

## Preparation and ESR Spectra of Manganese(III) Complexes with 2-[Bis(benzimidazol-2-ylmethyl)-amino]ethanol

Yuzo Nishida<sup>a,\*</sup>, Naoko Oshino<sup>a</sup>, and Tadashi Tokii<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa Yamagata 990, Japan

<sup>b</sup> Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

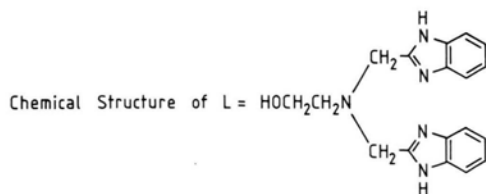
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Manganese(III) Complexes,  $\mu$ -Oxo-di- $\mu$ -acetato Bridges, ESR Spectra

Manganese(III) complexes with 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol were prepared. Based on the analytical data, IR, magnetic and ESR ("16-line ESR signal" was observed in the frozen state) properties, these complexes are assumed to be of the binuclear structure with  $\mu$ -oxo and di- $\mu$ -acetato bridges.

### 1. Introduction

Manganese is required in living systems to perform diverse redox functions including water splitting by photosynthetic enzymes [1] and disproportionation of hydrogen peroxide [2]. As evidence implying polynuclear centers in several of these enzymes has accumulated, various attempts have been made to prepare and characterize manganese complexes having analogous spectroscopic and magnetic properties [3–5] and catalytic function [6]. Very recently the manganese(III) complexes containing the ( $\mu$ -oxo)-bis( $\mu$ -acetato)dimanganese core have been prepared for the ligands of 1,4,7-triazacyclononane [7] and potassium hydrotris(1-pyrazolyl)borate [8]. In this article we wish to report that similar binuclear complexes with  $\mu$ -oxo and  $\mu$ -acetato bridges are obtained with the ligand 2-[bis(benzimidazol-2-ylmethyl)-amino]ethanol (hereafter abbreviated as L). The



\* Reprint requests to Dr. Y. Nishida.

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complexes exhibited interesting ESR spectra in the frozen state.

### 2. Materials and Methods

The ligand was obtained according to the method described in the literature [9]. Manganese(III) complexes with L were prepared from the reaction mixture (methanol) of the ligand, manganese(III) acetate dihydrate, and NaClO<sub>4</sub> (or NH<sub>4</sub>PF<sub>6</sub>).

$[Mn_2O(CH_3COO)_2L_2](ClO_4)_2$   
Calcd C 44.25 H 4.09 N 12.90 Mn 10.1,  
Found C 44.03 H 4.20 N 12.68 Mn 9.9.

$[Mn_2O(CH_3COO)_2L_2](PF_6)_2 \cdot H_2O$   
Calcd C 40.22 H 3.88 N 11.72 Mn 9.2,  
Found C 40.10 H 3.94 N 11.82 Mn 9.0.

ESR spectra were obtained with a JEOL ESR apparatus model JES-FE-3X at liquid nitrogen temperature using an X-band. Magnetic susceptibility ( $\chi$ ) were measured by the Faraday method at Saga University in the temperature range 81–290 K. Magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.878 \sqrt{\chi T}$ .

### 3. Results and Discussion

In Fig. 1, the temperature dependence of magnetic susceptibility of the perchlorate salt is shown. The magnetic moments are 5.04 and 5.16  $\mu_B$  at 289.7 and

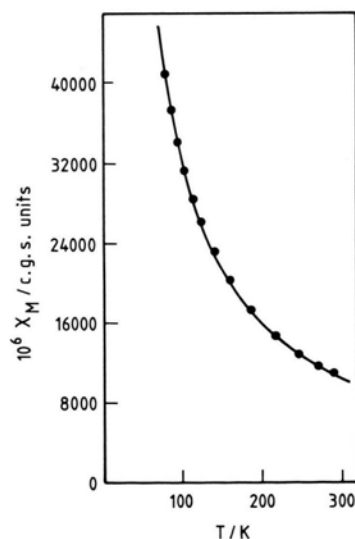


Fig. 1. Temperature dependence of magnetic susceptibility of  $[Mn_2OL_2(CH_3COO)_2](ClO_4)_2$ ; ●●● experimental value; — calculated curve based on the isotropic Heisenberg model where  $g$ ,  $J$ , and  $N\alpha$  were assumed to be 2.00, +1.72  $\text{cm}^{-1}$ , and 0, respectively.



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81.4 K, respectively, indicating that the manganese ion in this compound is of +3 oxidation state. Attempts to fit the  $\chi_M$  vs T data to the expression derived from the spin exchange Hamiltonian  $\mathcal{H}' = 2J S_1 \cdot S_2$  for  $S_1 = S_2 = 2$  led to  $J$  value of  $1.72 \text{ cm}^{-1}$  (cf. Fig. 1). This is suggesting that the magnetic interaction between the metal ions is negligible in the solid state. The magnetic moments of the  $\text{PF}_6$  salt are 4.92 and  $4.99 \mu_B$  at 286.6 and 81.3 K, respectively. In the IR spectra, strong bands were observed in the range 1590–1620, 738–740, and 550–560  $\text{cm}^{-1}$ , which may be assigned to  $\nu_{\text{as}}(\text{OCO})$ ,  $\nu_{\text{as}}(\text{Mn-O-Mn})$ , and  $\nu_s(\text{Mn-O-Mn})$ , respectively, as done by Lippard *et al.* [8].

In Fig. 2, the ESR spectrum of the perchlorate salt (in DMF, X-band) is illustrated. Clearly, 16 hyperfine lines are observed in the range 260–400 mT. As

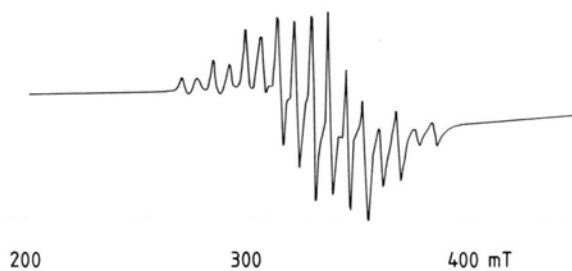


Fig. 2. ESR spectrum of  $[\text{Mn}_2\text{OL}_2(\text{CH}_3\text{COO})_2](\text{ClO}_4)_2$  (in DMF, 77 K, X-band).

the nuclear spin ( $I$ ) of the manganese atom is  $5/2$ , this spectrum is suggesting that multinuclear manganese site(s) are involved in this complex. The spectrum of the  $\text{PF}_6$  salt is essentially the same as that of the perchlorate salt. Very recently we have found [10] that the acetonitrile frozen solution (77 K) of  $\mu$ -oxo-di- $\mu$ -acetato binuclear manganese(III) complexes with 1,4,7-triazacyclononane show a "16-line ESR signal".

Based on the analytical data and the above discussion, it seems to be reasonable to assume that the manganese(III) complexes obtained in this study are of the binuclear structure with  $\mu$ -oxo and di- $\mu$ -acetato bridges.

It is generally known that tripod ligands containing benzimidazole groups such as L, prefer the lower oxidation state of the metal ion. For example, the stable manganese(II) and iron(II) complexes with L has been prepared, and characterized [11]. In fact, no color change was observed when the DMF solution of the manganese(III) complex obtained in this study was left to stand for several hours in air, which is quite different from those of Wieghardt [7] and Lippard [8]; the latter two complexes (we observed that the DMF solution of the Wieghardt complex turns from red to green in air [10]) are readily oxidized in solution under an aerobic condition, yielding the greenish-black Mn(III)–Mn(IV) complexes [8, 12]. Thus, it is very likely that the "16-line ESR signal" observed for the present complexes is due to the dimeric Mn(III) pair.

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