

Schiff base Mn(III) complexes have been of considerable interest in recent years mainly due to their important roles as models for biological systems, *e.g.*, of many metalloenzymes, redox and non-redox proteins [1, 2] and also in catalysts for olefin epoxidation [3] and various photocatalytic reactions, including photocleavage of DNA [4], and to their photophysical properties [5] and the occurrence in photosystem II models [6]. Manganese complexes have also been studied widely because of their structural and novel electronic and magnetic properties [7]. Exchange interaction between paramagnetic centres of multinuclear complexes has already been investigated [8, 9]. The nature and the tuning of magnetic interactions between metal centres are crucial points in the conception of molecule-based magnetic materials [10]. Manganese(III) complexes of tetradentate Schiff base ligands have a clear tendency to form infinite linear or helical chains, due to the predisposition of these ligands to occupy a planar configuration in an octahedral coordination geometry, leaving the axial positions free to allow for stacking through bidentate bridges [11]. I report here on the synthesis, crystal structure and magnetic properties of $[Mn(III)L(H_2O)_2]^+ClO_4^-$, **1** [L = *N*,*N*′-bis(rac-3,5-dichlorosalicylidenato)-1,2-diaminopropane] (Fig. 1). To my knowledge, in the general class of manganese(III) Schiff base complexes, the present work gives only the second example of a hydrogen-bonded zigzag chain manganese(III) complex, the other example being the related $[MnL(H_2O)_2]^+ClO_4^- \cdot H_2O$ [L = *N*,*N*′-bis(5-chlorosalicylidene)-1,3-propanediaminato] [12].

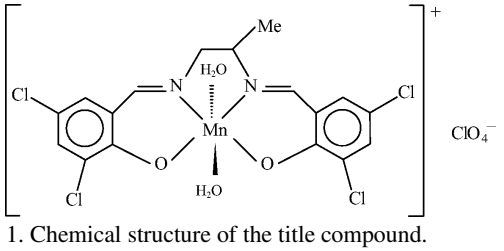

Fig. 1. Chemical structure of the title compound.

Experimental Section

Reagents

1,2-Diaminopropane, 3,5-dichlorosalicylaldehyde, manganese(III) acetate dihydrate and sodium perchlorate were purchased from Aldrich Chemical Co. Methanol and ethanol were purchased from Riedel. Elemental (C, H, N) analyses were carried out by standard methods. FT-IR spectra were measured with a Perkin-Elmer Model Bx 1600 instrument with the samples as KBr pellets in the 4000 – 400 cm^{-1} range. The temperature dependence of the mag-

Table 1. Crystallographic and refinement data for **1**.

Formula	$C_{17}H_{16}Cl_5MnN_2O_8$
Formula weight	608.51
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$C2/c$
a [Å]	18.320(4)
b [Å]	16.497(3)
c [Å]	15.111(3)
β [deg]	101.97(3)
Volume [Å^3]	4467.4(2)
Z	8
Density (calculated) [g cm^{-3}]	1.8
Absorption coefficient [mm^{-1}]	1.2
$F(000)$ [e]	2440
θ Range for data collection [deg]	2.27 – 27.48°
Index ranges	$-23 \le h \le 23$, $-21 \le k \le 21$, $-18 \le l \le 19$
Reflections collected	25129
Independent reflections	5108 ($R_{(int)}$ = 0.043)
Data / restraints / parameters	5108 / 4 / 328
Goodness-of-fit on F^2	1.115
Final R indices [$I \ge 2\sigma(I)$]	R_1 = 0.044, wR_2 = 0.097
R indices (all data)	R_1 = 0.054, wR_2 = 0.101
Largest peak / hole in fin. diff. map [e Å^{-3}]	1.5 / −0.68

netic susceptibility of polycrystalline samples was measured between 5 and 300 K at a field of 1.0 T using a Quantum Design model MPMS computer-controlled SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants [10b].

Synthesis

Caution: Although no problems have been encountered in the present work, perchlorates are potentially explosive and should be handled in small quantities and with care.

The ligand was prepared by reaction of racemic 1,2-diaminopropane (1 mmol) with 3,5-dichlorosalicylaldehyde (2 mmol) in hot ethanol (100 mL). The yellow compound precipitated from solution on cooling. Complex **1** was prepared by addition of manganese(III) acetate dihydrate (1 mmol) in 40 mL of hot ethanol to the ligand (1 mmol) in 50 mL of hot methanol. The resulting solution was stirred for 30 min. After the solution had been filtered, a methanol solution of sodium perchlorate (1 mmol) was added to the filtrate. The solution was warmed to 60 °C, 20 mL of hot water were added and this solution was filtered rapidly. A deep-brown solution was obtained and then allowed to stand at r. t. Several weeks of standing led to the growth of deep-brown crystals of **1** suitable for X-ray analysis. IR (KBr): ν (C=N) = 1620, $\nu(ClO_4)$ = 1095, 630 cm^{-1}. – $C_{17}H_{16}Cl_5MnN_2O_8$ (608.51): calcd. C 33.55, H 2.65, N 4.60; found C 33.65, H 2.40, N 4.68.

Table 2. Selected bond lengths (Å) and angles (deg) for **1**.

Mn(1)-O(1)	1.910(2)	Mn(1)-O(4)	2.165(2)
Mn(1)-O(2)	1.916(2)	Mn(1)-N(1)	1.990(2)
Mn(1)-O(3)	2.187(2)	Mn(1)-N(2)	1.991(2)
O(1)-Mn(1)-O(2)	96.75(8)	O(1)-Mn(1)-O(3)	89.91(8)
N(1)-Mn(1)-N(2)	81.15(1)	O(1)-Mn(1)-O(4)	87.11(8)
O(1)-Mn(1)-N(1)	91.14(9)	O(2)-Mn(1)-O(3)	88.87(8)
O(2)-Mn(1)-N(2)	90.94(9)	O(2)-Mn(1)-O(4)	91.89(8)
O(1)-Mn(1)-N(2)	172.01(9)	N(1)-Mn(1)-O(3)	90.33(9)
O(2)-Mn(1)-N(1)	172.07(9)	N(1)-Mn(1)-O(4)	89.32(9)
O(4)-Mn(1)-O(3)	176.99(8)	N(2)-Mn(1)-O(3)	88.05(9)
		N(2)-Mn(1)-O(4)	94.85(9)

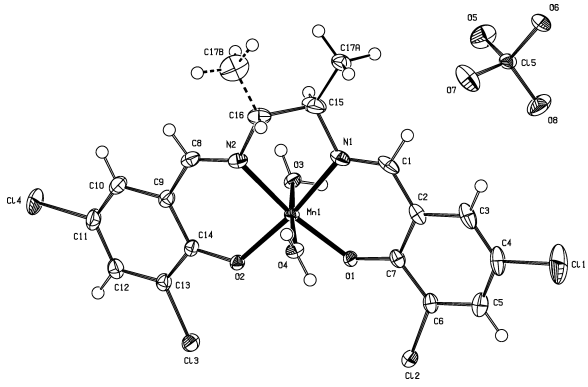

Fig. 2. The molecular structure of the components of the title compound. Displacement ellipsoids are plotted at the 50 % probability level. The alternative position of the disordered methyl group is shown with broken bonds.

X-Ray structure determination

Diffraction measurements were made on a three-circle CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at −100 °C. The intensity data were integrated using the SAINT [13a] program. Absorption, Lorentz and polarisation corrections were applied. The structure was solved by Direct Methods and refined using full-matrix least-squares against F^2 using SHELXTL [13a]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.5 times the U_{equiv} of their attached carbon atoms for methyl hydrogens, and 1.2 times the U_{equiv} of their attached carbon atoms for all others. The 1,2-diaminopropane portion of the ligand is disordered over two positions, which manifests itself as a terminal methyl group (atoms C17A or C17B) being attached to either C15 or C16. They were refined with occupancies of 0.64 and 0.36, respectively. The crystallographic data, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 1. Selected bond lengths and angles are summarised in Table 2,

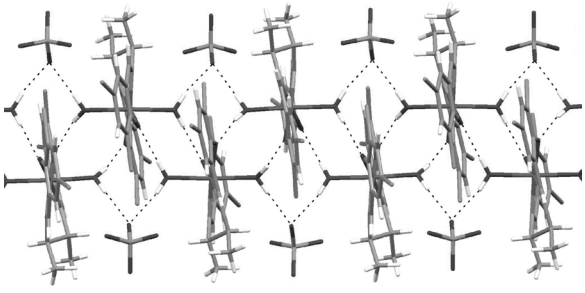

Fig. 3. Packing diagram of the title compound.

and an ORTEP view of the molecular structure is shown in Fig. 2.

CCDC 630147 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Description of the crystal structure

Complex **1** crystallises in the monoclinic space group $C2/c$ with $Z = 8$. As this space group is centrosymmetric and individual molecules of **1** are chiral, this implies that single crystals contain a racemic mixture. The 1,2-diaminopropane portion of the ligand was found to be disordered over two positions (Fig. 2), which manifests itself as a terminal methyl group (atoms C17A or C17B) being attached to either C15 or C16, with 64 and 36 % occupancy, respectively. The disorder of the methyl groups does not affect the handedness of the molecules at an individual site in the crystal as the disordered molecules are related by a *pseudo* two-fold axis.

The molecular structure of **1** consists of $[MnL(H_2O)_2]^+$ octahedra, with *trans*-coordinated water molecules, which are linked into infinite helices by hydrogen bonds. The monomeric octahedral unit is given in Fig. 2 and the polymeric representation of the structure in Fig. 3. The roughly octahedral manganese(III) centre contains an $N_2O_2O'_2$ coordination sphere made up of the Schiff base ligand in the equatorial plane and *trans*-coordinated water molecules. The Mn–$O_{phenolic}$ bonds of 1.910(2) and 1.916(2) Å and Mn–N_{imine} bonds of 1.990(2) and 1.991(2) Å are typical of such complexes whilst a substantial axial elongation in the *trans* Mn–O_{water} bonds of 2.165(2) and 2.187(2) Å is observed. Such elongations are typical of d^4 systems but in this case may also be attributed to the poorer donor power of the water molecules.

Table 3. Hydrogen bond geometry for **1**.

D–H···A	D–H	H···A	D···A	D–H···A
O3–H3A···O1^{i}	0.85	1.904	2.745	171.46
O3–H3B···O6^{ii}	0.85	1.976	2.809	167.27
O4–H4A···O2^{iii}	0.850	1.978	2.824	172.88
O4–H4B···O6^{iv}	0.83	2.030	2.854	172.60

Symmetry codes: ^{i} $-x, y, -z+1/2$; ^{ii} $-x+1/2, y+1/2, -z+1/2$; ^{iii} $-x, -y+2, -z+1$; ^{iv} $-x+1/2, -y+3/2, -z+1$.

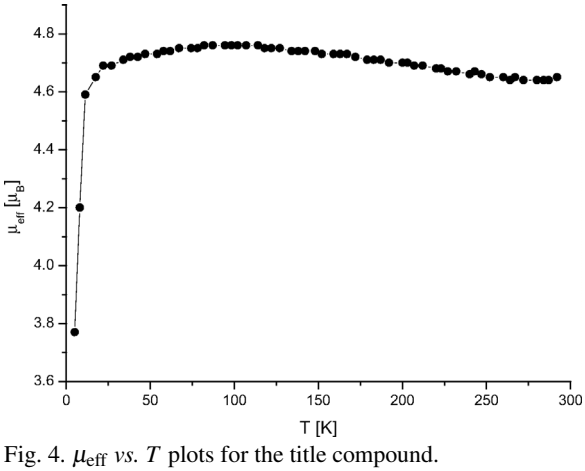

Fig. 4. μ_{eff} *vs.* T plots for the title compound.

In the crystal individual molecules of **1** are linked into helices through hydrogen bonds between the coordinated water molecules and the phenoxy oxygen atom of the ligand on a neighbouring molecule. Just as single crystals contain both enantiomers of **1**, the helices are of both handednesses. The hydrogen-bonding scheme is completed by lattice perchlorate anions (Table 3). This results in an infinite zigzag chain of six-coordinated Mn(III) ions (Fig. 3) and Mn···Mn separations of 5.012, 5.034, and 7.557 Å. In the zigzag chains, two arrays of parallel molecules may be distinguished: starting from a molecule ranked number n, the molecules ranked n, $n+2$, $n+4$, and so forth, are parallel to each other, while the molecules $n+1$, $n+3$, and so forth, form a second array of parallel molecules. The angle between the two arrays is 41.1°.

Magnetic properties

The temperature dependence of the molar magnetic susceptibility, χ_m, for compound **1** was measured on a polycrystalline sample in the temperature range 5 – 300 K. The temperature dependence of the effective

magnetic moment, μ_{eff} *versus* T, for **1** is shown in Fig. 4. The μ_{eff} values at r. t. for **1** is 4.65 μ_{B}, this being compatible with the spin-only value of S = 2, 4.90 μ_{B}, expected for an isolated high-spin manganese(III) ion. On lowering the temperature, the μ_{eff} value of **1** decreases gradually to reach 3.77 μ_{B} at 5 K. This behavior indicates that a weak antiferromagnetic interaction is operating in crystals of **1**.

The X-ray analysis of **1** verified that the title compound adopts a one-dimensional chain structure formed by hydrogen bonding. This compound therefore might be considered to have magnetically isolated manganese(III) species, because the magnetic interaction between Mn(III) ions through the hydrogen bonds and perchlorate ions should be negligible. However, the decrease in μ_{eff} in the low temperature region can be ascribed to intermolecular magnetic interactions or/and to zero-field splitting of the electronic states of the Mn(III) ion.

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