

Binuclear iron, manganese and copper centres in biology: Synthetic analogue approach

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Identification of binuclear (oxo-/hydroxo-/carboxylato bridged) iron, manganese and copper centres of biology are of comparatively recent origin. Noteworthy among them and of relevance to this article are: (i) the marine-invertebrate respiratory protein, hemerythrin (bridged diiron centre), (ii) oxygen-evolving centre of photosystem II (bridged manganese centres), (iii) manganese-containing catalase, pseudocatalase and ribonucleotide reductase (bridged dimanganese centres) and (iv) dicopper centre of tyrosinase. The presence of such bridged centres in biology has inspired bioinorganic chemists interested in synthetic model studies to synthesize and characterize such biological motifs in the laboratory, using designed ligands. Emphasis is directed toward their molecular structure, electronic structure and functional properties to compare with that present in biology. This article summarizes the results obtained in the author's laboratory along these lines.

THE field of bioinorganic chemistry^{1,2} is burgeoning and the problems of this rapidly expanding field are some of the most fascinating ones at the interface of chemistry, biology, agriculture and medicine. Hence scientists from a variety of disciplines are attracted to this field.

A principal theme of bioinorganic chemistry is the design of metal complexes which mimic active sites in functional metalloproteins. The veracity of these synthetic mimics can be measured by the congruence between their spectroscopic, structural and chemical properties and those features of the metalloproteins. The synthetic analogue approach^{3,4} is based on the premise that the chemistry of the metal binding site is dependent, for the most part, on the immediate coordination environment of the metal ion. For most metalloproteins, the immediate coordination environment consists of donors from the side-chains of amino acids. Sometimes, a prosthetic group (e.g. a porphyrin ring) completes the coordination sphere of the metal ion.

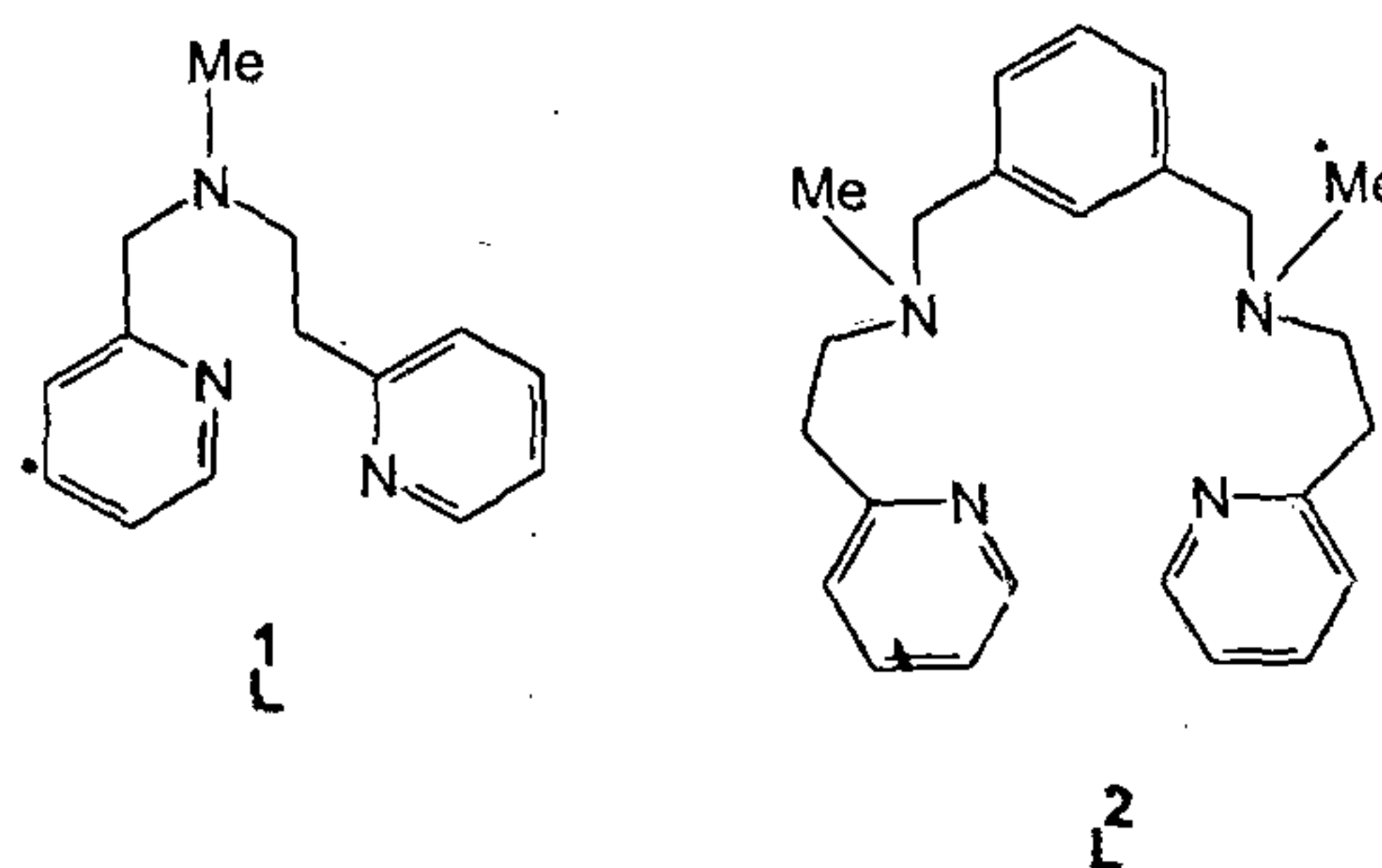
Our own involvement in this area began in 1989. Our studies have been aimed at mimicking both the molecular and electronic structural aspects (however, electronic structural in particular) and in some cases functional aspects of the relevant proteins or enzymes, using designed ligands. We have used magnetic, spectroscopic and electrochemical techniques to determine the structures

of the binuclear model complexes. These synthetic binuclear complexes have helped/augmented our knowledge in understanding the physico-chemical properties of the natural systems (see below).

In this article we present a brief summary of the current status of our synthetic models for the non-heme oxygen-transport iron protein hemerythrin (and its ruthenium analogue), water-oxidizing manganese complex of the photosynthetic apparatus and a binuclear copper monooxygenase (tyrosinase) that hydroxylates aromatic phenols.

The ligand design approach

Ligand design plays a key role in mimicking active sites of metalloproteins. Here a chelating ligand is viewed as a collection of adjustable components. These components are: (i) the donor atoms and their basicities; (ii) the donor functional groups and their spatial orientation and electronic and steric properties; (iii) the chelate rings and their sizes, structures, strains, and relationships to each other; (iv) the ring substituents and their electronic and steric effects; etc. In essence, ligand design can be viewed as the process by which the components are varied to control the properties of a targeted system. The synthetic model studies presented here use two pyridine-rich ligands: a tridentate nitrogen-donor ligand, having a five-membered and a six-membered chelate ring (L^1), and a binucleating ligand providing two terminal nitrogen coordination having six-membered chelate rings to each metal centre connected by a *m*-xylyl spacer (L^2).



Binuclear iron centres in biology

O₂-carrier protein hemerythrin and structures of its various forms

Hemerythrin is the oxygen-carrier protein found in marine invertebrates, containing two nonheme iron atoms per subunit. It is prototypical of an emerging class of oxo-bridged non-heme iron proteins and enzymes⁵⁻¹⁰. It functions in a manner directly comparable to the mammalian proteins myoglobin and hemoglobin. In the reduced deoxy form, the core is asymmetric (Figure 1), having one five and one six-coordinate iron atom. Two protein carboxylates and one solvent-derived hydroxide bridge link the two iron atoms. In the met form, the bridge is deprotonated. Terminal ligation sites are occupied by nitrogen atoms from the imidazole side chains of five histidine residues, and in the met and oxy forms by an additional exogenous ligand. As dioxygen approaches the diiron centre, it binds to the five-coordinate site. Electron transfer then occurs with oxidation of both ferrous ions to ferric and reduction of the dioxygen to peroxide. This is accompanied by transfer of the hydroxo proton to the peroxide to give a hydroperoxide ion (Figure 1).

Developments in hemerythrin model studies

Since the initiation of the hemerythrin model studies⁵⁻¹⁰ by Lippard *et al.* and Wieghardt *et al.* in 1983 there has been a growing interest in the synthesis of triply bridged (μ -oxo)bis(μ -carboxylato)diiron(III) complexes using a variety of tridentate nitrogen, containing facially capping ligands. The synthetic strategy adopted has mainly been the 'self-assembly' method of Ibers and Holm³. Some workers also used basic ferric acetate as their starting materials. However, our approach¹¹ resembles that of Lippard *et al.* using preformed $[\text{Fe}_2\text{OCl}_6]^{2-}$ ion.

Using an unsymmetrical triamine ligand L^1 , we synthesized¹¹ an orange-brown compound $[\text{Fe}_2(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2(L^1)_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$ (**1**). The complex **1** exhibits infrared [bridging acetate groups, asymmetric $\nu(\text{FeOFe})$ vibration mode, water of crystallization, and vibrations due to ionic perchlorate], electronic (Figure 2) and

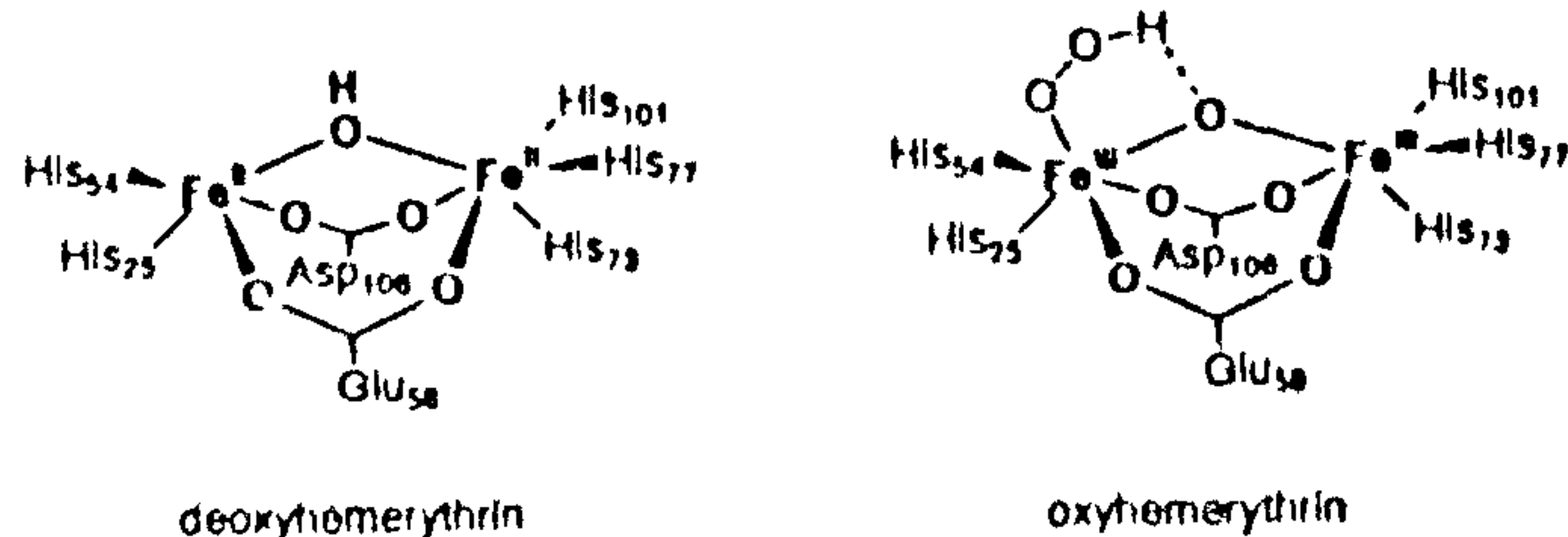
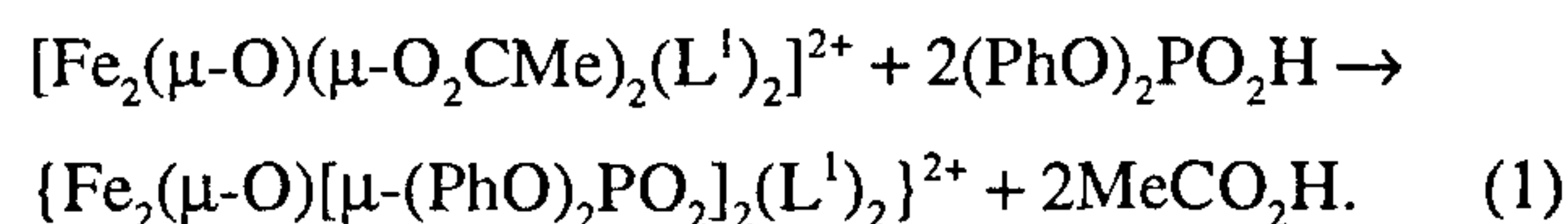


Figure 1. X-ray crystal structures of deoxy- and oxyhemerythrin.

Mössbauer spectral features similar to those of structurally characterized μ -oxo-bis(μ -carboxylato)diiron(III) complexes. The temperature-dependence of the magnetic susceptibilities of **1** is as expected for strongly coupled $S = 5/2$ dimers. The inequivalence in the chelate rings around each iron(III) might have caused the asymmetry in this compound which is reflected in its distinctively strong antiferromagnetic coupling ($J = -125 \text{ cm}^{-1}$) (ref. 11).

The lability of the bridging acetate groups in **1** has been demonstrated¹¹ by exchange with diphenyl phosphate (eq. (1)) as revealed by UV-vis spectroscopy (Figure 2). This study has relevance to the functioning of purple acid phosphatases⁷.



Interestingly, we synthesized¹² a ruthenium(III) analogue of complex **1**, $[\text{Ru}_2^{\text{III}}(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2(L^1)_2][\text{ClO}_4]_2 \cdot 4\text{H}_2\text{O}$ (**2**). From the success of hemerythrin core model studies, others¹³⁻¹⁶ have also synthesized this kind of ruthenium analogues. In dry acetonitrile solution complex **2** can be oxidized by $1e^-$ using constant-potential electrolysis or chemical oxidation by Ce^{4+} . The one-electron oxidized species $[\text{Ru}_2^{\text{III,IV}}(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2(L^1)_2]^{3+}$ reverts to complex **2** by the addition of water, implying oxidation of water. This reaction is presented schematically in Figure 3.

Thus we have synthesized an accurate electronic structural model for the met form of hemerythrin (for example, metazidohemerythrin). Analogous diruthenium(III) complex when oxidized by one electron is capable of oxidizing water. This property is important for understanding the water oxidation mechanism.

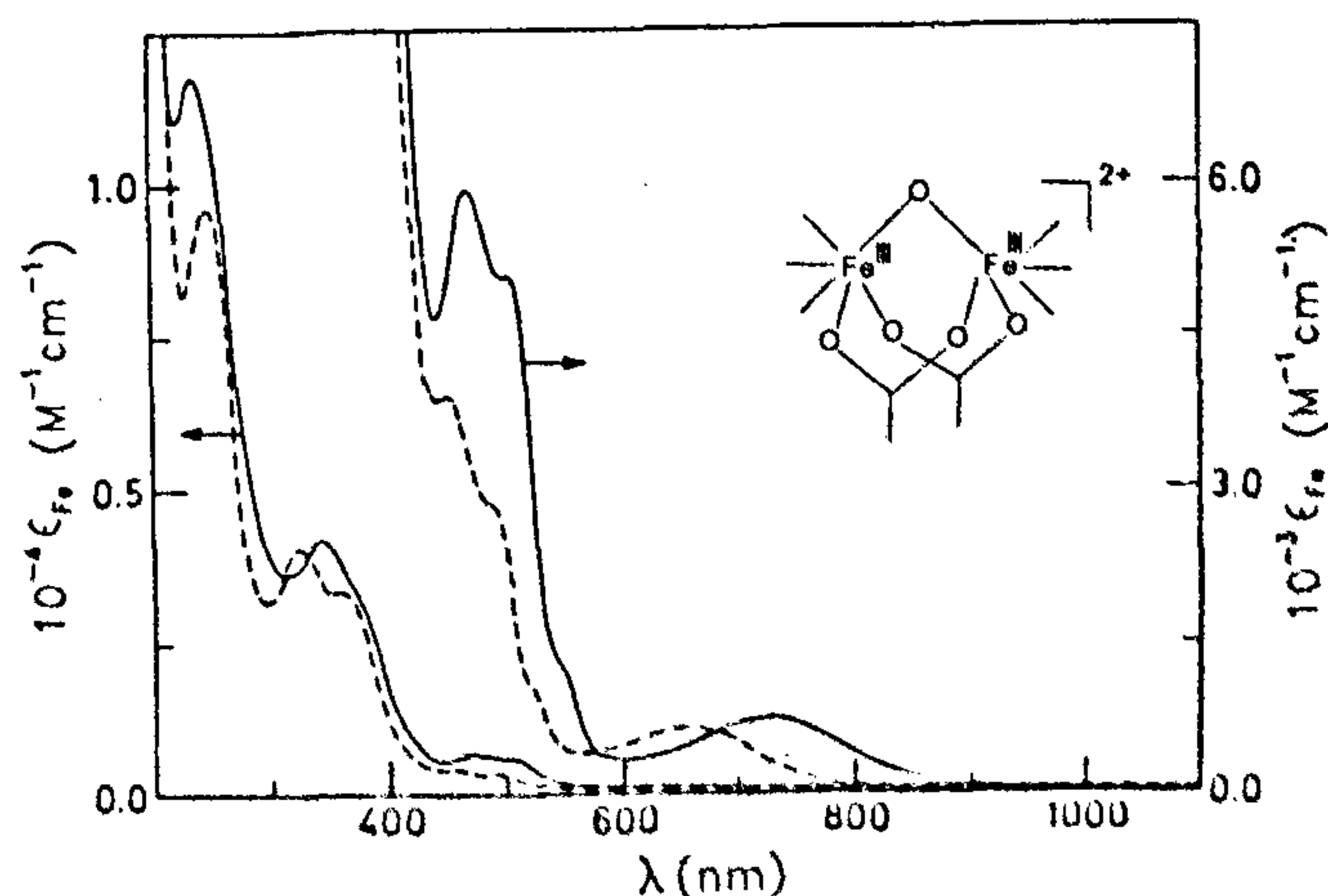
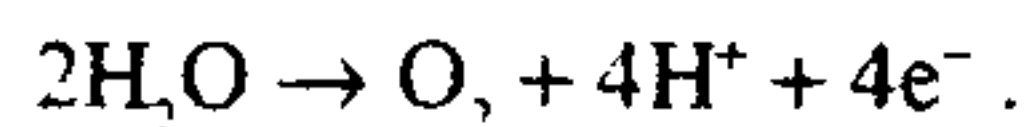


Figure 2. Acetate exchange reaction of $[(L^1)_2\text{Fe}_2(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$ with diphenyl phosphate as monitored by absorption spectroscopy in acetonitrile solution (—) before and (---) after addition of 2 equivalents of $(\text{PhO})_2\text{PO}_2\text{H}$.

Coupled manganese centres in biology

*Photosynthetic apparatus*¹⁷⁻²⁷

The most important role in nature for the metal manganese is its involvement at the water oxidation/oxygen evolution centre within the photosynthetic apparatus of green plants and cyanobacteria. In the water-oxidizing photosynthesis, generation of chemical energy from light, proceeds by light-induced, transmembrane charge separation of protons and electrons at the reaction centres photosystem I (PS I) and photosystem II (PS II), during which the water is oxidized in the active site of PS II.



The mechanism of oxygen evolution in PS II is typically discussed in terms of the so-called S-states. The model is based on the measurement of oxygen release after a series of short flashes of light, so that, in each reaction centre, there is a single charge separation event taking place per flash. The yield of O₂ in response to short flashes of light shows a characteristic oscillation pattern with a periodicity of four flashes. To account for this result, it was proposed that PS II cycles through five states [S₀-(S₄)], the index of which refers to the number of oxidizing equivalents stored (Figure 4).

The intermediate states are each defined by the number of electrons extracted from the water-oxidizing complex of PS II. The species which is oxidized in each of the S transitions appears to be a tetramanganese cluster, except possibly for the S₂ → S₃ transition. Here EPR evidence has implicated a protein residue close to the manganese cluster, possibly a histidine residue. One essential feature of the above scheme is that, during the S₀ → S₃ transitions, water is not oxidized. Water oxidation apparently takes place only after the third step, in one concerted four-electron reaction or two two-electron reactions.

Structure of the O₂-evolving centre in photosystem II

It is generally agreed that, stoichiometrically, four

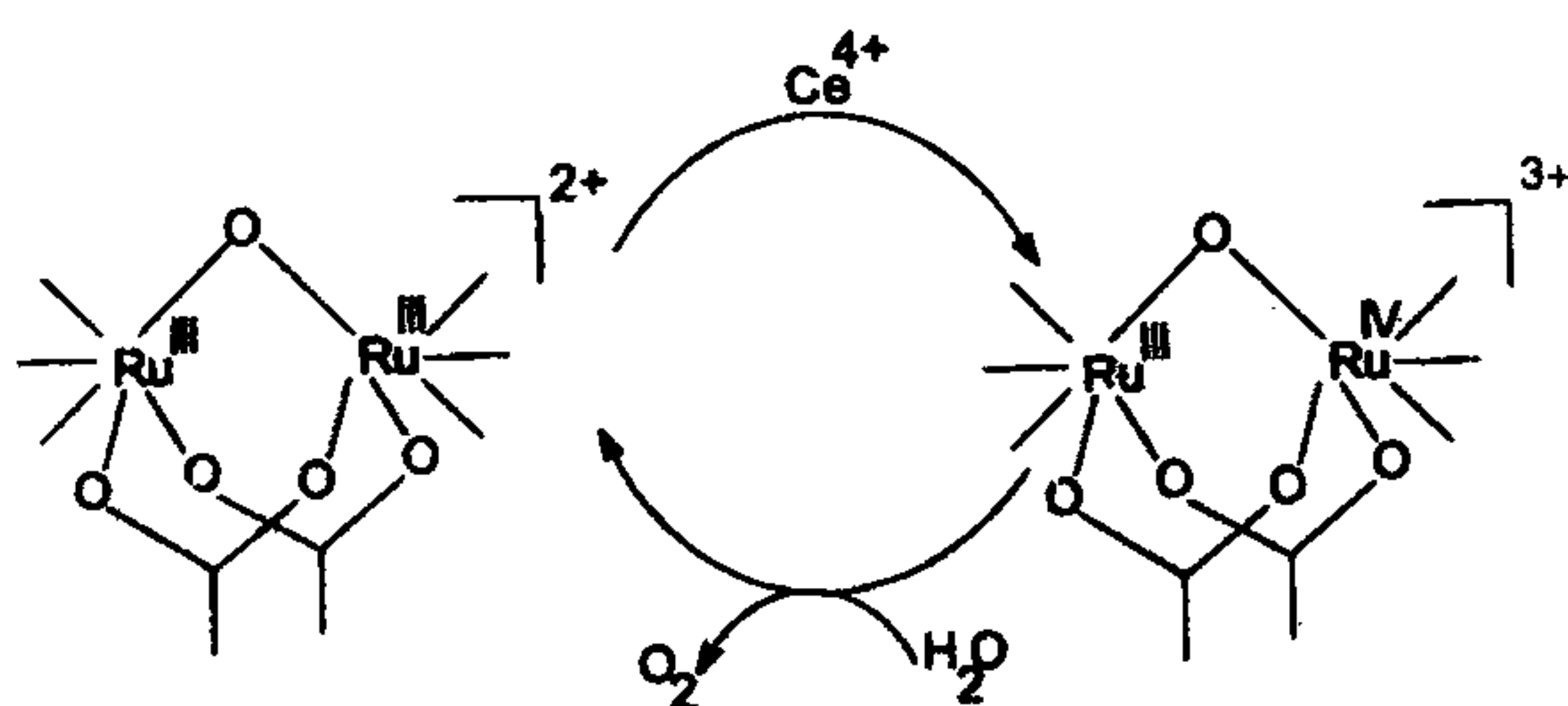


Figure 3. Transformations of $[(\text{L}^1)_2\text{Ru}_2^{\text{III}}(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})_2]^{2+}$ to $[(\text{L}^1)_2\text{Ru}^{\text{III}}(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})_2\text{Ru}^{\text{IV}}]^{3+}$ by Ce^{4+} ion and its rereduction by H_2O in acetonitrile.

manganese ions are associated as an indispensable co-factor with each PS II unit, but the question of how the metal ions organize within the protein is still the subject of considerable debate.

Recently, Klein and co-workers²⁵ have proposed from their EXAFS experiments a structural model which is summarized in Figure 5. The active site would contain two di- μ -oxo units linked by a μ -oxo-bis- μ -carboxylato bridge. The Mn-Mn distances would be $\text{Mn}_a\text{-Mn}_b = \text{Mn}_c\text{-Mn}_d = 2.7 \text{ \AA}$ and $\text{Mn}_b\text{-Mn}_c = 3.3 \text{ \AA}$.

Dinuclear manganese centres in biology^{8,22-24,27}

Recently, proteins with proposed (μ -oxo)dimanganese active sites have emerged. In this group are the ribonucleotide reductases found in coryneform bacteria, and catalases found in aerobic lactic acid bacteria. Carboxylate-bridged binuclear manganese centres that catalyse the disproportionation of hydrogen peroxide appear to exist in the active sites of pseudocatalase and catalase,



Unlike heme catalases, these Mn-containing catalases are only weakly inhibited by cyanide or azide.

A low-resolution X-ray crystallographic analysis of the latter enzyme demonstrated that two manganese ions are located at a distance of $\sim 3.6 \text{ \AA}$, and an EPR study indicated that the binuclear core can exist in three oxidation levels, $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$, $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$. These enzymes have been proposed to have manganese analogues of the hemerythrin active site based on spectroscopic similarities of the enzymes with corresponding dimanganese models.

Recently, a new type of ribonucleotide reductase that did not require coenzyme-B12 or iron for activity was discovered; this enzyme requires manganese instead. The electronic spectrum of the B2 subunit closely resembles

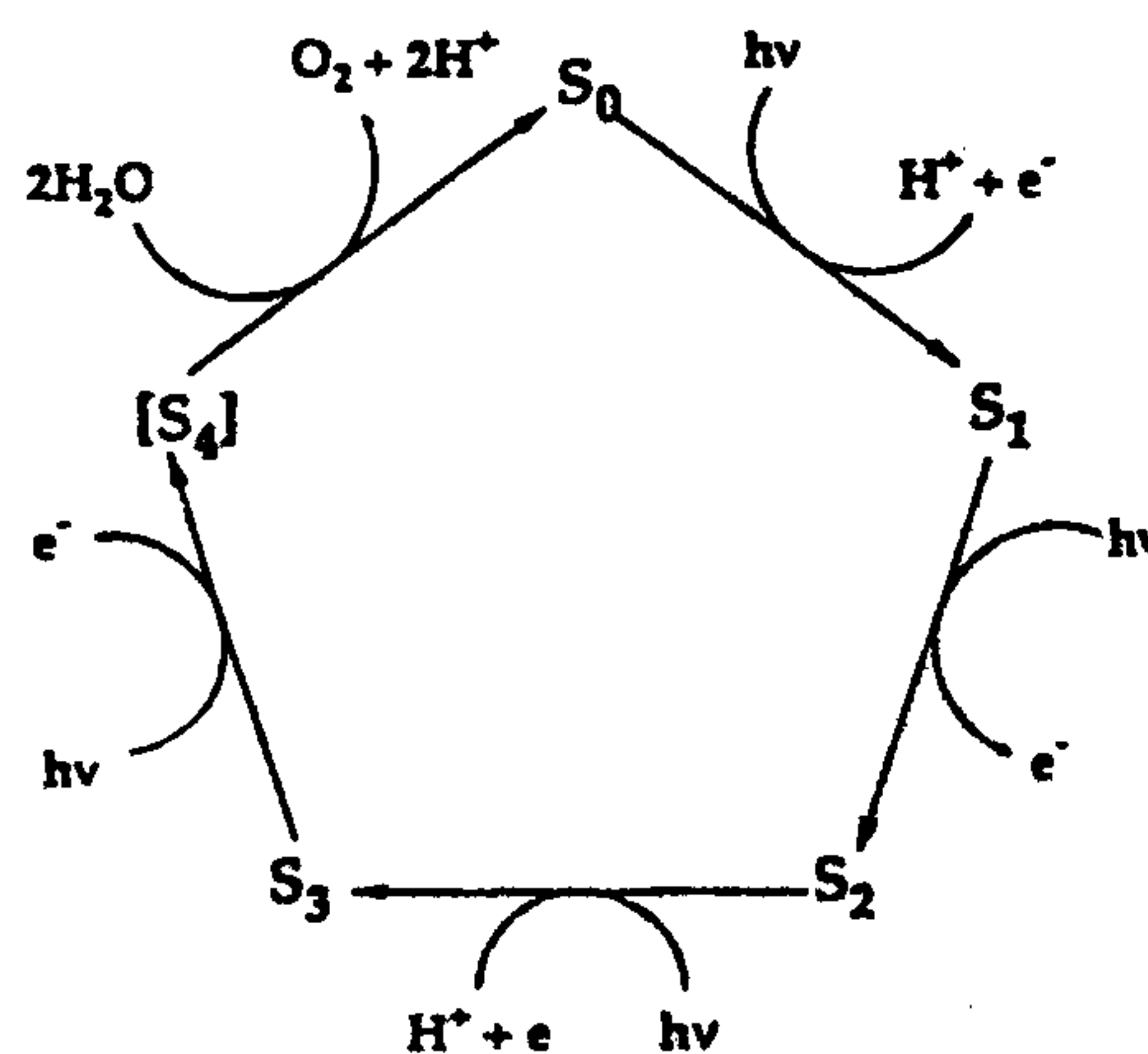


Figure 4. The S-states of the mechanism of O₂ evolution in PS II.

those of Mn-catalase and synthetic tribridged complexes with $[\text{Mn}_2^{\text{III}}(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2]^{2+}$ cores.

High-valent manganese systems

From the foregoing discussion it is understandable that the search for accurate synthetic models is on to mimic manganese cluster of water-oxidizing complex and manganese catalase. The structural motifs of relevance to these enzymes are higher-valent dimanganese systems with oxo and carboxylato bridges. We looked for new model systems in our laboratory and hence we prepared²⁸ a green mixed-valent complex, $[\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})\text{Mn}^{\text{IV}}(\text{L}^1)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ (**3**). From variable-temperature (19.8–300 K) solid-state magnetic susceptibility data we found that it has a doublet ground state with $J = -144 \text{ cm}^{-1}$ (antiferromagnetically coupled Mn centres). The X-band EPR spectrum at 77 K exhibits a 16-line Mn hyperfine signal centred at $g = 2$ (Figure 6). This is representative of binuclear Mn systems including the S_2 state of the manganese centre of PS II. The observed spectrum comes exclusively from the doublet ground state of two inequivalent manganese ions. The observed spectral pattern is indicative of a situation in which one of the ions has about twice the hyperfine coupling constant of the other.

An important test for the merit of any PS II model system is the thermodynamics of its redox reaction. Cyclic voltammetric measurement shows a one-electron oxidation at 1.0 V vs SCE to the dimanganese(IV) species as well as a one-electron reduction at -0.1 V vs SCE. Interestingly, coulometric or perchloric acid oxidation generates an orange Mn_2^{IV} species.

We found that acidification with glacial acetic acid of the mixed-valent (III,IV) dimer **3** produced a reddish brown dimanganese(III) complex $[\text{Mn}_2^{\text{III}}(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2(\text{L}^1)_2][\text{PF}_6]_2$ **4** (ref. 29). A case for a disproportionation reaction. For **4** on repetitive scanning of the potential between the limits 0.60 and 1.50 V vs SCE, at the expense of the higher potential response a new redox

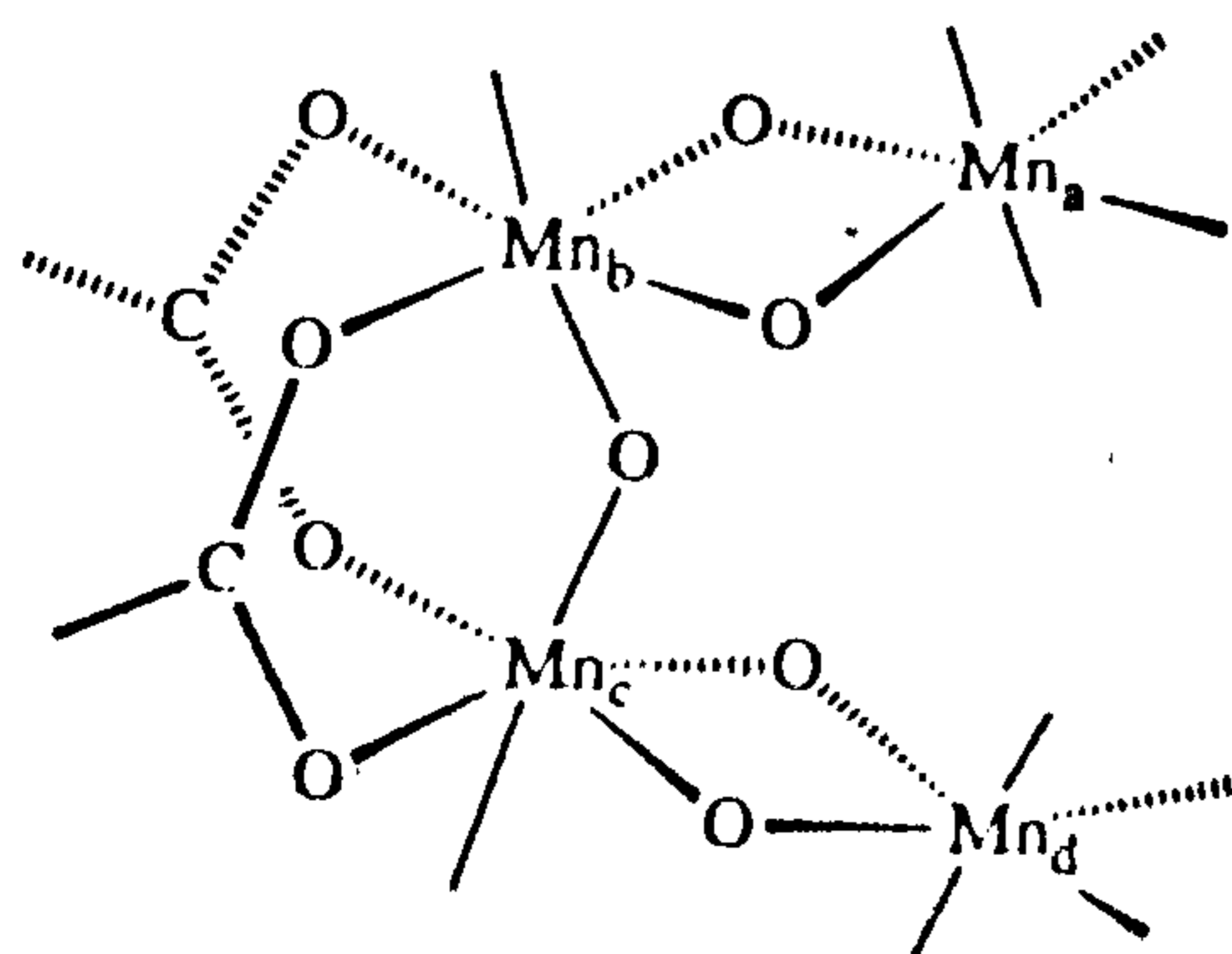


Figure 5. Klein's model for the oxygen evolving centre.

wave is being formed (Figure 7). The above experiment point towards redox transformation of **4** to the one-electron oxidized form of **3** under oxidative conditions. Thus, as the potential scanning is made up to the oxidative couple of **4**, $[(\text{L}^1)_2\text{Mn}_2^{\text{III}}(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})]^{2+}$ is oxidized to $[(\text{L}^1)_2\text{Mn}_2^{\text{III,IV}}(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2]^{3+}$ which in turn transforms to $[(\text{L}^1)_2\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})\text{Mn}^{\text{IV}}]^{3+}$.

The above results suggest that using our capping ligand L^1 it is possible to isolate manganese dimers with bis(μ -oxo) and (μ -oxo)bis(μ -acetato) motifs. These cores give rise to similar electronic structure as that of the natural systems. Redox chemistry neatly demonstrates interconversion of one core to other, having different oxidation levels. This is a finding of considerable interest in understanding the molecular events associated with water oxidation.

Binuclear copper centres in biology

Copper proteins carry out a variety of reactions that have long interested inorganic chemists. What has been of particular fascination are the structurally novel coordination sites and their associated physical and spectroscopic properties. Among the binuclear copper proteins or enzymes of relevance to this article, one of the fascinating properties is the presence of magnetically coupled binuclear copper centres. The interaction and subsequent reactivity of dioxygen (O_2) with copper ions is of great interest due to the importance of O_2 -binding and/or activating proteins in biological systems³⁰⁻³³.

Hemocyanin is an O_2 -carrier protein found in arthropods and molluscs. The deoxy dicopper(I) form reversibly binds O_2 via its reduction to O_2^{2-} . Tyrosinase, a monooxygenase that catalyses *ortho* hydroxylation of phenols to catechols with further oxidation to quinones. A dicop-

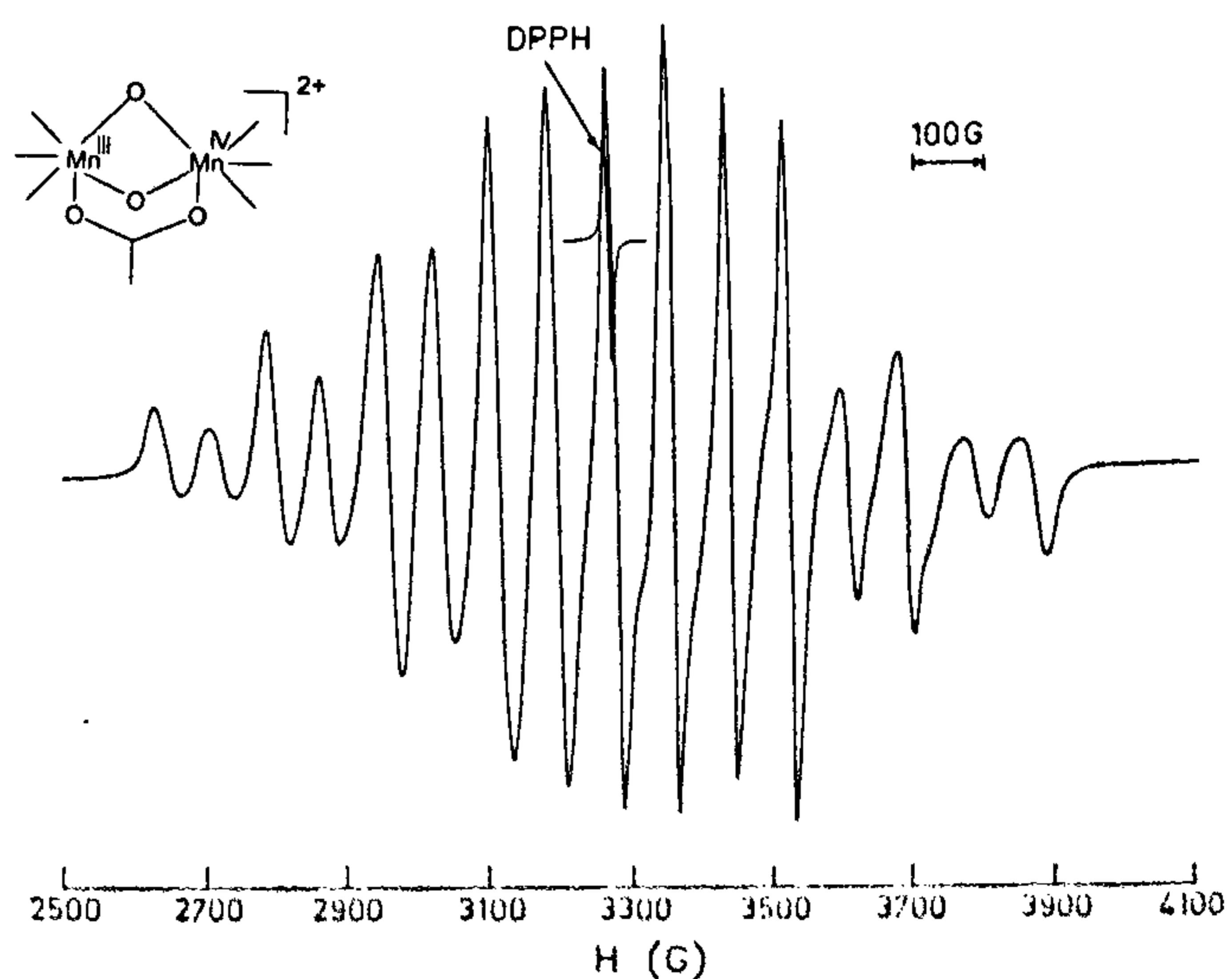


Figure 6. X-band EPR spectrum of $[(\text{L}^1)_2\text{Mn}_2^{\text{III}}(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ in dichloromethane at 77 K.

per(I) centre is readily amenable to the 2e oxidation by O_2 to generate a dicopper(II) species with concomitant reduction of dioxygen to reduction of dioxygen to oxide. The resulting $Cu_2(O_2^{2-})$ species is recognized as an active intermediate or product in hemocyanin and tyrosinase.

Developments in tyrosinase model studies

Notable progress has been made to mimic tyrosinase activity using tailor-made binucleating N-donor ligands having *m*- $CH_2C_6H_4CH_2$ spacers between the coordination units. Karlin and Gultneh³⁰ reported the first model, consisting of a ligand that provides two tridentate *bis*[2-(2-pyridylethyl)amine] donor units to each copper ion. In the meantime a number of modified-xylyl ligand systems demonstrating aromatic ring hydroxylation have appeared in the literature. To pinpoint ligand donor atom

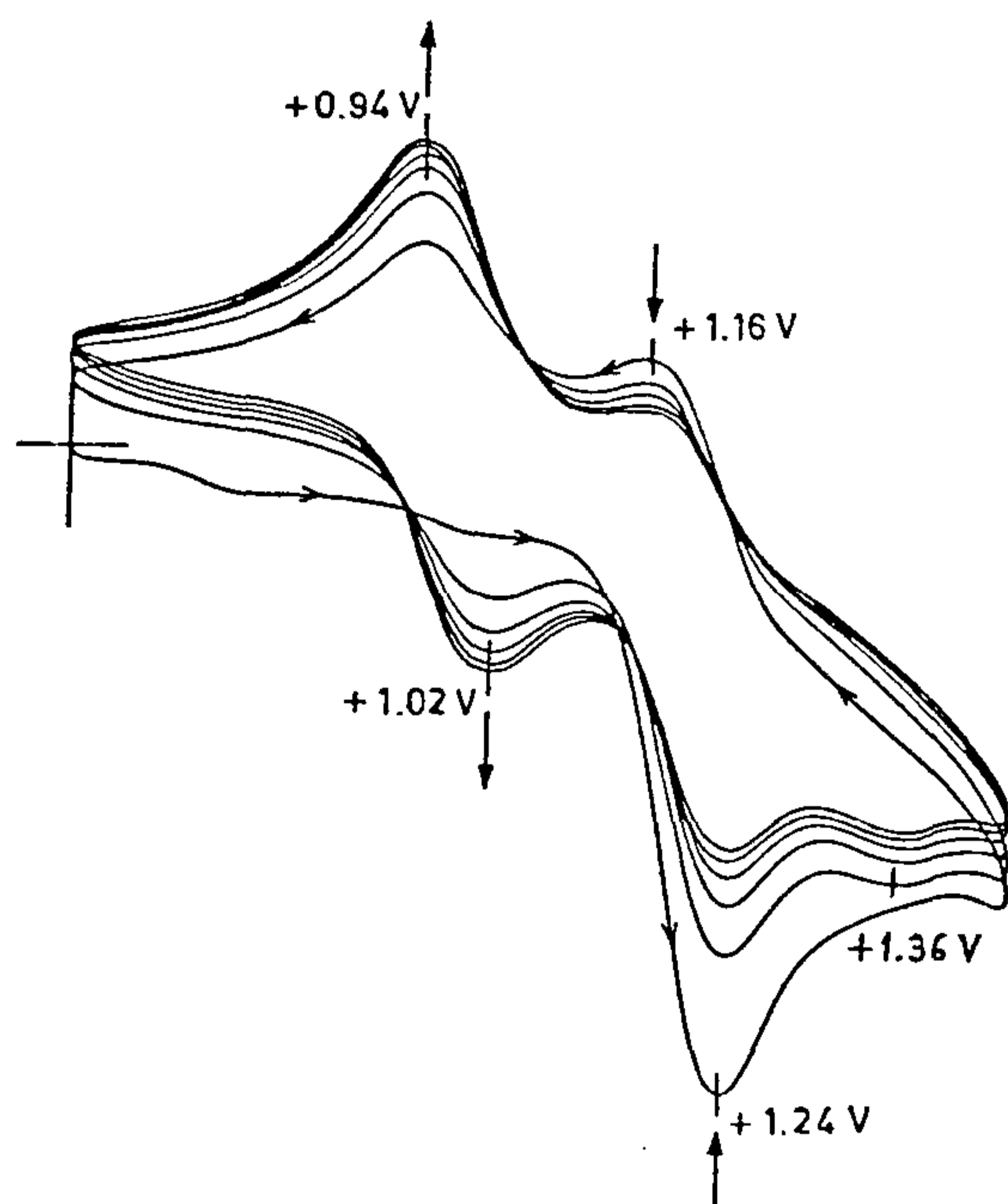


Figure 7. Repetitive scan cyclic voltammograms of $[(L^1)_2Mn^{III}(\mu-O)(\mu-O_2CMe)_2][ClO_4]_2 \cdot H_2O$ in acetonitrile at a platinum electrode; supporting electrolyte, tetra-*n*-butylammonium perchlorate.

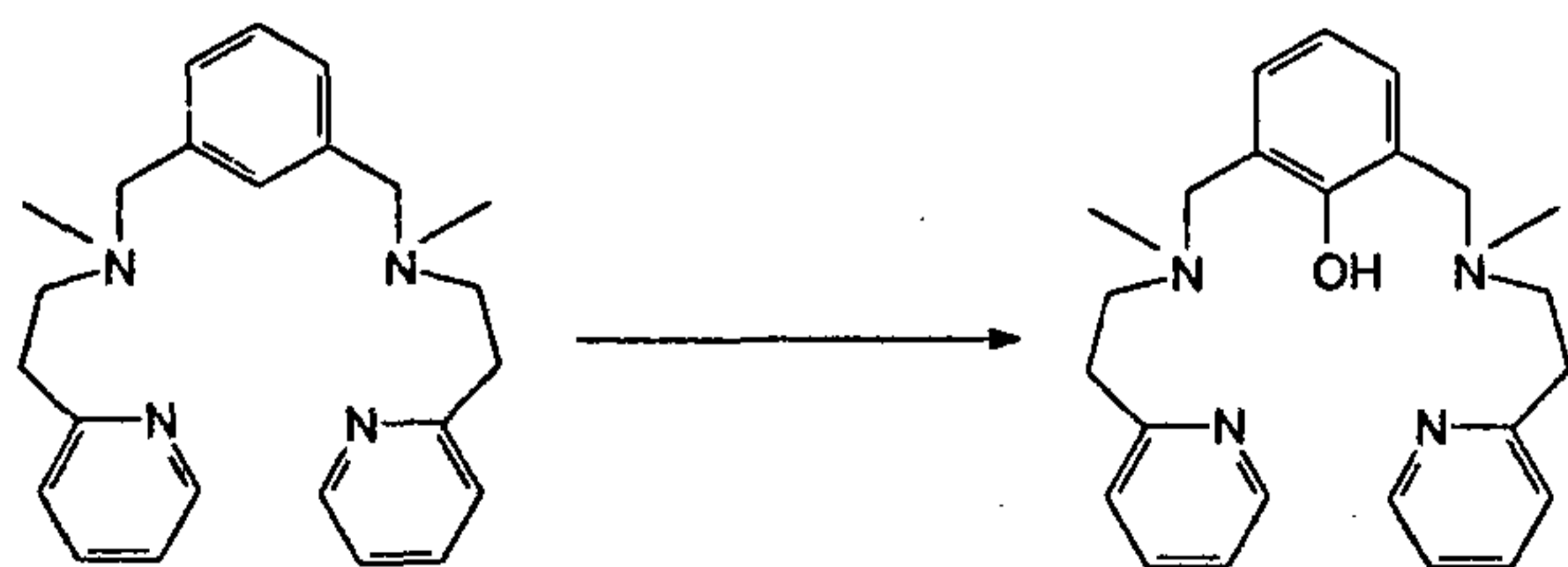


Figure 8. Demonstration of aromatic hydroxylation with our new ligand system.

characteristics (nature, number and their stereochemical factors etc.) necessary for bringing about aromatic ring hydroxylation in model systems, we became interested in mimicking tyrosinase-like activity using a new model system. Hence we designed a new non-Schiff base ligand (L^2), providing only two nitrogen coordination sites at each copper centre and demonstrated hydroxylation of the aromatic ring³⁴ (Figure 8).

The X-ray structure of the hydroxylated product provides, within the non-Schiff base family, the first example of a μ -phenolato and μ -hydroxo bridged copper(II) complex (Figure 9). This is a finding of considerable interest in the context of biomimetic studies aimed at the functional properties of tyrosinase.

Concluding remarks

A few potential synthetic models for (i) accurate electronic structural model for binuclear oxo-bridged iron centre of met form of hemerythrin and its ruthenium analogue, (ii) binuclear oxo-bridged manganese centres of oxygen-evolving complex of PS II (S_2 state) and catalase and (iii) binuclear copper centre of tyrosinase have been synthesized and thoroughly characterized. These models have provided electronic structural and functional properties of the aforesaid metalloproteins and enzymes. Most noteworthy results are (i) use of unsymmetrical tridentate nitrogen-donor capping ligand L^1 and a new *m*-xylyl ligand system L^2 in these models, (ii) bridge-exchange reaction on iron(III) dimer, (iii) demonstration of water oxidation with the one-electron oxidized form ruthenium analogue, (iv) redox transformations of $[Mn_2^{III}(\mu-O)(\mu-O_2CMe)_2]^{2+}$ to $[Mn^{III}(\mu-O)_2(\mu-O_2CMe)Mn^{IV}]^{2+}$ under oxidative conditions and (v) aromatic hydroxylation with a new *m*-xylyl ligand system. The results on the diiron(III) system provided us with the impetus to carry out research in this fascinating field. Our results on dimanganese systems demonstrated that redox-driven structural changes play an important role at the active site of PS II to increase the oxidation levels of manganese centres to oxidize water and hence

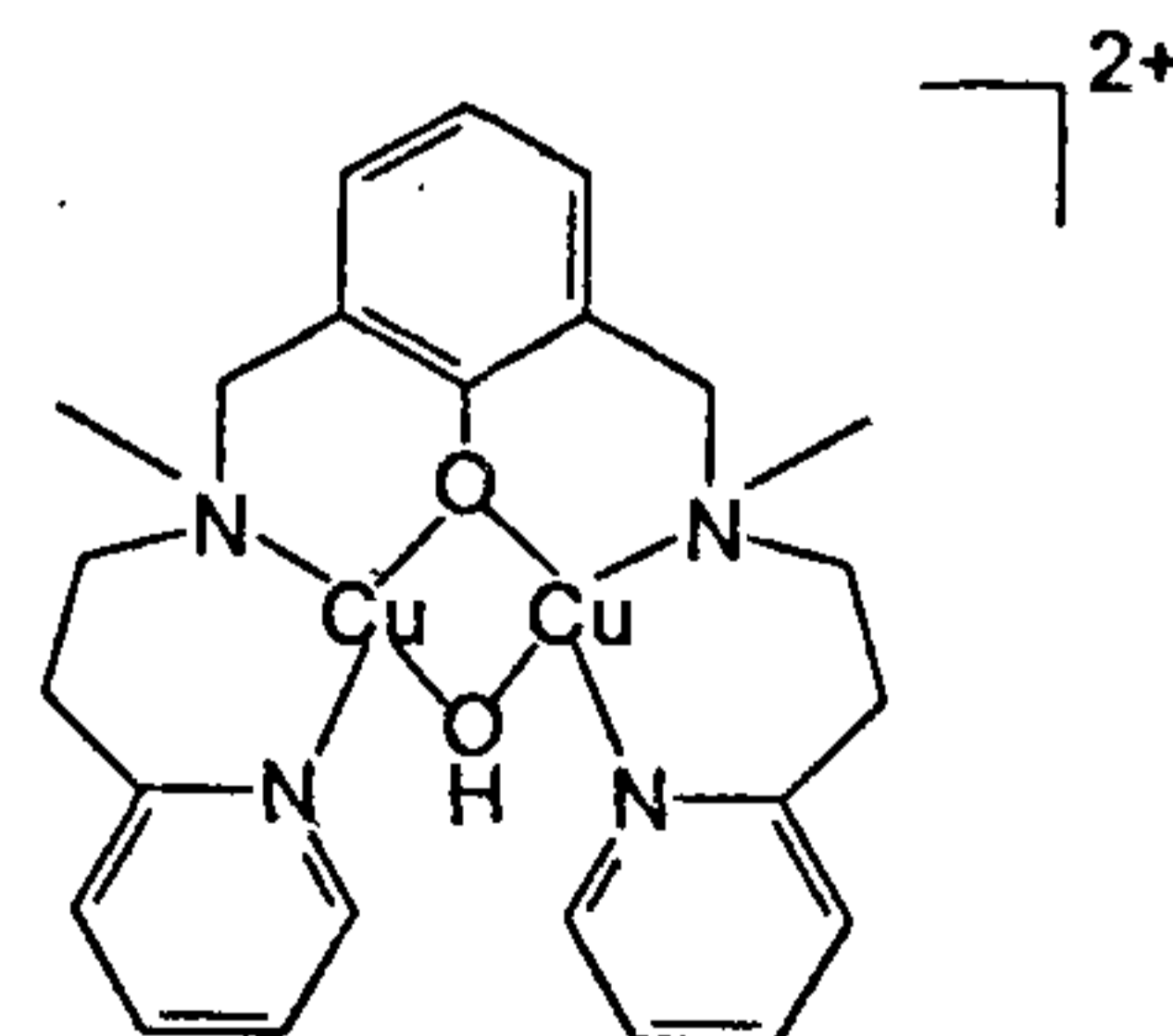


Figure 9. X-ray structure of the μ -phenoxo μ -hydroxo bridged dicopper(II) complex.

to liberate molecular oxygen. Our results on a new tyrosinase model is the demonstration of functional properties of this monooxygenase. It is obvious that there is a need and scope for understanding, at the molecular level, the fascinating properties of oxo-bridged binuclear iron, manganese and copper centres, which are still ill-understood. These include: (i) to model the functional properties of hemerythrin; at least the magnetic properties of oxyhemerythrin (hydrogen-bonded oxo-bridge), (ii) functional properties of PS II and (iii) to identify the electronic and steric factors responsible for bringing about aromatic ring hydroxylation (tyrosinase functional mimicking), etc. Such studies are in progress in our laboratory.

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