



Synthesis, crystal structure and magnetic properties of dimeric Mn^{III} Schiff base complexes including pseudohalide ligands: Ferromagnetic interactions through phenoxo bridges and single molecule magnetism

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ABSTRACT

Three new phenoxo-bridged dimeric compounds of Mn^{III} with tetradentate Schiff bases (salpnH₂, salmenH₂ and acphpnH₂) and pseudohalide ligands have been synthesized and characterized by crystallography and *dc* and *ac* magnetic measurements. Mn(salpn)NCO (**1**) and Mn(salmen)N₃ (**2**) exhibit intradimer ferromagnetic exchange ($J = 0.42(2) \text{ cm}^{-1}$ for **1**, $J = 0.58(1) \text{ cm}^{-1}$ for **2**, $\hat{H} = -2J\hat{S}_1\hat{S}_2$). The $\chi_m T$ product of **1** continuously increases upon lowering temperature, reaching a value of $10.01 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 1.98 K. In the case of **2**, the $\chi_m T$ product reaches a maximum value of $7.85 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5.82 K and decreases upon further cooling to a value of $6.34 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K, indicating the operation of interdimer antiferromagnetic interactions. Frequency dependence of *ac* magnetic susceptibility shows single-molecule-magnetic (SMM) behavior in the temperature range 2–10 K for both compounds. In sharp contrast, Mn(acphpn)N₃ (**3**) exhibits antiferromagnetic exchange interactions. salpnH₂ = N,N'-bis(salicylidene)-1,3-diaminopropane, salmenH₂ = N,N'-bis(salicylidene)-1,2-diaminopropane and acphpnH₂ = N,N'-bis(2-hydroxyacetophenone)-1,3-diaminopropane.

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1. Introduction

Schiff base complexes of Mn^{III}, though well known, continue to generate interest due to their potential applications in fields as diverse as homogeneous catalysis and magnetic materials [1]. Complexes of general formula Mn(SB)X, where SB is a tetra-dentate Schiff base and X is usually an anionic ligand, often crystallize as phenoxo-bridged dimers which may exhibit a range of magnetic interactions depending upon the bridge geometry [2–21]. Some of these complexes have been investigated in detail for their SMM (single molecule magnet) properties [4,6,21]. Magnetic properties of one-dimensional chains formed by bridging ligands (for example, azide [22]) and more recently, coordination networks resulting from second coordination sphere interactions [23] have also been reported. In this paper we report on three new phenoxo-bridged complexes, Mn(salpn)NCO (**1**), Mn(salmen)N₃ (**2**), and Mn(acphpn)N₃ (**3**); the Schiff bases involved are depicted in Scheme 1. Even though these new complexes do not greatly enlarge the range of bridge geometries already reported for this class of compounds, they do demonstrate the role of intermolecular interactions in causing dramatic differences between otherwise

similar magnetically coupled systems. In particular, compound **1**, unlike any other previously reported phenoxo-bridged Mn(III,III) system remains ferromagnetic in the entire temperature range 2–300 K with a high spin ($S = 4$) ground state.

2. Experimental

2.1. Materials and physical measurements

All chemicals used for synthesis were reagent grade. The Schiff bases were formed *in situ* in the presence of the appropriate metal salt. *Caution*: Azide compounds are potentially explosive and should be prepared only in small quantities and handled with care. IR spectra (KBr disc) were obtained with a Shimadzu FT-IR 8000 spectrometer. Absorption spectra in methanol were recorded on a Shimadzu UV-3100 PC spectrometer. Elemental analysis for C, H and N was performed on a Perkin–Elmer 240C analyzer.

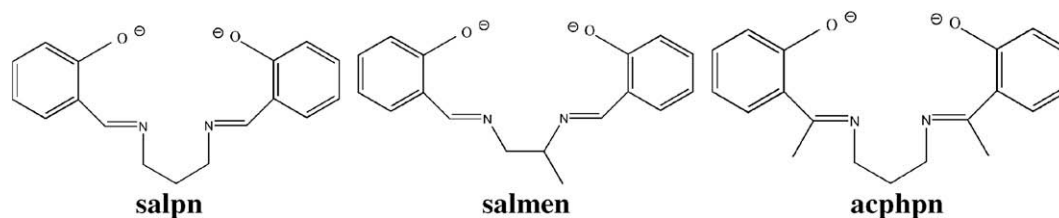
2.2. Synthesis

2.2.1. [Mn(salpn)NCO]₂ (**1**)

In a beaker open to the atmosphere, salicylaldehyde (0.244 g, 1.00 mmol) and 1,3-diaminopropane (0.071 g, 1.0 mmol) were stirred in 40 mL of ethanol. Mn(CH₃COO)₂ · 4H₂O (0.245 g, 1.00 mmol) was added, and stirring was continued for about 1 h.

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Scheme 1.

To the resulting solution, NaOCN (0.130 g, 2.00 mmol) dissolved in a minimum amount of water was added, stirring continued for 3 h, to complete the aerial oxidation of Mn^{II} . The filtered solution was kept in a refrigerator (5 °C) for 1 week when dark green crystals deposited. Yield: 0.234 g (0.62 mmol, 62%). *Anal. Calc.* for $\text{C}_{36}\text{H}_{32}\text{N}_6\text{O}_6\text{Mn}_2$: C, 57.1; H, 4.27; N, 11.14. Found: C, 57.20; H, 4.23; N, 11.23%. Characteristic IR absorptions (cm^{-1}): $\nu_{\text{a}}(\text{NCO})$ 2160, $\nu_{\text{s}}(\text{NCO})$ 1313, $\delta(\text{NCO})$ 615, $\nu_{\text{schiff base}}(\text{C}=\text{N})$ 1620. Electronic absorption bands ($\bar{\nu}_{\text{max}}/10^3 \text{ cm}^{-1}$, $\epsilon_{\text{max}}/100 \text{ cm}^{-1} \text{ M}^{-1}$): 17.11, 3.47(sh); 26.34, 66.0; 32.94, 108(sh); 35.65, 180.

2.2.2. $[\text{Mn}(\text{salmen})\text{N}_3]_2$ (**2**)

In a beaker open to the atmosphere, salicylaldehyde (0.244 g, 1.00 mmol) and 1,2-diaminopropane (0.074 g, 1.0 mmol) were stirred in 40 mL of methanol. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.245 g, 1.00 mmol) was added, and stirring was continued for about 1 h. To the resulting solution, NaN_3 (0.130 g, 2.00 mmol) dissolved in a minimum amount of water was added and stirring continued for 3 h to complete the aerial oxidation of Mn^{II} . The resulting microcrystalline precipitate was filtered off and dried. Yield: 0.306 g (0.81 mmol, 81%). It was recrystallized by slow evaporation of an acetonitrile solution at room temperature yielding dark-brown X-ray quality crystals. *Anal. Calc.* for $\text{C}_{36}\text{H}_{32}\text{N}_{10}\text{O}_4\text{Mn}_2$: C, 54.12; H, 4.27; N, 18.57. Found: C, 54.19; H, 4.32; N, 18.98%. Characteristic IR absorptions (cm^{-1}): $\nu_{\text{a}}(\text{N}_3)$ 2035, $\nu_{\text{s}}(\text{N}_3)$ 1309, $\delta(\text{N}_3)$ 599, $\nu_{\text{schiff base}}(\text{C}=\text{N})$ 1612. Electronic absorption bands ($\bar{\nu}_{\text{max}}/10^3 \text{ cm}^{-1}$, $\epsilon_{\text{max}}/100 \text{ cm}^{-1} \text{ M}^{-1}$): 20.20, 12.1(sh); 24.44, 45.7; 28.35, 61.5(sh); 32.16, 124, 35.87, 192.

2.2.3. $[\text{Mn}(\text{acphpn})\text{N}_3]_2$ (**3**)

In a beaker open to the atmosphere, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.245 g, 1.00 mmol) and NaN_3 (0.130 g, 2.00 g) were dissolved in 30 mL methanol and filtered. 2-Hydroxyacetophenone (0.272 g, 2.00 mmol) and 1,3-diaminopropane (0.071 g, 1.0 mmol) were dissolved in 30 mL methanol and filtered. The two solutions were mixed and stirred for 2 h to complete the aerial oxidation of Mn^{II} . The filtered solution was kept at room temperature for three days to obtain dark green crystals. Yield: 0.254 g (0.63 mmol, 63%). *Anal. Calc.* for $\text{C}_{38}\text{H}_{40}\text{N}_{10}\text{O}_4\text{Mn}_2$: C, 56.25; H, 4.98; N, 17.26. Found: C, 56.45; H, 4.98; N, 17.36%. Characteristic IR absorptions (cm^{-1}): $\nu_{\text{a}}(\text{N}_3)$ 2038, $\nu_{\text{s}}(\text{N}_3)$ 1300, $\delta(\text{N}_3)$ 522, $\nu_{\text{schiff base}}(\text{C}=\text{N})$ 1587. Electronic absorption bands ($\bar{\nu}_{\text{max}}/10^3 \text{ cm}^{-1}$, $\epsilon_{\text{max}}/100 \text{ cm}^{-1} \text{ M}^{-1}$): 18.00, 8.04; 26.32, 67.0(sh); 30.01, 89.0; 36.67, 191.

2.3. Magnetic studies

The magnetic susceptibility was measured in the 1.98–300 K temperature range using a Quantum Design MPMS SQUID susceptometer. The samples were pressed into pellets to avoid orientation effects of the microcrystals during magnetic measurements. Diamagnetic corrections were applied using Pascal's constants [24]. The magnetic susceptibilities have been computed both with the program SUSCEP [25] based on the expression derived from the isotropic spin-exchange Hamiltonian, $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ($S_1 = S_2 = 2$) and

van Vleck's equation [26], and by exact calculations of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry [27]. In the latter case, least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT [28].

2.4. X-ray crystallography

X-ray data were collected for compounds **1–3** on a Bruker SMART APEX CCD X-ray diffractometer, using graphite-monochromated Mo K radiation ($\lambda = 0.71073 \text{ \AA}$). Data were reduced using SAINTPLUS [29], and a multi-scan absorption correction using SADABS [30] was performed. The structures were solved using SHELXS-97 and full matrix least-squares refinements against F^2 were carried out using SHELXL-97 [31]. All ring hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. All hydrogen atoms were assigned fixed U_{iso} values, equal to $1.2U_{\text{eq}}$ of the parent atom for ring and $1.5U_{\text{eq}}$ for methyl hydrogens. Crystallographic data and structure refinement parameters are presented in Table 1. Selected bond distances and angles are collated in Tables 2–4.

3. Results and discussion

3.1. Crystal structures

All three complexes crystallize in the $P2_1/n$ space group. Complexes **1** and **2** have almost identical formula weights and nearly equal unit cell dimensions, even though their chemical compositions are different. The crystals of all three complexes contain dinuclear Mn^{III} entities (Fig. 1), wherein the two centrosymmetrically related five-coordinate metal centers are held by two weak phenoxo bridges ($\text{Mn}\cdots\text{O}$ in the 2.49–2.59 Å range). Within each five-coordinate unit, the tetradentate Schiff base ligand chelates in the equatorial mode, while the axial position is occupied by a nitrogen atom from the pseudo-halide ion, azide or cyanate, coordinating in a bent mode. The equatorial donor atoms (O_2N_2) are very nearly coplanar even though the manganese atom deviates significantly from this plane (0.16 Å in **1**; 0.20 Å in **2**; 0.13 Å in **3**). The mean planes of the two halves of the Schiff base ligands (excluding the methylene groups) are inclined with respect to each other by 15° in the three crystals. There are only slight differences in the $\text{Mn}-(\text{N},\text{O})$ distances in the three complexes: $\text{Mn}-\text{O}(\text{eq.})_{\text{av}}$, $\text{Mn}-\text{N}(\text{eq.})_{\text{av}}$, $\text{Mn}-\text{N}(\text{ax.})$ are, respectively, 1.90, 2.01, 2.14 Å in **1**; 1.88, 1.99, 2.14 Å in **2**; 1.89, 2.01, 2.17 Å in **3**. The overall coordination geometry of each Mn^{III} ion is thus distorted octahedral with the Jahn–Teller elongation along the $\text{OCN}/\text{NNN}-\text{Mn}\cdots\text{O}$ axis.

Coming to the dimer formed by bridging the five-coordinate complex molecules, the plane of the Mn_2O_2 bridge is nearly perpendicular to the equatorial coordination plane: dihedral angle, 88.5° in **1**, 87.4° in **2**, 89.7° in **3**. The axial N atom deviates only slightly from the bridging plane (0.08 Å in **1**; 0.16 Å in **2**; 0.03 Å in **3**). The most important difference between the three dimers

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