Crystal Structure and Magnetic Property of the Binuclear Manganese(III) Complex with \( \mu \)-Acetate and Di-\( \mu \)-Alkoxo Bridges

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Binuclear Manganese(III) Complex, Crystal Structure, ESR Spectra, Magnetic Property

Binuclear manganese(III) complex, \([\text{Mn}_2\text{L}(\mu\text{-OCH}_3)(\mu\text{-CH}_3\text{COO})(\text{OHCH}_3)\text{ClO}_4]\), was prepared and characterized in terms of crystal structure determination, magnetic measurement, and ESR spectroscopy, where \(\text{H}_3\text{L}\) represents the Schiff base derived from salicylaldehyde and 1,5-diamino-3-pentanol.

1. Introduction

Multinuclear manganese sites that are involved in the catalysis of reactions vital to biological systems are being steadily recognized and studied. Besides the photosynthetic water-oxidizing complex, which is known to utilize 4 Mn ions for the oxidation of water to molecular oxygen [1], evidence has accumulated that the Mn site of the pseudo-catalase from Lactobacillus planatrum is comprised of two Mn ions per protein subunit [2]. Thus there is compelling interest in the characterization of multinuclear manganese complexes in various oxidation states in order to unravel the more complex behaviour of the biological sites by serving as models of the structural, spectral, of functional properties. In the previous papers, Nishida et al. have studied the catalytic function of binuclear Mn(III) complexes for the decomposition of \(\text{H}_2\text{O}_2\) [3], and the ESR spectra of binuclear Mn(II) [4], and Mn(III) [5] complexes.

In this article we wish to report the preparation, crystal structure, and magnetic properties of the binuclear manganese(III) complex, \([\text{Mn}_2\text{L}(\mu\text{-OCH}_3)(\mu\text{-CH}_3\text{COO})(\text{OHCH}_3)\text{ClO}_4]\), where \(\text{H}_3\text{L}\) represents the Schiff base derived from salicylaldehyde and 1,5-diamino-3-pentanol.

2. Materials and Method

The ligand \(\text{H}_3\text{L}\) was obtained by the published method [6]. The manganese(III) complex was obtained as green prisms from the reaction mixture (methanol solution) of \(\text{Mn(CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}, \text{H}_3\text{L}, \text{triethylamine, and NaClO}_4\) [7].

The crystal (0.2\(\times\)0.2\(\times\)0.4 mm) was mounted on a Rigaku AFC-5 four-circle automatic diffractometer with graphite monochromated MoK\(\alpha\) radiation (\(\lambda = 0.71069\) \(\AA\)). Automatic centering and least-squares routines were carried out on 25 reflections to obtain the cell constant. Crystal data: \([\text{Mn}_2\text{L}(\text{OCH}_3)(\text{CH}_3\text{COO})(\text{OHCH}_3)\text{ClO}_4]_n\) orthorhombic, space group \(\text{Pca}_2_1\), \(a = 20.006(10)\), \(b = 15.445(2), c = 8.5058(9)\) \(\AA\). The \(\theta-2\theta\) scan technique was employed to record the intensities of a unique set of reflections, and 3640 of independent non-zero (\(\text{Fo} > 3\text{Fe(Fo)}\)) reflections with \(2\theta\) between 2.5° and 55° were used for the crystal structure determination. Three check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects; the data collection was performed at 294 ± 1 K. The structure was solved by direct methods (MULTAN) [8], and successive Fourier syntheses. The structure was refined by block-diagonal least-squares including anisotropic thermal parameters, giving \(R(=\Sigma|\text{Fo}| - |\text{Fc}|/\Sigma|\text{Fo}|) = 0.047\), and \(R_e(=\Sigma w(|\text{Fo}| - |\text{Fc}|)/\Sigma w|\text{Fo}|^2)^{1/2} = 0.052\) where \(w = 1\). The final shifts of the parameters were less than 0.4 times their estimated standard deviations.

All the calculations were performed on a Facom M-200 computer with local versions of UNICS III [9] and ORTEP [10]. The thermal ellipsoids of the ORTEP plots were drawn at the 50% probability...
level. The atomic scattering factors were taken from ref. [11]*.

3. Results and Discussion

An ORTEP drawing of the [Mn₂L(OCH₃)(CH₃COO)(OHCH₃)]⁺, including the atomic numbering scheme, is given in Fig. 1, and the selected bond distances and angles are summarized in Table I. Two manganese(III) ions are bridged by three groups; two alkoxo oxygen atoms and one acetate ion. The coordination numbers of manganese ions are six and five for Mn₂ and Mn₁, respectively, and the Mn—Mn distance is 2.931(2) Å. The temperature dependence of the magnetic susceptibility (81—298 K) is shown in Fig. 2. The magnetic moment per manganese ion is 4.28 and 3.08 μ_B at 298.3 and 81.5 K, respectively. The exchange integral parameter, J, derived from the equation based on the isotropic Heisenberg model (σ = −2JS₂) [12].

Table I. Selected bond lengths (Å) and angles (°) of the coordination sphere in [Mn₂L(OCH₃)(CH₃COO)(OHCH₃)]⁺ with their estimated standard deviations in parentheses.

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<tr>
<th>Bond length (Å)</th>
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<tr>
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<td>Mn₁—O₃</td>
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<td>Mn₂—O₄</td>
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* Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated structure factor amplitudes have been deposited as the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopolds- hafen 2. The registry-Nr., CSD 52937, the names of the authors, and the reference should be given.
et al. inferred that the electrons of the atoms are aligned in an antiparallel fashion via a superexchange mechanism [13]. Since Mn=O (oxo oxygen atom) bonding is the strongest in [Mn₂O₂(bip)₄]²⁺, the dₓᵧ orbital which is located along the Mn=O bond is vacant, and thus it is most likely that strong antiferromagnetic interaction observed in the complex should be attributed to notable direct overlap between dₓᵧ orbitals, as illustrated below. This is supported by the fact that the magnetic interaction is negligible in μ-oxo-di-μ-acetato dimanganese(III) complex, [Mn₂O(CH₃COO)₂(C₆H₁₃N₃)₂]²⁺ [14] where the Mn-Mn distance (3.08 Å) is much longer than that (2.716 Å) of [Mn₂O₂(bip)₄]²⁺. In our present manganese(III) complex, it can be anticipated that no electron lies in the dₓᵧ orbital because the in-plane Mn-O and Mn-N bonds are stronger than those of out-of-plane bonds. Thus, the small −J value of the present complex can be attributed to a smaller overlap between two dₓᵧ orbitals due to a longer Mn-Mn distance (2.931 Å).

The present dimanganese(III) complex is ESR non-detectable at 77 K (frozen solution state), whereas two other complexes, [Mn₂O₂(bip)₄]³⁺ and [Mn₂O(CH₃COO)₂(C₆H₁₃N₃)₂]²⁺ are ESR detectable [15, 5]. The ESR non-detectable nature of the present complex may be attributed to the diamagnetic ground state due to weak antiferromagnetic interaction, because the other two have paramagnetic ground states.

[7] Found: C 42.49; H 4.62; N 4.52; Mn 16.4%. Caled for
[Mn₂L₃(OCH₃)₃(CH₃COO)](OHCH₃)ClO₄: C 42.19; H 4.46; N 4.28; Mn 16.78%.