Asian Journal of Chemistry; Vol. 27, No. 10 (2015), 3883-3886

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19042

Synthesis, Crystal Structures and Magnetic Property of Manganese(III) Schiff-Base Enantiomers

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Received: 20 January 2015; *Accepted*: 2 March 2015; *Published online*: 22 June 2015; AJC-17366

A pair of manganese(III) Schiff-base enantiomers with the formula {[Mn(*R,R*-3-MeOSalcy)(H_2O)(DMF)]ClO_4}$_2$ (**1**) and {[Mn(*S,S*-3-MeOSalcy)(H_2O)(DMF)]ClO_4}$_2$ (**2**) (3-MeOSalcy = N,N'-(1,2-cyclohexanediylethylene)*bis*(3-methoxy salicylideneiminato)dianion) have been prepared and characterized by elemental analysis and X-ray structure determination. X-ray diffraction reveals the Mn(III) ion is involved in an elongated octahedron formed by a N_4O_2 unit. Furthermore, two mononuclear manganese(III) Schiff-base compounds are self-complementary through coordinated aqua ligand from one complex and the free O_4 compartment from the neighboring complex, giving supramolecular dimer structure. Investigation over magnetic susceptibilities of these two complexes reveals the overall weak antiferromagnetic interactions between the adjacent Mn(III) ions.

Keywords: Manganese(III) Schiff-base, Enantiomer, Crystal structure, Magnetic property.

INTRODUCTION

Molecular magnetic materials are one of the current issues in coordination chemistry. During the past several decades, many interesting results in this field include bulk materials with spontaneous magnetization in high T_C even above room temperature[1-5], hybrid magnetic compounds with dual properties exemplified as magneto-chiral dichroism[6,7], photomagnetic effects[8-11] and porous magnetic metal-organic frameworks[12,13], spin crossover materials[14-17], as well as nanoscale magnets such as single-molecule magnets (SMMs)[18-21] or single-chain magnets (SCMs)[22-25] exhibiting slow relaxation of magnetization.

Among of all the paramagnetic metal ions used to prepare molecular magnetic material, the manganese(III) ion have been given particularly attention by the molecular magnetism chemists because of its large spin (S = 2) and the strong uniaxial magnetic anisotropy created by the Jahn-Teller effect in an octahedral ligand field. The $[Mn^{III}(\text{Schiff-base})]^+$ cations, especially for those ones with Salen types of chelating ligands, whose apical sites can be filled by incoming bridges and/or their phenoxides have been utilized as useful assembling segments for the construction of coordination compounds with desirable properties[26]. Recently, we reported a serials of cyanide-bridged complexes with interesting metamagnetic properties based on polycyanidemetalates and schiff base manganese(III) compounds containing bicompartmental Schiff-base ligands and the results indicated that schiff base manganese(III) compounds containing N_2O_2 and O_4 coordination cavities are good candidates for assembling cyanide-bridged heterometallic magnetic complexes[27-30]. Here, we report the synthesis, structural and magnetic characterization of two manganese(III) chiral enantiomers {[Mn(*R,R/S,S*-3-MeOSalcy)(H_2O)(DMF)]ClO_4}$_2$ (**1,2**) [3-MeOSalcy = N,N'-(1,2-cyclohexanediylethylene)-*bis*(3-methoxy salicylideneiminato)dianion] based on the bicompartmental Schiff-base ligand.

EXPERIMENTAL

All the reactions 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.

Preparation of complexes 1 and 2: To a solution of *R,R/S,S*-H_2-3-MeOSalcy (1 mmol, 382 mg) in methanol and acetonitrile (20 mL, v:v = 1:1) was added $[Mn(ClO_4)_2]\cdot 6H_2O$ (1 mmol, 362 mg) and the mixture was stirred in air at room temperature until the colour of the mixture changed into dark-brown. The suspension was filtered to remove any insolvable material and the volume of the filtration was reduced to about one-fifth on a rotation evaporator. The dark-brown solid obtained by adding excess ether was collected by filtration, washed with ether and dried in air. Single crystals suitable for X-ray diffraction were obtained by dissolving the solid in DMF layered with ether after one month. Yield: about 60 %. Anal. calcd. for $C_{50}H_{66}N_6O_{20}Cl_2Mn_2$ (**1**): C, 47.97; H, 5.31; N, 6.71. Found: C, 48.31; H, 5.68; N, 6.38; $C_{50}H_{66}N_6O_{20}Cl_2Mn_2$ (**2**): C, 47.97; H, 5.31; N, 6.71. Found: C, 48.39; H, 5.70; N, 6.35.

Elemental analyses 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: Data were collected on a Oxford Diffraction Gemini E diffractometer with MoK$_\alpha$ radiation (λ = 0.71073 Å) 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 the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97)[31] on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Crystallographic data and experimental details for structural analyses are summarized in Table-1. CCDC: 104277 and 104278.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR THE COMPOUNDS **1** AND **2**

	Compound **1**	Compound **2**
m.f.	$C_{50}H_{66}N_6O_{20}Cl_2Mn_2$	$C_{50}H_{66}N_6O_{20}Cl_2Mn_2$
m.w.	1251.87	1251.87
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)	P2(1)
a (Å)	11.5022(7)	11.5292(3)
b (Å)	16.3727(8)	16.4076(3)
c (Å)	15.2633(9)	15.2675(3)
α (°)	90	90
β (°)	106.196(6)	106.396(3)
γ (°)	90	90
F(000)	1304	1304
Reflections/collected/unique	11065/7768/6194	13390/9218/7837
Data/restraints/parameters	7768/1/729	9218/1/729
Goodness-of-fit on F^2	1.025	1.028
Final R indices [I>2σ(I)]	0.0533	0.0486
R indices (all data)	0.1402	0.1219
Largest diff. peak and hole (e/Å^3)	0.601 and -0.484	0.521 and -0.390

RESULTS AND DISCUSSION

Some important structural parameters for compounds **1** and **2** are collected in Table-2. The perspective view of the enantiomeric structure of complexes **1** and **2**, 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-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE COMPOUNDS **1** AND **2**

	Compound **1**	Compound **2**
Mn1-N1	1.989(6)	1.980(5)
Mn1-N2	1.983(5)	1.979(4)
Mn1-O1	1.876(5)	1.877(4)
Mn1-O2	1.881(5)	1.883(4)
Mn1-O5	2.314(4)	2.316(3)
Mn1-O6	2.268(4)	2.275(4)
Mn2-N4	1.977(6)	1.986(5)
Mn2-N5	1.989(5)	1.987(4)
Mn2-O7	1.884(4)	1.876(4)
Mn2-O8	1.873(5)	1.884(4)
Mn2-O11	2.317(4)	2.318(3)
Mn2-O12	2.288(4)	2.292(4)
O6-Mn1-O5	175.7(2)	175.37(18)
O12-Mn2-O11	173.3(2)	173.72(18)

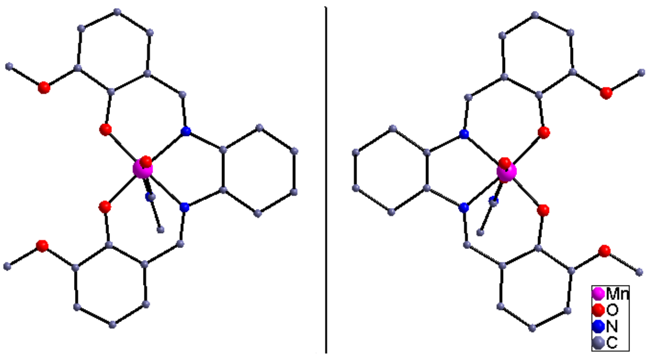

Fig. 1. Perspective view of the cationic structure of compound **1** (R,R isomer, left) and compound **2** (S,S isomer, right), respectively. All the H atoms and the balanced anion have been omitted for clarity

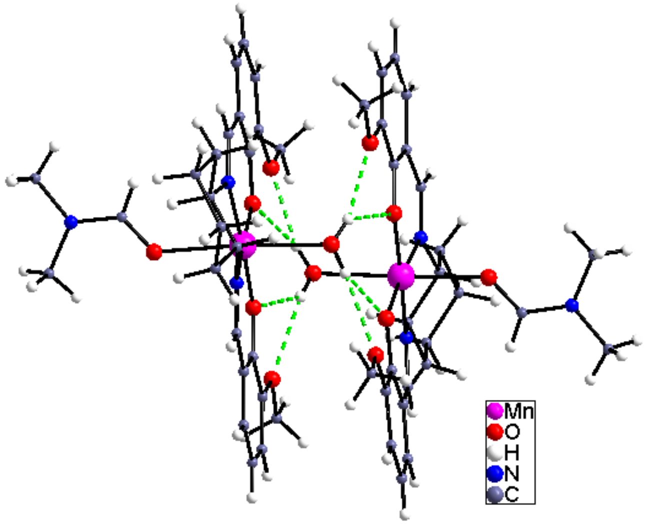

Fig. 2. Supramolecular dimer structure of compounds **1** and **2** formed by the intermolecular H-bond interactions. The balanced anion have been omitted for clarity

As can be found in Table-2, these two compounds, crystallizing both in monoclinic space group P2(1) and contain two independent units in the unit cell, are a pair of enantiomers.

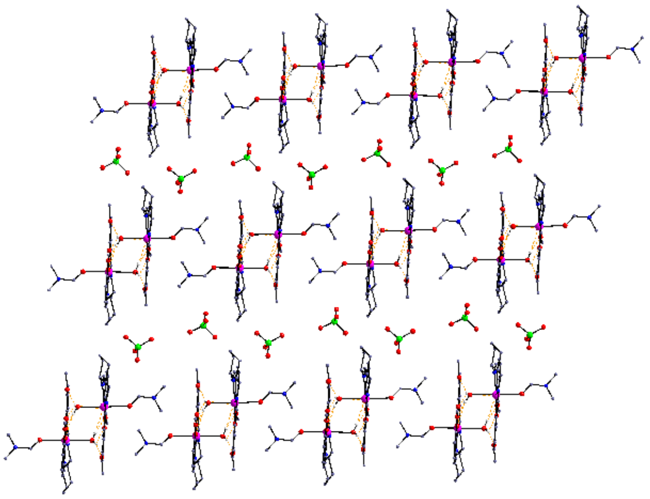

Fig. 3. Representative cell packing diagram of complexes **1** and **2** along b axis. All the H atoms except those used to form H-bond interactions have been omitted for clarity

The Mn(III) ions in these two complexes is hexa-coordinated involved in a distorted octahedral coordination sphere, 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 DMF molecules. The distances between the Mn atom (with Mn1 in complex **1** as representative) and the N, O atoms of the schiff-base ligand are 1.989(6), 1.983(5), 1.881(5) and 1.876(5) Å, respectively, which are obviously shorter than the Mn-$O_{solvent}$ bond lengths with the values of 2.268(4) and 2.314(4) Å, giving further information about the elongation octahedron surrounding the Mn(III) ion, typically accounting for the well known Jahn-Teller effect. The bond angle of $O_{solvent}$-Mn-$O_{solvent}$ in the realm of 173.3(2)-175.7(2)° demonstrates that the three atoms are in a good linear configuration. It should be pointed out, due to the excellent encapsulating ability of the O4 unit from the Schiff-base ligand, the mononuclear units of these two complexes are self-complementary through 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, giving supramolecular dimer structure (Fig. 2).

The temperature dependence of magnetic susceptibility for complex **1** was measured in the temperature range of 2-300 K in the applied field of 2000 Oe and its $\chi_m T$ *vs.* T and χ_m *vs.* T curves is presented in Fig. 4. The room temperature value of $\chi_m T$ is about 6.10 $cm^3 mol^{-1}$ K, which correspond for two high spin manganese(III) ions with S = 2. With the temperature cooling, $\chi_m T$ remains almost constant down to about 50 K, then decreases more and more and reaches about 4.1 $cm^3 mol^{-1}$ K at 2 K.

Taking into account the structural characteristic of this complex, such the magnetic behaviour 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, for the latter, which have been proven by the previous reports and our recent study results[27,31-34]. The magnetic susceptibility data for complex **1** was simultaneously fitted by full-matrix diagonalization of the following spin Hamiltonian[35]:

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

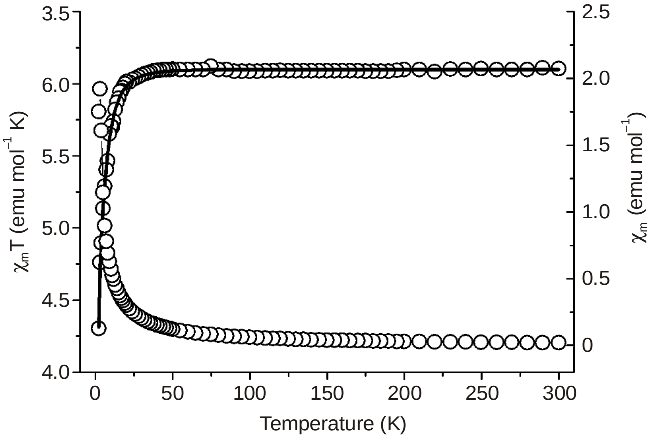

Fig. 4. The $\chi_m T$ *vs.* T and χ_m *vs.* T curves for compound **1**

The first term points to the exchange interaction between the manganese(III) ions within the supramolecular dimer. The second and third terms take into account 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), a negative sign is expected for D[36]; therefore, D was constrained to negative values in our calculations. The best set of parameters which match the experimental data were found to be $J = -0.89$ cm^{-1}, D = -2.13 cm^{-1}, g = 1.99. These results are comparable to those found in other Mn(III) dimer containing the same Schiff-base ligand[37].

ACKNOWLEDGEMENTS

This work was supported by the Natural Science Foundation of China (21171107) and the Natural Science Foundation of Shandong Province (ZR2011BM008) and the Science and Technology Project of High Education, Shandong Province (No. J11LB09).

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