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Origin of Multiline ESR Signal Observed for Manganese(III) Complexes with N-Alkyl-N,N-bis(benzimidazol-2-ylmethyl)amine

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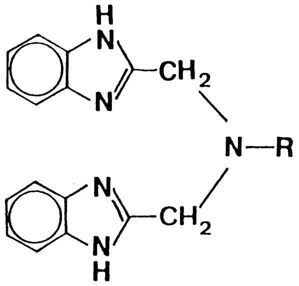
We have observed that some manganese(III) complexes with N-alkyl-N,N-bis(benzimidazol-2-ylmethyl)amine exhibit a multiline ESR signal around g=2 in the frozen state(below 77 K), and this has been attributed to the superposition of at least three components with 11 lines due to the dimeric manganese(III) pair.

Very recently we have observed that several manganese(III) complexes with oxo and acetate bridges, $[Mn_2O(CH_3COO)_2L_2]^{2+}$ exhibit a "multiline ESR signal" in the frozen state(77 K)[1,2] where L represents tridentate ligands such as 1,4,7-triazacyclononane and 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol. These spectra are very similar to those of Mn(III)-Mn(IV) mixed-valence complexes[3,4] and also to that reported for spinach PS II membrane where peripheral proteins of a molecular mass of 17 and 24 kD are removed.[5] On the basis of the chemical nature of these compounds, especially for the complex with the latter ligand, we have concluded that the "multiline ESR signal" observed can be attributed to the dimeric Mn(III) pair.[1,2] In this article we wish to report that some manganese(III) complexes with the ligands illustrated below(R=n-propyl, L_a; R=benzyl, L_b) show a "multiline ESR signal" around g=2 and another peaks centered at g=4(hereafter called as "signal II") in the frozen state(below 77 K), and the origin of the appearance of these signals for the manganese(III) complexes will be developed based on the temperature dependence (77-15 K) of signal intensity.



The manganese(III) complexes studied in this work were prepared according to the published method.[2] Analytical and IR data[6] are consistent with the assumed structure,[2] $[Mn_2O(CH_3COO)_2L_2](ClO_4)_2$($L=L_a$ and L_b), e.g., binuclear manganese(III) complex with oxo and acetate bridges. The magnetic susceptibility measurements(295-80 K) revealed that the oxidation state of Mn ion is of +3, and there is a very weak ferromagnetic interaction between manganese(III) ions(J was estimated to be in the range 0-10 cm^{-1} based on the isotropic Heisenberg model. For J, see the later text). The solutions(N,N-dimethylformamide(dmf), N,N-dimethylsulfoxide(dmso), and acetonitrile) are brown, and no color change was observed for the solutions, which is similar to the case of the complexes with 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol.[2] All these manganese(III) complexes showed a "multiline ESR signal" around g=2 at 77 K, as shown for

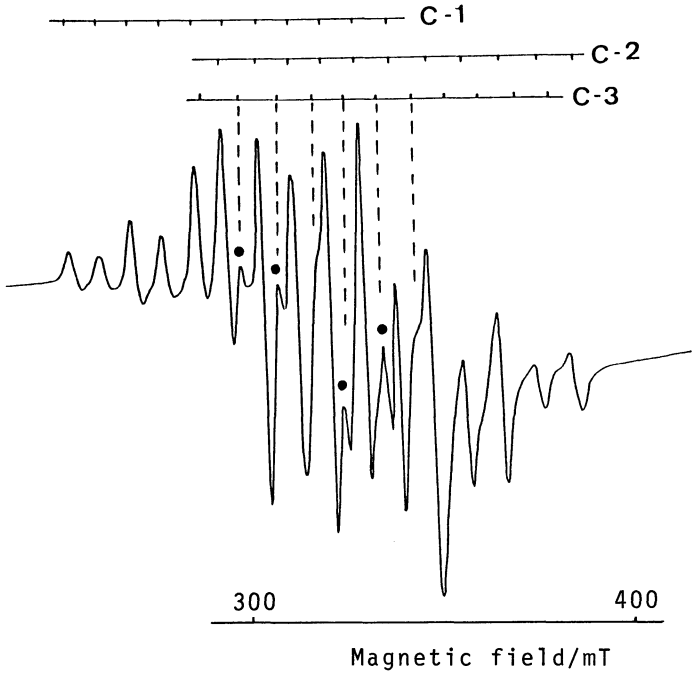


Fig. 1. ESR spectrum(X-band, 77 K) of $[Mn_2O(CH_3COO)_2(L_a)_2](ClO_4)_2$ in dmf.

$[Mn_2O(CH_3COO)_2(L_a)_2](ClO_4)_2$ in Fig. 1. This spectral pattern is slightly different from those reported for the complexes in references 1 and 2, e.g., more than 16 lines are observed for the present complex, whereas a "distinct 16-line ESR signal" was observed for the latter two compounds.[1,2]

Two drastic changes were observed in the ESR spectrum on decreasing of temperature from 77 to 15 K(spectra were recorded at 63, 33, and 15 K). First, the intensities of peaks marked by ● in Fig. 1 decreased with lowering of temperature, and thus the spectrum at 15 K in Fig. 2 resembles the "16-line ESR signal" reported previously.[1,2] Second, new signals centered at g=4 have appeared at very low temperature, as shown in Fig. 2; the intensity of "signal II" at 77 K is much smaller than those of the multiline signal around g=2, and the relative intensity of the "signal II" compared with that of the "multiline ESR signal" is the highest at 15 K. Almost the same facts were observed for the compound with L_b as observed for L_a.

Spins on neighboring metal ions in dimeric compounds may exchange through direct overlap of their orbitals or via overlap with intervening atoms. Exchange interaction is generally represented by the isotropic or Heisenberg type coupling

$$\mathcal{H}_{ex}=-2JS_1\cdot S_2.$$

Here negative J means a singlet(antiferromagnetic) lowest state and a positive J indicates a high spin state(ferromagnetic) as having the lowest energy. The

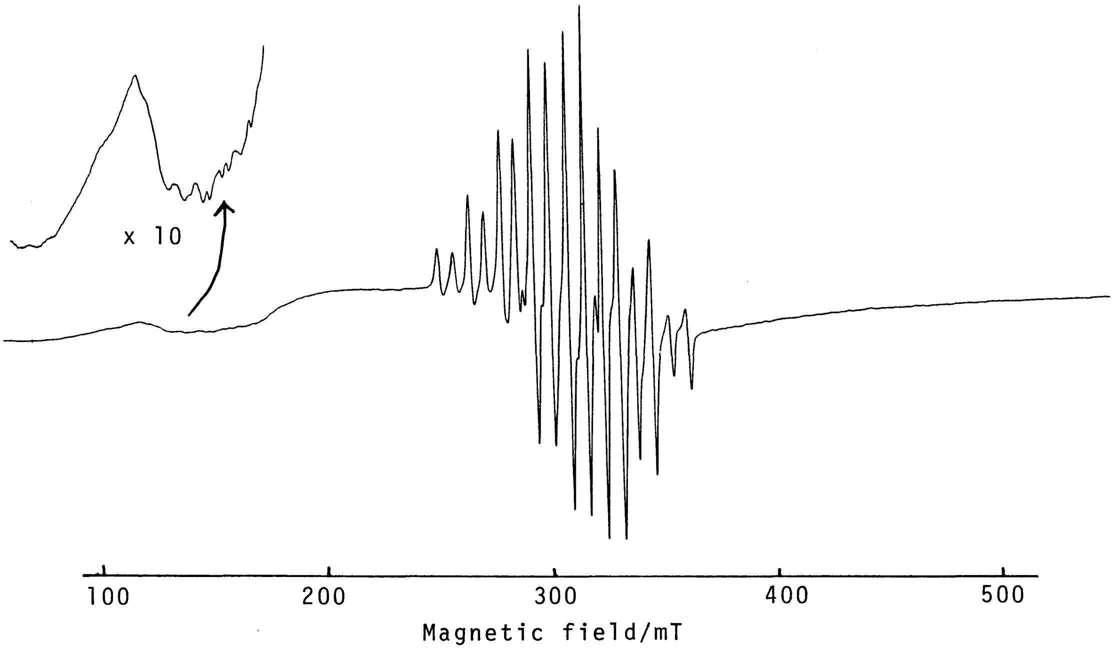


Fig. 2. ESR spectrum of $[Mn_2O(CH_3COO)_2(L_a)_2](ClO_4)_2$(X-band, in dmf, 15 K).

ESR spectra of the dimeric compounds can usually be characterized by the parameters, J, D, and E.[7)] The hyperfine interaction for such a pair is given by,

$$A_iS_i\cdot I_i + A_jS_j\cdot I_j + B_iS_i\cdot I_j + B_jS_j\cdot I_j$$

where A_i is the coupling at nucleus i due to spin at i, and B_j is the coupling at nucleus j due to spin i.[7)] In the case of $S_i=S_j$, $A_i=A_j$, $B_i=B_j$, and transfered hyperfine coupling constant B is small relative to A, the patterns for two exchanged-coupled atom with I=5/2(in the case of Mn) will be 11 hyperfine lines with relative intensities 1:2:3:4:5:6:5:4:3:2:1 separated essentially by A/2,[7)] as observed for several cases.[8,9)] For the exchange-coupled Mn^{2+} in MgO(or CaO), the signal due to the higher spin levels(S_t=2,3,4, and 5) have been observed in the spectrum.[10)] Each line appears splitted by hyperfine interaction into 11 lines and these are overlapping, yielding 22 peaks at room temperature.[10)]

Thus, it seems most reasonable to assume that the "16-line ESR signal" observed in the previous papers[1,2)] is due to the suitable overlapping of 11 lines of three components of the four possible spin levels(S_t=1,2,3, and 4) in dimeric Mn(III) pair, as suggested in the case of Mn^{2+} pair. If the overlapping of peaks due to three components are not complete, we can anticipate the more complicated spectrum; the spectrum of $[Mn_2O(CH_3COO)_2(L_a)_2](ClO_4)_2$ in dmf at 77 K should correspond to this case. In Fig. 1, a simple stick diagram of three components is illustrated for this case. The peak intensities of component-3(C-3 in Fig. 1) are greatly reduced at 15 K compared with those at 77 K, indicating that three components are not due to the anisotropic terms of g-tensor in the single spin ground state, and this is consistent with our assumption described above.

The ESR spectral behaviour observed in this study is inconsistent with that expected for the Mn(III)-Mn(IV) mixed-valence complexes[3,4)] and it is thus very likely that three components in the "multiline ESR signal" and the "signal II" may be due to the four spin levels(S_t=1,2,3, and 4) in the dimeric Mn(III) pair, although we cannot assign the ESR signals to each spin state at present.

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