

A Dimeric Mn(III) Complex of a Quadridentate Schiff Base Ligand. Synthesis, Structure and Ferromagnetic Exchange

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The synthesis, crystal structure and magnetic properties of $[\text{Mn}(\text{III})\text{L}(\text{H}_2\text{O})]_2(\text{H}_2\text{O})(\text{ClO}_4)$ (**1**) ($\text{L} = N,N'$ -bis(*rac*-5-chlorosalicylidenato)-1,2-diaminopropane) are reported. Compound **1** consists of a structurally dinuclear system in which two Mn ions are bridged by the oxygen atoms of μ -phenoxo ligands. Low temperature magnetic susceptibility measurements show a ferromagnetic intra-dimer interaction with $J = +1.75 \text{ cm}^{-1}$, $g = 2.01$ and $\alpha = -0.32$.

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

Introduction

Studies on the coordination properties of bi- and polynuclear manganese(III) complexes have attracted a lot of attention in recent years, because of the variable structures of manganese complexes, the wide occurrence of manganese enzymes in plants and bacteria [1] and the application of manganese compounds in industrial catalysis, for example epoxidation [2], bleaching [3] and paint drying [4]. Manganese complexes have also been studied widely because of their structural and novel electronic and magnetic properties [5]. Exchange interaction between paramagnetic centers of multi-nuclear complexes has already been investigated [6,7]. The nature and the tuning of magnetic interactions between metal centers are crucial points in the conception of molecule-based magnetic materials [8]. The investigation of the magnetic properties of such compounds has also been an active field of research, since the study on the correlation between magnetism and structure for manganese(III) complexes can help not only in further understanding the interaction between magnetic coupling centers in metalloproteins and enzymes, but also to develop the field of molecular magnetism [9]. Manganese(III) Schiff base complexes are known to serve as paramagnetic building blocks required for multidimensional extended architectures. Mn^{III} with this ligand environment could afford a ground state $S = 2$ for the monomeric entity, but $S = 4$ for dimeric forms *etc.* In fact, dozens

of dimeric manganese(III) compounds with salen-type ligands exhibiting antiferromagnetic or ferromagnetic intra-dimer interactions have been published [10]. Reports on ferromagnetic dimers ($S = 4$) are still sparse indicating the difficulty to control magnetic interactions between manganese(III) ions.

Experimental Section

Reagents

1,2-Diaminopropane, 5-chlorosalicylaldehyde, 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 range $4000\text{--}400 \text{ cm}^{-1}$. The temperature dependence of the magnetic 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 [8b].

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 5-chlorosalicylaldehyde

Table 1. Crystallographic and refinement data for the title compound.

Formula	C ₃₄ H ₃₄ Cl ₆ Mn ₂ N ₄ O ₁₆
Formula weight	1077.23
Temperature, K	100(2)
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	7.147(1)
<i>b</i> , Å	20.999(4)
<i>c</i> , Å	13.784(3)
β, deg	96.35(3)
Volume, Å ³	2056.0(7)
<i>Z</i>	2
Density (calculated), g cm ⁻³	1.740
Absorption coefficient, mm ⁻¹	1.082
<i>F</i> (000), e	1092
θ Range for data collection, deg	1.94 to 27.48
Index ranges	-9 ≤ <i>h</i> ≤ 9, -27 ≤ <i>k</i> ≤ 27, -17 ≤ <i>l</i> ≤ 17
Reflections collected	23065
Independent reflections	4707
<i>R</i> _{int}	0.10
Data/restraints/parameters	4707/2/304
Goodness-of-fit on <i>F</i> ²	1.216
Final <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.114/0.225
Final <i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.138/0.236
Largest diff. peak and hole, e Å ⁻³	1.38/-1.23

(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 crystallographic examination. – IR (KBr): ν(C=N) = 1618, ν(ClO₄) = 1097, 628 cm⁻¹. – C₃₄H₃₄Cl₆Mn₂N₄O₁₆ (1077.23): calcd. C 37.91, H 3.18, N 5.20; found C 37.60, H 3.40, N 5.28.

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 [11a] program. Absorption [11b], Lorentz and polarization corrections were applied. The structure was solved by Direct Methods and refined using full-matrix least-squares against *F*² using SHELXTL [11a]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without po-

Table 2. Selected bond lengths (Å) and angles (°) for the title compound^a.

Mn(1)–O(1)	1.883(5)	Mn(1)–O(3)	2.160(6)
Mn(1)–O(2)	1.907(5)	Mn(1)–O(2) ⁱ	2.404(5)
Mn(1)–N(1)	1.985(6)	O(2)–Mn(1) ⁱ	2.404(5)
Mn(1)–N(2)	1.976(6)	Mn(1)–Mn(1) ⁱ	3.326(5)
O(1)–Mn(1)–O(2)	95.0(2)	N(1)–Mn(1)–O(3)	95.6(2)
O(1)–Mn(1)–N(1)	91.6(2)	N(2)–Mn(1)–O(3)	89.6(2)
O(1)–Mn(1)–N(2)	173.9(3)	O(1)–Mn(1)–O(2) ⁱ	91.0(2)
O(2)–Mn(1)–N(1)	168.9(2)	O(2)–Mn(1)–O(2) ⁱ	79.7(2)
O(2)–Mn(1)–N(2)	90.9(2)	N(1)–Mn(1)–O(2) ⁱ	91.3(2)
N(2)–Mn(1)–N(1)	82.3(3)	N(2)–Mn(1)–O(2) ⁱ	88.6(2)
O(1)–Mn(1)–O(3)	91.6(2)	O(3)–Mn(1)–O(2) ⁱ	172.5(2)
O(2)–Mn(1)–O(3)	93.1(2)	Mn(1)–O(2)–Mn(1) ⁱ	100.3(2)

^a Symmetry transformations used to generate equivalent atoms: ⁱ -*x* + 1, -*y* + 1, -*z* + 1.

sitional constraints. Hydrogen atoms were included in idealized 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. These groups were refined with occupancies of 0.72 and 0.28, respectively. Geometrical calculations were done with PLATON [11c]. 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 summarized in Table 2.

CCDC 626597 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** (Fig. 1) crystallizes in the monoclinic space group *P*2₁/*c* with *Z* = 4. As individual molecules of **1** are chiral, this implies that single crystals contain molecules of opposite chirality in a strictly 1 : 1 molar ratio. The 1,2-diaminopropane portion of the ligand was found to be disordered over two positions (Fig. 2).

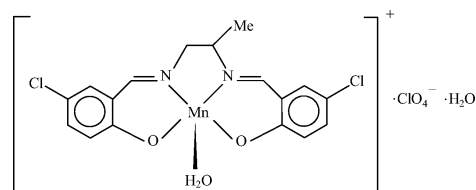


Fig. 1. Chemical structure of the title compound.

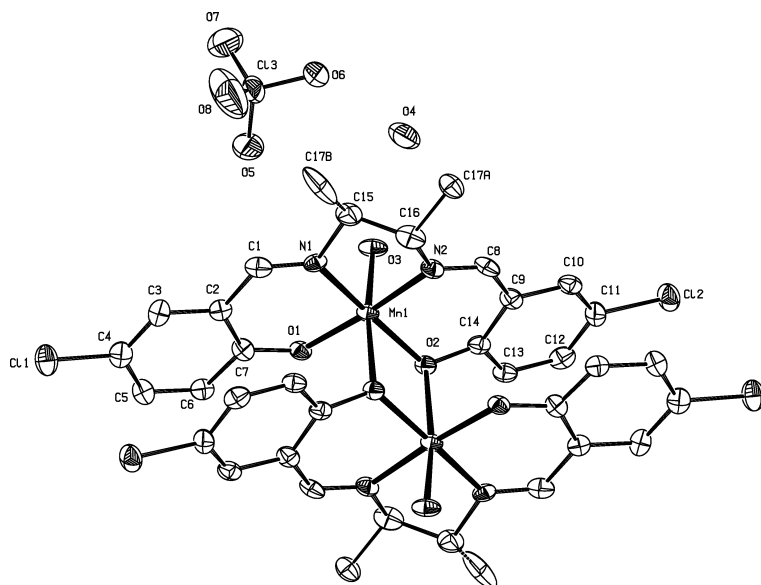


Fig. 2. The molecular structure of the title compound in the crystal. (ORTEP drawing [11d], displacement ellipsoids are drawn at the 50 % probability level; the alternative position of the disordered methyl group is shown with broken bonds; H atoms are omitted for clarity).

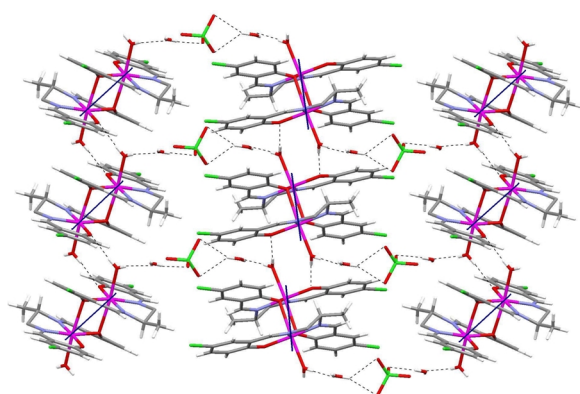


Fig. 3. Packing diagram of the title compound.

The disorder of the methyl groups does not affect the handedness of the molecules at an individual site in the crystal.

As shown in Fig. 2, the $[\text{Mn}_2(\text{L})_2(\text{H}_2\text{O})_2]^{2+}$ motif lies on an inversion center, and hence the asymmetric unit contains only one Mn^{III} atom that assumes an axially elongated square-bipyramidal six-coordination geometry. The Mn^{III} atom is surrounded by N_2O_2 atoms of the ligand in the equatorial plane and two axial oxygen atoms, $\text{O}(3)$ and $\text{O}(2)^*$, from the $\{\text{H}_2\text{O}\}$ molecule and the neighboring $\{\text{Mn}(\text{L})(\text{H}_2\text{O})\}$ moiety, respectively. In the equatorial plane, the average $\text{Mn}(1)-\text{X}$ bond length is $1.938(6)$ Å ($\text{X} = \text{N}$ or O of the ligand). As usually observed for octahedral Mn^{III} ions, the Jahn-Teller distortion leads to elongated

Table 3. Hydrogen bond geometry for the title compound (Å, deg)^a.

D–H...A	D–H	H...A	D...A	D–H...A
O3–H3A...O1 ⁱ	0.89(9)	1.93(9)	2.816(8)	177(10)
O3–H3B...O4	0.89(5)	1.75(4)	2.636(9)	170(12)
O4–H4B...O8 ⁱⁱ	0.9(2)	2.2(2)	2.995(13)	138(17)
O4–H4B...O7 ⁱⁱ	0.9(2)	2.37(19)	3.234(13)	155(13)
O4–H4A...O6	0.9(2)	1.92(19)	2.787(11)	174(1)

^a Symmetry codes: ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $x, -y+3/2, z+1/2$.

axial $\text{Mn}(1)-\text{O}(3)$ and $\text{Mn}(1)-\text{O}(2)^*$ bonds ($2.160(6)$ and $2.404(5)$ Å).

Two symmetrical arrangements of Mn^{III} dimers are found in the crystal packing. The Jahn-Teller axes of these two units lie roughly in the ab plane and are arranged along the b axis (Fig. 3). The interdimer $\text{Mn}\cdots\text{Mn}$ separations are particularly large: 5.214 and 11.135 Å in the a and b axis directions, respectively. The two Mn-linked water molecules form hydrogen bonds between the different dimers ($\text{O}(3)\cdots\text{O}(1)$, 2.815 Å) as well as with a perchlorate ion ($\text{O}(4)\cdots\text{O}(8)$, 2.995 Å, $\text{O}(4)\cdots\text{O}(7)$, 3.233 Å). The free H_2O is linked by hydrogen bonds with the coordinated H_2O molecule ($\text{O}(3)\cdots\text{O}(4)$, 2.635 Å) and with the perchlorate oxygen atom ($\text{O}(4)\cdots\text{O}(6)$, 2.788 Å) (Table 3).

Magnetic properties

The temperature-dependence of the molar magnetic susceptibility, χ_m , for compound **1** was measured on a polycrystalline sample in the temperature

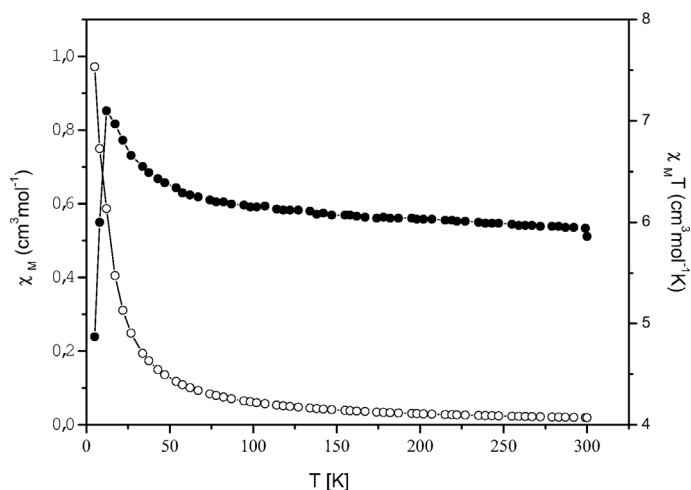


Fig. 4. χ_m (-o-) and $\chi_m \cdot T$ (-●-) vs. T plots for the title compound. The solid line shows the best-fit theoretical curve.

range 5–300 K. Results are depicted in a graph of χ_m and $\chi_m T$ versus T in Fig. 4. At 300 K, the value for $\chi_m T$ is $5.86 \text{ cm}^3 \text{ K mol}^{-1}$ ($6.84 \mu_B$) and in good agreement with the expected contribution of two non-interacting Mn(III) ions with $S = 2$ spin. For lower temperatures, the value of $\chi_m T$ steadily increases to reach $7.1 \text{ cm}^3 \text{ K mol}^{-1}$ ($7.53 \mu_B$) at 12 K before suddenly dropping to $4.87 \text{ cm}^3 \text{ K mol}^{-1}$ ($6.24 \mu_B$) for 5 K, the lowest temperature investigated. The behavior in the 300–12 K temperature domain is indicative of a ferromagnetic interaction between the Mn(III) ions within the dimer, whereas the drop of $\chi_m T$ for lower temperatures can be ascribed to two possible contributions. One is due to the zero field splitting (ZFS) of the states of the Mn(III) ions, the second arises from intermolecular exchange interactions, and these effects might be concomitant. The structural features for compound **1** show that the dimers are linked through hydrogen bonds established between the H_2O ligands and the perchlorate oxygen atoms. Such links are known to mediate an exchange interaction between magnetic centers [12]. Moreover, the maximum value reached for $\chi_m T$ of $7.1 \text{ cm}^3 \text{ K mol}^{-1}$ is lower than the $10 \text{ cm}^3 \text{ K mol}^{-1}$ expected for a $S = 4$ ground state (assuming $g = 2$), confirming indeed that the decrease of $\chi_m T$ can be ascribed to inter-dimer exchange interactions.

Therefore, the magnetic properties were analyzed by a theoretical model considering the interaction be-

tween two $S = 2$ spin centers and, to account for the low temperature behavior, a contribution arising from inter-dimer interactions. The magnetic susceptibilities were well reproduced by Eq. 1:

$$\chi = \frac{Ng^2\beta^2}{k(T - \alpha)} \left[\frac{A}{B} \right], \quad (1)$$

derived from the isotropic spin-Hamiltonian $H = -2JS_1S_2$, with $A = 30 + 14\exp(-8J/kT) + 5\exp(-14J/kT) + \exp(-18J/kT)$ and $B = 9 + 7\exp(-8J/kT) + 5\exp(-14J/kT) + 3\exp(-18J/kT) + \exp(-10J/kT)$, where an intra-dimer interaction term α is introduced in order to reproduce the decrease of μ_{eff} in the very low temperature region. The observed susceptibility data were fitted by a least-squares method. The best-fit parameters $J = +1.75 \text{ cm}^{-1}$, $g = 2.01$ and $\alpha = -0.32$ were obtained. The parameters indicate that there exists a weak intra-dimer ferromagnetic interaction.

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