Synthesis and Magnetic Properties of Oxo-Bridged Tetranuclear Iron(III) and Manganese(III) Complexes

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Oxo-bridged Tetranuclear Complex, Magnetic Property of Fe(III) and Mn(III)

New tetranuclear iron(III) and manganese(III) complexes with 1,4-bis[N,N-bis(2-benzimidazolylmethyl)amino]butane, and their hexane derivatives were prepared. Magnetic measurements suggest that these have an oxo-bridged structure of Toftlund type.

1. Introduction

Structural studies on met-hemerythrin (Hr) have shown that the subunits contain binuclear Fe(III) center in which the metal ions are bridged by one μ-oxo and two μ-carboxylato groups. The metal ions are bound to the protein by histidine nitrogen atoms, as well as by the carboxylate groups [1]. Spectroscopic properties similar to those of the Hr active site suggest that similar active site structures exist in ribonucleotide reductase [2] and purple acid phosphatase [3]. In 1983 Wieghardt et al. succeeded in preparing the model compound for met Hr, Fe₄O(CH₃COO)₄(L-4)Cl · 4 H₂O [14], where L represents 1,4,7-triazacyclononane [4]. After this, several groups reported the preparations of binuclear iron(III) complexes with a μ-oxo bis(μ-acetato) core [5, 6]. In 1986 Toftlund et al. have reported the preparation of tetranuclear iron(III) compounds where two dinuclear iron(III) with a (μ-oxo)bis(μ-acetato) core are linked by alkyl chains [7], as illustrated below.

We are now interested in the relationship between the enzymatic activity and the structure of metal enzymes with a μ-oxo bridge, which are ubiquitous in biological systems. For example, the presence of a μ-oxo bridge has been shown in the manganese enzyme of the oxygen evolving center of the photosystem II [8]. In previous papers [9–12], we have reported the preparation and properties of binuclear iron(III) and manganese(III) complexes with a μ-oxo bis(μ-acetato) core by the use of the ligands N,N-bis(benzimidazol-2-ylmethyl)amine and its homologues (as illustrated below). In this article we prepared tetranuclear iron(III) and manganese(III) complexes with the hexadentate ligands shown below, and the magnetic properties of these compounds are reported.

2. Materials and Method

The ligands used in this study, (L-4) and (L-6), were prepared according to the published method [13]. The metal compounds were prepared as follows: An aqueous solution (5 ml) of [Fe₄O(CH₃COO)₄(H₂O)₃]Cl · 4 H₂O [14] (0.002 mol) and a methanol solution (15 ml) of (L-4) (0.001 mol) were mixed, and to this solution was added NaClO₄ (500 mg). After one day, the deposited green prisms were filtered.

Fe₄O₄(CH₃COO)₄(L-4)/(ClO₄)·2H₂O
Calcd C 44.84 H 4.14 N 13.07 Fe 10.42
Found C 44.73 H 4.14 N 13.09 Fe 10.60.
To the methanol solution (20 ml) of (L-4) (0.001 mol) were added manganese(III) acetate dihydrate (0.002 mol) and NH$_4$PF$_6$ (500 mg), and the solution was filtered once. After several days brown needles deposited from the solution.

\[ Mn_4O_2(CH_3COO)_4(L-4)_2(PF_6)_3(CH_3COO) \]

Calcd: C 44.78, H 3.99, N 12.74, Mn 9.99.

Found: C 44.98, H 4.43, N 12.58, Mn 9.60.

By a similar way the corresponding (L-6) compound was obtained as brown needles.

\[ Mn_4O_2(CH_3COO)_4(L-6)_2(PF_6)_3(CH_3COO) \]

Calcd: C 45.80, H 4.15, N 12.42, Mn 9.74.

Found: C 45.52, H 4.57, N 12.34, Mn 9.60.

ESR spectra were obtained with a JEOL ESR apparatus model JES-FE-3X at liquid nitrogen temperature using the X-band. Magnetic susceptibilities (\(\chi\)) were measured by the Faraday method at Saga University in the temperature range 81-293 K. Magnetic moments were calculated by the equation \(\mu_{\text{eff}} = 2.878 V/\sqrt{T}\).

### 3. Results and Discussion

Analytical data of the compounds obtained in this study are consistent with tetranuclear complexes where two binuclear units of (\(\mu\)-oxo)bis-(\(\mu\)-acetato) core are linked by the alkyl chains, similar to the case of Toftlund et al. [7]. The temperature dependence of the magnetic susceptibility of the iron(III) compound is shown in Fig. 1. The observed values can be explained in terms of the theoretical expression for binuclear units based on the Heisenberg spin Hamiltonian, \(H = -2JS_1S_2\). The \(-J\) value, 109.6 cm$^{-1}$, clearly demonstrates the presence of a \(\mu\)-oxo bridge in this compound [15].

The temperature dependence of the magnetic susceptibility of 
\[ Mn_4O_2(CH_3COO)_4(L-4)_2(PF_6)_3(CH_3COO) \]
is illustrated in Fig. 2. The magnetic moments of (L-4) and (L-6) compounds are 5.13 (293 K) and 5.58 (81 K), and 5.13 (293 K) and 5.65 (81 K), respectively, indicating that these complexes are of Mn(III) oxidation state, and weak ferromagnetic interaction (\(J\) is estimated to be 4.8 and 5.6 cm$^{-1}$ for (L-4) and (L-6) complexes, respectively) operates in the dimeric units. These properties of the tetranuclear compounds are very similar to those observed for other binuclear Mn(III) compounds with a (\(\mu\)-oxo)bis(\(\mu\)-acetato) core [10, 12].

Although the magnetic properties of the present tetranuclear compounds are similar to those of binuclear ones, a great difference was observed in...
the ESR spectra. As reported in previous papers [10, 12], we can observe a "16-line ESR signal" in the frozen solutions (dmf, dmso, and acetonitrile) of manganese(III) compounds with a (μ-oxo)bis-(μ-acetato) core. Some authors have pointed out that this signal should be due to a Mn(III)-Mn(IV) species produced in the course of disproportionation reactions of oxo-bridged binuclear manganese(III) compounds [16]. Contrary to this, no ESR signal was detected in the frozen solutions of tetranuclear Mn(III) complexes with (L-4) and (L-6), as illustrated in Fig. 3, which were measured under almost the same experimental conditions as those of binuclear ones (concentration, solvents, and gain). In general, the ESR spectra of the binuclear compounds are different from the corresponding mononuclear complexes, and this has been attributed to the presence of interaction between mononuclear species [17]. Thus, the present result may indicate that there is some interaction between binuclear cores in the tetranuclear compounds.

If disproportionation reactions occur in the solutions of μ-oxo binuclear Mn(III) complexes, the formation of a Mn(II) species is expected as follows,

$$2 \text{Mn(III)} - \text{Mn(III)} \rightarrow \text{Mn(III)} - \text{Mn(IV)} + \text{Mn(II)} + \text{Mn(III)}$$

and the formation of a Mn(II) species should be detected by means of ESR spectroscopy. In Fig. 3, the ESR spectrum of the Mn(II) complex [18] of 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol, Mn(bbt)(NCS)$_2$, is also shown. We have also found that the ESR spectrum of binuclear Mn(II) complex, Mn$_2$(L-4)(NCS)$_4$, is almost the same as that of Mn(bbt)(NCS)$_2$ in Fig. 3. These facts are suggesting that there is no formation of a Mn(II) species in the solutions of the tetranuclear compound of (L-4).

The reduction of Mn(III) to Mn(II) was observed when H$_2$O$_2$ was added to the solution of the binuclear Mn(III) complex of (bbt). On the other hand, no color change was observed in the cases of tetranuclear compounds of (L-4) and (L-6) on the addition of H$_2$O$_2$. This suggests that the reactivity of the tetranuclear compounds is different from that of the corresponding binuclear species, and this may give an important key to understand the mechanism of the O$_2$ evolution reaction catalyzed by tetranuclear manganese cluster in the photosystem II [19].

Fig. 3. ESR spectra (in dmf, 77 K, X-band, [Mn] ~ 1-2·10^{-3} \text{mol dm}^{-3}).
A: [Mn$_3$O(CH$_3$COO)$_2$(bbt)$_2$(ClO$_4$)$_2$] [10];
B: [Mn$_2$O$_2$(CH$_3$COO)$_4$(L-4)$_2$(PF$_6$)$_3$(CH$_3$COO)];
C: [Mn(bbt)(NCS)$_2$].