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# First Example of a Mixed Valence $Mn^{III}Mn^{II}Mn^{III}$ Schiff-Base Polymeric Complex Having a Trimeric Repeat Unit. Crystal Structure of $[Mn_3(Hsaladhp)_2(acetato)_2(5\text{-}Cl\text{-}salicylato)_2]_n$

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One of the most important processes in nature occurs in the oxygen evolving complex (OEC) of photosystem II (PSII), where the four electron oxidation of water to molecular oxygen is believed to be catalyzed by a cluster of four manganese ions.[1−5] The available data strongly suggest that a polynuclear cluster is responsible for the EPR detectable signals in the $S_1$ ($g = 4.8$ in parallel polarization) and $S_2$ ($g = 2$ multiline and $g = 4.1$ with fine structure) oxidation states of the OEC.[7]

Our previous efforts have centered on the preparation and characterization of a variety of mononuclear, binuclear and trinuclear complexes with predominantly oxygen-derived donor ligands in order to understand the fundamental coordination, structural, and magnetochemistry of complexes potentially relevant to the active site of the OEC.[6] A number of workers have prepared binuclear or trinuclear complexes containing $\mu_2$-oxo[8] and carboxylato bridges.[9] However, very few polymeric complexes have been synthesized.[6e,10−12]

In this communication, we report the synthesis and characterization of $[Mn^{III}{}_2Mn^{II}(Hsaladhp)_2(acetato)_2(5\text{-}Cl\text{-}salicylato)_2]_n$ (**1**) [$H_3$saladhp = 2-(salicylideneaminato)-1,3-dihydroxy-2-methylpropane] the first example of a manganese polymer having a trimeric mixed valence repeat unit. The X-ray structure[14] of **1** (Figure 1) consists of a trimeric Mn(III/II/III) repeating unit, and these atoms are labeled Mn1, Mn2, and Mn1b respectively. The asymmetric unit comprises two manganese atoms, Mn1 which occupies a general position and Mn2 which lies on a crystallographic 2-fold axis. The saladhp ligand acts as a tridentate chelating agent by using an imine nitrogen and phenolate and alkoxide oxygen atoms to coordinate to Mn(III). The central (Mn2) and the terminal (Mn1 and Mn1b) ions are bridged by an alkoxide oxygen from the saladhp ligand, an acetato ligand, and a carboxylato oxygen from the 5-Cl-salicylato ligand resulting in a 3.482(1) Å Mn1−Mn2 separation with an 118.2° Mn1−O(alkoxide)−Mn2 angle. The phenolate oxygen atom O(1) forms a bridge between the trimers linking Mn1 to Mn1a, which is related to Mn(1) by a center of symmetry, resulting in an intertrimer Mn1···Mn1a distance of 3.417(2) Å. The cluster is valence trapped, as evidenced by the long central Mn(II) to heteroatom bond lengths and by the Jahn−Teller distortion of the terminal high spin Mn(III) ions. The Jahn−Teller axis is defined by the carboxylato oxygen of the 5-Cl-salicylato ligand and the phenolate oxygen from the saladhp ligand on an adjacent trimeric unit. The three coordinated atoms of the saladhp ligand and an acetato oxygen make up the Mn(III) equatorial plane. The bridging alkoxides [O(2)−Mn(2)−O(2b) = 89.2°] and the carboxylato oxygens of the 5-Cl-salicylato ligands [O(102)−Mn(2)−O(102b)] = 87.2°] are bound to the Mn(II) octahedron in a *cis*-configuration, while

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(14) Crystal data: $[C_{40}H_{40}N_2O_{16}Cl_2Mn_3]_n$, MW = 1040.5, monoclinic, space group *C*2/*c*, $a = 18.275(2)$ Å, $b = 12.964(3)$ Å, $c = 17.796(6)$ Å; $\beta = 102.75°$, $V = 4112.4(14)$ Å$^3$, $Z = 4$, brown prisms, crystal dimensions, 0.16 × 0.18 × 0.11 mm. The intensities of 3844 reflections were measured ($-21 \le h \le +21$, $0 \le k \le 15$, $0 \le l \le 20$) at room temperature ($3 < 2\theta < 65°$) on a CAD4-F diffractometer using Cu Kα ($\lambda = 1.5418$ Å) radiation. A total of 3499 independent reflections were used in refinement. The structure was solved by direct methods, using the program SHELX86. The refinement was carried out using the program CRYSTALS. Anisotropic thermal parameters were used for all non-H atoms except the disordered oxygen atoms. For 2353 unique observed reflections[$I > 3\sigma(I)$], the final $R$ value was 0.0367.

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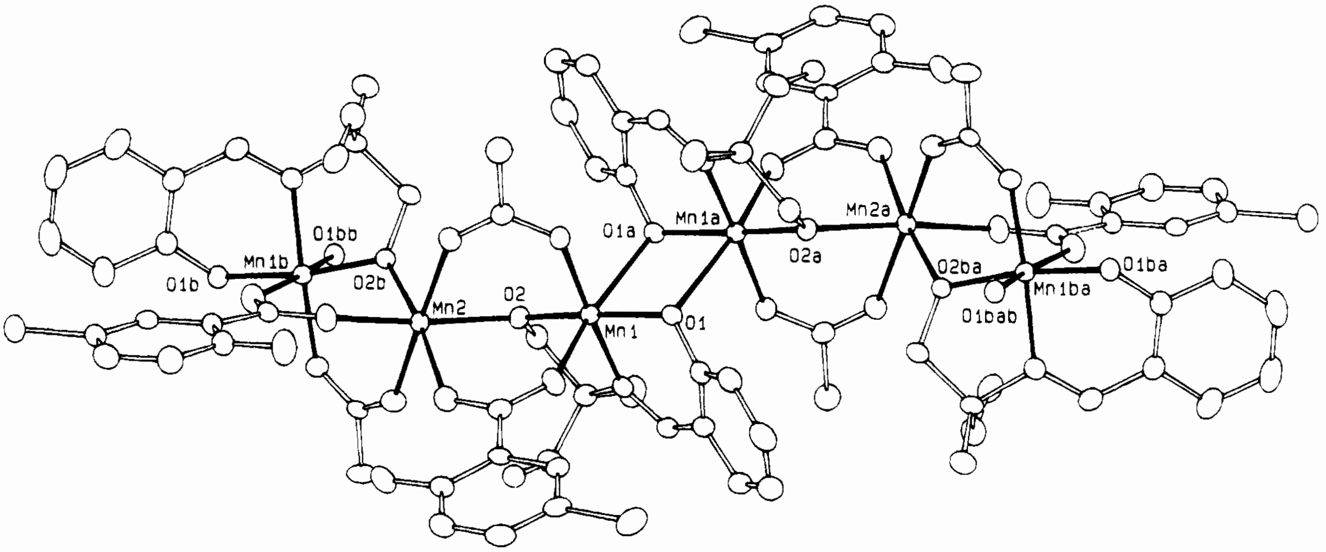


**Figure 1.** ORTEP diagram of $[Mn_3(Hsaladhp)_2(acetato)_2(5\text{-}Cl\text{-}salicylato)_2]_n$ (1). Important distances (Å) and angles (deg). Mn(1)−O(1) = 1.919(3), Mn(1)−N(1) = 1.986(4), Mn(1)−O(2) = 1.866(3), Mn(1)−O(101) = 2.102(4), Mn(1)−O(201) = 2.134(3), Mn(1)−O(1a) = 2.470(3), Mn(2)−O(2) = 2.188(3), Mn(2)−O(102) = 2.176(4), Mn(2)−O(202) = 2.134(3); N(1)−Mn(1)−O(1) = 90.2(1), O(2)−Mn(1)−O(1) = 170.4(1), O(2)−Mn(1)−N(1) = 82.0(1), O(101)−Mn(1)−O(1) = 88.0(1), O(101)−Mn−(1)−N(1) = 92.8(2), O(101)−Mn(1)−O(2) = 97.9(1), O(201)−Mn(1)−O(1) = 90.7(1), O(201)−Mn(1)−N(1) = 174.5(2), O(201)−Mn(1)−O(2) = 96.5(1), O(201)−Mn(1)−O(101) = 92.6(2), O(1)−Mn(1)−O(1a) = 78.4(1), N(1)−Mn(1)−O(1a) = 90.8(1), O(2)−Mn(1)−O(1a) = 95.9(1), O(101)−Mn(1)−O(1a) = 166.0(1), O(201)−Mn(1)−O(1a) = 84.1(1), O(2)−Mn(2)−O(2b) = 89.2(2), O(102)−Mn(2)−O(2) = 93.4(1), O(102)−Mn(2)−O(2b) = 171.1(1), O(102)−Mn(2)−O(102b) = 85.3(2), O(202)−Mn(2)−O(2) = 84.2(1), O(202)−Mn(2)−O(2b) = 91.8(1), O(202)−Mn(2)−O(102) = 96.9(1), O(202)−Mn(2)−O(102b) = 87.2(1), O(202)−Mn(2)−O(202b) = 174.4(2).

the bridging acetato oxygens [O(202)−Mn(2)−O(202b) = 174.4(2)°] are arranged in a *trans*-configuration about the central Mn(II). As a result of this bridging geometry, the distance between the two terminal Mn(1)−Mn(1b) ions in the trimeric unit is 6.491(1) Å and the Mn(1)−Mn(2)−Mn(1b) angle is 137.5(4)°.

Variable temperature magnetic susceptibility measurements indicate the presence of weak antiferromagnetic interactions in this polymer. Due to multiatom bridging and the long 6.491 Å terminal Mn1−Mn1b distance, the exchange interaction between these paramagnetic centers ($J_{terminal}$) is assumed to be negligible. Therefore, the magnetic interactions within the trimeric unit can be described by the following exchange Hamiltonian.

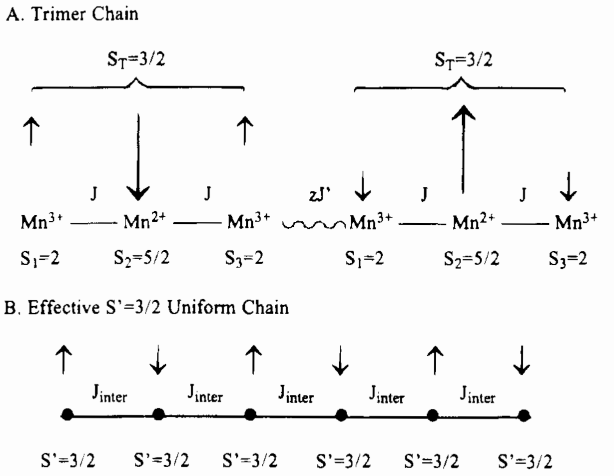
$$H = -2J[(S_1 \cdot S_2) + (S_2 \cdot S_3)]$$

The energy levels for such a trimer are given by standard vector coupling relations[13]

$$E = -J[S_T(S_T + 1) - S_{13}(S_{13} + 1) - S_3(S_3 + 1)]$$

where $S_{13}$ assumes values $S_1 + S_3$ ... $|S_1 - S_3|$ and $S_T$ assumes values $S_{13} + S_2$ ... $|S_{13} - S_2|$. The spin eigenfunctions in the coupled representation are given by $|S_T S_3\rangle$. The intertrimer interactions ($zJ'$) was accounted for by the use of a molecular field approximation.[13,15] The relevant exchange interactions within this polymeric trimer chain are shown schematically in Scheme 1A. The best fit parameters obtained from this model are $g = 1.95$, $J = -5.5$ cm$^{-1}$, and $zJ' = -0.2$ cm$^{-1}$. The ground state of the isolated trimer units is $|{}^3/_2, 4\rangle$, a spin quartet. Since $J \gg zJ'$, the polymer may be described as an effective $S' = {}^3/_2$ antiferromagnetic linear chain in the low temperature limit ($T < \sim 10$ K). This is depicted schematically in Scheme 1B.

**Scheme 1**



In conclusion, the compound $[Mn_3(Hsaladhp)_2(acetato)_2(5\text{-}Cl\text{-}salicylato)_2]_n$ represents a novel polymeric manganese complex that is composed of trimeric repeating units. Variable temperature magnetic susceptibility data show that intratrimer exchange coupling is dominant over intertrimer exchange coupling; thus the magnetic description of the complex as a trimer chain parallels the geometric structural description.

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**Supplementary Material Available:** Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations and a drawing of an alternate molecule as well as plots of magnetic susceptibility data (16 pages). Ordering information is given on any current masthead page.

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(15) It is difficult to ascertain the relative contributions of weak intertrimer exchange and zero-field splitting of the $S_T = {}^3/_2$ ground state to the low temperature magnetic behavior. Due to the presence of a single atom bridge between the terminal Mn ions of adjacent trimers, an intertrimer interaction is expected. However, this interaction is predicted to be small as a result of the Mn(III) Jahn−Teller distortion weakening the Mn−$O_{phenolate}$ bond and the terminal Mn(III) $d_{z^2}$ orbital not being a magnetic orbital.