ESR of an Oxidized Manganese Binuclear Cluster: a Possible Model of the Highest Oxidized State of the Oxygen-evolving Complex of Photosynthesis

S. V. Khangulov, M. G. Goldfeld, N. P. Kirpichnikova, S. N. Dobryakov, and V. B. Ilyasova
U.S.S.R. Academy of Sciences, Institute of Chemical Physics, Moscow, 117977 U.S.S.R.

The oxidation of the manganese-bipyridyl dinuclear μ-oxo-complex leads to a paramagnetic species with 170 mT wide, multiline ESR spectrum visible below 15 K, consistent with a spin-exchange coupled Mn^{IV}–Mn^{IV} cluster; this valence-state being similar to that of the extremely oxidized state of the oxygen-evolving complex in photosynthesis.

Dinuclear manganese complexes with various ligands have attracted much attention in recent years as models of the manganese cluster in the oxygen-evolving system of photosynthesis[1] and in manganese-pseudo-catalases of selected bacteria.[2—4] The ESR characteristics have been obtained for manganese dinuclear clusters in various valence-states of the metal: Mn^{I}–Mn^{II},[5,6] Mn^{II}–Mn^{II},[7] Mn^{II}–Mn^{III},[8—10] and Mn^{III}–Mn^{IV}.[11—14] Selected ESR data provided important information on the structure and mechanisms of the oxygen-evolving system. It is widely accepted that this enzymatic system is oxidized up to the Mn^{IV}–Mn^{IV} state at the final step of dioxygen formation, this extremely oxidized state having a very short life-time. However, as far as we know, there have been no reports on ESR spectra of any synthetic manganese

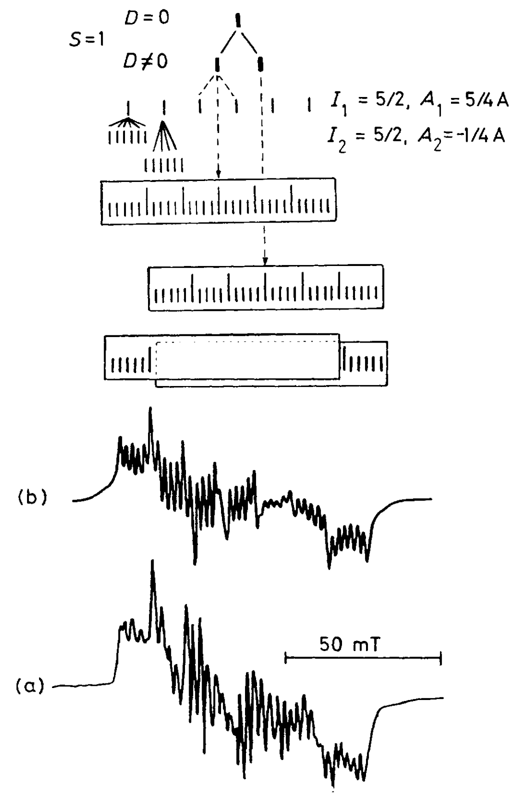

Figure 1. (a) X-Band ESR spectrum of the oxidation product of Mn–bipyridyl complex at 12 K. The amplitude of 100 kHz modulation H_m = 0.5 mT, microwave power P = 25 mW. (b) Computer simulation with $S = 1$, D = 13.8 mT, E = O, g = 2.0, $h\nu/\beta$ = 600 mT, A_1 = 2.1 mT, A_2 = 11.7 mT, line-width Δ = 0.5 mT (see text), and the scheme of the signal reconstruction.

complex in the Mn^{IV}–Mn^{IV} redox state. Here we report on an oxidation product of the manganese-bipyridyl dinuclear μ-oxo-complex with a new-type low-temperature signal being consistent with this valence-state.

The preparation of the crystalline (Mn^{III}–Mn^{IV})-bipyridyl binuclear species $[(bipy)_2Mn]_2O_2(ClO_4)_3{\cdot}2H_2O$ was performed according to a reported procedure,[11] and the product was characterized by its well-resolving 16-line ESR spectrum at 50 K. A solution of this complex (0.1 mM) in sodium acetate buffer (0.2 M, pH 4.5) was mixed with the equimolar solution of KIO_4, $KMnO_4$ or ClO_2 (7 mM). The resulting mixture was frozen in liquid nitrogen and used in ESR measurements. Occasionally the binuclear (Mn^{III}–Mn^{IV})-bipyridyl complex was not isolated, and Mn^{II}-acetate solution (0.1 mM) in the same buffer containing 2,2′-bipyridyl (2 mM) was titrated with KIO_4 or $KMnO_4$ (0.1 mM). The reaction with oxidant was followed by ESR between 10 and 50 K. Prior to the reaction with oxidant the usual six-line signal of Mn^{II}-ions was visible at 50 K. The oxidation caused this signal to decrease with concomitant rise of the 16-line Mn^{III}–Mn^{IV}-signal. In the course of further titration with oxidant this signal decreased, and a new broad signal appeared with its hyperfine structure (hfs) well resolved below 15 K [Figure 1(a)]. This broad, *ca.* 170 mT-wide, multiline signal centred at g = 2.0 has some peculiarities. There are six groups of nearly equidistant sextets, each sixth line being twice as intense as the others. The spectrum is abruptly cut off at the wings. It is distorted and loses its hfs above 30 K, presumably as the result of the relaxation broadening and overlap of the individual hfs lines.

Computer simulation of this spectrum, using the Program of the Fast Reconstruction of Anisotropic Spectra,[16,17] is given in Figure 1(b). The calculations have been carried out in terms of the model of strong antiferromagnetic coupling between the manganese ions, with an effective spin-Hamiltonian [equation (1)] where A_1,A_2 are the effective hfs constants for manganese ions in the dinuclear cluster, all other symbols having their usual meaning.

$$H = g\beta HS + D[S_z^2 - S(S+1)] + E(S_x^2 - S_y^2) + S(A_1I_1 + A_2I_2) + JS_1S_2$$

Satisfactory agreement with the experimental spectrum has been obtained using $S = 1$, D = 13.8 mT, E = O, A_1 = 2.1 mT, A_2 = 11.7 mT, and the line-width of 0.5 mT for individual hfs components. The term JS_1S_2 representing the spin-exchange coupling can be omitted in calculations, as it does not affect the hfs, only the position of the signal.

The calculated A_1, A_2 values essentially limit the possible spin-states of manganese ions. Theory predicts that these dimer hfs constants can be related to those of the individual manganese ions, A'_1, A'_2, within the same ligand system, by a scaling factor equal to the projection of the individual spins S_1, S_2 onto the resulting spin S of the dimer: $A_i = A'_i\,(S_iS/S^2)$.[18] For manganese in various redox states A'_i-values do not differ considerably, being within an 8 to 10 mT interval. Thus, the multiline spectrum in Figure 1 should arise from the coupling of two manganese ions with $S_1 = 3/2$ ($A_1 = 4A'_1$ = 8.4 mT) and $S_2 = 1/2$ ($A_2 = 4/5\ A'_2$ = 9.36 mT). These spin-values are consistent with the valence-state Mn^{IV}–Mn^{IV}. Other, more oxidized states, should be excluded both on the chemical background and as being incompatible with the required S_1, S_2 values. Such an assignment is not quite trivial as we assume the spin-states of the manganese ions to be different, their redox states being identical.

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