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An Electrochemical and Spectroelectrochemical Investigation of Metal-Substituted Bacteriochlorophyll *a*

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Abstract: A series of transmetalated bacteriochlorophyll *a*, [M]-BChla (M = Mn, Zn, Cd, Co, Ni, Cu, Pd), and the corresponding 13^2-hydroxy derivatives, [M]-OH-BChla, were investigated by low-temperature cyclic voltammetry and by spectroelectrochemistry in the vis/near-IR range. This is the first systematical investigation of bacteriochlorin macrocycles with electrochemical methods. In the cyclic voltammetry measurements, we were able to generate the dianions and dications of all species. Furthermore, we have observed the trianions for the Ni and Cu derivatives as well as the tetraanions of the Co derivatives. With the exception of the tri- and tetraanions, the redox potentials exhibit a linear relationship with the E_N/r_i values (E_N = electronegativities, r_i = radius of the divalent metal ion). Deviations are observed for the Ni, Co, and Cd derivatives and are interpreted in terms of structural deformations. Kinetic electrochemical measurements show that the native BChla has the highest rate constant for the heterogeneous charge transfer. Using VIS/near-IR spectroelectrochemistry, we were able to distinguish between metal-centered and ring-centered redox processes. For the Co and Mn derivatives, metal-centered redox reactions are observed. A "π-anion-state-marker" band positioned between 927 and 974 nm is proposed.

Introduction

Bacteriochorophyll *a* (BChla) (for structure, see Figure 1) is part of the bacterial photosynthetic reaction center (RC).[1] The cofactors form two branches (A and B), of which only the A branch is involved in the electron transfer (ET).[2,3] ET takes place between the primary donor P870, a dimer of BChla, via bacteriopheophytin (BPheo) (H_A) to the acceptor quinone (Q_A). Whether the monomeric BChla (B_A), located between the primary donor and the H_A, is involved in the ET is discussed controversely. Early studies with sufficient time resolution indicated that B_A is not involved in the ET,[4] and a direct ET from the primary donor to H_A requires a "superexchange" mechanism.[3] More recently, measurements of an additional ~1 ps time constant in *Rhodobacter sphaeroides* (*Rb. sphaeroides*) raised the possibility that $P^+B_A^-$ is an electron tranfer intermediate.[5]

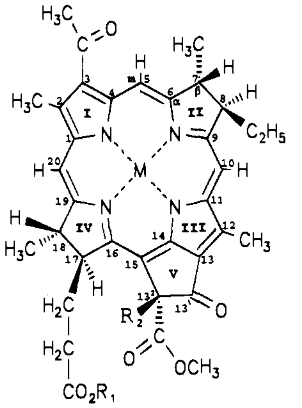

Figure 1. Structures of transmetalated bacteriochlorophylls [M]-BChla (M = H_2, Mg, Zn, Mn, Cd, Co, Ni, Cu, Pd) and the respective 13^2-hydroxy derivatives [M]-OH-BChla; ($R_1 = C_{20}H_{39}$, R_2 = H, OH).

B_A (and also B_B) can be substituted by chemically modified pigments in order to examine structure–function relationships in RC. For instance, monomeric BChla was substituted by 13^2-hydroxybacteriochlorophyll *a* and [3-vinyl]-13^2-hydroxybacteriochlorophyll *a* for BChla in *Rb. sphaeroides*.[6] In the latter case, the primary ET rate was lowered by a factor of approximately 10.

It has been known for some time that the substitution of the central metal in various porphyrin systems ([M]-Por) and transmetalated chlorophylls ([M]-Chla) alters their redox potentials.[7] Recently, Hartwich et al. succeeded in the substitution

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of the central Mg(II) ion of BChla and its respective 13^2-hydroxy derivative by the divalent ions of the transition metals Mn, Co, Ni, Cu, Zn, Pd, and Cd.[8] This opens the possibility to test whether the electrochemistry of the metal-substituted bacteriochlorophylls ([M]-BChla) and the respective 13^2-hydroxy derivatives ([M]-OH-BChla) correspond to that of normal porphyrins or [M]-Chla. Furthermore, electrochemistry yields the *in vitro* redox potentials, and thus provides the basis for a systematic change in the $B_{A/B}$ energetics in RCs of purple bacteria.

The visible absorption spectra of [M]-Por and [M]-Chla are well known.[8,9] Much less is known about the absorption spectra of the monoanions and monocations of [M]-Por.[10] Additionally, the four absorption bands of [M]-Por are not well resolved.[9] Therefore, it is difficult to get reliable relationships between structure and optical spectra. The [M]-BChla, however, show four well-resolved absorption bands[8,9c] and should thus facilitate correlations between structure and optical spectra. Moreover, spectroscopical data on the monoanions of [M]-BChla are needed to determine a participation of B_A in photosynthetic ET by spectroscopic methods.

In this paper, we present an electrochemical investigation of the [M]-BChla and [M]-OH-BChla in highly purified, superdry tetrahydrofurane (THF). We also report the visible and near-infrared absorption spectra (vis/near-IR) of the monocations and monoanions of [M]-BChla. We emphasize that this is the first investigation of bacteriochlorin-type systems.

Materials and Methods

Pigments were prepared by the method of Hartwich et al.[8] They were purified on silica gel (1.5% sodium ascorbate admixed) with toluene/acetone/triethylamine (88/10/2, v/v/v) as eluent and characterized by ^{1}H NMR, absorption, fluorescence, and FAB mass spectra. All pigments are sensitive to oxidation by oxygen and light.

Electrochemical Measurements. The solvent THF (Fluka, HPLC grade) was purified by distillation with Na/K alloy under nitrogen for 2 h. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as the electrolyte (0.1 M). It was purified according to a procedure described elsewhere.[11]

All electrochemical measurements were carried out in specially designed cells with an internal drying column filled with highly activated alumina.[12] As working electrodes, we have used either a Pt electrode (0.5 or 1 mm in diameter) or a Au electrode (0.25 mm in diameter) sealed in soft glass. A Pt wire, wrapped around the glass of the working electrode, was used as the counter electrode. The reference electrode was a Ag wire, immersed in the electrolyte solution. Potentials were calibrated with cobaltocenium perchlorate ($Cc^+ClO_4^-$) ($E_{1/2}^-(Cc^+/Cc^0) = -0.96$ V vs Ag/AgCl). All experiments were carried out in the dark and in oxygen free solution.

Cyclic voltammetry was performed with a JAISSLE potentiostat-galvanostat IMP 88 and a PAR 175 programmer. Data were recorded with a Philips Model PM 8131 $X-Y$-recorder.

The experiments were carried out in a temperature range between −65 °C and −20 °C in order to avoid adsorption effects and followup reactions. Moreover, at these temperatures the solution was stable over several days, thus facilitating a profound investigation of the pigments. A positive feedback IR compensation was used throughout all experiments.

Spectroelectrochemical Measurements. THF was used as the solvent with 0.3 M $TBAPF_6$ as the electrolyte. Purification was done as above. All measurements were carried out in a specially designed IOTTLE cell (infrared and optical transparent thin-layer electrochemical cell) described elsewhere.[13] This cell has a path length of 55 μm, allows measurements in the UV/vis/IR spectral range (190−10000 nm), and is equipped with a three-electrode configuration for constant potential electrolysis (CPE). The working electrode was a 6 μm Au minigrid (Buckbee-Mears Co., St. Paul, MN) sputtered with Pt. A Pt sheet was used as the counter electrode and a Ag wire served as the reference electrode. Potentials were calibrated against cobaltocene. In each case, the potential was stepped 200 mV beyond the redox potential of the monocations and monoanions. CPE was carried out with a computer-controlled potentiostat built in our laboratory (Sevenich-Gimbel Model II). Optical absorption spectra in the range of 400−1100 nm were recorded at 5 °C on a modified Cary 14 computer-controlled spectrophotometer. For experimental reasons, the temperature could only be lowered down to 5 °C. CPE was completed after 10 min for the forward and backward reactions. Under these conditions, no followup reactions were observed except where stated. A data acquisition program ("MSPEK") developed by S. Grzybek in our laboratory was used to control the spectrophotometer and the potentiostat.

Results and Discussion

THF was chosen as the solvent because of its wide "potential window"(−3.2 to +1.4 V vs Ag/AgCl, Pt working electrode).

A problem with chlorophylls is aggregation, which affects the electrochemical[14] and spectroscopical properties.[15] As judged from the Q_x band at 594 nm, BChla is hexacoordinated and therefore monomeric in THF,[8] although *in vivo* the Q_x band for the pentacoordinated BChla is positioned around ~590 nm likewise. However, this red shift *in vivo* is an effect of the protein environment.[6d]

Transition metals like Ni and Pd are known to form tetracoordinated species[16] and are, therefore, not prone to Katz-type aggregates between the central metal and peripheral carbonyl groups.[15] All other metals carried an extra ligand as judged from the Q_x band position in diethyl ether.[8] These band positions were similar to those in dioxane, where circular dichroism (CD) gave no indication by either M—C=O aggregation or π-interactions.[8]

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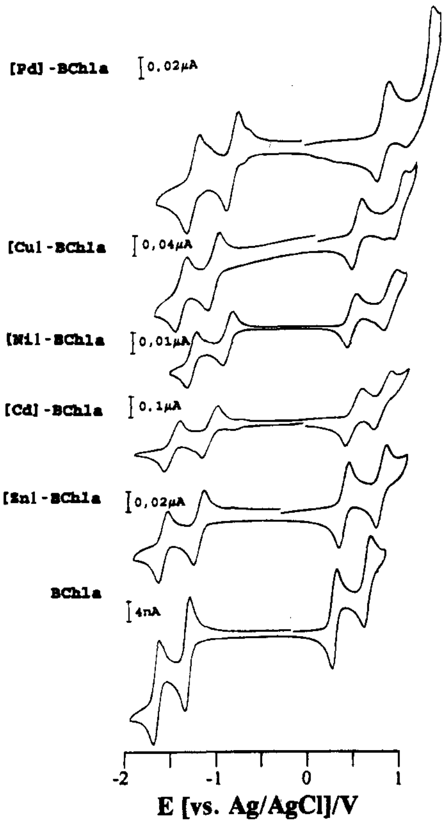

Figure 2. Cyclic voltammograms of transmetalated bacteriochlorophylls [M]-BChla (M = Zn, Cd, Ni, Cu, Pd) and BChla in THF/0.1 M TBAPF$_6$. The following conditions were used: (BChla) $c \cong 10^{-4}$ M, $v = 0.01$ V/s, $T = 228$ K; ([Zn]-BChla) $c \cong 1.5 \times 10^{-4}$ M, $v = 0.1$ V/s, $T = 209$ K; ([Cd]-BChla) $c \cong 2 \times 10^{-4}$ M, $v = 0.05$ V/s, $T = 218$ K; [Ni]-BChla) $c \cong 8 \times 10^{-5}$ M, $v = 0.02$ V/s, $T = 233$ K; ([Cu]-BChla) $c \cong 1.9 \times 10^{-4}$ M, $v = 0.1$ V/s; $T = 228$ K; ([Pd]-BChla) $c \cong 2.2 \times 10^{-4}$ M, $v = 0.1$ V/s, $T = 209$ K. All cyclic voltammograms were measured with a 0.5 mm ϕ Pt working electrode, except that for [Cd]-BChla (1 mm ϕ Pt working electrode).

Electrochemistry of [M]-BChla. Ring-centered redox reactions. Figure 2 shows the cyclic voltammograms of [M]-BChla (M = Zn, Cd, Ni, Cu, Pd) and BChla (cyclic voltammograms of the respective [M]-OH-BChla and BPheoa are similar). Table 1 lists the redox potentials of all [M]-BChla and [M]-OH-BChla investigated. The value of $\Delta(E_{1/2}^{-} - E_{1/2}^{2-})$ is 0.35 ± 0.08 V. The values of $\Delta(E_{1/2}^{2+} - E_{1/2}^{+})$ are somewhat more scattered and lie between 0.25 V ([Cd]-OH-BChla) and 0.47 V ([Cu]-BChla). These data imply ring-centered redox reactions by comparison with similar redox reactions in [M]-Por and [M]-Chl.[7]

To distinguish ring-centered redox reactions from metal-centered ones, Fuhrhop[7] established the empirical "electrochemical rule" for [M]-Por. It states that in the case of ring-centered redox reactions the difference between the redox potentials of the monoanions and the dianions $\Delta(E_{1/2}^{-} - E_{1/2}^{2-})$ is 0.42 ± 0.05 V and that between the monocations and the dications $\Delta(E_{1/2}^{2+} - E_{1/2}^{+})$ is 0.26 ± 0.05 V for [M]-OEP (OEP = 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin dianion). For [M]-Chla, the corresponding values are in the same range.[7d] On the other hand, a metal-centered redox reaction generally does not obey the electrochemical rule.

Since the redox behavior of a compound is related to the energy levels of its molecular orbitals (MO), one can relate the $E_{1/2}^{-}$ to the lowest unoccupied molecular orbital (LUMO) and $E_{1/2}^{+}$ to the highest occupied molecular orbital (HOMO). $\Delta(E_{1/2}^{+} - E_{1/2}^{-})$ lies between 1.52 and 1.6 V for both [M]-BChla and [M]-OH-BChla (M = Zn, Cd, Cu, Pd). The calculated value of $\Delta(E_{1/2}^{+} - E_{1/2}^{-})$ for BChla is 1.54 V.[17] It agrees well with our values measured by cyclic voltammetry. For the Ni derivatives, $\Delta(E_{1/2}^{+} - E_{1/2}^{-})$ is 1.31 V. This can be explained by a deformation from a planar form toward a nonplanar conformer by ruffling of the macrocycle, as will be discussed shortly.

Table 1. Redox Potentials of Transmetalated Bacteriochlorophylls [M]-BChla and Their Corresponding 13^2-Hydroxy Derivatives [M]-OH-BChla

compound	$E_{1/2}^{4-}$[a]	$E_{1/2}^{3-}$	$E_{1/2}^{2-}$	$E_{1/2}^{-}$	$E_{1/2}^{+}$	$E_{1/2}^{2+}$
BPheoa			−1.35	−1.01	0.66	0.95
BChla			−1.58	−1.24	0.35	0.69
13^2-OH-BChla			−1.57	−1.25	0.34	0.74
[Mn]-BChla[b,e]			−1.5	−1.22	0.69	0.91
[Mn]-OH-BChla[b,e]			−1.51	−1.22	0.71	
[Zn]-BChla			−1.52	−1.15	0.38	0.77
[Zn]-OH-BChla			−1.48	−1.13	0.42	0.85
[Cd]-BChla			−1.46	−1.09	0.43	0.68
[Cd]-OH-BChla			−1.43	−1.05	0.48	0.74
[Co]-BChla[e]	−3.0[c]	−2.76	−1.54	−1.03[d]	0.34	0.79
[Co]-OH-BChla[e]	−3.04	−2.7	−1.55	−1.04[d]	0.35	0.82
[Ni]-BChla		−2.8[c]	−1.31	−0.95	0.36	0.76
[Ni]-OH-BChla		−2.76[c]	−1.33	−0.95	0.36	0.78
[Cu]-BChla		−2.62[c]	−1.42	−1.09	0.42	0.86
[Cu]-OH-BChla			−1.31	−1.09	0.42	0.86
[Pd]-BChla			−1.37	−0.94	0.66	1.06
[Pd]-OH-BChla			−1.35	−0.93	0.67	1.06

[a] All potentials in volts vs Ag/AgCl, measured in THF/0.1 MTBAPF$_6$ in the temperature range between −65 °C and −20 °C. [b] Metal-centered oxidation Mn(II)/Mn(III) at −0.07 V vs Ag/AgCl. [c] Quasireversible peak. [d] Metal-centered reduction Co(II)/Co(I). [e] Signals are disturbed by adsorption effects.

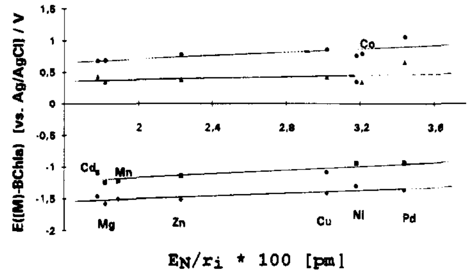

Figure 3. Correlation of the redox potential of a series of transmetalated bacteriochlorophylls, [M(II)]-BChla (M = Zn, Mn, Cd, Ni, Co, Cu, Pd), BChla, and BPheoa with E_N/r_i values of the divalent central metal. E_N is the Pauling electronegativities and r_i is the radius of the respective divalent metal ion: ◆, dianion; ■, monoanion; ▲, monocation; ●, dication).[18]

Correlations between the E_N/r_i values (r_i = radius of the divalent metal ion)[18] of the central metals versus the redox potentials of all observed redox states are shown in Figure 3.

As seen in Figure 3, the redox potentials show a systematic shift with E_N/r_i-values for all redox states. This trend is similar to that observed for the [M]-Chla[7d] and [M]-Por[7] for E_N alone and is rationalized in terms of an electron density decrease in the HOMO and LUMO of the bacteriochlorin π-system as a consequence of increased charge density and electron-withdrawing power of the more electronegative central metal.

The mismatches seen for the reduction and oxidation of [Cd]-BChla and the oxidation of [Ni]-BChla and [Co]-BChla in this correlation can be rationalized by structural deviations from planarity.

The ionic radius of Cd(II) (95 pm) is much larger than that of the other metals including the Mg(II) ion (72 pm) of native

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BChla. This size is too large to be accommodated by the geometry of the macrocycle. It is therefore displaced from the plane formed by the four nitrogen atoms and forms an out-of-plane square-pyramidal complex. This is also supported by the fact that it is easily transmetalated and demetalated (e.g., with acids as weak as water).[8]

The Ni and Co derivatives exhibit 10- to 5-fold stronger CD intensities than the other complexes in the series of [M]-BChla.[8] Since CD is very sensitive to geometric deformations, we assume that in the Co and Ni complexes the macrocycle is distorted toward a nonplanar form. This is reasonable in view of the small ionic radii (60 pm for low-spin Ni(II) and 65 pm for Co(II)), which tend to shorten the metal–nitrogen bonds and thus deform the macrocycle.[18,19]

In the four-orbital model,[9,10] the visible absorption bands of the [M]-BChla are composed of transitions among HOMO − 1 (a_{2u}), HOMO (a_{1u}), LUMO (e_{gx}), and LUMO + 1 (e_{gy}).[20] The electron density for a_{2u} is highest close to the inner hole of the macrocycle, especially at the nitrogen atoms, for a_{1u} it is mostly at the α-carbon atoms (C-1,4,9,11,14,16,19).[9c,21] e_{gx} and e_{gy} have approximately identical electron densities, which are rotated by 90°, and concentrate on all β-carbons (C-5,10,15,20), on the outer carbons of two opposite rings and to a minor extent on the α-carbons of these rings. An out-of-plane movement of the α-carbons, as is necessary for distortion, should have no significant effect on the e_{gx}, e_{gy}, and a_{2u} orbitals, since there is almost no electron density on the α-carbons in these MOs. The a_{1u}, however, carries most of its electron density on the α-carbons and is thus destabilized by distortion from planarity. The result is a decreased $E_{1/2}^{+}$ value for [Ni]-BChla and [Co]-BChla, as is observed here. The decreased HOMO–LUMO gap, observed for the [Ni]-BChla, can thus be attributed to a distortion of the macrocycle. A decrease in the $E_{1/2}^{+}$ value is also described by Fajer et al.[22] for nonplanar [Ni]-Por. We cannot observe this effect for the [Co]-BChla since the first reduction is a metal-centered instead of a ring-centered one (see below).

Since this is the first systematical work on bacteriochlorin systems, we have tested whether the central metal excerts a similar influence on the electronic states in [M]-Por and [M]-BChla. We have correlated our redox potentials with the redox potentials of [M]-TPP (TPP = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin dianion) (Figure 4).

As expected, we obtained a good correlation between the [M]-TPP and [M]-BChla. Watanabe and Kobayashi[7d] obtained a similar plot in the case of [M]-Chla. Thus, metallohydroporphyrins show the same redox behavior upon exchange of the central metal as metalloporphyrins. The mismatch in the linear correlation is due to the difference in the avarage single excitation energy in [M]-BChla (1.54 V)[17] and [M]-TPP (2.2 V).[23]

For the [M]-OH-BChla, we have obtained a E_N/r_i correlation similar to that for the [M]-BChla. The redox potentials shift slightly higher (up to 0.04 V) than the corresponding potentials of the unsubstituted [M]-BChla. In the case of [Cu]-OH-BChla, the redox potentials of all redox states are raised by 0.11–0.2 V. A possible explanation for the slightly higher redox potentials is that, by introduction of a hydroxy group at position C-13,[2] the otherwise possible keto–enol tautomerism is disconnected. Thus, the π-electron increasing effect of this tautomerism is excluded, leading to a stabilization of the MOs.

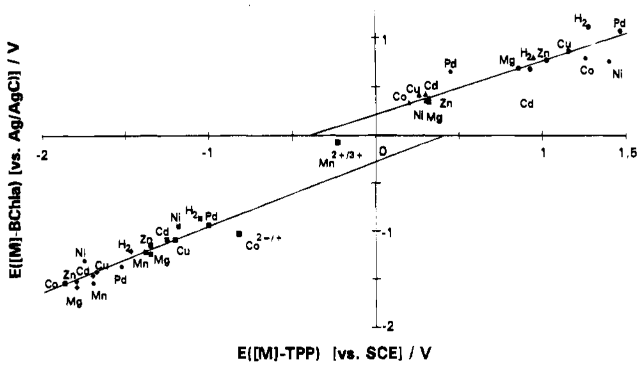

Figure 4. Redox potential correlation between transmetalated bacteriochlorophylls [M]-BChla and the respective metal-substituted 5,10,-15,20-tetraphenyl-21*H*,23*H*-porphyrins [M]-TPP, measured at room temperature (for legend see Figure 3).[7]

The relatively high stabilization in the case of [Cu]-OH-BChla cannot be answered unequivocally at the moment. We have speculated about a deformation of the macrocycle, but there is presently no evidence for it from CD.

For [Ni]-BChla, [Ni]-OH-BChla and [Cu]-BChla, even the trianions could be generated . $\Delta(E_{1/2}^{2-} - E_{1/2}^{3-})$ is 1.2 V for [Cu]-BChla, 1.49 V for [Ni]-BChla, and 1.43 V for [Ni]-OH-BChla.

Clack and Hush[24] observed four reduction peaks in the case of Mg-, Cu-, and Zn-substituted porphyrins. They pointed out that $\Delta(E_{1/2}^{2-} - E_{1/2}^{3-})$ is 0.75 ± 0.06 V and $\Delta(E_{1/2}^{3-} - E_{1/2}^{4-})$ is 0.24 ± 0.06 V. Subsequent studies showed that these reductions involved a two-electron transfer step with simultaneous uptake of protons.[25] Cosmo et al.[26] studied the generation of the trianion and tetraanion of [Zn]-OEP in superdry dimethylamine, where protons and other impurities can be excluded. The value for $\Delta(E_{1/2}^{2-} - E_{1/2}^{3-})$ is 0.81 V and that for $\Delta(E_{1/2}^{3-} - E_{1/2}^{4-})$ is 0.17 V, rather close to the values reported for the redox reaction involving proton uptake.

Our $\Delta(E_{1/2}^{2-} - E_{1/2}^{3-})$ values (between 1.2 V for [Cu]-BChla and 1.49 V for [Ni]-OH-BChla) are significantly higher (0.34–0.68 V) than the value reported by Clack and Hush. This can be explained by the altered electronic properties in the [M]-BChla compared to the [M]-Por. The e_{gy} is shifted to higher energies due to the reduced double bonds of rings II and IV in the bacteriochlorin system compared to [M]-Por.

Metal-Centered Redox Reactions. [Co]-BChla, [Mn]-BChla and their hydroxy derivatives not only undergo redox reactions on the ring but also can show a change of the redox state of the central metal. The cyclic voltammograms of [Co]-BChla and [Mn]-BChla are shown in Figure 5 (the cyclic voltammograms of the respective hydroxy derivatives are similar).

[Co]-BChla. We observed ring-centered redox oxidations for the monocation and dication. The value for $\Delta(E_{1/2}^{2+} - E_{1/2}^{+})$ is 0.45 V for [Co]-BChla. At negative potentials, we have observed four distinct reduction peaks. The value for

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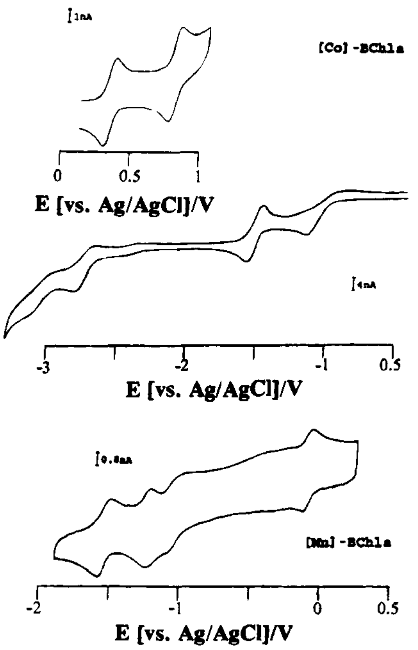

Figure 5. Cyclic voltammograms of [Co]-BChla ($c \cong 2 \times 10^{-4}$ M, T = 217 K, $\nu = 0.05$ V/s for the oxidation and $\nu = 0.02$ V/s for the reduction. A 0.25 mm ϕ Au working electrode for the reduction and a 1 mm ϕ Pt working electrode for the oxidation) and of [Mn]-BChla ($c \cong 1.5 \times 10^{-4}$ M, $\nu = 0.1$ V/s, $T = 212$ K; 0.25 mm ϕ Au working electrode).

$\Delta(E^{-}_{1/2} - E^{2-}_{1/2})$ is 0.51 V, the highest observed in the series of [M]-BChla. We surmised that the monoanion product is not a ring-centered redox product but rather the result of reduction at the central metal, as shown by the spectroelectrochemical measurements reported below. Fuhrhop[7] reported a value of −1.02 V vs Ag/AgCl for the reduction of [Co(II)]-OEP to [Co(I)]-OEP. This agrees well with our measured value. Nevertheless, this has to be verified by electron spin resonance (ESR) measurements.

The first reduction wave leading to the metal-centered reduction product [Co(I)]-BChla seems to be irreversible at a scan rate of 0.02 V/s. When the scan rate is increased to 0.1 V/s, the irreversible peak is split into two peaks. Increasing the scan rate further increases the second peak, the postwave, with respect to the initial, more positive peak. Thus, we presumed that the postwave is due to an adsorption effect at the electrode surface. The relative intensity of an adsorption peak in contrast to a peak associated with diffusion-controlled ET is dependent on the scan rate and concentration. An increase in the scan rate should result in an increased adsorption peak relative to the diffusion-controlled one.[27] Adsorption is known to cause prewaves in the case of the one-electron reduction of BChla on Hg in dimethyl sulfoxide (DMSO).[28] By contrast, we observed a postwave. This then might be due to a strong adsorption of the neutral species at the electrode surface, as described by Wopschall and Shain,[29] whereas a prewave appears upon adsorption of the reduced species. This is supported by the spectroelectrochemical measurements (see below). There is no indication for an irreversible electron transfer reaction, but there is at least for a quasi-reversible one.

[Co]-BChla shows a third and fourth reduction peak. $\Delta(E^{4-}_{1/2} - E^{3-}_{1/2})$ is 0.27 V for [Co]-BChla. According to the electrochemical rule, this is an indication that both peaks are due to ring-centered redox reactions. $\Delta(E^{2-}_{1/2} - E^{3-}_{1/2})$ has a value of 1.22 V for [Co]-BChla. This value is similar to the values obtained for the Ni and Cu derivatives. Since protic and other impurities were excluded in our special cell, we conclude that the reduction waves must be due to formation of the trianion ([Co(I)]-BChla^{2-}) and tetraanion ([Co(I)]-BChla^{3-}). These and the related species of the Ni and Cu complexes, to our knowledge, are the first data on tri- and tetraanions of naturally occuring cyclic tetrapyrroles.

Table 2. Kinetic Parameters of Transmetalated Bacteriochlorophylls [M]-BChla (M = Mg, Zn, Ni, Cu, Pd) and Their Corresponding 13^2-Hydroxy Derivatives [M]-OH-BChla (M = Mg, Zn, Ni, Cu)[a]

compound	D (cm^2 s^{-1})	T (K)	$k°$ (cm s^{-1})
BChla	8×10^{-7}	228	2×10^{-2}
13^2-OH-BChla	4×10^{-6}	227	9.2×10^{-3}
[Zn]-BChla	1.2×10^{-6}	228	5×10^{-3}
[Zn]-OH-BChla	2.3×10^{-7}	209	1.84×10^{-3}
[Ni]-BChla	1.8×10^{-6}	225	2.8×10^{-3}
[Ni]-OH-BChla	8×10^{-6}	225	4×10^{-3}
[Cu]-BChla	1.3×10^{-7}	228	1.54×10^{-3}
[Cu]-OH-BChla	1.2×10^{-7}	248	1×10^{-3}
[Pd]-BChla	4.3×10^{-7}	225	1.08×10^{-3}

[a] All parameters are calculated from cyclic voltammogramms in THF/0.1 M TBAPF$_6$.

[Mn]-BChla. Compared to other [M]-BChla, [Mn]-BChla shows an additional redox wave in the cyclic voltammogram at −0.07 V (Figure 5). Since the electrochemical rule does not hold for this peak, we suspected that this wave is due to a metal-centered redox process. Loach and Calvin reported a value of −0.18 V vs NHE for the reduction of Mn(III) to Mn(II) in manganese methylpheophorbide *a*, the first described manganese porphyrin-type complex.[30] Watanabe and Kobayashi[7d] reported a value of 0.0 V vs Ag/AgCl for the reduction of [Mn(III)]-Chla to [Mn(II)]-Chla. The assignment of the redox wave at −0.07 V to the reduction of [Mn(III)]-BChla to [Mn(II)]-BChla is also supported by the absorption spectra (see below).

All other observed waves in the cyclic voltammogram correspond to ring-centered redox reactions, as indicated by their $\Delta(E^{-}_{1/2} - E^{2-}_{1/2})$ and $\Delta(E^{2+}_{1/2} - E^{+}_{1/2})$ values of 0.28 and 0.29 V, respectively.

In Figure 5, one can observe a pronounced shoulder at more positive potentials at the first reduction peak. This prewave disappears when the scan rate is increased to 0.5 V/s (data not shown). This might be due to a preequilibrium, like, e.g., a conformational change of the macrocycle. However, in spectroelectrochemical measurements, we did not observe any indication of such a preequilibrium. Another possibility is an adsorption process of the π-anion of the Mn(II) species at the electrode surface. At the moment, we are not able to understand this prewave completely.

Measurements of Heterogeneous Kinetics. Cyclic voltammetry at varying scan rates can be used to measure ET rates of heterogeneous charge transfer reactions. The relationship between the peak separation ΔE_p and the rate constant for a heterogeneous charge transfer k^0 has been introduced by Nicholson.[31]

To calculate k^0, we had to measure D_R, the diffusion constant, which we did by using cyclic voltammetry. The values for k^0 and D_R are reported in Table 2 for BChla and [M]-BChla (M = Zn, Ni, Cu, Pd) and their hydroxy derivatives. We have measured k^0 in a temperature range between −65 and −20 °C

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Table 3. Absorption Band Positions in the Vis/Near-IR Region of the Neutral, Monoanion, and Monocation Species of Transmetalated Bacteriochlorophylls [M]-BChla and Their Corresponding 13^2-Hydroxy Derivatives [M]-OH-BChla[a]

compound	neutral [M(II)]		anion species		cation species		
	Q_x	Q_y			*b*		
BChla	594	771	637	992	423	680	866
[Mn]-BChla[c]	594	772	625	931	591		830
[Mn]-OH-BChla[c]	590	773	625	934	592		828
[Zn]-BChla	567	764	628	974	416	670	847,895
[Zn]-OH-BChla	561	764	634	970	414	670	879[e]
[Cd]-BChla	580	763	623	969		681	865[d]
[Cd]-OH-BChla	574	761	631	967	422	683	865[e]
[Co]-BChlad	540	763	567	816		664	
[Co]-OH-BChla[d]	537	766	562	815		663	
[Ni]-BChla	531	782	607	973	415	663	854[e]
[Ni]-OH-BChla	529	775	610	971	415	662	858[e]
[Cu]-BChla	552	771	616	968		669	888[e]
[Cu]-OH-BChla	547	774	624	969	413	670	879[e]
[Pd]-BChla	529	755	621	927	413	650	856[e]
[Pd]-OH-BChla	530	755		930	423	652	858[e]

[a] Experiments carried out in THF/0.3 M $TBAPF_6$ at T = 5°C. All values are in nanometers. [b] Absorption band of the oxidation product [M]-[3-acetyl]-Chla. [c] Metal-centered redox reaction Mn(II)/Mn(III). [d] Metal-centered redox reaction Co(II)/Co(I). [e] Broadened band structure.

at different scan rates (between 10 and 500 mV/s) and found no significant change in the k^0 values in this range.

The values for D_R are very low (10^{-7} to 8×10^{-6} cm²/s). However, the measurements were done at very low temperatures. Cotton and Heald[32] reported a value for the diffusion constant of 4.7×10^{-6} cm²/s at a platinum electrode in CH_2Cl_2 at 295 K for BChla measured with a rotating disk electrode. The decrease of our value for BChla by a factor of 6 at 228 K in THF appears to be reasonable. The k^0 values vary between 2×10^{-2} cm/s for BChla and 10^{-3} cm/s for [Cu]-OH-BChla. The value reported by Cotton and Heald[32] of 1.2×10^{-2} cm/s for BChla, measured under the same conditions as described above, agrees reasonably well with the value obtained here.

A reasonable explanation why Mg was chosen during the evolution as the central metal in BChla may be, among other reasons, its high ET rate as compared to other [M]-BChla.

Spectroelectrochemical Measurements. The vis/near-IR absorption spectra of the neutral species as well as of the monoanions and monocations of [M]-BChla and [M]-OH-BChla were recorded between 400 and 1050 nm (Table 3). The respective spectra of [Zn]-BChla, shown in Figure 6, are typical for most other [M]-BChla (M = Mg, Cd, Ni, Cu, Pd).

Absorption Spectra of the Neutral Species. All neutral species exhibit the absorption spectra typical for monomeric pigments. The position of the Q_y band ($a_{1u} \rightarrow e_{gx}$ transition) in the near infrared (near-IR) lies between 755 nm ([Pd]-BChla) and 783 nm ([Ni]-BChla); that of the visible Q_x band ($a_{2u} \rightarrow e_{gy}$ transition) shows much larger shifts between 529 nm ([Pd]-BChla) and 596 nm (BChla). The values for BChla agree well with the value reported by Mäntele et al.[33] in THF/0.1 M $TBAPF_6$. All spectra are similar to those reported by Hartwich et al. in diethyl ether.[8] The exceptions for the Q_x band for [Zn]-BChla (558 nm (diethyl ether) vs 567 nm (THF)) and [Cu]-BChla (538 nm (diethyl ether) vs 553 nm (THF)) are probably due to a shift in the axial ligation equilibrium by changing the solvent from diethyl ether to THF. The red shift in the Q_y band for the Ni derivatives with respect to BChla mirrors the electrochemically determined differences in $\Delta(E^{+}_{1/2} - E^{-}_{1/2})$ and thus can be attributed to a distortion of the planar macrocycle. This is also reported for various nonplanar [Ni]-Por.[22]

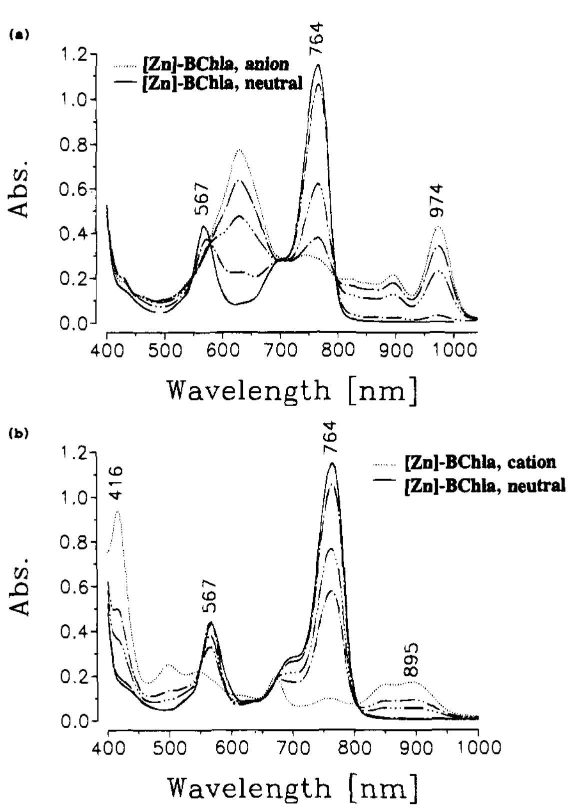

Figure 6. (a) Visible and near-infrared absorption spectra of the neutral and the fully evolved monoanion of [Zn]-BChla after electrolysis at −1.4 V vs Ag/AgCl in THF/0.3 M $TBAPF_6$. (b) Visible and near-infrared absorbance spectra of the neutral species and the fully evolved monocation of [Zn]-BChla after electrolysis at 0.6 V vs Ag/AgCl in THF/0.3 M $TBAPF_6$.

Absorption Spectra of the Monoanions. As compared to the monocation, there is little information about the monoanions of BChla, Chla, or the [M]-Por.[10,34] Such information is of general interest, because the monoanion is discussed as an intermediate in photosynthesis.[5] Spectra obtained for the first reduction step show up to four clear isobestic points. π-anion formation results in a decrease of the Q_y band, as reported by Mäntele et al.[33] and Fajer et al.[34a] for the parent compound BChla. Reoxidation of the anion species to the neutral species shows a reversibility of 80−100%. The most prominent features are two new absorption bands around 630 nm, and one in the near-IR region between 927 and 974 nm. In MO calculations of the monoanion of BChla,[9d,17,35] these bands were predicted, albeit with lower intensities. No side products are observed during CPE time.

Fajer et al.[35a] pointed out that the near-IR band of the monoanion of BChla is a marker band. The results presented here clearly show that this statement can be generalized to the π-anion radicals of [M]-BChla.

The spectra of the monoanions of the Co derivatives differ from those of all other π-monoanions of [M]-BChla (Figure

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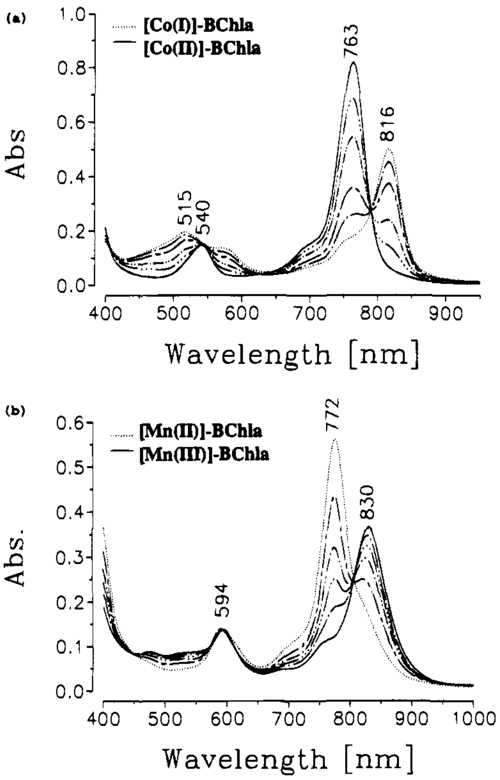

Figure 7. Visible and near-infrared absorption spectra of the transmetalated bacteriochlorophylls undergoing metal-centered redox processes: (a) neutral and monoanionic species of [Co]-BChla in THF/0.3 M TBAPF$_6$ after electrolysis at -1.5 V vs Ag/AgCl. (b) Neutral and monocationic species of [Mn]-BChla in THF/0.3 M TBAPF$_6$ after electrolysis at 0 V vs Ag/AgCl.

7a). Anion formation is accompanied with a 53 nm red shift of the Q_y band. The intensity of this band decreases by only 50%, whereas the near-IR band around 950 nm is missing. Since only the Q_x band is sensitive for axial ligation in bacteriochlorin systems,[8] we can exclude a ligation effect for the red shift of the Q_y band for the Co derivatives. We conclude that reduction takes place at the central metal instead of at the ring. Wollberg and Manassen[36] reached the same conclusion for [Co]-TPP.

Absorption Spectra of the Monocations. The isosbestic points in the monocation absorption spectra are less well defined than in monoanion formation (Figure 6). This is most obvious in the region between 630 and 680 nm, where a new absorption band appeared. Its intensity increases with prolonged CPS time, and does not decrease after reduction back to the neutral species. The dehydrogenation product of BChla, [3-acetyl]-Chla, has a characteristic absorption in this region.[37] In analogy, we assign the irreversibly formed products to chlorin structures. A new absorption band in the Soret region (between 400 and 430 nm) is also due to this product type.

In the near-IR region, a slight increase in intensity was observed. There is again one exception of this general behavior: the one-electron oxidation absorption spectra of the Mn derivatives differ strongly from the π-radical cation spectra (Figure 7b). Watanabe and Kobayashi[7d] and Loach and Calvin[30] obtained a spectrum for the oxidation for [Mn(II)]-Chla similar to that for [Mn(III)]-Chla and manganese methylpheophorbide *a*; Boucher[38] reported this one-electron oxidation for various [Mn]-Por. All these spectra resemble the one-electron reduction absorption spectra of the Co derivatives. This is a clear sign that the central metal is the redox site instead of the ring. Again, the effect of a change in axial ligation can be excluded (see above).

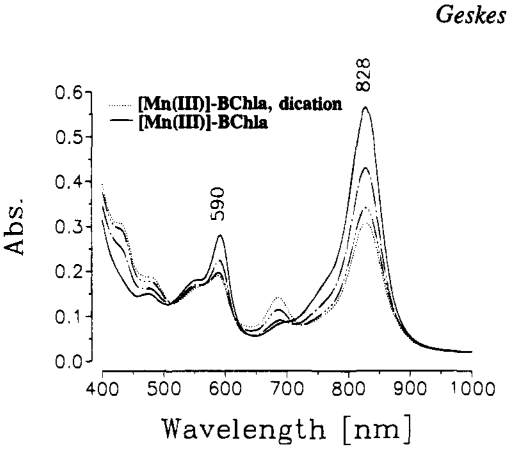

Figure 8. Visible and near-infrared absorption spectra of [Mn(III)]-OH-BChla at 0.0 V vs Ag/AgCl and of the dication [Mn(III)]-OH-BChla$^{\bullet+}$ after electrolysis at 0.8 V vs Ag/AgCl in THF/0.3 M TBAPF$_6$.

We have also obtained the two-electron oxidation absorption spectrum for the [Mn]-OH-BChla (Figure 8). Like the absorption spectra of [M]-BChla undergoing ring-centered oxidation, it is characterized by the bleaching of the Q_y and Q_x bands and the appearance of the red-shifted Soret band. Thus, the second-electron oxidation step generates the dication [Mn(III)]-OH-BChla$^{\bullet+}$ with the typical π-monocation spectra for an oxidized bacteriochlorin ring system. The same is observed for the oxidation of [Co(III)]-TPP and [Fe(III)]-TPP.[36]

Conclusions

In this paper, the first detailed electrochemical and spectroelectrochemical investigation of [M]-BChla and their 13^2-hydroxy derivatives [M]-OH-BChla is described. In particular, the dianions and dications of all [M]-BChla and [M]-OH-BChla could be generated. In a few cases, we obtained the trianions (M = Cu, Ni) as well as the tetraanions (M = Co). These are the first highly reduced anions observed for naturally occurring metal-substituted porphyrin systems.

The measured redox potentials correlate well with the E_N/r_i-values. Within the examined range of the E_N/r_i-values, both the HOMO and LUMO are changed by about 2000 and 1900 cm^{-1}, respectively, indicating a Q_y transition which is almost independent of the E_N/r_i values. The inductive influence of the central metal in this series of [M]-BChla can now be specified. From shifts in the B_y ($a_{2u} \rightarrow e_{gy}$ transition) and Q_x ($a_{2u} \rightarrow e_{gx}$ transition) on the order of 2300 and 1600 cm^{-1}, respectively, it was derived earlier that $\Delta E_{a_{2u}} > \Delta E_{a_{1u}} \approx \Delta E_{e_{gx}} \approx \Delta E_{e_{gy}}$.[8] With the data reported here, the maximum of the energetic shift in the series of [M]-BChla is $\Delta E_{a_{2u}} \approx 3600$ cm^{-1} $> \Delta E_{a_{1u}} \approx 2000$ cm^{-1} $\geq \Delta E_{e_{gx}} \approx 1900$ cm^{-1} $\geq \Delta E_{e_{gy}} \approx 1400$ cm^{-1}. Furthermore, in the case of the Co, Cu, and Ni derivatives, the e_{gy} orbital is accessible for reduction, providing the tri- and tetraanions of these species. Deviations from the E_N/r_i correlation with the redox potentials for the Cd, Co, and Ni derivatives can be explained in terms of structural deformations. In the latter two cases, a destabilization of the a_{1u} MO through distortion of the planar macrocycle toward a nonplanar form results in a decreased $E_{1/2}^{+}$ value. The red shift in the Q_y transition with respect to BChla in these derivatives mirrors the electrochemical data. In the Cd derivatives, the Cd(II) ion is sitting atop of the planar porphyrin plane.

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Although a thorough analysis of the electrochemical behavior can distinguish between ring-centered and metal-centered redox reactions in porphyrin systems, spectroelectrochemical measurements are the method of choice to discern the redox sites. Using optical absorption spectroscopy, we can show that the Co and Mn derivatives undergo metal-centered redox reactions.

In the π-radical anion absorption spectra, we established an absorption band in the near-IR as an "π-anion-state marker". The position of this absorption band is altered with respect to the central metal between 927 and 974 nm.

Kinetic electrochemical measurements indicated that the naturally occurring BChla exhibits the highest rate constant of the heterogeneous charge transfer of all examinined [M]-BChla. This could play a role in the choice of Mg as the central metal in the evolutionary process leading to the complex photosynthetic apparatus.

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