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ESR Spectral Evidence for Existence of Electron-localized Species in Binuclear Manganese(III/IV) Compounds with Di-μ-oxo Bridge

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We have observed that the binuclear manganese(III/IV) compounds with di-μ-oxo bridge exhibit solvent-dependent solution ESR spectra at room temperature, and have concluded that there are two ESR-detectable species, electron-localized and electron-delocalized ones, in the solution.

Since the discovery of the so-called multiline ESR signal of the S_2-state in the oxygen-evolving center,$^{1)}$ the magnetic properties of binuclear manganese(III/IV) compounds with di-μ-oxo bridge have received considerable attention.$^{2)}$ Cooper et al.$^{3)}$ have carried out extensive studies including spectroscopic, magnetic and electrochemical measurements on the complex, $[Mn_2O_2(bpy)_4]^{3+}$ where bpy represents 2,2'-bipyridine, as well as the 1,10-phenanthroline analogue. The features of ESR spectrum of a frozen solution (below 77 K) of the compounds may be accounted for by the following spin Hamiltonian,

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) + (A_1 I_1 + A_2 I_2)S - 2JS_1 \cdot S_2$$

where $g_{\parallel}$ and $g_{\perp}$ are the principal g-tensor components for the assumed symmetry, and others have the usual meanings.$^{4)}$ The terms with subscript 2 refer to the Mn(IV) ion. The 16-line ESR signal observed in the frozen solution indicates that the exchange coupling results in a doublet ground state with little anisotropy in the g-tensor. The large difference in the hyperfine coupling constants of $A_1=167\pm 3$ G and $A_2=79\pm 3$ G indicates that the unpaired electron in the ground spin state is transferred between them at a rate much slower than $|A_1|-|A_2|$. The slow rate of the electron transfer is a consequence of the electronic structure of the high-spin Mn(III) ion; the electron transferred is in the e_g antibonding orbital, and the transfer to the Mn(IV) requires considerable changes in the bond distances about the manganese ions.

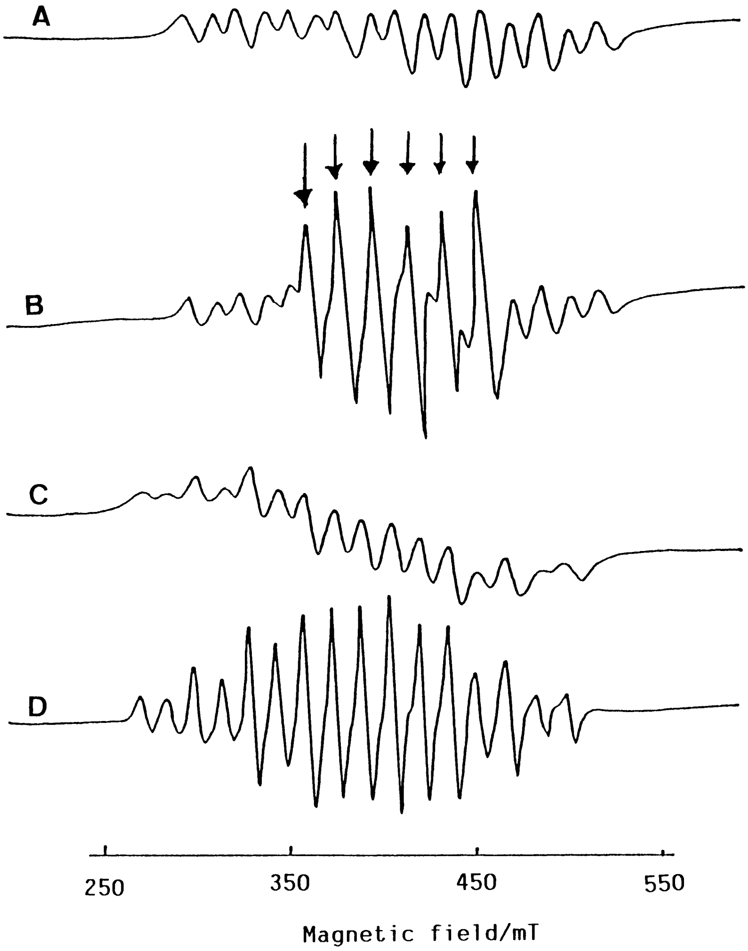

Fig. 1. ESR spectra of the cyclam compound (X-band) In AN (1/1000 mol dm^{-3}) at 295 K (A) and 77 K (C). In dmf (1/500 mol dm^{-3}) at 295 K (B) and 77 K (D).

In this article, we have observed that some di-μ-oxo binuclear Mn_2(III/IV) compounds exhibit solvent-dependent solution ESR spectra at room temperature. In the course of the study on the solution ESR spectra of these compounds, we have concluded that there are two ESR-detectable species, electron-localized and electron-delocalized ones, in the solution. The binuclear manganese(III/IV) compounds used in this study are $[Mn_2O_2(cyclam)_2](ClO_4)_3$,[5] $[Mn_2O_2(tpa)_2](ClO_4)_3$,[6] $[Mn_2O_2(pda)_2]ClO_4$,[7] and $[Mn_2O_2(Me\text{-}en\text{-}py)_2](ClO_4)_3$,[8] where cyclam, tpa, Hpda, and Me-en-py denote 1,4,8,11-tetraazacyclotetradecane, tris(2-pyridylmethyl)amine, N,N-bis(2-pyridylmethyl)glycine, and N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)ethylenediamine, respectively. ESR spectra were obtained by a JEOL ESR apparatus model RE-2X ESR spectrophotometer by the use of an X-band. The solvents, acetonitrile(AN) and N,N-dimethylformamide(dmf) were obtained commercially, and were used without further purification. The ESR spectra of the solutions were measured both at 295 and 77 K.

In Fig. 1, the ESR spectra of the cyclam compound are shown; in AN, a 16-line ESR signal is observed at both 295 and 77 K. In dmf, the ESR spectrum at 295 K is very similar to that observed in AN, except for the appearance of strong 6 lines(see the trace B in Fig. 1; the 6 lines are indicated by arrows). However, the spectrum at 77 K in dmf is completely consistent with that in AN, i. e., a 16-line signal is observed. Similar facts are also observed for the tpa compound(cf. Fig. 2). In a dilute AN solution, a 16-line signal is observed at 295 K as shown in Fig. 2. On the other hand, only a 6-line signal is observed in the dmf solution(see

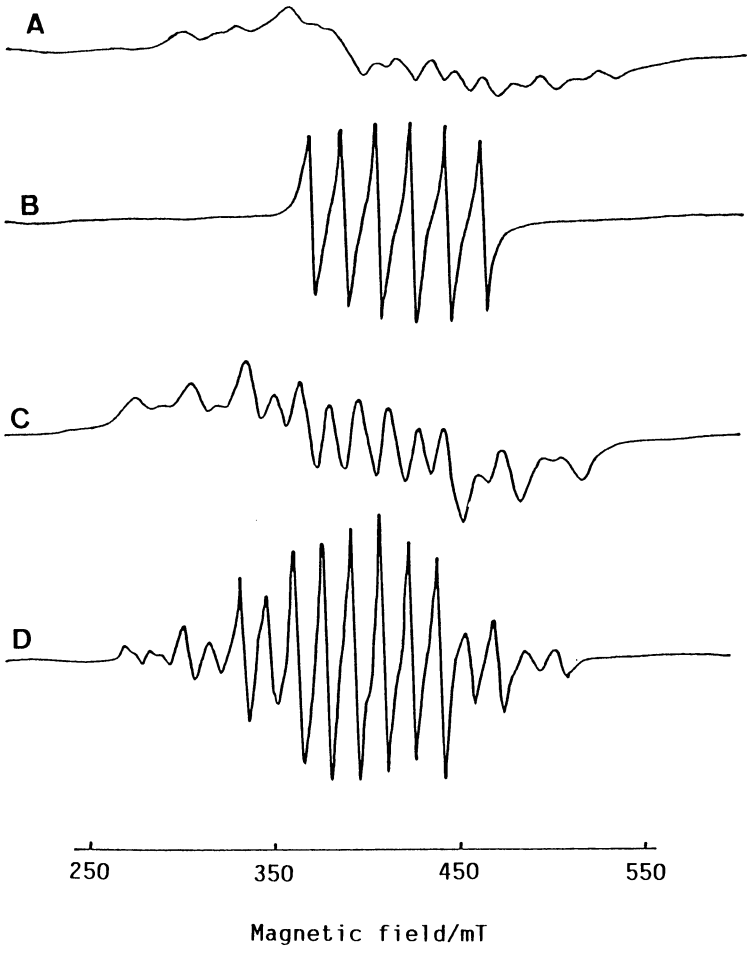

Fig. 2. ESR spectra of the tpa compound(X-band)
In AN(1/1000 mol dm^{-3}) at 295 K (A) and 77 K (C).
In dmf(1/500 mol dm^{-3}) at 295 K (B) and 77 K (D).

the trace B in Fig. 2). However, the frozen solution ESR spectra at 77 K in both the solutions are very similar to each other as illustrated in Fig. 2. In the case of the Hpda compound, only a 16-line signal was observed for both AN and dmf solutions at 295 K, although the spectral properties of both AN and dmf solutions at 77 K are completely the same as those of the cyclam and tpa compounds. The spectral properties of the Me-en-py compound are very similar to those of the tpa compound.

If we assume that the 6-line signal observed at 295 K for the tpa and the cyclam compounds in dmf is due to a Mn(II) species which may exist in the solution as a contamination, we can expect that strong ESR signal due to this Mn(II) ion appears in the spectra at 77 K. But this assumption is not consistent with the facts observed. Based on these facts, it seems reasonable to conclude that the 6-line signal observed in this study should be due to the binuclear manganese(III/IV) species, and that this should be attributed to an electron-localized form of the compound. Our data also suggest that the equilibrium between the electron-localized and the electron-delocalized forms depends on the solvent and temperature. More detailed investigation on this problem is now in progress.

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