biguously established by hydroboration–oxidation (4.0 equiv of $BH_3 \cdot THF/THF/1$ h/0 °C; 30% $H_2O_2/3.0$ M NaOH, 1:1/1 h/55 °C) to yield 7-hydroxypentalenane (**4**)[17a,d] as a 20:1 mixture of epimers, followed by oxidation with PCC in CH_2Cl_2 (1 h/25 °C) to give pentalen-7-one (**5**)[17a,e] that was essentially devoid of tritium.

The preceding experiments firmly demonstrate the enzymatic conversion of farnesyl pyrophosphate to pentalenene and are consistent with the pathway illustrated in Scheme I. The proposed cyclization mechanism is further supported by the biomimetically modeled synthesis of pentalenene via cation **7**, reported earlier by Shirahama and Matsumoto,[5b] and used for the preparation of racemic pentalenene in the present study. On the basis of incorporation experiments with intact cells, we have previously suggested on stereochemical grounds that the enzymatic formation and further cyclization of the intermediate humulene (**6**, Scheme I) may take place at a single active site.[8,18] Further experiments to test this prediction and to establish the details of the pentalenene synthetase reaction are in progress.

Acknowledgment. The Bruker WM-250 NMR spectrometer used in this work was purchased with funds provided by the National Science Foundation and the Montedison Group of Milan. High-resolution mass spectra were obtained on a VG Micromass 7070H at the University of Pennsylvania. Strains of UC5319 were provided by Dr. L. J. Hanka of the Upjohn Co. We thank Professor Haruhisa Shirahama of Hokkaido University for providing us with a detailed experimental description of the synthesis of 2 reported in ref 5b.

---

[18] For a discussion of related dimethylcyclopentane sesquiterpenes see: Cane, D. E.; Nachbar, R. B. *J. Am. Chem. Soc.* **1978**, *100*, 3208. See also ref 3.

Models for the Photosynthetic Water Oxidizing Enzyme. 1. A Binuclear Manganese(III)-β-Cyclodextrin Complex

Balachandran Unni Nair and G. Charles Dismukes*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received September 15, 1982

The involvement of discrete binuclear and possibly tetranuclear clusters of Mn(III) and Mn(IV) in the enzyme that catalyzes the oxidation of water to oxygen in green plant photosynthesis[1] has prompted us to synthesis a binuclear Mn(III) model compound utilizing β-cyclodextrin (β-CD) as a ligand. β-CD is a naturally occurring cyclic oligomer containing seven glucose units.[2] The 7.0-Å internal diameter of the cavity of β-CD permits the formation of a large number of inclusion complexes.[3] This offers a method for modifying the redox properties and electron-transfer kinetics of coordinated metal sites. Although the Mn ligands in the enzyme have not been identified, they appear not to include thiol or thiolate[4] but may include nitrogen[1b] or oxygen donor ligands. α-CD and β-CD complexes with Cu(II) have been reported.[5] Stable coordination of Mn(III) and Mn(IV) by nonmacrocyclic polyhydroxy ligands such as sorbital and gluconate has been observed.[6]

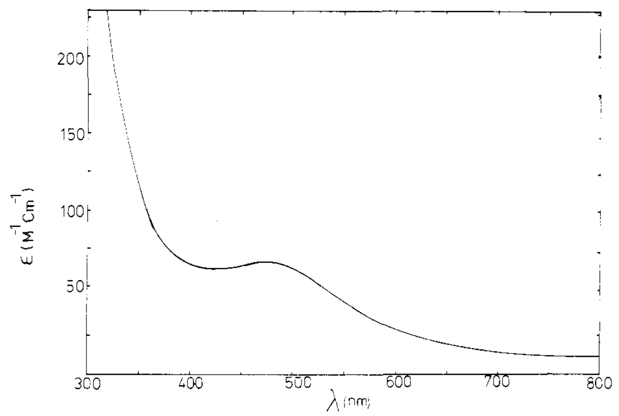


Figure 1. UV–visible spectrum of bis(μ-hydroxo)(β-cyclodextrin)dimanganese(III,III) in DMF.

Synthesis of Bis(μ-hydroxo)(β-cyclodextrin)dimanganese(III,III). β-CD (0.56 g, 0.5 mM) was dissolved in 30 mL of Ar-flushed DMF, Mn(II) acetate (0.26 g, 1.0 mM) was added, and the reaction mixture was stirred under Ar for 1 h. An alcoholic solution of NaOH (10 mL, 0.2 M) was added, and the resulting solution was exposed to bubbling air. After the solvent was stripped under vacuum, an excess of ethanol was added to precipitate the compound. It was filtered, washed with ethanol, and air-dried. The compound was recrystallized from 3:1 DMF–ethanol, yield 55%. An alternate procedure starting with Mn(III) acetate and the absence of oxygen also yielded the same compound, yield 20%. Mn was analyzed spectrophotometrically by oxidation to permanganate[7] and checked by EDTA titration of a reduced sample. These methods consistently gave 2.01 ± 0.04 Mn per $\beta\text{-CD} \cdot 2H_2O$ unit.

The compound is found to be soluble only in water, DMF, and Me_2SO. An aqueous solution of the compound is quite unstable and decomposes to hydrated oxides of Mn. However, in phosphate buffer (0.1 M, pH 9.2) the aqueous solution of the compound is comparatively more stable, observable precipitation occuring after 10–15 min. DMF and Me_2SO solutions of the compound are stable for days. The electronic spectrum of the compound in DMF exhibits a band at 482 nm, presumably due to an $^5E_g \rightarrow {}^5T_{2g}$-type transition typical of Mn(III)[8] (Figure 1). The oxidation state of Mn was confirmed to be 3+ by treating the compound with aqueous acid to remove the metal ion from the coordination sphere of cyclodextrin and reacting with Fe(II). No reaction is observed without prior release of Mn. The amount of Fe(III) generated was determined spectrophotometrically as the thiocyanate complex. One mole of the compound is found to react with 1.94 mol of Fe(II). Thus both of the Mn ions are in the trivalent state. The infrared spectrum shows the presence of all the prominent bands due to β-CD. A weakly enhanced infrared band is found in the complex at 652 cm^{-1}. This falls in the region for the $Mn_2(OH)_2$ stretching mode[9] and apparently excludes a μ-oxo bridge. ^1H NMR revealed that all the β-CD protons in the compound were not observable, even though the free ligand protons were easily identified. This shows broadening due to relaxation from the spin in the metal sites. Alternating current conductivity measurements in DMF showed an equivalent conductance of 8 mho cm^2 $equiv^{-1}$, indicating the compound to be essentially nonionic. A magnetic moment measurement by the Evans method gave a value of 3.51 μ_B per Mn at 302 K, which decreased to 3.38 μ_B at 224 K. This is well below the spin-only value (4.9 μ_B) for a mononuclear Mn(III) species, suggesting a possible weak antiferromagnetic

---

[1] (a) Dismukes, G. C.; Siderer, Y. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 274. (b) Dismukes, G. C.; Ferris, D.; Watnick, P. *Photobiochem. Photobiophys.* **1982**, *3*, 263.

[2] Cramer, F.; Hettler, H. *Naturwissenschaften* **1967**, *54*, 625.

[3] (a) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. (b) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer Verlag: Berlin, 1978.

[4] Takahashi, M.; Asada, K. *Eur. J. Biochem.* **1976**, *64*, 445.

[5] Matsui, Y.; Kurita, T.; Yagi, M.; Okayama, T.; Mochida, K.; Date, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2187.

[6] (a) Richens, D. T.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1979**, *18*, 706. (b) Bodini, M. E.; Willis, L. A.; Riechel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1538.

[7] Vogel, A. "Textbook of Quantitative Inorganic Analysis", 4th ed.; Longman: London, 1978; p 746.

[8] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: 1966; pp 846.

[9] Boucher, L. J.; Coe, C. G. *Inorg. Chem.* **1975**, *14*, 1289.

0002-7863/83/1505-0124$01.50/0 © 1983 American Chemical Society

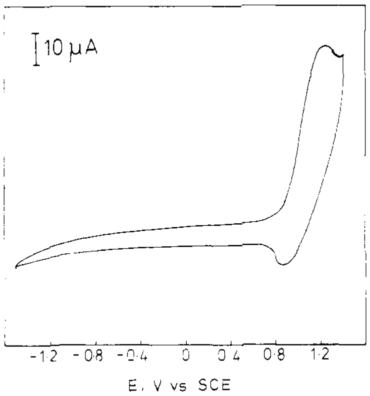
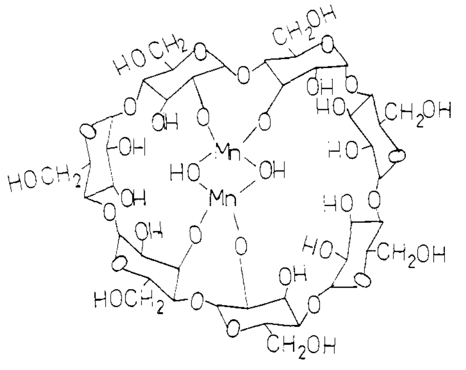


Figure 2. Cyclic voltammogram of 2 mM Mn–β-CD complex in DMF and 0.1 M tetrabutylammonium perchlorate (scan rate 100 mV s^{-1}).

coupling of the Mn spins. This could be fostered readily by the bis(μ-hydroxo)-bridged structure I. The bis(μ-hydroxo)structure



I

results in an uncharged complex, which is consistent with the conductivity data. EPR at 4.2 K revealed only a weak signal at $g' = 4$, which is presumably due to a small Mn(IV) impurity.

In order to establish which side of the β-CD ligand the Mn coordinates to, we treated the complex with 1 equiv of terephthaloyl chloride, which selectively esterifies the primary hydroxy groups.[10] This resulted in a "capped"-β-CD product that retained the original manganese. This experiment conclusively shows that it is the secondary hydroxyls of β-CD that coordinate both Mn ions. Cyclic voltammetry of the compound in DMF showed a quasi-reversible two-electron oxidation wave with a peak potential of +1.28 V (vs. aqueous SCE). The corresponding reduction wave has a peak potential of +0.81 V (Figure 2). The two-electron oxidation process was confirmed by use of an internal standard of ferrocene and also by constant potential electrolysis of the compound at 1.3 V (vs. SCE). The latter did not give rise to the mixed-valence Mn(III)–Mn(IV) product (assayed for spectrophotometrically) expected for a one-electron oxidation of Mn(III)–Mn(III) species. The Mn(IV) species so obtained was unstable, and at room temperature it decomposed within a few hours. This instability may be due to oxidation of the ligand. No evidence for reduction to the Mn(II) state was observed out to potentials of −1.5 V (vs. SCE). This indicates that the usually unstable Mn(III) oxidation state is stabilized considerably by coordination of β-CD in preference to the Mn(II) state.

Reaction of the compound with various oxidizing agents has been investigated. The compound in 80:20 DMF–H_2O (was not oxidized by excess potassium ferricyanide ($E_0 \simeq 0.44$ V). On treatment with 2 equiv of Ce(IV) ($E_0 \simeq 1.4$ V), the 482-nm band was bleached. One equivalent produced only partial bleaching, with no evidence again for the intervalence transition for a Mn(III)–Mn(IV) oxidation state. Evidently a two-electron oxidation to the (IV,IV) state is preferred, with eventual decomposition of ligand or water over hours, at least in aqueous DMF and Me_2SO.

Acknowledgment. This work was supported by a grant from the U.S. Department of Energy/Solar Energy Research Institute (DE-FG02-80CS84003) and by an award from the Chicago Community Trust/Searle Scholars Program (G.C.D.).

---

(10) Tabushi, I.; Shimokawa, K.; Shimizu, N.; Shirakata, H.; Fujita, K. *J. Am. Chem. Soc.* **1976**, *98*, 7855.

Solution Structure of Thianthrene: Dihedral Angle between the Benzene Rings Determined from the Analysis of NMR Spectra in Nematic Phase

Hideaki Fujiwara,* Akio Kawamura, Tatsuya Takagi, and Yoshio Sasaki

Faculty of Pharmaceutical Sciences, Osaka University
Suita, Osaka 565, Japan

Received June 7, 1982

Thianthrene is a typical example of the tricyclic compounds that have a "butterfly structure" folded along one of the principal molecular axes. The folded angle, i.e., the dihedral angle between the two benzene rings, has been repeatedly studied by several methods in different states.[1-6] This angle was first determined to be 128° from X-ray analysis with crystals[1,2] and later to be 131.4° from the electron diffraction study in gaseous state.[3] As for the solution structure of this molecule, on the other hand, values between 140 ± 10 and 144 ± 8° have been suggested from the dipole moment[4,5] and Kerr constant[4] measurements. Recent study on the molecular optical anisotropy similarly suggested the angle of 142°.[6] These studies all supported evidence that the dihedral angle is opened in solution, or otherwise the values in solution might be misleading. However, to make sure of the fact, it is necessary to determine the dihedral angle unambiguously in solution by means of a more direct and unequivocal procedure. For this purpose, NMR spectroscopy using liquid–crystal solvents[7] is quite useful. In the present communication we have analyzed the ^{1}H NMR spectra of thianthrene in a nematic-phase (Merck ZLI1167) mixture of three cyanocyclohexanes and determined the molecular structure in solution. The thus-derived solution structure of the molecule has led to a dihedral angle of 141.6±0.2°, and dependence of the angle on the molecular state of investigation has been proved.

The ordered spectra are analyzed by a modified LAOCN3 program extended to 9-spin system,[8] by using published values[9] of the indirect coupling constants. Direct coupling constants were processed to the program SHAPE[10] after extension from the original 7-spin system. The spectrum of 0.1 M (M = mol dm^{-3}) thianthrene dissolved in ZLI1167 was taken with a Hitachi R-900M FT NMR spectrometer operating at 90 MHz, the probe temperature being held constant at 34.1 °C. The experimental and simulated spectra are depicted in Figure 1, where 224 lines were used for the simulation. Deviation between the observed and the simulated lines is 1.6 Hz at its maximum and 0.43 Hz in the rms value, the latter being smaller than the NMR computer resolution. Analysis of the ordered NMR spectrum is summarized in Table I, and the structural as well as order parameters are cited in Table II. Large amplitude vibration of the "butterfly motion"

---

(1) Lynton, H.; Cox, E. G. *J. Chem. Soc.* **1956**, 4887.

(2) Rowe, I.; Post, B. *Acta Crystallogr.* **1958**, *11*, 372.

(3) Gallaher, K. D.; Bauer, S. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1173.

(4) Aroney, M. J.; Le Fêvre, R. J.; Saxby, J. D. *J. Chem. Soc.* **1965**, 571.

(5) Davies, M.; Swain, J. *Trans. Faraday Soc.* **1971**, *67*, 1637.

(6) Canselier, J. P.; Clement, C. *J. Chim. Phys. Phys.-Chim. Biol.* **1979**, *76*, 699.

(7) (a) Emsley, J. W.; Lindon, J. C. "NMR Spectroscopy Using Liquid Crystal Solvents"; Pergamon Press: Oxford, 1975. (b) Khetrapal, C. L.; Kunwar, A. C.; Tracey, A. S.; Diehl, P. In "NMR Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: Heidelberg, 1975; Vol. 9. (c) Khetrapal, C. L.; Kunwar, A. C. *Adv. Magn. Reson.* **1977**, *9*, 302.

(8) Fujiwara, H.; Takahashi, K.; Sasaki, Y. *J. Magn. Reson.* **1980**, *41*, 171.

(9) Lim, T. K.; Taurins, A.; Whitehead, M. A. *Can. J. Chem.* **1964**, *44*, 1211.

(10) Diehl, P.; Henrichs, P. M.; Niederberger, W. *Mol. Phys.* **1971**, *20*, 139.

0002-7863/83/1505-0125$01.50/0 © 1983 American Chemical Society