

" $n\pi^*$ " and " $\pi\pi^*$ " excitation energies calculated by the INDO/S method¹³ at these geometries (Table I) reflect the experimental trends correctly but are a little too low, as was also the case for other imines.^{5,6}

The structure assignment of the nitrene **4** is based on its ESR signal at 0.8124 T (9.3 GHz; assuming $E = 0$, $|D/hc| = 1.65 \text{ cm}^{-1}$),¹⁴ a sharp UV peak at $33\,560 \text{ cm}^{-1}$, whose intensity follows that of the ESR signal,¹⁵ and on photochemical trapping with CO in Ar at 36 K. The IR spectrum of this matrix, containing **2**, **3**, CO, and presumably **4**, was unchanged for many hours in the dark, but on UV irradiation^{7c} a weak band of 1-norbornyl isocyanate at 2263 cm^{-1} appeared¹⁶ (IR, MS, and GC comparison with an authentic sample).

To our knowledge, the above results represent the first observation of geometrical isomerism at a strained bridgehead double bond. Taken together with prior work,²⁻⁶ they suggest that the C=N stretching frequencies are typically reduced by about 100 cm^{-1} in *trans*-azacycloheptene rings and by about 200 cm^{-1} in *trans*-azacyclohexene rings, respectively, relative to an unstrained imine.

Acknowledgment. This work was supported by the National Science Foundation (CHE 81-21122).

Registry No. **1**, 65864-91-7; (*E*)-**2**, 95673-67-9; (*Z*)-**2**, 95673-68-0; **3**, 95673-69-1; **4**, 95673-70-4.

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Mixed-Valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ Complexes: Models for the Manganese Site in the Photosynthetic Electron-Transport Chain

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Two or four manganese ions serve as the active site for oxygen evolution in the photosynthetic electron-transport chain.² Recently two research groups³ independently reported an EPR signal for the S_2 oxidation state of this manganese site, and, on the basis of the magnitude of observed hyperfine structure, they attributed the signal to a binuclear $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ site³ or a tetranuclear $\text{Mn}_3^{\text{III}}\text{Mn}^{\text{IV}}$ site.⁴ The limited number of mixed-valence manganese complexes needs to be increased to characterize better the EPR signal for the S_2 state.

The complexes $\text{Mn}^{\text{II}}(\text{saldien})$ and $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$,^{5,6} where *saldien* and 5- $\text{NO}_2(\text{saldien})$, respectively, result from the

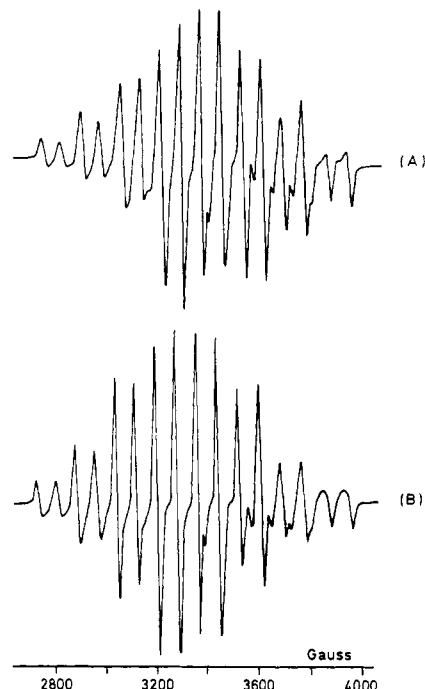
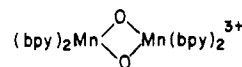


Figure 1. X-band EPR spectrum (A) for the oxygenation product of $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$ in frozen DMF-toluene glass at 120 K (63 mW and field modulation of 10 G). Trace (B) illustrates the simulated spectrum obtained with the parameters and approach¹¹ described in the text.

Schiff base condensation of diethylenetriamine and either salicylaldehyde or 5-nitrosalicylaldehyde, have proven to be useful precursors to new mixed-valence manganese complexes. A solution of either of these complexes when allowed to react with O_2 and then frozen gives a 16-hyperfine-line EPR spectrum as is illustrated in Figure 1A for $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$ in a DMF-toluene glass at 120 K. This EPR spectrum looks like the spectrum reported⁷ for frozen glasses of the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ complex



However, as indicated below, the mixed-valence complexes derived from O_2 oxidation of $\text{Mn}^{\text{II}}(\text{saldien})$ and $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$ are $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complexes. A caveat concerning the identification of manganese oxidation states based on magnitudes of hyperfine interactions is advanced in this paper.

The time development of the O_2 oxidation of the two *saldien* Mn^{II} complexes under strictly anhydrous conditions was monitored with EPR. The rate of O_2 oxidation of $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$ in solution is slow in comparison to $\text{Mn}^{\text{II}}(\text{saldien})$. In the case of the former complex dissolved in $\text{C}_2\text{H}_4\text{Cl}_2$, within a few minutes of exposure to dry oxygen, a 16-line EPR spectrum for a frozen solution is readily visible superimposed on a very broad, wide ranging Mn^{II} spectrum.³ If the solution is warmed to room temperature for periods of time, then refrozen, the intensity of the 16-line spectrum grows slowly at the expense of the Mn^{II} spectrum. A double integration of the whole 7000 G X-band spectrum as a function of time shows a continuous decrease in the total EPR signal. After 120 h, the intensity of the total EPR signal remains constant at $\sim 1/10$ of that of the initial Mn^{II} complex whose wide-ranging spectrum has totally disappeared. During this reaction, the yellow orange solution turns slowly brown-green and a green powder precipitates very slowly. EPR spectra run for the green powders exhibit a temperature dependence. At room temperature, the signal is characterized by several fine structure resonances spread out over 5000 G. As the sample temperature is decreased, the $g = 2$ resonance grows at the expense of the other

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transitions, to give finally a $\Delta M_S = -1/2 \rightarrow 1/2$ transition at 100 K. EPR spectra of frozen green-brown solutions obtained by dissolving the green complex in solvents such as DMF, Me_2SO , or CH_3CN gives a typical mixed-valence 16-line pattern. Magnetochemistry studies show that $\mu_{\text{eff}}/\text{Mn}$ for the green powder decreases from 2.1 μ_B at 300 K to 0.71 μ_B at 1.9 K. An intramolecular antiferromagnetic interaction with $J = -54 \text{ cm}^{-1}$ was found on fitting the experimental data to the equations for an exchange interacting ($S_1 = 5/2$, $S_2 = 2$) dimer.

Variable-temperature susceptibility results (from 5.9 μ_B at 300 K to 1.86 μ_B at 1.7 K) for a solid sample of the $\text{Mn}^{\text{II}}(\text{saldien})$ complex indicate a dimeric structure, i.e., $[\text{Mn}^{\text{II}}(\text{saldien})]_2$, which is probably similar to that reported⁸ for $[\text{Cu}^{\text{II}}(\text{saldien})]_2$. Compared to the IR spectrum of $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$, the CsBr pellet IR spectrum of the green O_2 oxidation product exhibits two peaks at 657 and 793 cm^{-1} which may be respectively assigned to the Mn-O and the O-O stretching vibrations of a coordinated peroxide group. When the green O_2 oxidation product is heated (180 °C) under vacuum, the color of the powder turns back from green to orange which is the color of $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$. Furthermore, the EPR characteristics (solid state and frozen solution) of the orange solid and $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$ are identical. Efforts are continuing to grow good crystals of the green compound. Taking into account the fact that the O_2 oxidation of Mn^{II} complexes with ligands such as saldien gives Mn^{III} as the most oxidized form of the manganese,⁹ we suggest that the green compound consists of two $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{saldien})_2$ units bridged by an O_2^{2-} ion.¹⁰

The frozen-solution EPR spectra of our mixed-valence complexes were simulated in the same manner¹¹ as employed by Cooper et al.⁷ The lower trace (B) in Figure 1 shows the best simulated spectrum obtained for a pair of inequivalent manganese ions; i.e., the $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complex has a localized structure. Small anisotropies in the manganese A and g tensors were incorporated to get the best simulation. The final parameters for the ground-state Kramers doublet of the pair are $g_x = g_y = 2.006$ and $g_z = 2.00$; $A_{1x} = A_{1y} = 170 \text{ G}$ and $A_{1z} = 156 \text{ G}$; $A_{2x} = A_{2y} = A_{2z} = 83 \text{ G}$. We can recast these hyperfine values into the single-ion values. If the complex is incorrectly assumed to be a $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ complex, we find $A_x = A_y = 85 \text{ G}$ and $A_z = 78 \text{ G}$ for Mn^{III} whereas $A_x = A_y = A_z = 83 \text{ G}$ for Mn^{IV} . If the complex is correctly assumed to be a $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complex $A_x = A_y = 73 \text{ G}$ and $A_z = 67 \text{ G}$ for Mn^{II} whereas $A_x = A_y = A_z = 62 \text{ G}$ for Mn^{III} . The hyperfine interaction calculated for the Mn^{IV} ion (83 G) in the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ formulation does not agree with the 97 G hyperfine interaction we have determined¹² for a frozen solution of $(\text{Mn}^{\text{IV}}[5\text{-NO}_2(\text{saldien})])(\text{ClO}_4)_2$, a mononuclear compound that was prepared electrochemically. For a frozen solution of $\text{Mn}^{\text{II}}[5\text{-NO}_2(\text{saldien})]$, we find a dimer-type EPR signal with an 11-line $S = 0$ to $S = 1$ manganese hyperfine pattern with a splitting of $A = 38 \text{ G}$. A value that is twice this dimer interaction (i.e., 76 G) is in better agreement with the 73 G interaction found for the Mn^{II} ion in the $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ formulation.

The above analysis suggests that caution has to be exercised in deciding which oxidation states of manganese are present in

a mixed-valence complex if only the magnitudes of manganese hyperfine interactions are known from EPR simulations. It is quite possible that the hyperfine interaction can vary considerably for a given oxidation state of manganese depending on the coordination number and geometry of the manganese ion.

Acknowledgment. We thank the National Institutes of Health for partial support of the work at the University of Illinois through a Grant HL13652 to D.N.H. Tuchagues and Hendrickson are thankful for a NATO grant for collaborative research. Helpful discussions with Dr. M. J. Nilges about EPR simulations are acknowledged.

Characterization of Transient Intermediates on Laser Flash Excitation of Cyclohexenones in the Presence of Amines¹

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Received October 15, 1984

Recently, we reported that upon laser flash photolysis of a series of 2-cyclohexenones, transient absorption could be observed in the ultraviolet region (260–320 nm) whose lifetime correlates with the ability of the enone to twist about the $\text{C}_2\text{--C}_3$ double bond.² This structural feature also determines the rate of energy transfer to triplet quenchers such as naphthalene (NA), 1,3-cyclohexadiene (CHD), and piperylene.³ Olefins such as 1,1-dimethoxyethylene (DME) and cyclohexene and amines such as 1,4-diazabicyclo-[2.2.2]octane (DABCO) and triethylamine quench certain photoreactions of these enones but have no effect on the observed transient.² We therefore concluded that for conformationally flexible enones, this transient does not lead to photoproducts.⁴ A "phantom" triplet state, which has not yet been directly detected, was proposed to be responsible for reaction with amines and olefins, as well as triplet energy transfer to NA and CHD.² For conformationally rigid enones, the distinction between the spectroscopically observable species and the chemically reactive triplet state becomes blurred.

We now report that flash photolysis of degassed samples of enones 1–5 in acetonitrile in the presence of tertiary amines using a 353-nm pulse from a mode-locked Nd:YAG laser yielded new long-lived transients absorbing from 260 to 500 nm. Figure 1 shows spectra generated from enones 1, 2, and 4 in the presence of DABCO and *N,N*-dimethylaniline (DMA).

Flash excitation of DABCO alone in acetonitrile with a 265-nm pulse produces a broad absorption which decays with a lifetime of 22 ns and narrow absorption which decays with $\tau = 4\text{--}7 \mu\text{s}$,

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(10) Peroxide-bridged binuclear manganese complexes have been suggested by Coleman and Taylor for the oxygenation products of the related $\text{Mn}^{\text{II}}(\text{XSaldPT})$ compounds.^{9b}

(11) (a) The frozen-glass, X-band, EPR spectra were simulated employing the following spin Hamiltonian: $\hat{H} = g\beta H_z \hat{S}_z + g\beta(H_x \hat{S}_x + H_y \hat{S}_y) + \hat{I} \hat{A} \hat{S}$. The EPR signal is attributable to the ground-state Kramers doublet resulting from an antiferromagnetic exchange interaction between two Mn ions. In the simulation a Gaussian line shape was assumed with the line width of a particular transition determined by the nuclear spin quantum number and the degree of strain in g and A tensors. A computer program based on the following sources was employed: (a) Nilges, M. J. Ph.D. Thesis, University of Illinois, Urbana, IL 1979. (b) Belford, R. L.; Nilges, M. J. "Computer Simulation of Powder Spectra", EPR symposium, 21st Rocky Mountain Conference, Denver, CO, 1979. (c) Maurice, A. M. Ph.D. Thesis, University of Illinois, Urbana, IL, 1980.

(12) Mabad, B.; de Montauzon, D.; Tuchagues, J.-P.; Hendrickson, D. N., manuscript in preparation which includes single-crystal X-ray structural results for a monomeric Mn^{IV} complex.

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(3) For rigid enones such as 4, quenching of the transient absorption at 280 nm by piperylene can be observed directly. However, for flexible enones (e.g., 1 and 3) quenching of this transient by piperylene is inefficient and nonlinear, while no quenching by CHD is observed. Quenching by NA cannot be directly measured at 280 nm due to NA ground-state absorption, but absorption of $^3\text{NA}^*$ at 413 nm is easily monitored.^{2a}

(4) Similar conclusions have been reached by Pienta based on complementary studies. See: Pienta, N. J. *J. Am. Chem. Soc.* 1984, 106, 2704.