Manganese(III) Complex Exhibiting a Multiline ESR Signal

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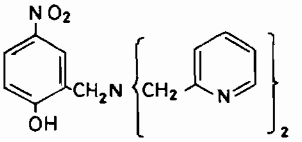
In the photosynthetic process of higher plants and algae, water is oxidized to dioxygen in four consecutive photoreactions of PS II. Manganese has been indirectly implicated as the site for water binding and direct observation of oxidation changes have indicated clear redox reactions [1, 2]. However, little is known about the arrangement of the metals or their ligation. It is generally believed that four atoms of Mn per PS II reaction center are essential for oxygen evolution, and that all are in close proximity to one another. The Mn aggregate is capable of cycling between four distinct oxidation levels labelled S_0–S_4 by the pioneering work of Kok [1].

In 1980, Dismukes and Siderer succeeded in measuring the ESR spectrum of the S_2-state which shows a 'multiline ESR signal' [3]. Since then, it has been believed that a 'mixed-valence state' is present in the S_2-state, based on the fact that only the Mn(III)–Mn(IV) mixed-valence complex $[Mn_2O_2(bip)_4](ClO_4)_3$ exhibits a 'multiline ESR signal' [4, 5]. Very recently, Nishida and Oshino have shown that several binuclear Mn(II) [6] and Mn(III) [7] complexes show a 'multiline ESR spectra', and proposed that the S_2-state in the active site contains a dimeric manganese(III) pair. In this article, we report that the manganese(III) complex with 2-bis[bis(2-pyridylmethyl)-aminomethyl]-4-nitrophenyl (hereafter abbreviated as HL) also shows a '16-line ESR signal' which resembles that of the S_2-state of the spinach photosystem membrane where peripheral proteins of molecular mass of 17 and 24 kD are removed [8].



HL

From the reaction mixture (methanol solution) of $Mn(CH_3COO)_3 \cdot 2H_2O$, HL [9], triethylamine and $NaClO_4$, brown needles of $Mn(L)(OCH_3)ClO_4$ were obtained†. The magnetic data (286–81 K, μ_{eff} = 4.88 and 4.80 μ_B at 287.4 and 81.4 K, respectively) indicate that the manganese ion in this complex is of a +3 oxidation state, and that a very weak antiferromagnetic interaction (J was estimated to be -0.88 cm^{-1} based on the equation of the isotropic Heisenberg model) is operating between the manganese ions. The ESR spectrum in *N,N*-dimethylformamide (frozen state, 77 K) exhibits a '16-line ESR signal', as illustrated in Fig. 1. This spectrum is very similar to those of the S_2-state in the spinach photosystem [8], mixed-valence Mn(III)–Mn(IV) [4] and also binuclear μ-oxo-di-μ-acetato Mn(III)–Mn(III) [7] complexes.

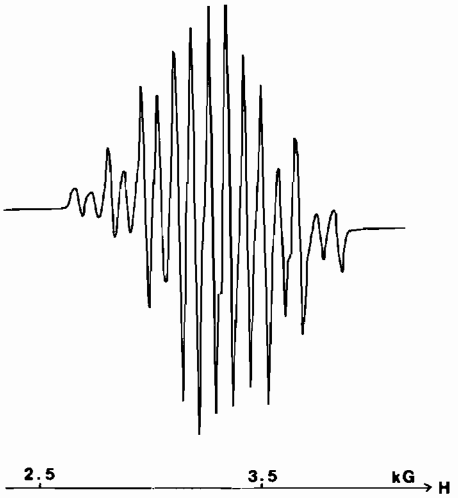


Fig. 1. ESR spectrum of $Mn(L)(OCH_3)ClO_4$ (in DMF, 77 K, X-band).

Since the $-J$ value in the trimeric manganese(III) complex with a μ-oxo bridge is large [10] it is unlikely that the present complex is of a trimeric structure. Very recently, the present author determined the crystal structure of the Mn(II) complex of HL, $Mn_2L_2(NCS)_2$, which is of a binuclear structure with a phenoxide bridge [6]. These facts suggest that the present complex is of a dimeric structure similar to that of the corresponding Mn(II) complex.

The results in this study and in our previous work [6, 7] clearly indicate that we can elucidate the ESR spectral feature of the S_2-state in PS II without taking into consideration the presence of a mixed-valence state of manganese ions.

References

1 G. C. Dismukes, *Photochem. Photobiol., 43,* 99 (1986).
2 Govindjee, T. Kambara and W. Colemann, *Photochem. Photobiol., 42,* 187 (1985).
3 G. C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci. U.S.A., 78,* 274 (1981).

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†*Anal.* Calc. for $MnC_{20}H_{20}N_4O_8Cl$: C, 44.92; H, 3.77; N, 10.48; Mn, 10.27. Found: C, 45.24; H, 4.04; N, 10.54; Mn, 10.0%.

0020-1693/88/$3.50

4 S. Cooper, G. C. Dismukes, M. Klein and M. Calvin, *J. Am. Chem. Soc.*, *100*, 7248 (1978).

5 J. C. de Paula, W. F. Beck and G. W. Brudvig, *J. Am. Chem. Soc.*, *108*, 4002 (1986).

6 Y. Nishida, in press.

7 Y. Nishida and N. Oshino, submitted for publication.

8 D. Hunziker, D. A. Abramowicz, R. Damoder and G. C. Dismukes, *Biochim. Biophys. Acta*, *890*, 6 (1987).

9 Y. Nishida, H. Shimo and S. Kida, *J. Chem. Soc., Chem. Commun.*, 1611 (1984).

10 J. Catterick and P. Thornton, *Adv. Inorg. Radiochem.*, *20*, 291 (1977).