

A Pair of Manganese(III) Schiff-Base Enantiomers: Synthesis, Crystal Structure and Magnetic Characterization

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ABSTRACT: Based on the quasi-planar tetra-dentate Schiff-base ligand, a pair of manganese(III) Schiff-base enantiomers formulated as $\{[Mn(R,R-3-MeOSalcy)(H_2O)(CH_3OH)]ClO_4\}_2$ (1) and $\{[Mn(S,S-3-MeOSalcy)(H_2O)(CH_3OH)]ClO_4\}_2$ (2) (3-MeOSalcy = *N,N'*-(1,2-cyclohexanediylethylene)bis(3-methoxysalicylideneiminato)dianion) have been synthesized and characterized by element analysis. Single X-ray structure analysis showed that the coordination sphere of the Mn(III) ion is an elongated octahedron with the four equatorial positions occupied by N_2O_2 unit from the Schiff-base ligand and two O atoms of the coordinated solvent molecules completing the additional two axial sites. The mononuclear manganese(III) Schiff-base compounds are self-complementary into a supramolecular dimer structure through the coordinated solvent ligand from one complex and the free O_4 compartment from the neighboring complex. Investigation of the magnetic susceptibility of the manganese complexes reveals the overall weak antiferromagnetic interactions between the adjacent metal centers.

KEYWORDS: Manganese(III) Schiff-base; Enantiomer; Crystal structure; Magnetic property.

INTRODUCTION

As has been known for a long time, a feasible approach to the preparation of the cyanide-bridged molecule-based magnets, which can exhibit interesting magnetic properties including bulk materials with spontaneous magnetization in high T_c [1-3], spin crossover materials [4-5], Single-Molecule Magnets (SMMs) [6-7] and Single-Chain Magnets (SCMs) [8-9] as well as the hybrid magnetic compounds with dual properties exemplified as magneto-chiral dichroism [10-11], photomagnetic effects [12-13], and porous magnetic metal-organic frameworks [14-15], consists of using the paramagnetic building block $[M(L)(CN)_m]^{n+}$ (M = first- or

second-row transition metal ion, L = block organic ligand) as a ligand towards other paramagnetic assemble segments.

Among of all the paramagnetic metal ions used to prepare molecular magnetic material, the Mn(III) ion attached to Schiff-base ligands mainly within N_2O_2 basal environments has strong uniaxial magnetic anisotropy created by the Jahn-Teller effect in an octahedral coordination field. The $[Mn(\text{Schiff-base})]^+$ cation whose apical sites can be filled by incoming bridges and/or their phenoxides have been utilized as useful segments for the construction of coordination compounds with desirable functional properties, especially in cyanide-bridged

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magnetism field[16]. On the other hand, because chirality can be reasonably introduced into magnetic system by using the appropriate chiral ancillary ligand for coordination with paramagnetic ions [17-21], several manganese Schiff-based chiral cyanide-bridged complexes with interesting magnetic properties have been reported[22-26], indicating that chiral Schiff-base manganese compounds are also good candidates for assembling molecular magnetic material. Here, we report the synthesis, structural and magnetic characterization of a pair of manganese(III) chiral enantiomers {[Mn(*R,R/S,S,S*-3-MeOSalcy)(H₂O)(CH₃OH)]ClO₄}₂ (**1,2**) (3-MeOSalcy = *N,N'*-(1,2-cyclohexanediylethylene) bis(3-methoxy salicylideneiminato)dianion) based on the chiral bicompartimental Schiff- base ligand.

EXPERIMENTAL SECTION

General procedures and materials.

The Schiff-base ligands were synthesized according to the reported method[27]. The preparation reactions for these two complexes were carried out under an air atmosphere and all chemicals and solvents used were reagent grade without further purification.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with care.

The preparation of complexes 1 and 2

[Mn(ClO₄)₂]-6H₂O (1 mmol, 362 mg) was added to a solution of *R,R/S,S,S*-H₂-3-MeOSalcy (1mmol, 382 mg) in methanol and acetonitrile (20 mL, V : V = 1:1), and the mixture was stirred at room temperature until the color of the mixture changed into dark-brown. The suspension was filtered to remove any insolvable material, and an additional 20 mL methanol was added to prevent the rapid precipitation of the product. After slow evaporation from the methanol/acetonitrile solution in air about one week, the dark-brown single crystals suitable for X-ray diffraction obtained were collected by filtration, washed with ether and dried in air. Yield: *ca.* 55%. Anal. Calcd. for C₄₆H₆₀Cl₂Mn₂N₄O₂₀ (**1**): C, 47.23; H, 5.17; N, 4.79. Found: C, 47.01; H, 5.38; N, 4.99; C₄₆H₆₀Cl₂Mn₂N₄O₂₀ (**2**): C, 47.23; H, 5.17; N, 4.79. Found: C, 47.03; H, 5.35; N, 5.01.

Physical measurements

Elemental analysis of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. Variable-

temperature magnetic susceptibility was performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Structure determination

Single crystals of all the complexes for X-ray diffraction analysis with suitable dimensions were mounted on the glass rod and the data were collected on a Oxford Diffraction Gemini E diffractometer with Mo *K* α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package and refined by full-matrix least-squares (SHELXL-97) on F² [28]. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms bonded to the C and N atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C), and their coordinates were allowed to ride on their respective C atoms using SHELXL97, except some of the H atoms of the solvent molecules. For these H atoms, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. Crystallographic data and experimental details for structural analyses are summarized in Table 1. CCDC: 104279 and 104280.

RESULTS AND DISCUSSION

Some selected structural parameters for complexes **1** and **2** are given in Table 2. The perspective view of the enantiomeric structure for these two complexes, the supramolecular dimer structure formed by the intermolecular hydrogen bond interactions and the cell packing diagram along *b* axis are shown in Figs. 1-3, respectively.

Table 1: Crystallographic Data and Structure Refinement Summary for the Compounds 1 and 2.

	1	2
Empirical formula	C ₄₆ H ₆₀ Cl ₂ Mn ₂ N ₄ O ₂₀	C ₄₆ H ₆₀ Cl ₂ Mn ₂ N ₄ O ₂₀
Formula weight	1169.76	1169.76
Temperature(K)	293	293
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)	P2(1)
a/Å	13.7904(6)	13.7732(4)
b/Å	14.5971(5)	14.6322(3)
c/Å	14.6001(7)	14.5776(5)
β/deg	117.412(6)	117.367(4)
Flack Parameter	0.05(2)	0.02(3)
F(000)	1216	1216
Reflections/collected/unique	18844 / 9090/7129	24326 / 9040/7627
Data/restraints/parameters	9090 / 1 / 673	9040 / 1 / 673
Goodness-of-fit on F ²	1.031	1.028
Final R indices [I>2σ(I)]	0.0645	0.0484
R indices (all data)	0.1840	0.1208
Largest diff. peak and hole (e/Å ³)	0.603 and -0.348	0.461 and -0.290

Table 2. Selected bond lengths (Å) and angles (°) for the compounds 1 and 2.

	1	2
Mn1-N1	1.967(6)	2.000(4)
Mn1-N2	2.003(6)	1.980(5)
Mn1-O1	1.858(5)	1.871(4)
Mn1-O3	1.894(5)	1.881(4)
Mn1-O5	2.250(4)	2.251(4)
Mn1-O6	2.304(5)	2.307(4)
Mn2-N3	1.960(6)	1.982(5)
Mn2-N4	1.989(6)	1.971(4)
Mn2-O7	2.327(5)	2.250(4)
Mn2-O8	2.239(5)	2.320(4)
Mn2-O11	1.887(5)	1.879(4)
Mn2-O12	1.866(5)	1.874(4)
O6-Mn1-O5	172.3(2)	171.87(15)
O12-Mn2-O11	174.5(2)	173.61(16)

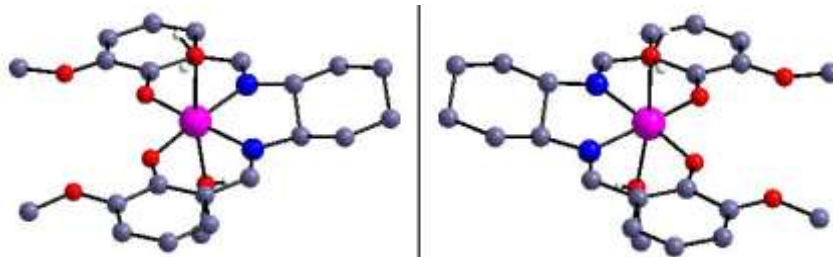


Fig. 1: Perspective view of the cationic structure of 1 (R,R isomer, left) and 2 (S,S isomer, right), respectively. All the H atoms except those used to form H bond interactions and the balanced anion have been omitted for clarity.

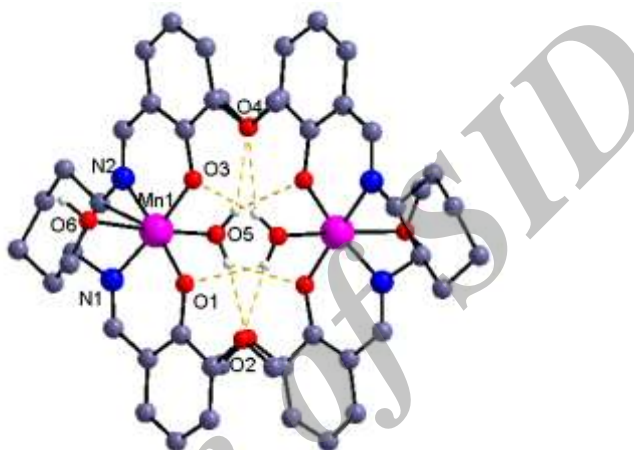


Fig. 2: The supramolecular dimer structure of compounds 1 and 2 formed by the intermolecular H-bond interactions. All the H atoms except those used to form H bond interactions and the balanced anion have been omitted for clarity.

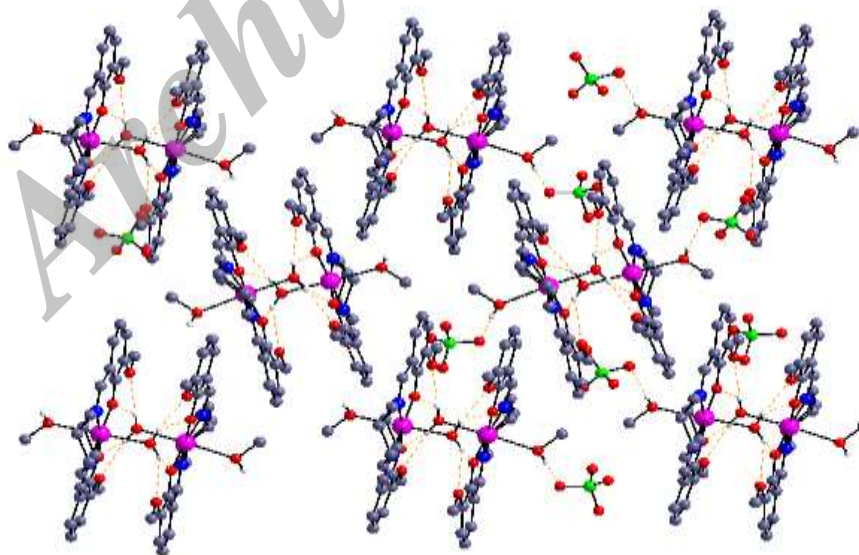


Fig. 3: The representative cell packing diagram of complexes 1 and 2 along b axis. All the H atoms except those used to form H-bond interactions have been omitted for clarity.

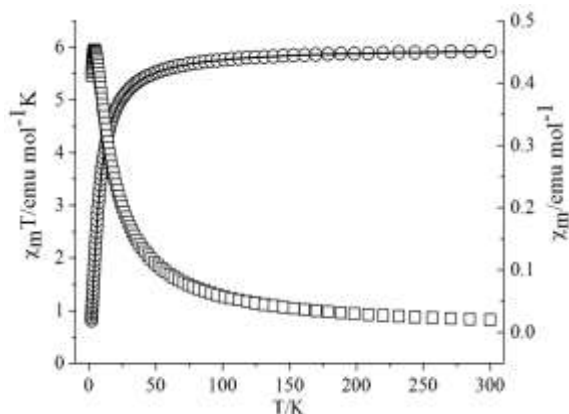


Fig. 4: χ_m vs T and $\chi_m T$ vs T curves for complex 1.

As tabulated in Table 2, this pair of enantiomers, which contain two independent units in the unit, crystallize both in monoclinic space group P2(1) with the Flack parameter 0.05(2) and 0.02(3), respectively. The coordination sphere of the Mn(III) ions in these two complexes is an octahedron, in which the four equatorial positions are occupied by two N atoms and two O atoms from the Schiff-base ligand, and the other two axial ones come from the O atoms of the coordinated solvent water and methanol molecule. The Mn-N and Mn-O_{Schiff-base} bond lengths (with Mn1 in complex 1 as representative) are 1.967(6), 2.003(6), 1.858(5) and 1.894(5) Å, respectively, markedly shorter than the distances between the manganese ion and the oxygen atom of the coordinated solvent molecules with the values of 2.250(4) and 2.304(5) Å, which provides further information about the elongated octahedron around the Mn(III) ion, typically accounting for the well known Jahn-Teller effect. The O_{solvent}-Mn-O_{solvent} bond angle in the narrow range of 171.87(15)-174.5(2)° indicates that the three atoms are in a good linear configuration. It should be pointed out, because of the excellent encapsulating ability of the O4 unit from the Schiff-base ligand, the supramolecular dimer structure can be formed with the help of the intermolecular O-H...O hydrogen bond interactions between the coordinated aqua ligand from one molecule and the phenolic oxygen atoms from the neighboring one (Fig. 2).

The temperature dependence of magnetic susceptibility for complex 1 measured in the temperature range of 2-300 K under the applied field of 2000 Oe

is shown in Fig. 4. The $\chi_m T$ value at room temperature of is about 5.95 cm³/mol K, which is consistent with the spin-only value 6.0 cm³/mol K for two high spin manganese(III) ions ($S = 2$). Within the temperature range of 300-50 K, the $\chi_m T$ remains almost constant. After that, the $\chi_m T$ value begins to decrease and reaches its lowest value about 0.82 cm³ mol⁻¹ K at 2 K.

As has been proven, the intermolecular hydrogen bond could result in obvious antiferromagnetic interactions between the paramagnetic metal centers [29-32]. Therefore, the magnetic behavior of this complex might be due to one of the following causes, or to a combination of them: (i) zero field splitting (D) of the ground state of Mn(III); (ii) antiferromagnetic interaction between the manganese(III) ions within the supramolecular dimer mediated by hydrogen bonds. The magnetic susceptibility data for complex 1 was simultaneously fitted by full-matrix diagonalization of the following spin Hamiltonian [33]:

$$H = -2JS_1S_2 + D_1[S_{1z}^2 - 1/3S_1(S_1 + 1)] + D_2[S_{2z}^2 - 1/3S_2(S_2 + 1)]$$

The J represents the exchange interaction between the manganese(III) ions within the supramolecular dimer, and the D represents the zero field splitting (ZFS) effects for the two manganese ions ($D_1 = D_2$). In view of the axially elongated structure around Mn(III) and the previous results[34], D was constrained to negative values in our calculations. The best set of parameters which match the experimental data were found to be $J = -0.98$ cm⁻¹, $D = -2.02$ cm⁻¹, $g = 2.01$. These results are comparable to those found in other Mn(III) dimer containing the same Schiff-base ligand[35].

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