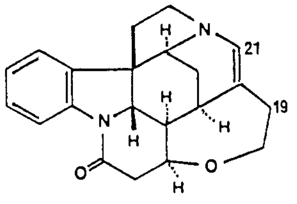

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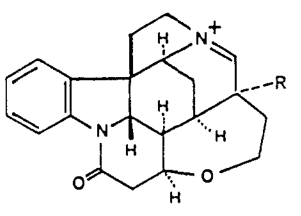

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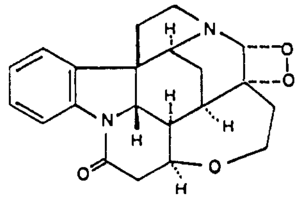

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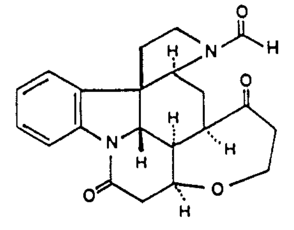

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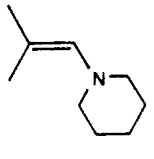
as anticipated, are highly unfavored. The neostrychnine employed in this work was prepared by Raney nickel treatment of strychnine[12] and fully characterized.[13]

An oxygen-bubbled solution of neostrychnine (3×10^{-3} mol L^{-1}) and methylene blue (10^{-4} mol L^{-1}) in methanol (100 mL) was irradiated at room temperature through Pyrex with a 100-W medium-pressure mercury arc. After 2 h, clean conversion to a single product was complete. No reaction was observed in the absence of light or oxygen. Isolation by preparative TLC (acetone/hexane, 7:3 on silica gel) and crystallization from methanol gave the *N*-formylketone **5** in 75% isolated yield, mp 206–212 °C. Spectral data[14] were in complete agreement with this structure. The molecule contains an additional two oxygens relative to neostrychnine and exhibits identical *N*-acylarylamine absorption in the ultraviolet. Two new infrared carbonyl stretching bands at 1654 cm^{-1} (*N*-formyl) and 1715 cm^{-1} (ketone) are apparent. In the 300 MHz PMR spectrum the one proton singlet at δ 5.73 due to the C(21) enamine proton in the substrate **2** has been replaced by two singlets at δ 8.26 and 8.38 (2:1) corresponding to the rotational isomers of the *N*-formyl grouping. Clearly the product is characteristic of normal enamines[15] indicating the intermediacy of the dioxetane **4**.[16]

In addition, under identical conditions, the rate for *chemical* reaction of **2** with $O_2(^1\Delta_g)$ was essentially the same (slightly less than a factor of 2 lower) as that for the simple unstrained model **6** which gives exclusively *N*-formylpiperidine and acetone under the same conditions.[17] There is no doubt[8,19] that, at the temperature of our experiments, reaction of both **2** and **6** involves pre-equilibrium formation of an exciplex followed by "slow" product formation. Were that irreversibly formed product a zwitterion of type **1**, one would, for reasons already emphasized, anticipate a very significant reduction in the rate constant for chemical reaction of **2** relative to that of **6**. Since no such difference is observed we are forced to the conclusion that it is possible, in a *polar protic* medium such as methanol, for $O_2(^1\Delta_g)$ to react to give dioxetanes via a mechanism which does not involve the intermediacy of open zwitterions.[20]



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[12] Chakravarti, R. N.; Robinson, R. *J. Chem. Soc.* **1947**, 78.

[13] This material[12] was twice recrystallized from ethanol, mp 224–225 °C (lit. 228 °C[12]): λ_{max} (ethanol) 252 (12 400), 279 (4240), 288 (3300); ν_{max} (Nujol) 1680 (s); δ ($CDCl_3$) 8.06 (d, 8 Hz, 1 H), 7.27 (m, 2 H), 7.08 (t, 8 Hz, 1 H), 5.73 (s, 1 H), 4.2–1.3 (17 H); *m/z* (%) 334 (100), 277 (28), 220 (11), 167 (23), 144 (16), 130 (16), 115 (14), 107 (21).

[14] λ_{max} (ethanol) 253 (12 500), 278 (3740), 288 (2920); ν_{max} (Nujol) 1715 (s), 1674 (s), 1654 (s); δ ($CDCl_3$) 8.38 (s, 0.3 H), 8.26 (s, 0.7 H), 8.14 (d, 8 Hz, 0.7 H), 8.12 (d, 8 Hz, 0.3 H), 7.35–6.80 (3 H), 4.4–1.7 (17 H); *m/z* (%) 366 (100), 337 (10), 294 (98), 220 (50), 180 (36), 168 (57), 123 (50), 130 (71), 115 (59).

[15] Foote, C. S.; Dzakpasu, A. A.; Lin, J. W.-P. *Tetrahedron Lett.* **1975**, 1247.

[16] The α-face of the molecule is by far the less hindered, hence the stereochemistry shown in **4**. This would certainly be correct if $O_2(^1\Delta_g)$ were "delivered" via an $N(b)/O_2(^1\Delta_g)$ complex.

[17] The relative rates of chemical reaction in methanol were essentially the same with either methylene blue or 2-acetonaphthone as sensitizer. Reactions were monitored by GLC with a 3.8 m by 0.22 mm (i.d.) vitreous silica capillary column coated with cross-linked methyl silicone BP-1(OV-1), 0.25 μm thickness, 0.15 kg cm^{-2} (hydrogen). For **2** and **5**: injection block 300 °C, isothermal at 270 °C, external standard stigmasterol. For **6** and *N*-formylpiperidine: injection block 150 °C, programmed at 50 °C (4 min) to 170 °C (10 °C min^{-1}), internal standard octan-1-ol. Overall rate constants for quenching of $O_2(^1\Delta_g)$ in methanol were determined by time-resolved IR emission spectroscopy as described.[18] These rate constants, 1.0×10^8 L mol^{-1} s^{-1} for **2** and 2.0×10^8 L mol^{-1} s^{-1} for **6**, were in the same ratio as the rates of chemical quenching. These data together with those of Foote and coworkers[15] indicate that both **2** and **6** are essentially exclusively chemical quenchers of $O_2(^1\Delta_g)$.

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[20] Clearly, some degree of electron donation from N(b) into the double bond of **2** must occur. Equally clearly, the inherent conjugative "electron-donating ability" of the activating group cannot be the dominant factor in controlling rate constants for chemical reaction.

A New Model for the Oxygen-Evolving Complex in Photosynthesis. A Trinuclear μ_3-Oxo-Manganese(III) Complex Which Contains a μ-Peroxo Group

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Oxidation of water by the photosynthetic process in plants is believed to involve a cluster of four (or three) manganese atoms.[3] Recently much effort has been devoted to the isolation of multinuclear manganese complexes, which it is hoped, will provide useful models for the oxygen-evolving complex in plants.[4-15] These

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[1] Victoria University of Wellington.

[2] Chemistry Division, D.S.I.R.

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investigations have revealed a rich and complex chemistry of polynuclear manganese complexes, and in one case the complex has been shown to oxidize water.[15] It has been known for some considerable time that polyamine complexes of Mn(II) are oxidized by molecular oxygen and that MnO_2 is precipitated from aqueous solution.[16,17] Until recently no Mn(III) and Mn(IV) complexes of polyamines with primary amine functional groups had been isolated although complexes with macrocyclic amines[5,6,18] and Schiff bases[19] were known. Very recently Armstrong[10] reported a dimeric Mn(III)–Mn(IV) complex with the tetradentate ligand tren. We have also discovered that high oxidation state manganese complexes of simple polyamines are readily isolated and herein report the properties of one of these complexes.

When a solution of Mn(II) acetate (1.2 g) and diethylenetriamine (dien) (0.5 g) in refluxing methanol (30 mL) is allowed to cool to room temperature in air, the original pale orange solution turns dark red brown, and a red brown solid may be obtained by the addition of sodium perchlorate. The same compound may be produced by using Mn(III) acetate (0.5 g), dien (0.3 g), and sodium acetate (0.6 g) in methanol (20 mL) followed by the addition of sodium perchlorate (0.7 g). In the absence of air the brown product is not obtained. The iodide salt can be obtained by using the latter preparative method by the addition of potassium iodide (0.96 g). The iodide can only be obtained in the buffered solution as more acidic conditions result in the formation of iodine. The dark brown powders are soluble in CH_3CN, and dimethylformamide (DMF) and crystals of $Mn_3(dien)_3(OAc)_2(ClO_4)_3O_3{\cdot}H_2O$, **1**, and $Mn_3(dien)_3(OAc)_2I_3O_3H_2O{\cdot}0.33CH_3OH$,[20] **2**, may be obtained by vapor diffusion of tetrahydrofuran into the DMF solutions.

Infrared spectra of these two compounds are very similar apart from the presence of a broad perchlorate peak centered at 1090 cm^{-1} in the perchlorate complex. Peaks at 1590, 1550, and 1430 cm^{-1} suggested the presence of bridging acetato groups.[5a,14] Mn–oxo bonds were suggested by the presence of strong absorptions at 715 cm^{-1}.[6] There is no evidence from the infrared spectra for any ligand oxidation. X-band EPR spectra of the two compounds obtained in frozen DMF solutions at −160 °C are shown in Figure 1. Both spectra show a 16-line hyperfine coupling centered on $g = 2$ and no evidence for the presence of Mn(II). Attempts to determine the oxidation state of the manganese by the addition of the perchlorate complex to an acidic Fe(II) solution and back titration with dichromate showed that only one Fe(III) was produced per trinuclear manganese unit. This suggested the presence of a Mn(III)·2Mn(II) unit which was incompatible with the EPR spectrum.

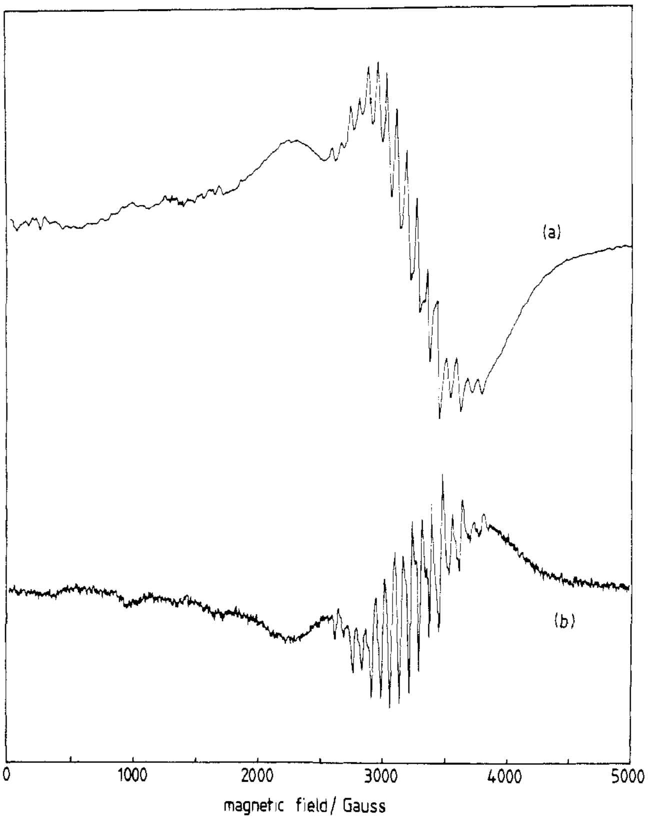

Figure 1. Frozen solution EPR spectra of **2** (a) and **1** (b) in DMF. Conditions: temperature −160 °C, (a) spectrometer power 2 mW, modulation amplitude 1.25 G, gain 6.3×10^3, frequency 8.99 GHz; (b) spectrometer power 0.2 mW, modulation amplitude 1.25 G, gain 4.0×10^4, frequency 8.99 GHz.

Crystals of **2** which were marginally suitable for X-ray studies were obtained.[21] Refinement of the structure is continuing with difficulty because of the highly symmetric but reasonable positions of the heavy atoms. Currently the R factor is less than 9%, and the analysis has revealed the presence of a μ_3-oxo bridged trinuclear Mn(III) cluster, two bridging acetato groups, and a bridging peroxo group. The structure of the cation is illustrated in Figure 2.[22] The oxo-centered Mn_3O unit is characteristic of Mn(III) carboxylates and has also been observed in a mixed valence Mn(II)·2Mn(III) complex.[23] The presence of the peroxo group is confirmed by the anomalous titration results mentioned above, which can be rationalized if in acid solution the Mn(III) oxidizes the peroxo group more rapidly than Fe(II) and by the observation of an intense band in the Raman spectrum at 814 cm^{-1} which may be assigned to the peroxy O–O stretching frequency.

Mn(II) complexes of tridentate and tetradentate Schiff bases take up dioxygen in a 2:1 Mn/O_2 ratio, and the initial products have been formulated as μ-peroxo derivatives but these have not been isolated.[24,25] Addition of oxygen to the manganese in the

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[20] Microanalyses were performed by the Microanalytical Service at Otago University. Manganese was determined by using atomic absorption spectroscopy. Anal. Calcd for **1**, $C_{16}H_{49}N_9O_{20}Cl_3Mn_3$: C, 20.04; H, 5.11; N, 13.15; Cl, 11.10; Mn, 17.20. Found: C, 19.87; H, 5.12; N, 13.19; Cl, 11.11; Mn, 17.55. Anal. Calcd for **2**, $C_{16.33}H_{48.33}N_9O_{8.33}I_3Mn_3$: C, 18.69; H, 4.61; N, 12.01; I, 36.27; Mn, 15.70. Found: C, 18.87; H, 5.01; N, 11.57; I, 35.71; Mn, 15.23.

[21] Crystal data: orthorhombic, space group $P2_1mn$, a = 8.685 Å, b = 12.292 Å, c = 17.666 Å, Z = 2.

[22] Selected interatomic distances in Å at the current state of refinement are as follows: Mn(1)–Mn(2) 3.32 (3), Mn(2)–Mn(2) 3.14 (4), Mn(1)–N(11) 2.2 (1), Mn(1)–N(12) 2.1 (1), Mn(1)–N(13) 2.3 (1), Mn(1)–O(1) 2.1 (1), Mn(1)–O(3) 1.8 (1), Mn(2)–N(21) 2.2 (1), Mn(2)–N(22) 2.1 (1), Mn(2)–N(23) 2.4 (1), Mn(2)–O(2) 1.7 (1), Mn(2)–O(3) 1.9 (1), Mn(2)–O(4) 2.0 (1), O(4)–O(4) 1.6 (1).

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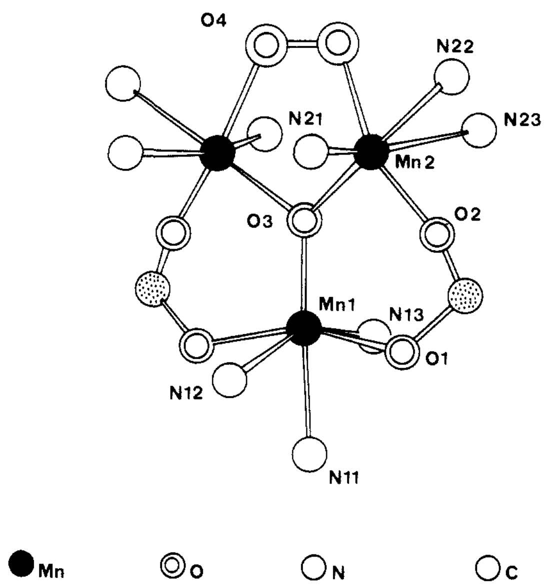

Figure 2. Structure of **2** showing the atomic numbering system used. Carbon atoms of the dien ligand and the methyl carbons of the acetato groups are not shown.

dien complex is apparently reversible as heating methanol solutions of **1** in a stream of nitrogen results in the disappearance of the brown color. Upon cooling the brown color of the solution is restored. This behavior could be due to oxidation of the methanol followed by regeneration of the complex in air and suggests that the complex may be a useful oxidation catalyst.[26]

Addition of small amounts of concentrated hydrochloric acid to a methanol solution of **1** results in the formation of deep red crystals formulated as $Mn_3(dien)_2(OAc)_2Cl(ClO_4)_2O_2{\cdot}CH_3OH$.[27] The Raman spectrum of this complex shows no O–O stretching frequency, and the X-band EPR spectrum of the material is indicative of a complex containing Mn(II). The spectrum is very similar to the spectrum of a 2Mn(III)·Mn(II) complex described recently by Pecoraro.[11] The photosynthetic oxygen evolving complex has a chloride ion requirement so the structure of this material would be of considerable interest. We are attempting to obtain crystals suitable for structural analysis.

In summary, we have shown the polyamine dien can coordinate to Mn(III) without undergoing oxidation and that the complex isolated by using this ligand is a stable μ-peroxy complex. This complex provides the first model for the binding of dioxygen to a manganese cluster in the photosynthetic oxygen evolving system, and the ease with which the peroxo group is oxidized in acidic solutions suggests a possible mechanism for oxygen release in photosynthesis.

The properties of these complexes and complexes produced by using the amines 2,3-tri, triethylenetriamine, 2,3,2-tet, 3,2,3-tet, and tren are under active investigation in this laboratory. It should be mentioned that the complex we have obtained by using the tren ligand is different from the complex described by Armstrong.[10]

Acknowledgment. The assistance of the Internal Research Committee of Victoria University is gratefully acknowledged. We are also grateful to Dr. E. Ainscough for assistance acquiring the EPR spectra, Joanne Rollo for assistance with the Raman spectra, and Dr. Ward T. Robinson for the collection of the X-ray data set.

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(27) Anal. Calcd for $C_{13}H_{36}N_6Cl_3O_{15}Mn_3$: C, 19.83; H, 4.58; N, 10.67; Cl, 13.51; Mn, 20.93. Found: C, 19.59; H, 4.71; N, 10.62; Cl, 13.67; Mn, 21.04.

Effect of Pressure on the Proton–Proton Vicinal Coupling Constants in 1,1,2-Trichloroethane and 1,1,2,2-Tetrachloroethane-*1*-^{13}C. A New Approach to High-Pressure Study of Molecular Conformations

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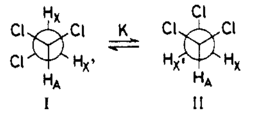
We report here the first observation of a pressure-induced change in J_{vic} and demonstrate that the experiment possibly provides a new, straightforward approach to conformation studies at high pressure.[1]

Our choice of title compounds[2] was governed by the availability of quantitative information of the NMR parameters characteristic of the trans and gauche conformers,[3,4] as well as by the simplicity of the proton spectra. Use of J_{vic} in the conformational study requires extremely precise measurement of doublet separations.[5] We employed a linear sweep rate of 108 Hz/250 s in a continuous wave mode (ν_0 = 100 MHz), while the field control was effected by means of an internal NMR lock.[6]

Figure 1 shows the pressure dependence of J_{vic} in trichloroethane, which exhibits a small but steady decrease upon increase in pressure.[7] The observed coupling constant, J_{vic}, can be expressed in terms of the weighted mean of the coupling constants in the trans and gauche isomers,[8] i.e.



$$J_{vic} = n_I J_I + (1 - n_I) J_{II} \qquad (1)^9$$

Since $J_I > J_{II}$ holds generally,[5] the decrease in J_{vic} demonstrates that the population of the gauche conformer II increases at high pressure. This agrees qualitatively with the observation of Christian et al. based on a high-pressure IR experiment.[12] This is also in accord with the general view that high pressure favors more polar conformers.

In order to provide quantitative understanding, it is necessary to use in eq 1 a reasonably consistent set of J_I and J_{II} values. Employing the Karplus-type eq 2,[13] with A = 11.1 Hz and B =

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(1) For reviews of high-pressure high-resolution NMR, see: Ando, I.; Webb, G. A. *Magn. Reson. Chem.* **1986**, *24*, 557. For the experimental technique employed, see: Yamada, H. *Rev. Sci. Instrum.* **1974**, *45*, 640.

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(5) For example, see ref 4.

(6) At least 10 measurements were made at a given pressure. Reproducibility better than ±0.03 Hz was generally attained.

(7) A 50 mol % solution gave a smaller pressure dependence, i.e., –0.13–0.16 Hz/300 MPa.

(8) Theoretically, conformers with any dihedral angle should be taken into account and weighted statistically.[3] In the present discussion, however, only the discrete stable conformers have been postulated as a first approximation.

(9) A basic assumption of this type of treatment is that J_I and J_{II} are pressure-independent. Evidence in support of this assumption can be obtained from an examination of J_{vic} in the "rigid" molecule such as 1,1-dichloroethane, for which the pressure-induced change in J_{vic} proved to be less than ±0.03 Hz. An observed constancy (±0.02 Hz) of J_{vic} in a "rigid" system,[10,11] upon changing the solvents (ϵ = 2–35), may be taken as further confirmation for the assumption.

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