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Osmium and Cerium Porphyrins: Metalloporphyrins with Unnatural Metals as Models for Active Sites of Electron-Transfer Enzymes

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Osmium and Cerium Porphyrins: Metalloporphyrins with Unnatural Metals as Models for Active Sites of Electron-Transfer Enzymes

Structure–function relationships can provide valuable insight into the function of enzymes. These relationships can be obtained by chemical variation or modification of the original enzyme. Many enzymes contain metal ions which either stabilize the tertiary structure or serve as active sites for the biochemical process catalyzed by the enzyme under consideration. This Comment is devoted to the use of "unnatural" metals in metalloporphyrins that may be regarded as enzyme models.

Key Words: *osmium porphyrins, cerium porphyrins, metal porphyrins, electron transfer*

1. IMITATION AND VARIATION AS A MEANS OF OBTAINING INFORMATION ON THE FUNCTION OF BIOMOLECULES

Synthetic chemists can contribute to the understanding of the function of an enzyme by its "imitation" or "variation." The latter may be done by stepwise replacing, modifying or omitting parts of the "original." In the case of imitation, the biochemical effect of the "original" is achieved in full or in part with simpler molecules, thereby showing the essential structural features. (Incidentally, imitation is a very fruitful way of drug design.) In a previous review concerning hemoglobin as a famous and well-studied example of an enzyme,[1] the results of variations and imitation have been discussed.

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Inorganic chemists can elucidate structure–function relationships of enzymes in two ways:

1. They can use the specific properties of the original metal ion to gain insight into the structure of the native enzyme or its active site ("inorganic biochemists"). All kinds of spectroscopy or physical measurements are applied in this approach. Only slight "variations" are allowed, e.g., the replacement of the "natural" metal ion with an "unnatural" one which has a similar coordination geometry, but different spectral properties, or the attachment of certain probes to the protein chains, e.g., spin traps or electron donor or acceptor sites.

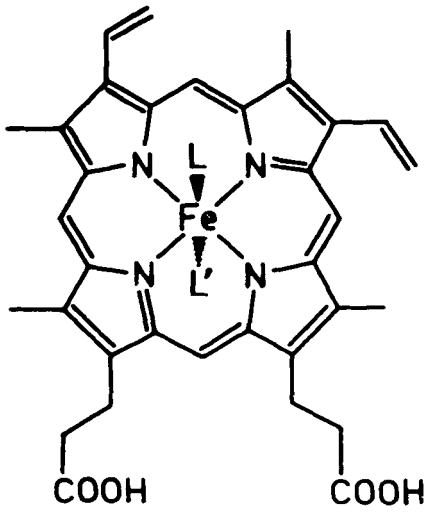
2. They can provide "imitations" of the original in the sense given above, reproducing structural or functional features of the latter ("bioinorganic chemists"). There are three criteria for evaluating these imitations[2]:

1. The synthetic analog should have a set of donor atoms about the metal that is very similar to the original. Configuration, structural type and oxidation state of the metal should also approach the situation in the original very closely. The compound should be crystalline ("structural model").
2. The spectral and magnetic properties should resemble the original ("spectroscopic model").
3. Reactions with substrates should occur as with the original, at least stoichiometrically, if not catalytically ("functional model").

The more the model fulfills all three of the above requirements, the better it will be.

Metal complexes with tetrapyrrole ligands constitute a large family of prosthetic groups in enzymes. They encompass the hemes (iron porphyrins[3,4]), chlorophylls (magnesium dihydro- and tetrahydroporphyrins[3]), vitamin B_{12} (cobalt corrinoids[5]), and, very recently, the factor F 430 (a nickel tetrahydrocorphin[6]). Porphyrin complexes of zinc, copper and manganese may also be found in living organisms; vanadyl porphyrins are constituents of petroleum and shale. As a whole, then, the "natural" metals in the above-mentioned tetrapyrroles are: Mg, V, Mn, Fe, Co, Ni, Cu and Zn. Because of their natural occurrence, porphyrin complexes of these metals have been widely studied.

An obvious way of trying to imitate the function of a heme protein is by using a simple iron porphyrin, the coenzyme or prosthetic group, instead of the holoenzyme. Here, the natural metal is still present. The variation is then simply the omission of the protein part. This means working with the coenzymes alone. The specific function of the heme protein is thus deteriorated or lost. Iron porphyrins alone are unable to reversibly bind molecular dioxygen at room temperature or act as stable electron-transfer agents; hence they cannot perform the functions of heme proteins: dioxygen transport and consumption or electron transport. The reason for this is their substitutional lability, bringing about the ultimate transformation of the heme **1**, Fe(proto-IX),[7] into its μ-oxo complex, $\langle Fe(proto\text{-}IX)\rangle_2O$ [8] according to Scheme 1 which shows, in fact, an inner-sphere autoxidation process.



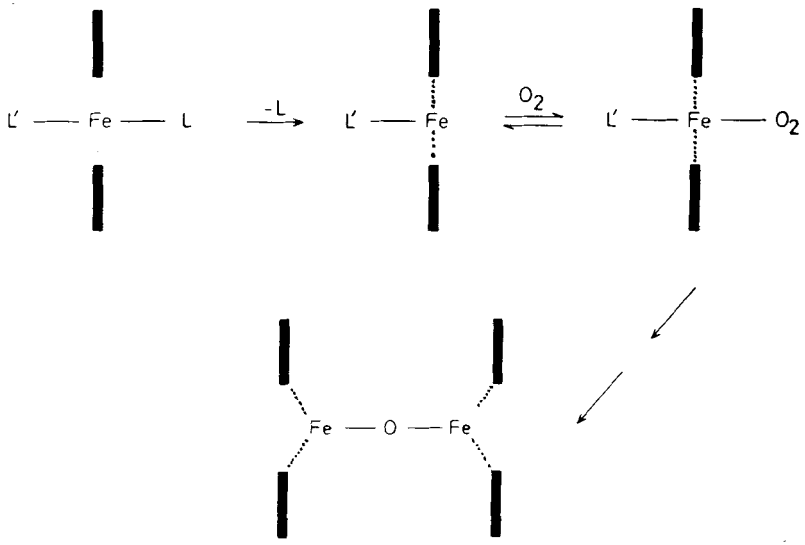
1: Fe(proto)LL'

No.	L	L'
1a	Py	Py

The working hypothesis that has emerged is that the protein somehow serves as a protection of the axial coordination sites (L and L′ in Scheme 1), preventing the formation of binuclear iron prophyrin complexes, or stabilizing the axial ligand system by connecting it directly to the protein (a chelate effect).

As a consequence, attempts have been made to imitate heme proteins by synthesizing iron porphyrins which carry substituents fulfilling the protective task of the protein in the natural system. The first documented attempt in this direction was made by Traylor *et al.* who synthesized a porphyrin in which the positions 8 and 18 (IUPAC numbering scheme) were bridged by a $-(CH_2)_4-C_6H_4-C_6H_4-(CH_2)_4-$ chain.[9] Since then, numerous iron porphyrins with modified side chains have been synthesized and the degree of analogy with the hemoglobins, the electron-transport cytochromes, the peroxidases, and the oxidizing cytochrome P 450 has been tested. A comprehensive review on the synthesis of these peripherally modified porphyrins is forthcoming.[10]

Very versatile compounds in this field are the 5,10,15,20-tetrakis(o-pivaloylamidophenyl)heme, the so-called "picket-fence



SCHEME 1 Inner sphere auto-oxidation of hemes.

heme" prepared by Collman *et al.*,[11] an "imitation" of myoglobin, and the 5,10,15,20-tetrakis(mesityl)heme which mimics in part the function of the high-oxidation-state iron porphyrins in cytochrome P 450 and peroxidases.[12,13] The bulky o-substituted phenyl groups protect the coordination sites of the central iron ions in these model compounds.

As already stated, the compounds described above still contain the natural metal, iron. The subject of this Comment is to answer the question whether "model compounds" of certain biologically active metal tetrapyrroles could be made which contain "unnatural" metals, i.e., metals that are not found in natural tetrapyrrole complexes. Contrary to the above-mentioned peripheral variations of the natural protoheme system **1**, these modifications may be termed "central variations."[1(a)]

2. PORPHYRIN COMPLEXES OF CHROMIUM, MOLYBDENUM, RUTHENIUM AND OSMIUM AS CYTOCHROME P 450 OR PEROXIDASE MODELS (VARIATION Fe → Cr, Mo, Ru, Os)

Cytochrome P 450 and the peroxidases are the heme proteins that catalyze the introduction of oxygen atoms into natural alkane or alkene moieties. In numerous studies it has been shown that this function can be imitated with natural or synthetic porphyrins containing iron,[13] manganese,[14] chromium,[15] molybdenum,[16] ruthenium[17] and osmium[18] in the absence of a protein. Cr, Mo, Ru, and Os certainly are "unnatural" metals in the porphyrin. So far, the best results seem to have been obtained with iron and manganese, natural metals, in the center of a porphyrin. Using the natural metal in the early studies, a quite obvious variation is to replace the natural iron with unnatural metals that can occur in "normal" and "elevated" oxidation states. Normal states are Fe^{III}, Mn^{III}, Cr^{III}, Mo^{V}, Ru^{II} and Os^{II}, elevated states are Fe^{IV}, Mn^{IV}, Cr^{IV} or Cr^{V}, Mo^{VI}, Ru^{VI} and Os^{VI}. Intermediates with terminal oxo groups as axial ligands of the respective metalloporphyrins are probably involved. A good example is the catalytic epoxidation of olefins with sodium hypochlorite catalyzed by porphyrinatomanganese complexes.[19]

Variations like the above, including unnatural metals, are quite obvious and yield useful information. Although the specificity of the originals is normally not attained, the study of synthetic analogs is becoming independent of bioinorganic chemistry and very promising in homogeneous catalysis or even industrial chemistry.

The following two sections will deal with model complexes that have not been developed on purpose by some systematic variation, but which have been found accidentally during fundamental investigations of osmium or lanthanoid porphyrins. These were part of a general research program aimed at elaborating the scope and the limits of the porphyrins as ligands in coordination chemistry.[1,20]

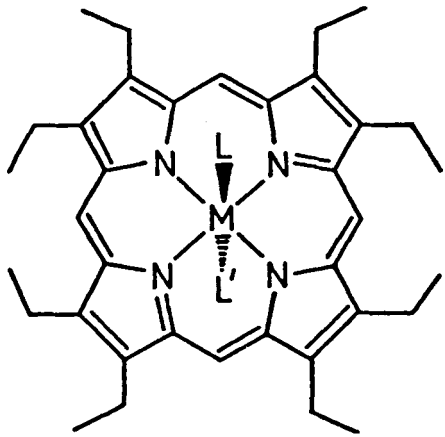
3. OSMIUM PORPHYRINS (VARIATION $Fe^{II} \rightarrow Os^{II}$)

Exploring the axial ligand chemistry of osmium porphyrins, we have found that the bis(1-methylimidazole)osmium(II) complex, Os(OEP)(1-Meim)$_2$ (**2a**),[20(d),21] and the 1-methylimidazole tetrahydrothiopheneosmium(II) complex, Os(OEP)(1-Meim) (THT) (**2b**),[20(d),22] could be regarded as cytochrome b_5 or c models, respectively.

Both cytochromes b_5 and c are electron carriers, i.e., they are members of certain electron-transport chains in living organisms. The essential function is the redox reaction shown in Scheme 2. These also occur in the hemochromes (which are the bis ligand iron(II) porphyrins, e.g., **1a** (L = L′ = Py) or **2c**, L = L′ = Py).

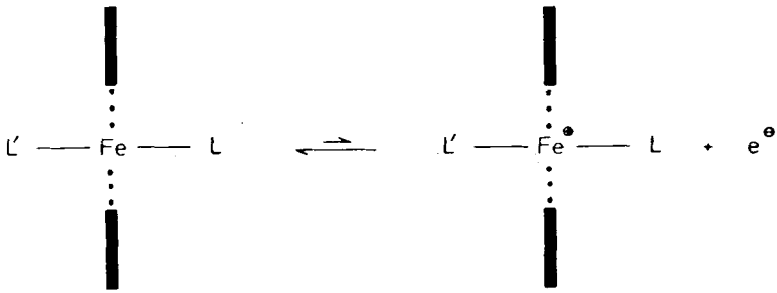
These heme proteins can fulfill this function only because their protein chain firmly binds the axial ligands to the iron center. In contrast to the cytochromes b_5 and c, simple hemochromes rapidly lose one of their nitrogen or sulfur donor ligands, forming a pentacoordinated species, which readily binds dioxygen and then is degraded to a μ-oxo complex (see Scheme 1). Apart from protecting the heme from μ-oxo complex formation, the protein here blocks substitutional lability and thus fixes and closes the axial coordination sphere. Therefore, the cytochromes b_5 and c do not rapidly react with carbon monoxide or dioxygen. The inner-sphere autoxidation is prohibited.

Hemes have been synthesized in which specifically designed side chains ("tails") carry the donor atoms and help to fix the latter to



2: M(OEP)LL'

No.	M	L	L'
2a	Os	1-Meim	1-Meim
2b	Os	1-Meim	THT
2c	Fe	Py	Py



hemochrome (e.g., **1a**)	hemichrome cation
$Fe(OEP)Py_2$	$E_0 = -0.15$ V (SCE)

reduced	oxidized cytochrome
$Fe(Cyt\ b_5)$	$E_0 = +0.02$ V (SHE) (E_1)
Fe(Cyt c)	$E_0 = +0.25$ V (SHE) (E_2)

SCHEME 2 The essential redox reaction of hemochromes and cytochromes.

the iron.[10] A typical example is the "tail heme" shown in Fig. 1.[23] This is the only way to prepare the mixed-ligand imidazole-thioether hemes that are analogous to cytochrome c, but these systems are still labile to inner-sphere autoxidation, and it may require further synthetic modifications at the porphyrin periphery to overcome this difficulty.

The above-mentioned symmetrical and unsymmetrical bis ligand osmium(II) porphyrins **2a** and **2b** were called osmochromes because of their structural and spectral analogy with the hemochromes, e.g., **2c**. The name "hemochrome" expresses the relation to the cytochromes: cytochrome b_5 carries two imidazole side chains of two histidines of the protein chain as axial ligands, while cytochrome c carries an imidazole of a histidine and the methyl thioether function of a methionine as *trans* ligands. What are the properties that might justify regarding the osmochromes **2a** or **2b** as cytochrome b_5 or c models?

Contrary to the hemochromes, the osmochromes **2a** and **2b** are substitutionally inert. The Os–N and Os–S bonds have inherent stability, thus a chelate effect fixing the axial ligands is not necessary. Therefore, the osmochromes can perform the reversible redox reaction depicted in Scheme 3 and do not suffer inner-sphere autoxidation like the one shown in Scheme 1.

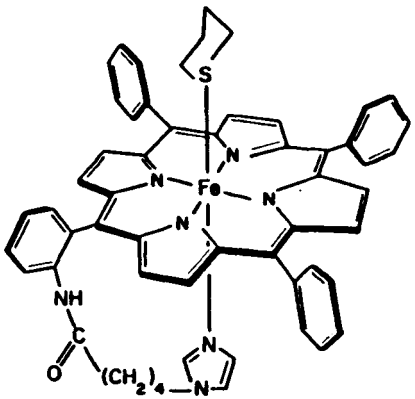
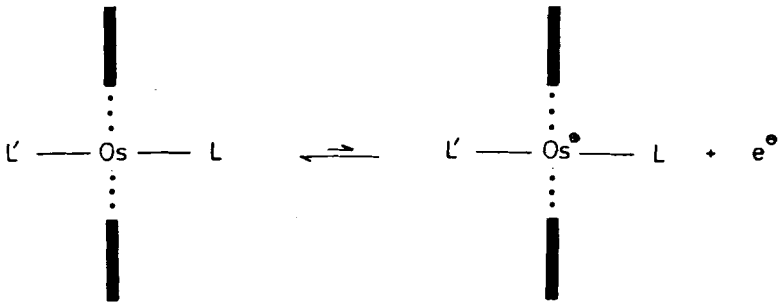


FIGURE 1 "Tail heme" of Reed and Scheidt. Drawing by courtesy of D. Dolphin (Ref. 10).



osmochrome
(2a, 2b)
$Os(OEP)(1\text{-}Meim)_2$ **(2a)**
Os(OEP)(1-Meim)(THT) **(2b)**

osmichrome cation
$E_0 = -0.63$ V (SCE) (E_1)
$E_0 = -0.45$ V (SCE) (E_2)

SCHEME 3 The essential redox reaction of osmochromes (bisligandosmium(II) porphyrins).

Apart from the unnatural metal, the osmochromes are significant cytochrome models under the structural, spectroscopic and functional aspects. The structural aspect becomes obvious on comparison of Schemes 2 and 3. The spectroscopic aspect is addressed by the fact that, apart from a hypsochromic shift, the optical absorption spectra of the components of both the osmochrome and the hemochrome systems are very similar.[21] Rapid electron transfer can be derived from the fact that a mixture of an osmochrome with its corresponding osmichrome cation gives only a single proton NMR spectrum with broadened lines, no individual species being seen. The osmochrome stage is diamagnetic; the osmichrome stage has a low-spin configuration. The oxidation is clearly metal-centered. Neither carbon monoxide nor dioxygen react with the osmochromes at room temperature in the absence of protic acids.

Nevertheless, a special feature of the osmochromes is their acid-induced autoxidation which has been shown to proceed via superoxide (Scheme 4(a)). The latter is present in stationary concentrations during hydrogen peroxide formation (Scheme 4(b)).

$$Os(OEP)(1\text{-}Meim)_2 + O_2 \longrightarrow Os(OEP)(1\text{-}Meim)_2^+ + O_2^- \quad (a)$$

$$2\,O_2^- + 2\,H^+ \longrightarrow O_2 + H_2O_2 \quad (b)$$

SCHEME 4 Acid-induced outer-sphere autoxidation of osmochromes.

Both O_2^- and H_2O_2 have been identified and quantitated in the course of the rather slow reaction. These reaction products could never be observed in the autoxidation of hemochromes even though kinetic experiments have shown that hemochromes may also suffer an outer-sphere autoxidation in the presence of excess axial ligand L.[24] This is due to the fact that neither superoxide nor hydrogen peroxide can be detected in the presence of the iron(III) porphyrins that are the products of autoxidation of hemochromes. The paramagnetism and ESR activity of Fe^{III} complexes interferes strongly with the ESR assay of superoxide, and the catalase activity of heme compounds prevents any accumulation of hydrogen peroxide, which would be the final product of the outer-sphere autoxidation of hemochromes.

The reverse of reaction (a) of Scheme 4 can be realized by titration of an osmichrome cation with potassium superoxide, a reaction which is known to occur with oxidized cytochrome c as well.

Although cytochrome b_5 does not bind either dioxygen or carbon monoxide, it also undergoes a slow autoxidation reaction which could be caused by an outer-sphere-electron transfer to the dioxygen molecule and disproportionation of hydrogen peroxide similar to Scheme 4.

Another functional aspect of the osmochrome/cytochrome analogy is the difference, $\Delta E = E_1 - E_2$, between the metal redox potential E_1 of the corresponding symmetrical bis(imidazole) and E_2 of the unsymmetrical thioether/imidazole systems. For the heme octapeptide obtained by partial hydrolysis of cytochrome c, $\Delta E = -160$ mV,[25] for the "tail heme" (Fig. 1), $\Delta E = -167$ mV,[23] for a mesoheme with covalently bonded N/N- or N/S-donors, $\Delta E = -147$ mV,[26] for the osmochromes **2a** and **2b**, $\Delta E = -180$ mV (see Scheme 4),[22] and for the corresponding osmochromes derived from 5,10,15,20-tetrakis (p-tolyl)porphyrin, $\Delta E = -200$ mV.[27] By comparison of cytochromes b_5 and c, one finds $\Delta E = -235$ mV (see Scheme 2). This large value may be attributed to a special protein effect. The osmochromes, nevertheless, approach the ΔE value of the natural system more closely than the models based on iron porphyrins.

As a whole, the structural, spectroscopic, and functional aspects justify the view that osmochromes behave as cytochrome models,

despite the fact that they do not contain the natural metal. On the other hand, the replacement Fe → Os introduces the inherent stability of the axial ligand bonds which is not seen with the Fe porphyrins. While the Fe^{II}/Fe^{III} redox potentials are rather similar to the corresponding Os^{II}/Os^{III} values, the Ru^{II}/Ru^{III} redox potentials are higher and ring oxidation is sometimes involved.[1(a),20(d)] Therefore, the "ruthenochromes" would be less well suited as cytochrome model compounds.

4. CERIUM PORPHYRINS (VARIATION 2 $Mg^{II} \rightarrow Ce^{IV}$)

Lanthanoid monoporphyrinates of the composition Ln(OEP)X (where X is thought to be OH) or Ln(TTP)(acac) have been known for some time.[28] In the course of our studies on porphyrin complexes with metals in high coordination numbers,[1] we have prepared a nearly complete series of novel lanthanoid bis(octaethylporphyrinates), $Ln(OEP)_2$ (Ln = La . . . Lu except for the radioactive Pm).[29] For both $Ce(OEP)_2$[29(c)] and $Eu(OEP)_2$,[29(f)] the double-decker structure with square-antiprismatic coordination about the lanthanoid ion as shown in Fig. 2 has been established by x-ray crystallography.

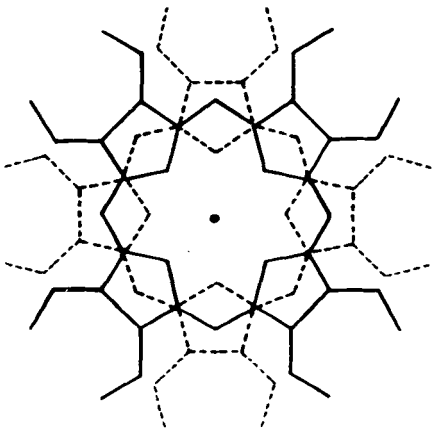


FIGURE 2 Schematic representation of the double-decker (biplan) structure of $Ln(OEP)_2$ (taken from Ref. 29(a)).

The composition $Ln(OEP)_2$ is to be expected for a tetravalent central ion like Ce^{IV}, by analogy to the phthalocyanine sandwiches $Th(Pc)_2$ and $U(Pc)_2$.[30] However, for $Eu(OEP)_2$ a question about the charge balance between the lanthanoid ion and the porphinate anions arises. The homologous species $Lu(OEP)_2$ is paramagnetic (μ_{eff} 1.49 . . . 1.83 B. M. between 2.6 and 285 K[29(e)]) and gives the ESR spectrum of an organic radical.[29(g)] Thus, as has been proved for the similar sandwich, $Lu(Pc)_2$,[31] the electron distribution is represented by Ln^{3+} $(OEP)^{2-}$ $(OEP\cdot)^{-}$.[29(a),(c),(d)] Further evidence for the presence of an electron-deficient porphyrinate system comes from specific IR and NIR (near infrared) bands.[29(a),(c),(d)] On the NMR timescale, the unpaired electron is delocalized over both porphyrin rings. Despite their different electronic configurations, the two rings are identical in the crystal structure.

The NIR bands occur between 1200 and 1500 nm in all complexes except $Ce(OEP)_2$. The wavenumber of these bands monotonously decreases with increasing ionic radius of the lanthanoid ion.[29(c)] As these bands have molar absorptivities of about 3000, they are regarded as internal charge-transfer transitions. Hence, these sandwich molecules are internal donor–acceptor complexes, the $(OEP)^{2-}$ ion being the donor, the radical ion $(OEP\cdot)^{-}$ being the acceptor. Both are firmly connected by the Ln^{III} ion. These electron-deficient species can be reduced chemically[29(e)] or electrochemically[29(k)] to anions of the type $Ln(OEP)_2^{-}$ which no longer show this NIR absorption.

This NIR absorption occurring in an electron-deficient pair of tetrapyrrole systems is reminiscent of the oxidized special pair $(Bchl)^{+}{}_2$ of bacteriochlorophyll-b molecules, Bchl (**3**), which is part of the photosynthetic reaction centers in purple bacteria, e.g., Rhodopseumonas viridis or spheroides. It had been postulated on the basis of various physical measurements that this special pair is the primary source of the electron produced according to Scheme 5(a) and entering into the reducing pathway of photosynthesis.

$$(Bchl)_2 \xrightarrow{h\nu} (Bchl)_2^{+} + e^{-} \qquad \text{NIR: 1300 nm} \qquad \text{(a)}$$

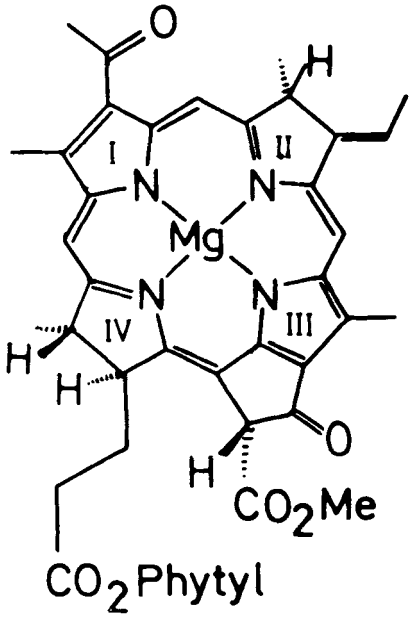
$$Ce(OEP)_2 \longrightarrow Ce(OEP)_2^{+} + e^{-} \qquad \text{NIR: 1270 nm} \qquad \text{(b)}$$

SCHEME 5 Oxidation of bis(tetrapyrrole) systems.

The oxidized special pair, $(Bchl)_2^+$, is recognized by a characteristic NIR absorption band at about 1300 nm.[32]

The structure of the protein subunits of the reaction center of R. viridis has been elucidated recently by x-ray crystallographic analysis[33] and clearly shows a pair of (Bchl) molecules **3** in a slipped coplanar situation, overlapping strongly at the pyrrole rings I, the planes of which lie about 300 pm apart.

In $Ce(OEP)_2$ the rings are also parallel. However, the following differences in the positions of the rings should be noted: (1) They are somewhat farther apart (distance of the mean planes 340 pm). (2) They are in a staggered conformation; the pyrrole rings do not strongly overlap. (3) They are coaxial instead of slipped. The first two statements imply a decrease of the interaction of the two rings while the third one means an increase. As a result, the interactions



3

TABLE I

Assessment of the model character of osmochromes and cerium bisporphyrinates

Aspect	Osmochromes Cytochromes	Cerium Bisporphyrinates Bacteriochlorophyll Dimer
Structural	Bisligandmetal(II) Porphyrin	Cofacial Porphyrin Dimer
Spectroscopic	UV/VIS spectrum of reduced and oxidized species	NIR spectrum of oxidized species
Functional	Rapid electron transfer and inertness to axial ligand substitution; outer-sphere autoxidation	Dramatic facilitation of electron abstraction; fluorescence quenching; reversible redox reactions

as a whole may be of similar magnitude. Indeed, electrochemical or chemical oxidation of the diamagnetic cerium(IV) double-decker yielded a paramagnetic double-decker cation according to Scheme 5(b). The cation $Ce(OEP)_2^+$ was isolated as its hexachloroantimonate and shows a NIR absorption band at 1270 cm^{-1},[29(d)] in close proximity to the "original."

There are two other physical similarities between $(Bchl)_2$ and $Ce(OEP)_2$: (1) Contrary to monomeric (Bchl) or the lanthanoid monoporphyrins, neither the dimer $(Bchl)_2$ nor the bisporphyrinate shows any fluorescence.[29(h)] This is a very essential functional aspect. The nonfluorescence discriminates the special pair from the other chlorophyll molecules present in the photosynthetic apparatus, especially from the so-called "antenna" chlorophylls which serve to harvest light quanta and to transduce them to the special pair by re-emission after absorption. (2) Compared with a suitable magnesium monotetrapyrrole, namely the monomeric (Bchl) or Mg(OEP), the bistetrapyrroles are much more easily oxidized to the cationic species. This is another feature that helps to locate the site of electron ejection to the special pair which is then more easily oxidized than the antenna chlorophylls. The cation $Ce(OEP)_2^+$ shows a broad ESR absorption at $g = 1.9924$ at room temperature,[29(i)] close to the value expected for an organic radical.

5. CONCLUSION

As a whole, there are structural, spectroscopic, and functional aspects that justify regarding the osmochromes as cytochrome b_5

or c models on the one hand, and the cerium(IV) bisporphyrinates as models of the "special pair" of the photosynthetic apparatus in purple bacteria on the other hand. Hence, tetrapyrrole complexes containing unnatural metals may well serve as models for biologically active tetrapyrrole complexes. The arguments are summarized in Table I.

Acknowledgments

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7. Abbreviations used: $(\text{proto-IX})^{2-}$, $(\text{OEP})^{2-}$, $(\text{P})^{2-}$, $(\text{TTP})^{2-}$, dianions of protoporphyrin IX, octaethylporphyrin, a general porphyrin, and tetra(p-tolyl)porphyrin, respectively; $(\text{acac})^{-}$, 2,4-pentanedionate; 1-Meim, 1-methylimidazole; Py, pyridine; THT, tetrahydrothiophene; Bchl, bacteriochlorophyll.

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