Metal Complexes with Tetrapyrrole Ligands, LXV[1]

Generation and ESR Spectra of the Cation Radicals of Bis(octaethylporphyrinato)zirconium(IV) and Bis(chelate)(octaethylporphyrinato)zirconium(IV) Complexes

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Electron spin resonance spectra of the cation radicals $\mathbf{A}^+$ and $\mathbf{B}^+$ generated from a zirconium(IV) monoporphyrin, bis(acetato)(octaethylporphyrinato)zirconium(IV), $Zr(OEP)(OAc)_2$ (**A**), and bis(octaethylporphyrinato)zirconium(IV), $Zr(OEP)_2$ (**B**), respectively, have been measured at 293 and 77 K. $[Zr(OEP^{\bullet})(OAc)_2]Br$ ($\mathbf{A}^+Br^-$) has been prepared in situ by oxidation of **A** with bromine, $[Zr(OEP^{\bullet/2})_2]PF_6$ ($\mathbf{B}^+PF_6^-$) by electrochemical oxidation of **B**. ESR parameters at 293 K are as follows: $\mathbf{A}^+Br^-$: $g = 2.0025$, $\Delta H_{pp} = 0.57$ mT; $\mathbf{B}^+ PF_6^-$: $g = 2.0024$, $\Delta H_{pp} = 0.39$ mT. The ratio of the line widths $\Delta H_{pp}(\mathbf{A}^+)$ and $\Delta H pp(\mathbf{B}^+)$ of the ESR signals of $\mathbf{A}^+$ and $\mathbf{B}^+$ is 1.46 at room temperature, i. e. very close to the value of $\sqrt{2}$ expected for a defect electron completely delocalized between the two porphyrin π electron systems in $[Zr(OEP^{\bullet/2})_2]^+$. The ESR signal of $\mathbf{A}^+Br^-$ persists on cooling to 77 K excluding any kind of π-π dimer formation. Treatment of (octaethylporphyrinato)bis(2,4-pentanedionato)zirconium(IV), $Zr(OEP)(acac)_2$, with bromine yields bis(3-bromo-2,4-pentanedionato)(octaethylporphyrinato)zirconium(IV), $Zr(OEP)(Bracac)_2$.

In the photosynthetic apparatus of purple bacteria, e. g. *Rhodopseudomonas viridis*, the so-called "special pair" of bacteriochlorophyll-b molecules, $[Mg(Bchl)]_2$[2], serves to transform the excitation energy of light into charge separation[3]. In the initial step a radical cation of the dimer, $[Mg(Bchl^{\bullet/2})]_2{}^+$, is produced (eq. 1). An electron is ejected, crosses two other tetrapyrrole pigments, and ultimately reduces a quinone moiety to a quinone radical anion.

$$[Mg(Bchl)]_2 \xrightarrow{h\nu} [Mg(Bchl^{\bullet/2})]_2^{+} + e^- \qquad (1)$$

Before the occurrence of the special pair had been proven[3], spectroscopic experiments had given serious hints at its existence[4], especially ESR and ENDOR spectroscopy[5]. An important early observation was the comparison of the line width of the ESR signals of chlorophyll radicals in vivo and in vitro; Katz et al.[6] concluded from the decreasing line width of the native radical signal as compared with the signal of known monomeric chlorophyll that the native radical was a chlorophyll dimer with a defect electron delocalized between the two π electron systems. These authors reasoned that the peak-to-peak line widths ΔH_{pp} of a Mg(Bchl) monomer and the dimeric species in the special pair, SP, were related as in eq. (2).

$$\Gamma_{SP}[\Delta H_{pp}(\text{monomer})/\Delta H_{pp}(\text{dimer})] = \sqrt{2} \qquad (2)$$

In this paper, it is shown that the above-mentioned technique used by Katz et al.[6] for the demonstration of the defect electron delocalization in the special pair may also be applied to cation radicals of synthetic metal monoporphyrinates and bisporphyrinates. For this comparison, a set of radicals are required which contain the same metal ion in order to cancel any line width effects or hyperfine splittings which might be caused by the central metal. Zirconium(IV) was chosen as a suitable metal ion because it contains only one isotope with a nuclear spin moment (^{91}Zr, nuclear spin 5/2). The abundance of this isotope is with its value of 11.2% comparable to the native system, in which ^{25}Mg (nuclear spin also 5/2) occurs in 10.1%. In this paper it is shown that this causes no trouble due to the electronic structure of the oxidized porphyrin ring.

Fortunately, zirconium(IV) monoporphyrinates and bisporphyrinates are stable, well-defined compounds which can serve as the sources of suitable π cation radicals. Zirconium(IV) monoporphyrins are easily prepared with two axial chelate ligands[7,8], e. g. bis(acetato)(octaethylporphyrinato)zirconium(IV), $Zr(OEP)(OAc)_2$ (**A**; see Figure 1); the zirconium(IV) porphyrin double-deckers $Zr(P)_2$ (P = OEP or TPP) have been prepared by different synthetical routes by Kim and Suslick[9] and in Darmstadt[10], e. g. bis(octaethylporphyrinato)zirconium(IV), $Zr(OEP)_2$ (**B**; Figure 1).

Zr(IV) bis(octaethylporphyrinate), $Zr(OEP)_2$, has been presented as a model of this special pair since the chemically or electrochemically oxidized form $[Zr(OEP^{\bullet/2})_2]^+$ is a sandwich-like porphyrin π radical, which like $[Mg(Bchl^{\bullet/2})]_2{}^+$ shows a strong near infrared (NIR) band at 966 nm and is

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much more easily generated than π cation radicals from metal monoporphyrinates[11], viz., as compared with monoporphyrinates, the one-electron oxidation potential of the corresponding octaethylporphyrinate sandwich system is lowered by about 0.9 V[9,10].

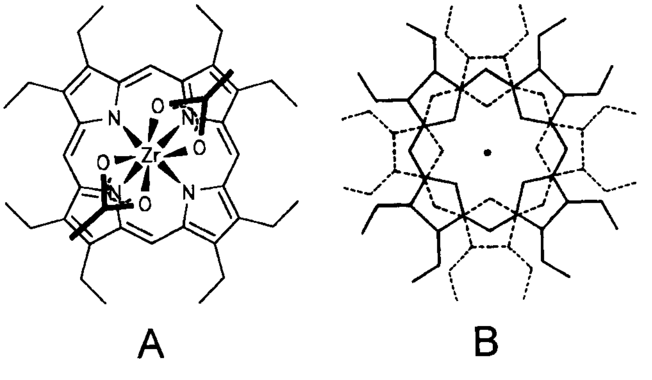

Figure 1. Structural formulae of the neutral monoporphyrin Zr(OEP)(OAc)$_2$ (**A**) and the double-decker Zr(OEP)$_2$ (**B**, ● = Zr)

Generation of π-Radical Cations

For the generation of the monoporphyrin radical cations, three different methods were employed: 1) Oxidation of neutral **A** by controlled potential coulometry with NBu$_4$PF$_6$ as supporting electrolyte in dichloromethane gave a solution of the desired defect electron species **A**$^+$PF$_6^-$ which was used to obtain the quantitative UV/Vis spectrum and to verify the stoichiometry of the reaction. 2) For obtaining the ESR spectra, oxidation was performed by adding a stoichiometric amount of a solution of bromine[12] ($\approx 10^{-2}$M) to a $\approx 10^{-4}$ M solution of a zirconium(IV) complex Zr(OEP)X$_2$ (X = OAc$^-$, acac$^-$) in anhydrous degassed dichloromethane under argon yielding **A**$^+$Br$^-$ · 3) In order to isolate the radical cation in a solid salt, oxidation of the neutral complex Zr(OEP)(OAc)$_2$ to its perchlorate, **A**$^+$ClO$_4^-$, was carried out with an excess of solid ferric perchlorate. Since the oxidation with bromine was most simple and convenient it was chosen for the ESR experiments.

Starting from the acetato complex Zr(OEP)(OAc)$_2$ (**A**) the corresponding radical cation [Zr(OEP$^{\bullet}$)(OAc)$_2$]$^+$Br$^-$ (**A**$^+$Br$^-$) was prepared in quantitative yield. Upon addition of bromine, the absorption spectra of Zr(OEP)(OAc)$_2$ acquired clear isosbestic points indicating the homogeneity of the reaction. Figure 2 shows the absorption spectra of Zr(OEP)(OAc)$_2$ and its one-electron oxidation product, [Zr(OEP$^{\bullet}$)(OAc)$_2$]$^+$Br$^-$. The oxidized complex exhibits characteristics of metalloporphyrin π radical cations: broad B-state absorption bands and a blue-shifted Soret band with a loss of intensity as compared with the neutral complex[13]. The features of the absorption spectrum of [Zr(OEP$^{\bullet}$)(OAc)$_2$]$^+$Br$^-$ do not differ from Bocian's hexachloroantimonate salt of [Zr(OEP$^{\bullet}$)Cl$_2$]$^+$[14]. To be sure that the removal of an electron from the neutral acetato complex **A** is the only reaction and that the irreversible oxidation to isoporphyrins does not occur, the obtained zirconium radical cation **A**$^+$Br$^-$ was reduced with potassium iodide/18-crown-6 or tetrabutylammonium iodide. ^{1}H-NMR and UV/Vis spectra showed the identity of the obtained product with the original metal complex Zr(OEP)(OAc)$_2$. Mass spectra of this re-reduced compound showed no signals at higher *m*/*z* ratio indicating a complete recovery.

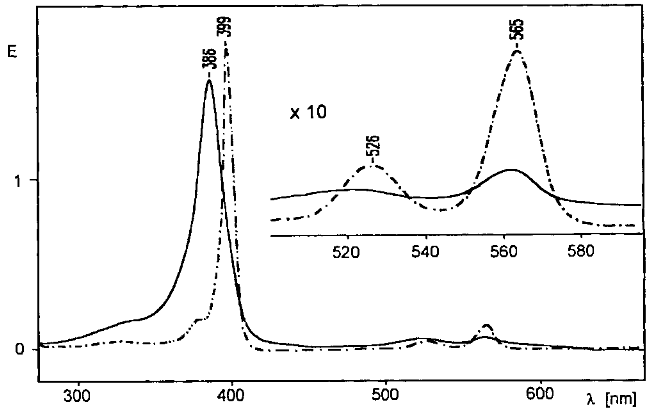

Figure 2. UV/Vis spectra of Zr(OEP)(OAc)$_2$ (**A**, – · –) and [Zr(OEP$^{\bullet}$)(OAc)$_2$]$^+$Br$^-$ (**A**$^+$Br$^-$, ——) in dichloromethane

The solid perchlorate [Zr(OEP$^{\bullet}$)(OAc)$_2$]$^+$ClO$_4^-$ (**A**$^+$ClO$_4^-$) was dissolved in [D$_6$]benzene and a NMR spectrum was taken which showed broad and slightly high-field shifted signals without multiplet structure for the ethyl protons as compared with the uncharged Zr(OEP)(OAc)$_2$ (**A**). This indicated paramagnetism of the solution. It cannot be excluded that the observed NMR spectrum is due to a mixture of **A**$^+$ClO$_4^-$ and adventitiously reformed **A**. For Zn(OEP$^{\bullet}$)$^+$ Fuhrhop et al. observed broad NMR signals, but did not quote chemical shifts[15]. By analogy to [Zr(OEP$^{\bullet/2}$)$_2$]$^+$ (**B**$^+$)[10b] and the double-decker radicals [Y(OEP$^{\bullet/2}$)$_2$][16] and [La(OEP$^{\bullet/2}$)$_2$][17], a very broad peak between δ = 2.5 and 3.5 would be expected for the methyl protons, i. e. low field-shifted as compared with a diamagnetic reference. Therefore, it seems premature to ascribe the NMR spectrum observed here to the radical cation **A**$^+$.

The UV/Vis spectra of the perchlorate **A**$^+$ClO$_4^-$ and the electrochemically obtained hexafluorophosphate **A**$^+$PF$_6^-$ and the ESR spectrum of the former (see below) are identical within experimental error with those of the bromide **A**$^+$Br$^-$. This indicates the existence of the same radical cation [Zr(OEP$^{\bullet}$)(OAc)$_2$]$^+$ in each salt with a negligible influence of the counterion.

Under identical conditions the acetylacetonato complex Zr(OEP)(acac)$_2$ showed a completely different behavior. After the addition of a stoichiometric amount of bromine unreproducible ^{1}H-NMR spectra were obtained indicating the presence of a mixture of compounds. It was suspected that the bromine oxidized the π electron system of the porphyrin and brominated the ligands of the complex at the same time. As the concentration and the excess of bromine were increased the ^{1}H-NMR signal of the methine protons of the acetylacetonato ligands decreased, and only one product was obtained which was suspected to be the bis(3-bromo-2,4-pentanedionato) complex Zr(OEP)(Bracac)$_2$ according to its field desorption mass spectrum.

In order to prove the formation of $\mathrm{Zr(OEP)(Bracac)_2}$ an independent synthesis was carried out. As the ligand 3-bromo-2,4-pentanedione is known to be very instable against heat and alkaline conditions[18] the usual method for the synthesis of the complex[7] was inappropriate. Simple standing of the acetato complex $\mathrm{Zr(OEP)(OAc)_2}$ with an excess of the ligand yielded a product mixture in which about one third of the sample was the bromoacetylacetonato complex $\mathrm{Zr(OEP)(Bracac)_2}$. Its existence could be proven by ^{1}H-NMR and mass spectra though it was never isolated in a pure form due to the instability of the $\mathrm{(Bracac)^-}$ ligand. Relating the likely bromination product to the mixture containing the independently synthesized $\mathrm{Zr(OEP)(Bracac)_2}$ it was concluded that the reaction of the acetylacetonato complex $\mathrm{Zr(OEP)(acac)_2}$ with bromine gives $\mathrm{Zr(OEP)(Bracac)_2}$. The observed bromination is not surprising as simple metal acetylacetonates react similarly[19].

The acetylacetonate radical cation $\mathrm{[Zr(OEP^{\bullet})(acac)_2]^+}$ was electrochemically generated as its hexafluorophosphate salt in solution. The Vis spectrum of this compound is quite similar to the other zirconium monoporphyrin radical cations though the absorption bands differ within 4 nm (for values, see Experimental).

The air-stable sandwich radical salt $\mathrm{[Zr(OEP^{\bullet/2})_2]PF_6}$ ($\mathbf{B}^+\mathrm{PF_6^-}$) was used as a solid sample prepared by controlled potential coulometry. As mentioned earlier[10b], in this compound formally only one porphyrin ring is oxidized. However, the resulting hole is delocalized over both tetrapyrrole systems.

Electron Spin Resonance Spectra

Dichloromethane solutions of solid $\mathrm{[Zr(OEP^{\bullet})(OAc)_2]^+ClO_4^-}$ ($\mathbf{A}^+\mathrm{ClO_4^-}$) (prepared in Darmstadt), and $\mathrm{[Zr(OEP^{\bullet})(OAc)_2]^+Br^-}$ ($\mathbf{A}^+\mathrm{Br^-}$) (prepared from **A** in Homburg) were subjected to ESR measurements.

At room temperature the examined monoporphyrin radical cation $\mathrm{[Zr(OEP^{\bullet})(OAc)_2]^+}$ ($\mathbf{A}^+$) showed only one resonance at $g = 2.0025$ ($\mathbf{A}^+\mathrm{Br^-}$, 2.0030 for $\mathbf{A}^+\mathrm{ClO_4^-}$) with a line width ΔH_{pp} of 0.57 mT ($\mathbf{A}^+\mathrm{Br^-}$, 0.60 mT for $\mathbf{A}^+\mathrm{ClO_4^-}$). Since a minor contamination of the perchlorate $\mathbf{A}^+\mathrm{ClO_4^-}$ with paramagnetic ferric ions remaining from the preparation cannot be excluded the values of the bromide $\mathbf{A}^+\mathrm{Br^-}$ are thought to be more reliable. For the bistetrapyrrole radical cation $\mathrm{[Zr(OEP^{\bullet/2})_2]^+}$ a line width ΔH_{pp} of 0.39 mT at a g value of 2.0024 was observed (Figure 3). Both the g factors of $\mathbf{A}^+\mathrm{Br^-}$ and $\mathbf{B}^+\mathrm{PF_6^-}$ are very close to the free spin value of 2.0023 so that a single delocalized electron without any strong spin-orbit contribution is the origin of the line.

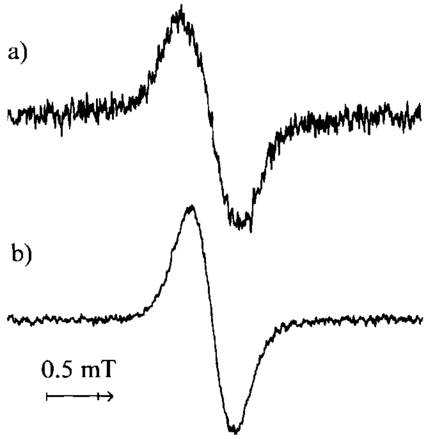

Figure 3. Electron spin resonance spectra of a) $\mathrm{[Zr(OEP^{\bullet})(OAc)_2]Br}$ ($\mathbf{A}^+\mathrm{Br^-}$), b) $\mathrm{[Zr(OEP^{\bullet/2})_2]\ PF_6}$ ($\mathbf{B}^+\mathrm{PF_6^-}$) in dichloromethane at 293 K. X Band modulation amplitude 0.05 mT, receiver gain $4 \cdot 10^5$ and $8 \cdot 10^4$, resp., microwave frequency 9.79 GHz, power 0.2 mW

The ratio of the line widths Γ_{Zr} [ΔH_{pp}(monoporphyrin) / ΔH_{pp}(bisporphyrin)] is 1.46 and thus in good agreement with the theoretical value of $\sqrt{2}$ (eq. 2). The less reliable data for $\mathbf{A}^+\mathrm{ClO_4^-}$ gives a line width ratio of 1.54. For the determination of the line width the concentration of the paramagnetic species must be as low as possible in order to prevent spin-spin exchange and an increase of the line width. Though spectra taken at 77 K were not used to determine the line width because dichloromethane is a non glass-forming solvent, they served to find a strong signal of the monoporphyrin radical cation at $g = 2.0030$. This is very important since the paramagnetic radical cations $\mathrm{[M(OEP^{\bullet})]^+}$ (M = Zn[15], Mg[20]) yield diamagnetic π dimers $\mathrm{[M(OEP)]_2^{2+}}$ below 220 K. The nonexistence of a diamagnetic π dimer at low temperatures is due to the saucer-like conformation of the porphyrin ligand in $\mathrm{[Zr(OEP^{\bullet})(OAc)_2]^+Br^-}$[21] which prevents the planes of two porphyrins to come to such a close proximity that electronic coupling is favored. Very recently, Scheidt et al.[22] obtained π radical cation derivatives in which one neutral and one oxidized porphyrin ring form a discrete dimer, $\mathrm{[M(OEP^{\bullet/2})]_2SbCl_6}$ (M = Cu, Ni), lacking any covalent bond between the two porphyrin rings. This aggregate was put forward by them as a photosynthetic special pair model though its existence is limited to the solid state. It could be related to our bistetrapyrrole sandwich radical $\mathrm{[Zr(OEP^{\bullet/2})_2]^+}$ as both substances contain a defect electron delocalized between the two porphyrin rings on the electronic timescale, a situation found in all single-hole sandwich complexes, e. g. the well-studied $\mathrm{Eu(OEP^{\bullet/2})_2}$[23], with the exception of the asymmetrical sandwich complex $\mathrm{[Ce\text{-}(OEP^{\bullet})(TTP)]^+}$[23].

Le Mest et al.[25] found that this delocalization depends on geometric conditions: When the two porphyrin rings of covalently linked cofacial bisporphyrins are sufficiently far apart, the diporphyrin behaves as the juxtaposition of two monoporphyrins. Only when the two porphyrin planes are very close, strong π-π interactions generate a new mixed-valence behavior resulting in the possible oxidation of the bisporphyrin to a totally delocalized monoradical cation, e. g. our double-decker radical $\mathrm{[Zr(OEP^{\bullet/2})_2]^+}$. The line width in the ESR experiment has to be figured out as a result of this delocalization: A greater delocalization of the defect electron causes a decrease of the line width.

Furthermore, time-resolved and steady-state optical measurements performed on $\mathrm{Ce(OEP)_2}$, $\mathrm{Ce(TTP)_2}$, Ce(OEP)(TTP)[26,27], $\mathrm{Th(OEP)_2}$[28], $\mathrm{Zr(TPP)_2}$, and $\mathrm{Hf(TPP)_2}$[29] have shown that considerable π-π interactions already exist in the neutral sandwich complexes, i. e. the two π systems of the porphyrinate rings are compressed by the central ion to such an extent that new electronic states are created which are not found in monoporphyrins.

It is well-known that there are two classes of porphyrin π radical cations. The assignment of these classes to a $^2A_{1u}$ or $^2A_{2u}$ ground state arises from the two highest nearly degenerate occupied molecular π orbitals of a_{1u} and a_{2u} symmetry from which withdrawal of an electron is possible[30]. It has been thought that for OEP those two classes of radical cations are clearly differentiated on the basis of their UV/Vis spectral pattern giving the complexes a green or grey color in solution for the electronic ground states $^2A_{1u}$ and $^2A_{2u}$, respectively[31]. According to this UV/Vis spectral criterion the grey radical cation $[Zr(OEP^{\bullet})(OAc)_2]^+$ ought to be a $^2A_{2u}$ electronic ground state using D_{4h} nomenclature.

But recently, Sandusky et al.[32] showed that the green and grey forms of octaethylporphyrinato radical cations do not belong to the $^2A_{1u}$ and $^2A_{2u}$ electronic ground state, respectively. The difference in the optical spectra seems to be only a matter of ring conformation and not a matter of difference in the electronic ground state since it was shown by ESR and ENDOR spectra that both classes of complexes have predominantly an $^2A_{1u}$ ground state. Thus, the grey color of our complexes in solution does *not* account for a $^2A_{2u}$ ground state. In agreement with the resonance Raman studies of Czernuszewicz et al.[33] and the earlier ENDOR study of Sandusky et al.[34] the defect electron species $[Zr(OEP^{\bullet})(OAc)_2]^+$ is suggested to have a $^2A_{1u}$ electronic ground state.

This assignment could be easily proved by ESR spectroscopy since $^2A_{2u}$-type porphyrin radicals show a hyperfine structure with nine lines due to coupling with spin-bearing nitrogen and *meso*-hydrogen atoms[5]. Our ESR spectra showed a single line without hyperfine splitting. Therefore, the generated monoporphyrin radical cations must be assigned with certainty to a $^2A_{1u}$ ground state.

This indicates that the pattern of the UV/Vis spectra does not necessarily provide correct information on the electronic ground state, though the use of such patterns has been one of the most convenient methods for the identification of electronic ground states of porphyrin radical cations. To our knowledge until now octaethylporphyrin radical cations with a dominant $^2A_{2u}$ ground state have not been found so far, but confusion in the literature is still continuing[35].

Any hyperfine splitting due to the spin-bearing ^{91}Zr in 11.2% natural abundance was not detected. The single line in the ESR spectra is consistent with what is expected by MO calculations for metalloporphyrins, i. e. according to Gouterman's four-orbital model[30] the a_{1u} orbital containing the unpaired electron has nodes on the nitrogen and *meso*-carbon atoms, and there is no overlap with the central metal orbitals. These features are the ones previously observed for the radical cations of Mg and Zn(OEP) complexes assigned as $^2A_{1u}$-type radicals where no hyperfine splitting due to the metal is detected.

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Experimental

MS: Finnigan MAT 311 A with data system SS 100 MS (direct insertion, ion source at 150°C, field-ion desorption). – UV/Vis: Spectrophotometer Bruins Instruments Omega 10. – ^1H NMR: Spectrometer Bruker WM 300 (300 MHz). – The electrochemical equipment and techniques are described in ref.[36]. – ESR: Bruker ESP 380 (NMR Gaußmeter, Hewlett Packard frequency detector), quartz sample tubes Spintec 707 SQ and quartz flat cell; 77 K: Spintec Dewar WG 804.

Materials: The following chemicals were purchased from the companies indicated in brackets: Dichloromethane (Fluka) was dried over 4-Å molecular sieve and degassed prior to use. Bromine (Fluka) was used without further purfication. The zirconium(IV) complexes $Zr(OEP)(acac)_2$, $Zr(OEP)(OAc)_2$[7], and $[Zr(OEP)_2]PF_6$[10] were prepared as described by using a recent variant of the metal inscrtion[8,10]. The radicals are rather stable in the dried solvent, but turned into the neutral precursors within 30 min in unpurified solvent. The supporting electrolyte, tetrabutylammonium hexafluorophosphate, was obtained from tetrabutylammonium bromide (Fluka) and ammonium hexafluorophosphate (Merck)[37]. All oxidation procedures were performed under argon.

Bis(3-bromo-2,4-pentanedionato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV), Zr(OEP)(Bracac)$_2$

Bromination of Zr(OEP)(acac)$_2$: A solution of 6.0 mg (7.3 μmol) of $Zr(OEP)(acac)_2$ in 0.5 ml CD_2Cl_2 was placed under argon into a dry NMR tube. With a Hamilton syringe bromine was added dropwise, until the signal of the methine protons of the $(acac)^-$ ligand diasappeared. Evaporation of the solvent in vacuo yielded 7.1 mg of $Zr(OEP)(Bracac)_2$. Due to the instability of the compound neither elemental analyses nor IR measurements were performed. – UV/Vis (CH_2Cl_2): λ_{max} = 403 nm, 530, 566. – MS, *m/z* (%): 978 (19) $[M^+]$. – ^1H NMR (CD_2Cl_2): δ = 2.00 (t, *J* = 7 Hz, 24 H, CH_2CH_3), 2.55 (s, 12 H, CH_3, $acac^-$), 4.27 (m, 16 H, CH_2CH_3), 10.87 (s, 4 H, OEP-C*H*).

Independent Formation of Zr(OEP)(Bracac)$_2$: A solution of 40 mg (53 μmol) of $Zr(OEP)(OAc)_2$ in an excess of 4 ml of H(Bracac) was stirred for 24 h at 20°C. Evaporation of the bromopentanedionate yielded 45 mg of a product mixture. $Zr(OEP)(Bracac)_2$ was detected in this mixture by ^1H-NMR and mass spectral analysis. Due to the instability of the ligand, all attempts to isolate pure $Zr(OEP)(Bracac)_2$ failed.

Generation of Radical Cations

(2,3,7,8,12,13,17,18-Octaethylporphyrinato)bis(2,4-pentanedionato)zirconium(IV) Hexafluorophosphate, $[Zr(OEP^{\bullet})(acac)_2]^+PF_6^-$: A solution of 1.150 mg (1.40 μmol) of $Zr(OEP)(OAc)_2$ in 50 ml of 0.1 M NBu_4PF_6/CH_2Cl_2 was electrolyzed at +0.93 V. Within 65 min the current dropped from 150 to 3 μA, and 0.135 C (1.0 F/mol) were transported. The color of the solution changed from red to grey. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 324 nm (4.41), 388 (5.20), 527 (4.07), 563 (4.37).

Bis(acetato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV) Hexafluorophosphate, $[Zr(OEP^{\bullet})(OAc)_2]^+PF_6^-$: A solution of 1.237 mg (1.67 μmol) of $Zr(OEP)(OAc)_2$ in 50 ml of 0.1 M NBu_4PF_6/CH_2Cl_2 was electrolyzed at +1.05 V. Within 1 h the current dropped from 150 to 5 μA, and 0.162 C (1.01 F/mol) were transported. The color of the solution changed from red to grey. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 386 nm (5.13), 523 (4.06), 564 (4.27).

Bis(acetato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV) Bromide, $[Zr(OEP^{\bullet})(OAc)_2]^+Br^-$*:* A solution of 1.8 mg (2.4 μmol) of $Zr(OEP)(OAc)_2$ in 6 ml of CH_2Cl_2 was flushed with argon. With a Hamilton syringe 50 μl of a $2.9 \cdot 10^{-2}$ M dichloromethane solution of bromine (1.4 μmol) was added dropwise. After 30 min the UV/Vis spectrum showed the presence of the radical cation. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 386 nm (5.15), 523 (4.07), 564 (4.32). – ESR (CH_2Cl_2): g (ΔH_{pp}) = 2.0025 (0.57 mT).

Bis(acetato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV) Perchlorate, $[Zr(OEP^{\bullet})(OAc)_2]^+ClO_4^-$*:* Two portions of about 5 mg of solid $Fe(ClO_4)_3$ were added to a solution of 16.1 mg (21.7 μmol) of $Zr(OEP)(OAc)_2$ in 5 ml of CH_2Cl_2 under argon. After 5 min, the UV/Vis spectra indicated the presence of radical cations. Crystallization with hexane yielded 13.7 mg (85%) of $[Zr(OEP^{\bullet})(OAc)_2]^+ClO_4^-$ as dark red crystals. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 387 nm (5.20), 524 (4.03), 564 (4.35). – ^1H NMR ([D_6]benzene): δ = 0.29 (s, 6H, CH_3COO), 1.62 (br, 24 H, CH_2CH_3), 3.91 (br, 8 H, CH_2CH_3), 4.21 (br, 8 H, CH_2CH_3), 10.07 (s, 4 H, CH). – MS, *m/z* (%): 740 (39) [M^+], 681 (100) [M^+ – OAc]. – ESR (CH_2Cl_2): g (ΔH_{pp}) = 2.0030 (0.60 mT).

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[1] Part of this work was presented as a poster at the DFG-Kolloquium "Bioinorganic Chemistry" in Bosen, Germany, 6. – 8. December 1992. – Part LXIV: J. W. Buchler, F. M. Künzel, U. Mayer, M. Nawra, *Fresenius Z. Anal. Chem.*, in press.

[2] Abbreviations: Bchl, bacteriochlorophyll b; $(P)^{2-}$, $(OEP)^{2-}$, $(TPP)^{2-}$ are the dianions of a general porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, 5,10,15,20-tetraphenylporphyrin; M = metal; H(acac) = acetylacetone; X^- = univalent anion.

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