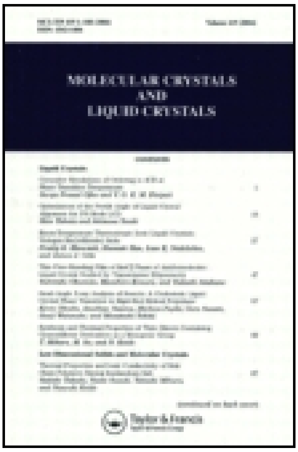

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Out-of-plane Dimer Structures and Magnetic Properties of Mn(III) Quadridentate Schiff Base Compounds with N, N′-(1, 1, 2, 2-Tetramethylethylene)bis(5-chlorosalicylideneiminato)

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Out-of-plane Dimer Structures and Magnetic Properties of Mn(III) Quadridentate Schiff Base Compounds with *N*, *N′*-(1, 1, 2, 2-Tetramethylethylene)bis(5-chlorosalicylideneiminato)

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Three Mn(III) quadridentate Schiff base compounds with *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(5-chlorosalicylideneiminato) (5-Clsaltmen^{2-}) were prepared and characterized: [Mn_2(5-Clsaltmen)$_2$(H_2O)$_2$](ClO_4)$_2$ (**1**), [Mn_2(5-Clsaltmen)$_2$(5-Clsal)$_2$](ClO_4)$_2$ (**2**; 5-Clsal = 5-chlorosalicylaldehydonato), and [NEt_4]$_2$[Mn_2(5-Clsaltmen)$_2$(MeOH)$_2$][Fe(CN)$_6$]ClO_4·2MeOH (**3**). All compounds contain Mn(III) out-of-plane dimer units. The magnetic measurements revealed intra-dimer ferromagnetic exchange interaction between Mn(III) ions via phenolate oxygen, producing a S = 4 spin ground state.

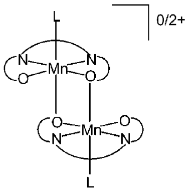
Keywords: Mn(III) quadridentate Schiff base compounds; out-of-plane dimers; ferromagnetic interaction; S = 4 spin ground state

INTRODUCTION

Recently, we have reported a family of out-of-plane dimeric compounds [Mn_2(SB)$_2$(L_2)]$^{0/2+}$ (**I**) (SB = *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(salicylideneiminato) (saltmen^{2-}: **II**); *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(naphthylideneiminato) (naphtmen^{2-}: **III**), L = H_2O, NCS^- and Cl^-), which exhibited ferromagnetic exchange interaction between Mn(III) ions through the bridging phenolate oxygens[1]. In this work, the correlation between ferromagnetic exchange parameters (J_F) and Mn-O* distances (O* is defined as a out-of-plane oxygen) was revealed and empirically estimated by the following equation:

$$J_F = 4.5724 - 1.1868x$$

$$(x\text{: Mn}\cdots\text{O* distance (Å) in the range of } 2.4 - 3.7 \text{ Å})$$



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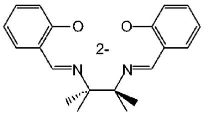
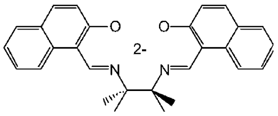
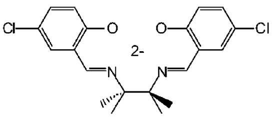


II



III



IV

Although the magnetic behavior for many Mn(III) salen analogues having out-of-plane dimeric motifs have been investigated up to date, few compounds exhibiting ferromagnetic interaction are reported[1,2]. Herein, new series of ferromagnetic out-of-plane dimers is described. Thus, three Mn(III) quadridentate Schiff base compounds with *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(5-chlorosalicylideneiminato) (5-Clsaltmen^{2-}: **IV**) were prepared and investigated on magnetic studies: $[Mn_2(5\text{-Clsaltmen})_2(H_2O)_2](ClO_4)_2$ (**1**), $[Mn_2(5\text{-Clsaltmen})_2(5\text{-Clsal})_2](ClO_4)_2$ (**2**; 5-Clsal = 5-chlorosalicylaldehydonato), and $[NEt_4]_2[Mn_2(5\text{-Clsaltmen})_2(MeOH)_2][Fe(CN)_6]ClO_4{\cdot}2MeOH$ (**3**).

EXPERIMENTAL

General Procedures and Materials

All chemicals and solvents used during the syntheses were reagent grade. The quadridentate Schff base ligand H_25-Clsaltmen was synthesized by mixing 1, 1, 2, 2-tetramethylethylenediamine with

5-chlorosalicylaldehyde in a 1:2 molar ratio in ethanol. Caution: Perchlorate salts are potentially explosive and should only be handled in small quantities.

Preparation of 1

A methanol solution (20 cm^3) of manganese(III) acetate dihydrate (1.34 g, 5 mmol) was added to a methanol solution (50 cm^3) of the Schiff base ligand $H_2$5-Clsaltmen (1.97 g, 5 mmol). After heating the brown solution at 50 °C and stirring for 30 min, sodium perchlorate (610 mg, 5 mmol) was added. Before filtration, 80 cm^3 of hot-water was added to the resulting hot solution. The filtrate was left to stand for one week at room temperature. Dark brown crystals were collected by suction filtration, washed with a minimum amount of water and dried in vacuo. Anal. Calcd for $C_{20}H_{22}N_2O_7Cl_3Mn$: C, 42.61; H, 3.93; N, 4.97. Found: C, 42.55; H, 3.96; N, 4.96. IR(KBr): ν (C=N), 1605 cm^{-1}; ν (Cl-O), 1067, 1099, 1123 cm^{-1}.

Preparation of 2

To a methanol solution (20 cm^3) of **1** (0.141 g, 0.25 mmol) was added a methanol solution (20 cm^3) containing 5-chlorosalicylaldehyde (0.078 g, 0.5 mmol) and triethylamine (0.037 g, 0.5 mmol). After stirring for 10 min at ambient temperature, to this mixture was added water (10 cm^3), then filtered. The filtrate was left to stand for one week at room temperature. Dark brown crystals were collected by suction filtration, washed with a minimum amount of water and dried in vacuo. Anal. Calcd for $C_{27}H_{24}N_2O_4Cl_3Mn$: C, 53.89; H, 4.02; N, 4.65. Found: C,

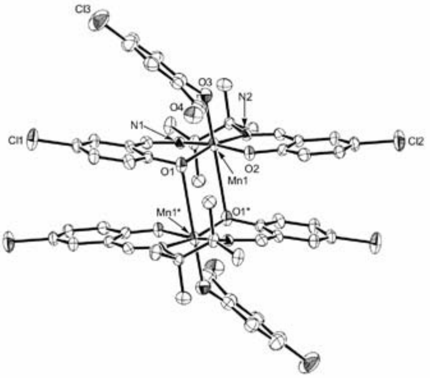


FIGURE 1 ORTEP drawing of **2**.

53.71; H, 4.04; N, 4.66. IR(KBr): ν (C=O), 1649 cm^{-1}; ν (C=N), 1607 cm^{-1}.

Crystal data: **2**: $C_{27}H_{24}N_2O_4Cl_3Mn$, M = 601.79, monoclinic, a = 12.5479(8), b = 12.9108(8), c = 16.5266(8) Å, β = 103.985(4) °, U = 2598.0(3) $Å^3$, T = 23 °C, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-Kα) = 8.54 cm^{-1}, 24999 reflections measured, 5923 unique (R_{int} = 0.035), refinement method: full-matrix least-squares on F^2. The final R indices: R_1 = 0.050, wR = 0.104 ($I > 3\sigma(I)$), GOF = 1.34.

Preparation of 3

A methanol solution (10 cm^3) of $[NEt_4]_3[Fe(CN)_6]$ (0.30 g, 0.5 mmol) was added to a methanol solution (50 cm^3) of **1** (0.141 mg, 0.25 mmol). After stirring for 10 min at ambient temperature, the solution was filtered. The brown solution was kept to stand for 3 days to form brown crystals of **3**. The crystals were collected by suction filtration and dried in air. Anal. Calcd for $C_{66}H_{96}N_{12}O_{12}Cl_5Mn_2Fe$: C, 49.78; H, 6.08; N, 10.55. Found: C, 49.14; H, 5.95; N, 10.85. IR(KBr): ν (C≡N), 2116 cm^{-1}; ν (C=N), 1609 cm^{-1}; ν (Cl-O), 1088, 1121 cm^{-1}.

Crystal data: **3**: $C_{66}H_{96}N_{12}O_{12}Cl_3Mn_2Fe$, M = 1592.55, triclinic, a = 8.7800(7), b = 14.446(2), c = 15.943(1) Å, α = 66.743(3) °, β = 81.603(3) °, γ = 87.125(3) °, U = 1837.8(3) $Å^3$, T = -170 °C, space group P-1 (no. 2), Z = 1, μ(Mo-Kα) = 7.81 cm^{-1}, 17341 reflections measured, 8287 unique (R_{int} = 0.052), refinement method: full-matrix least-squares on F^2. The final R indices: R_1 = 0.083, wR = 0.220 ($I > 3\sigma(I)$), GOF = 1.60.

RESULTS AND DISCUSSION

Structures

Compounds **2** and **3** are structurally characterized by the single-crystal X-ray crystallography. ORTEP drawing of **2** is depicted in Figure 1. Compound **2** is found to be exactly out-of-plane dimer with the bond distances and angles of Mn···Mn* = 3.776(2) Å, Mn-O(1) (O(1) : intramolecular phenolate oxygen) = 1.880(4) Å, Mn-O(1)* (O(1)*: intermolecular phenolate oxygen) = 2.911(5) Å, Mn-O(1)*-Mn* = 101.9(2) °, and O(1)-Mn-O(1)* = 78.1(2) ° (*; 1-x, -y, -z). The average bond distances in the equatorial plane occupied with 5-Clsatmen^{2-} are av. Mn-N = 1.981(5) Å and av. Mn-O = 1.879(4) Å. The another apical site is occupied by phenolate oxygen of

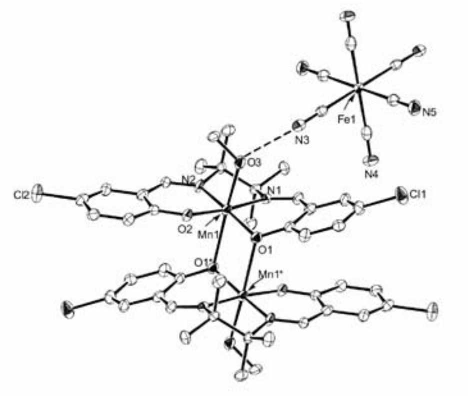


FIGURE 2 ORTEP drawing of the parts $[Mn_2(5\text{-}Clsaltmen)_2(MeOH)_2]^{2+}$ and $[Fe(CN)_6]^{3-}$ of **3**.

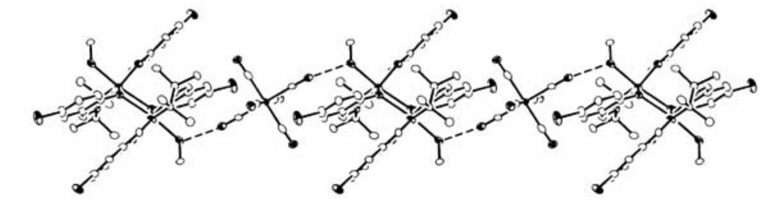


FIGURE 3 Hydrogen-bonded 1-D chain structure (the dashed line expresses hydrogen bonds).

5-chlorosalicylaldehydonato with the bond distance of Mn-O(3) = 2.029(5) Å, thus taking the Jahn-Teller distortion in an elongated octahedron geometry around Mn(III) ion.

ORTEP drawing of the parts $[Mn_2(5\text{-}Clsaltmen)_2(MeOH)_2]^{2+}$ and $[Fe(CN)_6]^{3-}$ of **3** is depicted in Figure 2. For the out-of-plane Mn(III) dimer, the structural feature of the dimeric core is almost the same as that of **2**. The bond distances and angles of the bridging core are found to be Mn···Mn* = 3.380(2) Å, Mn-O(1) (O(1) : intramolecular phenolate oxygen) = 1.929(4) Å, Mn-O(1)* (O(1)*: intermolecular phenolate oxygen) = 2.396(4) Å, Mn-O(1)*-Mn* = 102.2(2) °, and O(1)-Mn-O(1)* = 77.8(2) ° (*; 2-x, -y, 1-z). The apical site is occupied by a methanol molecule with the distance of Mn-O(3) =

2.221(4) Å, in which the methanol makes a hydrogen bond with cyano group of $[Fe(CN)_6]^{3-}$ (O(3)···N(3) = 2.718(7) Å), forming an alternating arranged 1-D chain as shown in Figure 3.

Magnetic Properties

Temperature-dependence of the magnetic susceptibility of **1** - **3** was measured on the ground polycrystalline samples in the temperature range from 1.9 to 300 K under 1 T. The χT vs T plots of **1** and **2** are shown in Figure 4. The χT values for these out-of-plane dimeric compounds at room temperature are 3.00 and 3.02 $cm^3 \cdot K \cdot mol^{-1}$ (per Mn(III) ion), respectively, which are compatible with 3.0 $cm^3 \cdot K \cdot mol^{-1}$ of a high-spin Mn(III) $S_{Mn} = 2$ ion calculated assuming $g_{Mn} = 2.0$. The χT value increases gradually upon lowering temperature to reach the maximum (3.59 $cm^3 \cdot K \cdot mol^{-1}$ at 11.0 K for **1** and 3.33 $cm^3 \cdot K \cdot mol^{-1}$ at 6.5 K for **2**). The decrease at low temperature region could be associated with principally two phenomena: the zero-field splitting (ZFS) arising from Mn(III) ion and/or possible intermolecular antiferromagnetic interaction between the neighboring dimer units. These magnetic behavior for the out of-plane Mn(III) dimers can be modelized by the

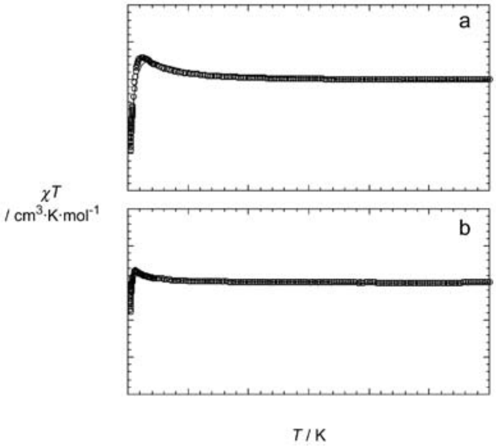


FIGURE 4 Temperature-dependence of χT of **1** (a) and **2** (b) (per Mn(III) ion). The solid line corresponds to the best-fitting (see text).

dinuclear equation for two equivalent $S = 2$ ($S_1 = S_2 = S$) magnetic spins including the ZFS term D. Following Hamiltonian was used:[3]

$$\boldsymbol{H} = 2g\mu_B HS - 2JS_1 \cdot S_2 + 2D[S^2_z - 1/3S(S + 1)]$$

where J is the intra-dimer magnetic exchange, D the zero-field splitting (ZFS) originated from each Mn(III) ion. For **1** and **2**, inter-dimer interactions (zJ) were introduced by the molecular field approximation in order to fit the magnetic susceptibility, where z is the number of neighbors and J is the magnitude of the inter-molecular interactions[4]. The obtained best-fitting parameters are g = 1.97, J = 1.74 cm^{-1}, D = -2.44 cm^{-1}, zJ = -0.60 cm^{-1} for **1** and g = 2.00, J = 0.55 cm^{-1}, D = -1.26 cm^{-1}, zJ = -0.28 cm^{-1} for **2**, and the fitting curve are described as a solid line in Figure 4. The positive J values are due to a contribution of ferromagnetic interaction between Mn(III) ions through phenolate oxygens. Thus, these parameters are reasonable for ferromagnetic out-of-plane Mn(III) salen-type dimers[1].

The magnetic behavior for **3** is essentially the same as **1** and **2** as shown in Figure 5. The metal-complex units as magnetic centers containing in **3** are given as $[\mathrm{Mn_2(5\text{-}Clsaltmen)_2(MeOH)_2}]^{2+}$ and $[\mathrm{Fe(CN)_6}]^{3-}$, where the latter possesses a S = 1/2 from a low-spin ground state of Fe(III) ion, and these units are separately situated in the crystal packing as mentioned in the structural section. Therefore, the Hamiltonian should be described as follow,

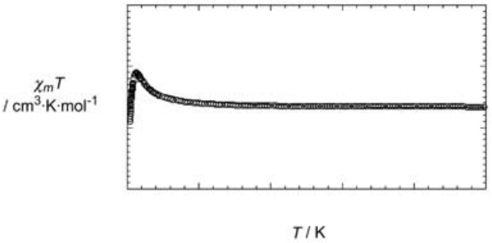


FIGURE 5 Temperature-dependence of $\chi_m T$ of **3**. The solid line corresponds to the best-fitting (see text).

$$\boldsymbol{H} = 2g\mu_B H S_{\mathrm{Mn}} - 2JS_{\mathrm{Mn}1}\cdot S_{\mathrm{Mn}2} + 2D[S_{\mathrm{Mn}}{}^{2}{}_{z} - 1/3S_{\mathrm{Mn}}(S_{\mathrm{Mn}} + 1)] + g\mu_B H S_{\mathrm{Fe}}$$

where the first and second terms are the same as the dimer model for $S = 2$ ($S_{\mathrm{Mn}1} = S_{\mathrm{Mn}2} = S_{\mathrm{Mn}}$) mentioned above, and the third term expresses paramagnetic contribution of $S = 1/2$ (S_{Fe}). The obtained parameters are $g = 2.08$, $J = 1.15$ cm^{-1}, $D = -1.56$ cm^{-1}, $zJ = -0.23$ cm^{-1} (the g is given as average contribution of Mn(III) and Fe(III) ions).

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