Metal Complexes with Tetrapyrrole Ligands, LVIII[1]

Zirconium(IV) and Hafnium(IV) Bisporphyrinate Double Deckers: Synthesis, Spectra, Redox Potentials, and Structure

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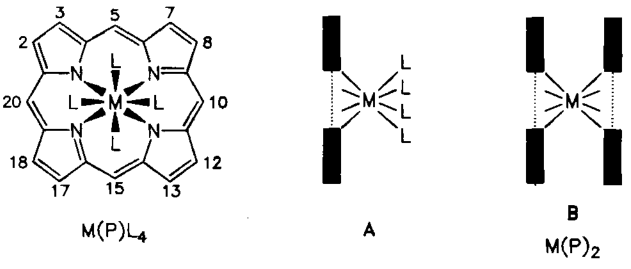
The synthesis of new zirconium and hafnium bisporphyrinate double deckers $M(P)_2$ (M = Zr, Hf; P = OEP, TPP)[2,3] is described. The complexes are characterized by UV/Vis/NIR and ^1H-NMR spectroscopy and cyclic voltammetry. As compared with M = Ce, the redox potentials or the energies of the near-infrared absorption bands of the corresponding radical cations $[M(P)_2]^{+\cdot}$ are lower by ≈ 0.2 V or higher by ≈ 2000 cm^{-1}, respectively. Hence, there is a stronger π-π interaction between the porphyrin ligands as compared with the cerium analogues due to the smaller ionic radii of Zr(IV) and Hf(IV). X-ray crystallography of $Zr(TPP)_2$ confirms the sandwich-like structure of the compound and the close proximity of the porphyrin ligands.

Sandwich-like metal(III) bisporphyrinate double-decker radicals $M(OEP)_2$[4,5] **1B** or $M(TPP)_2$[6] **2B** (M = Y, La – Lu) show a linear correlation of the redox potentials and the near infrared (NIR) absorption bands with the radii of the central ions. Sandwich complexes $M(P)_2$ (**B**) with tetravalent metal ions have been reported with cerium[4b,4c,5,6,7,8] and with uranium and thorium[9]. The synthesis of zirconium and hafnium bisphthalocyaninates $M(Pc)_2$ (**B**) (M = Zr, Hf) has been described only recently[10] and has stimulated our preparation of the corresponding bisporphyrinates which is reported here. Certain spectroscopic and electrochemical properties of these compounds should show the effect of the smaller ionic radii of Zr(IV) and Hf(IV) compared to Ce(IV), Th(IV), and U(IV) if the regularities that are known from the series of the trivalent lanthanoid bisporphyrinates may be transferred to the complexes of the tetravalent ions.

Scheme 1. Constitution $M(P)L_4$ of octacoordinated metal monotetrapyrroles and configurations **A** and **B** of monotetrapyrroles and bistetrapyrroles $M(P)_2$; M = Zr, Hf



Specification of porphyrins

Nr.	P in $M(P)L_4$	R in positions 2–20
1	OEP	C_2H_5 in 2,3,7,8,12,13,17,18
2	TPP	C_6H_5 in 5,10,15,20
3	Pc	Phthalocyanine
4	TTP	p-$CH_3C_6H_4$ in 5,10,15,20

Synthesis of Zirconium and Hafnium Bisporphyrinates

The reaction of metal acetylacetonates $M(acac)_4$ (M = Zr, Hf) with metal-free porphyrins $H_2(P)$ yields monoporphyrinates which may be isolated with two bidentate ligands in the *cis* configuration **A**, e.g. $M(P)(acac)_2$ or $M(P)(OAc)_2$ (LL = acac or OAc)[11,12]. The lanthanoid double deckers $Ln(P)_2$ **B** with Ln = Dy – Lu can be prepared by a "raise-by-one-story reaction" using the corresponding monoporphyrinates M(P)(acac) and dilithium porphyrinate $Li_2(P)$[13]. Zirconium and hafnium sandwiches cannot be synthesized this way. The smaller ionic radii and the higher charge of Zr(IV) and Hf(IV) compared to M(III) probably make the monoporphyrinates $M(P)(acac)_2$ more stable and therefore less reactive for the reaction with $Li_2(P)$ than M(P)acac. As regards the synthesis of the corresponding sandwich complexes, the important effect of radius and charge of the metal ion on stability and reactivity of monoporphyrinates can be seen with cerium complexes. The reaction of cerium(III) acetylacetonate with $H_2(TTP)$ yields only the double decker $Ce(TTP)_2$ and no monoporphyrinate[8], whereas cerium(IV) acetylacetonate yields only the monoporphyrinate Ce(TPP)$(acac)_2$ and no sandwich complex[14].

The metal acetylacetonates are therefore not suitable for preparing the double deckers of zirconium and hafnium.

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Suslick et al.[9a,b)] have succeeded in preparing bisporphyrinates of uranium and thorium which are not accessible from $M(acac)_4$[7,15a)] or MCl_4[15b)] using the diethylamido compounds $M(NEt_2)_4$ (M = U, Th)[16)]. We looked for organometallic compounds which are particularly useful for the synthesis of porphyrin complexes of metal ions which are hard Lewis acids[11a,b)]. For example, bis(cyclopentadienyl)titanium dichloride $TiCp_2Cl_2$ has been used for the preparation of titanium porphyrin complexes[11a,b,17)]. Indeed, the zirconium and hafnium analogues MCp_2Cl_2 are suitable for the synthesis of the desired sandwich complexes, as is subsequently shown.

The new double deckers $M(P)_2$ (M = Zr, Hf; P = OEP, TPP) are prepared from equimolar amounts of MCp_2Cl_2 and $Li_2(P)$ in refluxing 1,2,4-trichlorobenzene (TCB) (eq. 1).

$$MCp_2Cl_2 + 2\,Li_2(P) \xrightarrow{\text{TCB, 200°C}} M(P)_2 + 2\,LiCl + 2\,Li(Cp) \qquad (1)$$

The OEP complexes are purified by chromatography on alumina. After elution of the neutral species $M(OEP)_2$ with toluene a fraction containing the cation salt $[M(OEP)_2]X^-$ is eluted; the anion X^- is not identified but may be methoxide from the solvent methanol. Obviously, the sandwich compounds are partially oxidized during the chromatography according to eq. (2).

$$4\,M(OEP)_2 + O_2 + 4\,MeOH \longrightarrow [M(OEP)_2]^+OMe^- + 2\,H_2O \qquad (2)$$

The cation can be reduced to the neutral species $M(OEP)_2$ by adding some hydrazine hydrate.

Due to the low solubility of the TPP complexes, the purification of the compounds $M(TPP)_2$ by chromatography is not efficient. These complexes can be separated from lithium salts, decomposition products, and unreacted porphyrin by repeated extractions and crystallizations.

Spectral Characterization of the Double Deckers

UV/Vis-Spectra: The spectra of the zirconium and hafnium bisporphyrinates closely resemble their cerium analogs but show markedly red-shifted visible bands. The shift of about 20 nm is probably due to the increased interaction of the π-electron systems of the two porphyrin rings which are held together by ions with smaller radii [Zr(IV): 84, Hf(IV): 83, Ce(IV): 97 pm[18)]]. UV/Vis data of all known metal(IV) bisporphyrinates are listed in Table 1 for comparison.

The bands I and IV which appear in the spectra of the bisporphyrinates and are absent in those of the monoporphyrinates of the same metal ions cannot be interpreted in terms of exciton coupling of the π-electron systems of the porphyrin ligands. These bands are assigned to π-π* transitions between delocalized molecular orbitals of the sandwich molecules which derive from the molecular orbitals of the isolated porphyrin systems by strong coupling in the double deckers[19)].

As found with thorium bisporphyrinates[19a)] the zirconium and hafnium sandwiches show light emission[19b)]. In this respect they differ from the cerium double deckers, the excited states of which suffer a very fast and radiationless decay via ligand-to-metal charge transfer (LMCT) states[19,20)]. In the thorium, zirconium, and hafnium compounds there are no low-lying LMCT states so that emission occurs from the lowest $^1(\pi\pi^*)$ state. This state is labeled Q′ by Holten; band I in the absorption spectra of the bisporphyrinates corresponds to the Q′(1,0) transition[19a)].

Table 1. UV/Vis spectra of metal(IV) bisporphyrinates $M(P)_2$ (λ_{max} [nm], lgε in parentheses)

Complex	Soret	IV	III	II	I	Ref.
$Zr(OEP)_2$[a)]	382	490	550	592	750	24
	(5.22)	(4.10)	(3.78)	(4.39)	(2.72)	
$Hf(OEP)_2$[a)]	380	486	548	592	750	24
	(5.18)	(4.04)	(3.67)	(4.31)	(2.69)	
$Ce(OEP)_2$[b)]	378	467	530	573	661	8
	(5.21)	(3.92)	(3.77)	(4.24)	(3.16)	
$Zr(TPP)_2$[c)]	396	506	554		696	24
	(5.54)	(4.42)	(3.97)		(3.15)	
$Hf(TPP)_2$[c)]	394	506	554		700	24
	(5.57)	(4.45)	(4.00)		(3.19)	
$Ce(TPP)_2$[c)]	396	486	540		630	8
	(5.35)	(4.15)	(4.03)		(3.49)	
$U(TPP)_2$[d)]	404	485	550		620	9a
	(5.69)	(4.34)	(4.18)		(3.77)	

[a)] In toluene. — [b)] In cyclohexane. — [c)] In CH_2Cl_2. — [d)] In $CHCl_3$.

Table 2. ^{1}H-NMR data of metal(IV) bis(octaethylporphyrinates) $M(OEP)_2$ ([D_8]toluene, δ)

Complex	=CH-	-CH2-		-CH3	Ref.
$Zr(OEP)_2$	9.21 (s)	4.17 (m)	3.80 (m)	1.56 (t)	24
$Hf(OEP)_2$	9.21 (s)	4.16 (m)	3.81 (m)	1.55 (t)	24
$Ce(OEP)_2$	9.11 (s)	4.20 (m)	3.88 (m)	1.68 (t)	4c

Table 3. ^{1}H-NMR data of metal(IV) bis(tetraphenylporphyrinates) $M(TPP)_2$ ($CDCl_3$, δ, signal shape in parentheses[a)], room temperature, if not otherwise stated)

Complex	H-pyrr	o-H	o′-H	m-H	m′-H	p-H	Ref.
$Zr(TPP)_2$	8.21	9.64	6.25	8.02	7.17	7.66	24
	(s)	(b)	(b)	(b)	(b)	(t)	
$Zr(TPP)_2$[b,c)]	8.21	9.61	6.24	8.07	7.17	7.68	24
	(s)	(d)	(d)	(t)	(t)	(t)	
$Hf(TPP)_2$	8.23	9.63	6.27	7.94	7.38	7.67	24
	(s)	(b)	(b)	(b)	(b)	(t)	
$Ce(TPP)_2$	8.32	9.61	6.38	8.11	7.10	7.66	8
	(s)	(b)	(b)	(b)	(b)	(t)	
$Th(TPP)_2$[d)]	8.34	9.33	6.56	8.0	7.23	7.75	9b
	(s)	(d)	(d)	(t)	(t)	(t)	

[a)] b: broad signal. — [b)] In CD_2Cl_2. — [c)] At −30°C. — [d)] At −40°C.

NMR Spectra: The ^{1}H-NMR spectra of Ce(IV) bisporphyrinates have already been discussed in detail[4c,7]. The spectra of the corresponding Zr(IV) and Hf(IV) derivatives do not differ very much from those (see Tables 2 and 3) and show the typical features of $M(P)_2$ sandwich complexes with diamagnetic metal centers.

Notable differences are observed in the line widths of the signals of the *ortho* and *meta* phenyl protons. They are much broader in $Zr(TPP)_2$ than in $Ce(TPP)_2$. This indicates a facilitated rotation of the phenyl groups which may be due to the increased saucer-like deformation of the TPP ligand in the zirconium complex (vide infra). Facilitation of aryl-ring rotation in tetraarylporphyrinates as a consequence of a deformation of the macrocycle has been mentioned earlier[21]. At −30°C the phenyl-ring rotation is frozen, and the expected multiplicity of the signals can be observed (Table 3).

Electrochemical Characterization of the Double Deckers

In the accessible voltage range for the solvents used, cyclic voltammetry of the zirconium and hafnium sandwich complexes shows the following electrode processes: Two oxidations for $M(OEP)_2$ and $M(TPP)_2$, two reductions for $M(TPP)_2$, and one reduction for $M(OEP)_2$ (Figures 1, 2). All redox processes are reversible one-electron transfer reactions only concerning the porphyrin ligands. The redox potentials of the new double deckers are compared with the corresponding data of $Ce(OEP)_2$[22], $Ce(TPP)_2$[8], $Th(TPP)_2$[9b], and $U(TPP)_2$[9b] in Table 4. The redox steps are labeled according to eq. (3).

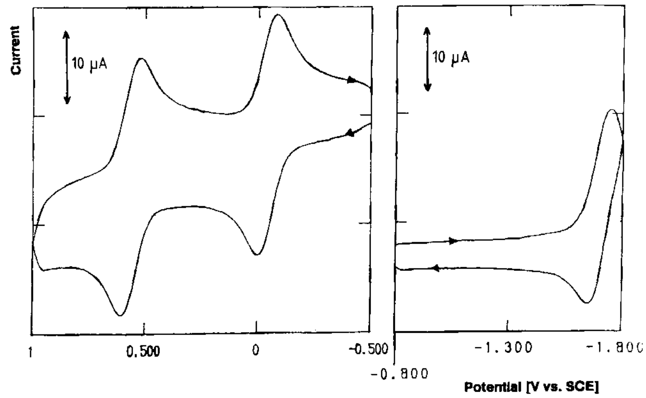

Figure 1. Cyclic voltammogram of $Zr(OEP)_2$; CH_2Cl_2, NBu_4PF_6, scan rate 1 V/s, SCE

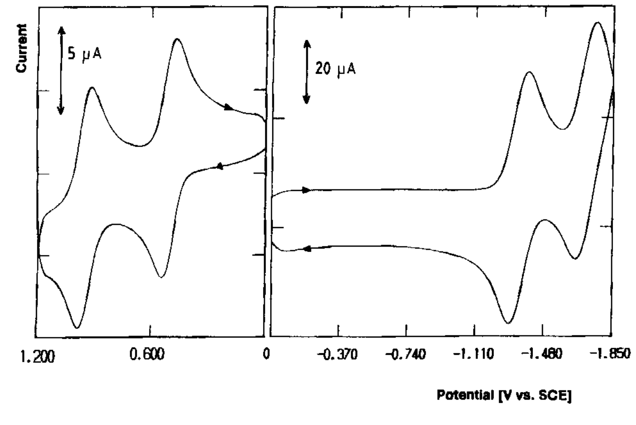

Figure 2. Cyclic voltammogram of $Zr(TPP)_2$; CH_2Cl_2, NBu_4PF_6, scan rate 0.4 or 5 V/s (left or right part of voltammogram, respectively), SCE

$$[M(P)_2]^{2+} \overset{E1}{\rightleftarrows} [M(P)_2]^{+} \overset{E2}{\rightleftarrows} M(P)_2 \overset{E3}{\rightleftarrows} [M(P)_2]^{-} \overset{E4}{\rightleftarrows} [M(P)_2]^{2-} \qquad (3)$$

The half-wave potentials E_1 and E_2 of $Zr(P)_2$ and $Hf(P)_2$ clearly show the effect of the smaller ionic radii of these ions as compared with cerium: both oxidations are remarkably facilitated. This cathodic shift of the oxidation potentials with decreasing ionic radii has already been stated for the OEP[4a,4c] and TPP[6] sandwich complexes of the trivalent lanthanoid ions. This effect can be explained by assuming an elevation of the HOMO of the sandwich complex due to the increased π-π interaction between the two macrocycles which approach one another when the ionic radius of the central ion decreases[4e,23].

Table 4. Redox potentials of metal(IV) bisporphyrinates $M(P)_2$ [Solvent/supporting electrolyte: CH_2Cl_2/NBu_4PF_6 or DMF/NBu_4PF_6 (values in italics)]

Complex	E_1	E_2	E_3	E_4	Ref.
$Zr(OEP)_2$	0.576	-0.026	-1.663	/[a]	24
	0.544	*0.133*	*-1.498*	/[a]	*24*
$Hf(OEP)_2$	0.573	-0.035	-1.661	/[a]	24
	0.530	*0.118*	*-1.525*	/[a]	*24*
$Ce(OEP)_2$	0.745	0.17	-0.58[b]	/[a]	8
	/	*0.33*	*-0.47*[b]	*-1.935*	8
$Zr(TPP)_2$	0.981	0.533	-1.310	-1.704	24
$Hf(TPP)_2$	0.986	0.542	-1.286	-1.647	24
$Ce(TPP)_2$	1.075	0.675	-0.27[b]	/[a]	8
$U(TPP)_2$[c]	0.990	0.580	/[d]	/[d]	9b
$Th(TPP)_2$[c]	0.990	0.580	/[d]	/[d]	9b

[a] Not observed. — [b] Metal reduction. — [c] In $CHCl_3$, supporting electrolyt not given. — [d] No data given for reduction processes.

Table 5. $\Delta E_{2,3}$[a] for different OEP complexes and radii of the central ions

Complex	r [pm] [18]	$\Delta E_{2,3}$	Ref.
$[La(OEP)]^-$	118	1.925	4e
$[Lu(OEP)]^-$	97	1.737	4e
$Hf(OEP)_2$	83	1.643	24
$Zr(OEP)_2$	84	1.631	24
$[La(TPP)_2]^-$	118	1.997	6c
$[Lu(TPP)_2]^-$	97	1.905	6b
$Zr(TPP)_2$	84	1.843	24
$Hf(TPP)_2$	83	1.828	24

[a] $\Delta E_{2,3}$ means the difference between the potentials of the first oxidation and the first reduction of the denoted species.

The facilitation of the oxidation of the porphyrin ligand in double deckers as compared with monoporphyrinates has been described earlier[22]. The half-wave potential of Ce-

Table 6. NIR absorptions and ionic radii of the central metals of the bisporphyrinate cations $[M(P)_2]^+$ and $[M(P)_2]^{2+}$ (CH_2Cl_2, λ_{max} [nm])

Complex	r [pm] [18]	$[M(P)_2]^+$	$[M(P)_2]^{2+}$	Ref.
$Zr(OEP)_2$	84	966	692	24
$Hf(OEP)_2$	83	958	684	24
$Ce(OEP)_2$	97	1280	808	24
$Hf(TPP)_2$	83	1054	768	24
$Zr(TPP)_2$	84	1074	784	24
$Ce(TPP)_2$	97	1350	1017	24
$U(TPP)_2$	100	1270	990	9b
$Th(TPP)_2$	106	1480	1080	9b

$(OEP)_2$ has been compared to that of Mg(OEP) because cerium monoporphyrinates have been described only recently[14] and their electrochemical properties are still unknown. In contrast, electrochemical data of zirconium monoporphyrinates are available[24]. A comparison of the first oxidation potentials of $Zr(OEP)(OAc)_2$ (+0.883 V) and $Zr(OEP)(acac)_2$ (+0.677 V) with that of $Zr(OEP)_2$ (−0.026 V) shows the drastic ease of the oxidation of the sandwich complex.

The quantity of $\Delta E_{2,3}$ is defined as the difference of redox potentials of the first oxidation (E_2) and the first reduction (E_3) of the porphyrin ring and corresponds to the difference in energy between the HOMO and the LUMO ("molecular band gap"). $\Delta E_{2,3}$ has been found to be always near 2.25 V for OEP complexes with redox-inactive metals[25]; for TPP complexes, $\Delta E_{2,3}$ tends to be smaller and varies from metal to metal (Zn 2.06, Mg 1.89 V[26]). For the zirconium and hafnium sandwich complexes $\Delta E_{2,3}$ is much smaller than in the series of the metal(III) bisporphyrinates $M(OEP)_2$[4e]. The decrease of $\Delta E_{2,3}$ with decreasing radius of the metal ion being observed in the lanthanoid series continues in the corresponding values of the zirconium and hafnium complexes (Table 5). This behavior can be explained by the increase of the π-π interactions between the two macrocycles with decreasing ionic radius of the metal ion[4c,6].

Salts of the mono- and dications of the zirconium and hafnium bisporphyrinates can be prepared electrochemically[24]. They show the characteristic NIR bands of bisporphyrinates having oxidized porphyrin ligands. The energies of the NIR bands of the lanthanoid bisporphyrinates $Ln(OEP)_2$[4a–c], $Ln(TPP)_2$[6], and $[Ln(TPP)_2]^+$ [6] have been shown to depend linearly on the ionic radii of the lanthanoid ions. The NIR bands of the zirconium and hafnium bisporphyrinate cations are shifted to the blue with respect to those of the cerium complexes, as it is expected for their smaller central ions. The "NIR" bands of the dications $[M(P)_2]^{2+}$ (M = Zr, Hf) are even shifted into the visible region of the spectrum (Table 6[24]).

Crystal Structure of $Zr(TPP)_2$

Small reddish-brown octahedra of $Zr(TPP)_2 \cdot 4\,H_2O$ are obtained by slow diffusion of toluene into a CH_2Cl_2 solution. The crystallographic data of these crystals are given in Table 7[27]. Table 8 lists the atomic coordinates of the independent non-hydrogen atoms. Figure 3 gives the perpendicular displacements of the metal and porphyrin-core atoms (in pm) relative to the 24-atom core mean plane of one ring and shows the numbering scheme used for these atoms.

Table 7. Crystallographic data of $Zr(TPP)_2$

$C_{88}H_{64}N_8O_4Zr$, 1388.76 g/mol; color: reddish-brown; crystal system: monoclinic, space group $C2/c$; a = 2117.3(5), b = 2121.5(5), c = 1244.9(2) pm; β = 124.49(2)°; $V = 6918.8 \cdot 10^6$ pm³; Z = 4; d(calcd) 1.333 g/cm³; crystal size: 0.25 × 0.28 × 0.35 mm; diffractometer: Enraf-Nonius CAD4-F, Θ/2Θ-mode; radiation: Mo-K_α, graphite-monochromated; μ = 2.131 cm⁻¹; temperature: 293 K; scan speed (°/s): variable; scan width (°): 1.00 +0.343 tg(Θ); Θ limits (°): 2/27.5; octants: $\pm h + k + l$; number of data collected: 8392; number of data with $I > 3\sigma(I)$: 4743; no absorption corrections were applied, the absorption coefficients being very small; solution of the structure by means of the heavy atom method; number of variables refined: 456; residual electron density not exceeding 0.1 e/Å³; $R(F)$ = 0.054; R_w(F) = 0.083; p = 0.08; GOF = 1.63

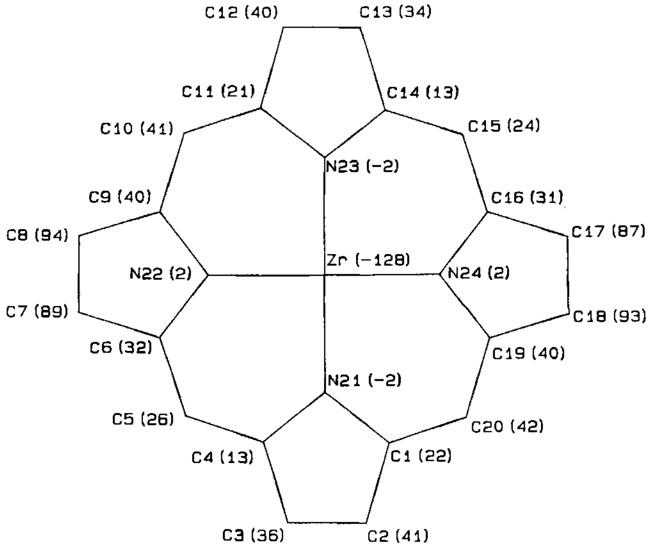

Figure 3. Stick-bond model projection of $Zr(TPP)_2$ along the Zr−Ct axis; Ct is the centroid of the 4 N_p atoms. The labeling scheme of the 24 core atoms of one TPP ring and their deviations [pm] from the mean plane of the porphyrin core is shown

The structure contains discrete $Zr(TPP)_2$ double-decker molecules which lie on a crystallographic twofold axis. This twofold symmetry axis passes through the zirconium ion and by symmetry connects the two tetraphenylporphyrin rings. Thus, the asymmetric unit of the crystals contains one half independent $Zr(TPP)_2$ molecule and also two water molecules of solvation. Figure 4 shows the ORTEP plot of a double-decker unit. Selected bond lengths and angles are given in Table 9.

Due to the two-fold crystallographic symmetry, the zirconium atom is equidistant from the four pyrrole nitrogen ($4N_p$) and 24-atom core (core) mean planes. The corresponding distances are: $\Delta(4N_p)$ = 128.4(1) and Δ(core) = 164.2(1) pm[3,28,29,30]. The porphyrin rings are rotated by an angle of 37° with respect to their eclipsed position setting up a distorted square antiprism about the zirconium atom.

Table 8. Fractional atomic coordinates[a,b] and equivalent thermal parameters[c] for $Zr(TPP)_2 \cdot 4\ H_2O$

Atom	x	y	z	B(Å^2)
ZR	0.000	0.12499(3)	0.250	1.789(9)
C1	0.0431(2)	0.2681(2)	0.3474(2)	2.44(9)
C2	0.0880(2)	0.3225(2)	0.3598(3)	3.0(1)
C3	0.1461(2)	0.3036(2)	0.3565(3)	2.8(1)
C4	0.1381(2)	0.2368(2)	0.3417(2)	2.24(8)
C5	0.1953(2)	0.1984(2)	0.3498(2)	2.32(9)
C6	0.1938(2)	0.1324(2)	0.3538(2)	2.32(9)
C7	0.2627(2)	0.0954(2)	0.3908(3)	2.9(1)
C8	0.2436(2)	0.0356(2)	0.3941(3)	2.9(1)
C9	0.1625(2)	0.0353(2)	0.3593(2)	2.31(8)
C10	0.1254(2)	-0.0186(2)	0.3601(2)	2.48(9)
C11	0.0543(2)	-0.0178(2)	0.3473(2)	2.50(9)
C12	0.0219(2)	-0.0725(2)	0.3596(3)	3.0(1)
C13	-0.0400(2)	-0.0536(2)	0.3559(2)	2.83(9)
C14	-0.0462(2)	0.0133(2)	0.3419(2)	2.31(8)
C15	-0.0956(2)	0.0515(2)	0.3496(2)	2.37(9)
C16	-0.0898(2)	0.1176(2)	0.3538(2)	2.25(8)
C17	-0.1222(2)	0.1548(2)	0.3903(2)	2.89(9)
C18	-0.0997(2)	0.2141(2)	0.3942(2)	2.83(9)
C19	-0.0530(2)	0.2147(2)	0.3595(2)	2.22(8)
C20	-0.0154(2)	0.2685(2)	0.3604(2)	2.41(9)
N21	0.0723(2)	0.2154(2)	0.3319(2)	2.20(7)
N22	0.1321(2)	0.0952(2)	0.3346(2)	2.07(7)
N23	0.0100(2)	0.0346(2)	0.3321(2)	2.15(7)
N24	-0.0476(2)	0.1548(2)	0.3348(2)	2.07(7)
C25	0.2664(2)	0.2286(2)	0.3645(2)	2.58(9)
C26	0.3119(2)	0.2682(2)	0.4343(3)	3.1(1)
C27	0.3758(3)	0.2964(3)	0.4461(3)	4.1(1)
C28	0.3950(3)	0.2851(3)	0.3888(4)	5.0(1)
C29	0.3512(3)	0.2449(3)	0.3199(3)	5.2(1)
C30	0.2867(2)	0.2166(3)	0.3077(3)	3.8(1)
C31	0.1718(2)	-0.0781(2)	0.3909(3)	2.82(9)
C32	0.1998(3)	-0.1008(3)	0.4726(3)	4.2(1)
C33	0.2486(4)	-0.1529(3)	0.5054(4)	5.9(2)
C34	0.2686(3)	-0.1826(3)	0.4553(4)	5.2(2)
C35	0.2403(3)	-0.1612(3)	0.3728(4)	4.9(1)
C36	0.1924(3)	-0.1091(3)	0.3409(3)	4.3(1)
C37	-0.1518(2)	0.0212(2)	0.3646(2)	2.59(9)
C38	-0.1280(2)	-0.0182(2)	0.4342(2)	3.1(1)
C39	-0.1794(3)	-0.0464(3)	0.4463(3)	4.0(1)
C40	-0.2563(3)	-0.0352(3)	0.3890(3)	4.9(1)
C41	-0.2816(3)	0.0056(3)	0.3194(3)	5.1(1)
C42	-0.2288(2)	0.0334(3)	0.3081(3)	3.9(1)
C43	-0.0308(2)	0.3282(2)	0.3908(3)	2.76(9)
C44	-0.1010(3)	0.3587(3)	0.3410(3)	4.2(1)
C45	-0.1174(3)	0.4117(3)	0.3727(3)	4.9(1)
C46	-0.0627(3)	0.4331(3)	0.4553(4)	5.3(1)
C47	0.0069(4)	0.4027(3)	0.5049(4)	5.7(2)
C48	0.0227(3)	0.3506(3)	0.4731(3)	4.1(1)
OW1	0.5502(4)	0.2412(4)	0.3384(6)	14.2(3)
OW2	0.5385(4)	0.0093(5)	0.3380(4)	14.7(3)

[a] Figure 3 displays the numbering scheme of all non-hydrogen atoms other than C25···C48 (phenyl groups) and OW1 and OW2 (water molecules). — [b] The estimated standard deviations of the last significant digits are given in parenthesis. — [c] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot \beta(1,1) + b^2 \cdot \beta(2,2) + c^2 \cdot \beta(3,3) + ab(\cos\gamma) \cdot \beta(1,2) + ac(\cos\beta) \cdot \beta(1,3) + bc(\cos\alpha) \cdot \beta(2,3)]$.

Although, the $4N_p$ and 24-atom core mean planes are not required by symmetry to be parallel, the dihedral angles between these planes are very small (0.08 and 0.04°, respectively).

The metal$-N_p$ bond lengths range from 238.9(3) to 239.4(3) pm. The corresponding mean value amounts to 239.1(2) pm. This distance is markedly longer than in the hafnium monoporphyrinate derivative $Hf(OEP)(OAc)_2$, where the average $Hf-N_p$ distance is 225.7(3) pm and the displacement of the metal $\Delta(4N_p)$ with respect to the $4N_p$ mean plane of the ring 101.2(3) pm. The corresponding mean value for $Zr-N_p$ and the value of $\Delta(4N_p)$ in $Zr(OEP)(OAc)_2$ should be similar since these molecules are reported to have isodimensional configurations[31]. The longer distances observed in $Zr(TPP)_2$ are probably due to the presence of two TPP rings which are stronger ligands than the OAc^- groups[32] but slightly weaker ligands than the OEP units present in $Zr(OEP)(OAc)_2$. "Back strain" caused by the mutual repulsion of hydrogen atoms at the phenyl groups and pyrrole units of the neighboring porphyrin rings may also be, at least partially, responsible for the larger distances observed in $Zr(TPP)_2$.

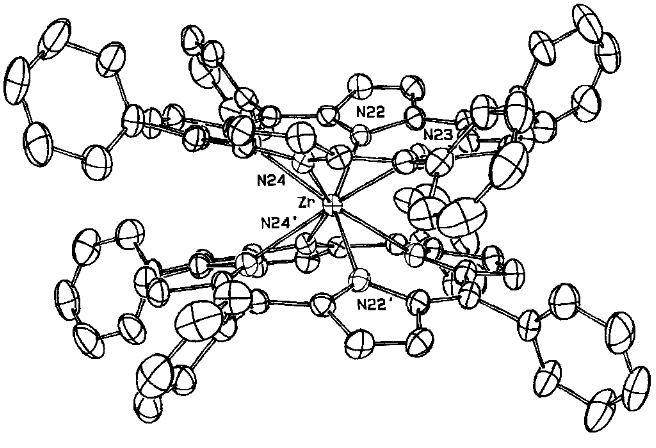

Figure 4. ORTEP plot of a $Zr(TPP)_2$ molecule as it exists in the crystal. Ellipsoids are scaled to enclose 50% of the electronic density. The numbering of the atoms is given in part. Hydrogen atoms are omitted

Table 9. Selected bond lengths [pm] and angles [°] of $Zr(TPP)_2$ (C_α, C_β, C_m, C_{Ph}, and $C_{Ph'}$ denote the α and β carbon atoms of the pyrrole ring, the methine carbon, and carbons of the phenyl ring, respectively)

Bonds		Core bond lengths	
Zr-N	238.9(3)	NC_α	138.1(5)
	239.0(3)	$C_\alpha C_\beta$	144.1(9)
	239.0(3)	$C_\beta C_\beta$	133.4(5)
	239.4(3)	$C_\alpha C_m$	139.4(7)
mean value:	239.1(2)	C_m-C_{Ph}	150.4(6)
		$C_{Ph}C_{Ph}'$	138.1(9)
Core bond angles			
$C_\alpha NC_\alpha$	104.3(2)	$NC_\alpha C_m$	126.4(8)
$NC_\alpha C_\beta$	110.7(3)	$C_\beta C_\alpha C_m$	122.4(8)
$C_\alpha C_\beta C_\beta$	107.0(1)	$C_{Ph}C_{Ph}C_{Ph}$	120.0(8)
$C_\alpha C_m C_\alpha$	123.2(5)		

The average metal$-N_p$ bond length in $Zr(TPP)_2$ (239.1 pm) is about 8.4 or 16 pm shorter than in $Ce(OEP)_2$ (247.5 pm[4c]) or $Th(TPP)_2$ (255 pm[9b]), respectively. Hence, the separation between the $4N_p$ mean planes of the two rings $\Delta(4N_p)\cdots\Delta'(4N_p)$ is significantly shorter: 256.8 pm, compared to 275.2 and 276.7 pm in cerium[4c,8] or 294 pm in thorium[9b] double deckers, respectively. The separations between the 24-atom core mean planes [Δ(core)$\cdots\Delta'$(core)] and the mean planes of the four *meso* carbons $\Delta(4C_m)\cdots\Delta'(4C_m)$ of the two rings are also shorter in the zirconium complex [Δ(core)$\cdots\Delta'$(core) = 328.4 in $Zr(TPP)_2$ and 340.0 pm in $Ce(OEP)_2$; $\Delta(4C_m)\cdots\Delta'(4C_m)$ = 323.3 in $Zr(TPP)_2$ and 339.4 pm in $Ce(OEP)_2$[4c)]]. These data confirm the closer proximity and hence stronger interaction of the π-electron systems of the porphyrin ligands in zirconium bisporphyrinates and confirm spectroscopic and electrochemical results (vide supra).

The saucer-like deformation of the porphyrin rings which is observed in all known molecular structures of porphyrin double deckers is particularly strong in $Zr(TPP)_2$. This is indicated by the separation between the $4N_p$ and 24-atom core mean planes of the independent macrocyclic ring and the dihedral angles occurring between the individual pyrrole ring mean planes and the 24-atom core mean plane of the porphyrin. The distance between the $4N_p$ and 24-atom core mean planes which measures the doming of the porphyrin[28)] is 35.8 pm in $Zr(TPP)_2$. Thus, it is significantly longer than in the two cerium compounds $Ce(OEP)_2$ (29.5 pm[4c)]) and Ce(OEP)(TPP) (32.4 pm[8)]). As usual, the individual pyrrole rings are almost planar, but the dihedral angles of their mean planes with the 24-atom core mean plane of the independent porphyrin range from 10.0(1) to 23.6(1)°. The average value of 17° of these dihedral angles is slightly larger than in $Ce(OEP)_2$ (15.4°) or in Ce(OEP)(TPP) (13.9°). Moreover, these angles are alternatively larger (average: 23°) and smaller (average: 10°) and thus show that a slight ruffling is superimposed on the doming of the porphyrins. A similar, but less expressed, distortion of the porphyrin macrocycles occurs in the cerium double deckers[4c,8)].

Conclusion

Ce(IV)[7,22)] and Th(IV)[9b)] porphyrin double deckers have been suggested as models for the special pair of bacteriochlorophyll molecules effecting the transformation of light energy into charge separation in photosynthetic bacteria. Do the Zr(IV) or Hf(IV) double deckers have any advantage over the Ce(IV) or Th(IV) analogues in studying the model character of these bisporphyrinates? As far as ease of oxidation is concerned, the Zr(IV) or Hf(IV) sandwiches are certainly superior to the other two M(IV) systems. Furthermore, their synthesis is less difficult as compared with those of the Ce(IV) or Th(IV) sandwiches. The preparation and the study of the magnetic properties of Ce(IV) bisporphyrinates is complicated by contamination of the product by Ce(III) double and triple deckers which have to be separated, but tend to be reformed when solutions of $Ce(P)_2$ are being stored. Such a difficulty is not encountered with Zr(IV) or Hf(IV). The preparation of Th(IV) sandwich systems requires $Th(NEt_2)_4$ which is not commercially available, contrary to the zirconocene and hafnocene dichlorides. Should the lack of light emission be important for the function of a "special pair", Ce(IV) might become more promising, since $Zr(P)_2$[19b)], $Hf(P)_2$[19b)], and $Th(P)_2$[19a)] show emission.

Very recently, a titanium(IV) bisphthalocyaninate, $Ti(Pc)_2$, has been described[33)]. Due to the small size of the Ti(IV) ions, the two phthalocyanine rings are compressed to such an extent that two covalent C–C bonds are formed between C5 and C5′ and C19 and C19′ of the two rings, respectively, thus producing a novel octadentate unsaturated ligand system with an optical spectrum totally different from the typical phthalocyanine chromophore. Attempts of synthesizing a titanium(IV) bisporphyrinate, $Ti(P)_2$, using $TiCp_2Cl_2$ and $Li_2(P)$ under the conditions of the preparation of the Zr(IV) and Hf(IV) double deckers described here have failed[34)]. The only detectable metal insertion products have been the oxotitanium(IV) porphyrins TiO(P), as observed earlier[17)].

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Experimental

MS: Varian MAT 311 A with data system SS 100 MS (direct insertion, ion source 150°C, field ion desorption). – IR: Perkin-Elmer 397, KBr pellets. – UV/Vis: Hewlett Packard HP 8451 A and Bruins Instruments Omega 10. – ^{1}H NMR: Bruker WM 300 (300 MHz). – Elemental analyses: Mr. *F. Roth*, Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Technischen Hochschule Darmstadt or Analytische Laboratorien Malissa & Reuter, DW-5250 Engelskirchen (AL). – The electrochemical equipment and techniques are described elsewhere[4c,35)]. – Diffraction data: Enraf-Nonius CAD4-F automated diffractometer. Details of the procedure of structure determination can be taken from Table 7 and previous papers[4c,d,8)].

The following chemicals were purchased: Octaethylporphyrin, $H_2(OEP)$ (Strem Chemicals), [D_1]chloroform, [D_2]dichloromethane, [D_8]toluene, bis(cyclopentadienyl)zirconium dichloride (Merck), bis(cyclopentadienyl)hafnium dichloride (Aldrich), butyllithium (1.6 mol/l in *n*-hexane, Merck), alumina type W 200 basic super I (Woelm-ICN-Biomedicals). 1,2,4-Trichlorobenzene (TCB) was a gift of Bayer AG, Leverkusen, and dried by passing it through an alumina column (basic, super I). Dimethylformamide (Fluka) for electrochemical purposes was purified by literature methods[36)]. Tetraphenylporphyrin, $H_2(TPP)$, was prepared according to ref.[37,38)]. Dichloromethane was distilled and passed through an alumina column (super I, basic) prior to use. – All the metal insertion procedures were performed under argon.

Bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV), $Zr(OEP)_2$: 1.6 mmol of butyllithium in 1 ml of hexane is added to a solution of 257 mg (0.48 mmol) of $H_2(OEP)$ in 50 ml of TCB under argon. After stirring at room temp. for 15 min, 148 mg (0.51 mmol) of $ZrCp_2Cl_2$ is added and the solution heated to reflux for 6 h. After removal of TCB in vacuo the residue is treated with 10 ml of cyclohexane and filtered. The residue is dissolved in CH_2Cl_2 and chromatographed on alumina (II, basic, 3.5 × 10 cm). The first reddish-brown fraction is eluted with CH_2Cl_2 and contains unreacted $H_2(OEP)$. A second pink fraction is eluted with CH_2Cl_2/

MeOH (95:5) and consists of an unidentified zirconium monoporphyrinate. The cyclohexane solution is chromatographed on alumina (II, basic, 3.5 × 15 cm). Fractions are obtained as follows: with cyclohexane/toluene (1:1) an orange forerun of unknown composition, with toluene the blue-violet fraction 1 containing Zr(OEP)$_2$, with CH_2Cl_2 the reddish-brown fraction 2 which contains unreacted H_2(OEP), with CH_2Cl_2/MeOH (95:5) the dark brown fraction 3 containing an unknown decomposition compound, and with MeOH the red fraction 4 of $[Zr(OEP)_2]^+X^-$. 0.1 ml of $N_2H_4 \cdot H_2O$ is added to the methanol solution of fraction 4 in order to reduce the cation. After stirring at room temp. for 30 min the solvent is removed. The blue-violet residue of Zr(OEP)$_2$ is crystallized together with the Zr(OEP)$_2$ obtained by evaporation of fraction 2 from hot CH_3CN. 132 mg (48%) of blue-violet needles of Zr(OEP)$_2$ is obtained. — IR (KBr), most intense bands: $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 2865, 1465, 1450, 1055, 1010, 955, 835, 685. — MS: *m/z* = 1155 $[^{90}Zr(OEP)_2^+]$.

$C_{72}H_{88}N_8Zr$ (1156.8)
Calcd. C 74.76 H 7.67 N 9.69
Found C 74.59 H 7.82 N 9.64 (AL)

Bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)hafnium(IV), Hf(OEP)$_2$: As described for Zr(OEP)$_2$ with 263 mg (0.49 mmol) of H_2(OEP) and 186 mg (0.49 mmol) of $HfCp_2Cl_2$; yield 70.0 mg (23.0%) of blue-violet needles of Hf(OEP)$_2$. — IR (KBr), most intense bands: $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 2870, 1465, 1450, 1365, 1010, 955, 835, 685. — MS: *m/z* = 1244 $[^{180}Hf(OEP)_2^+]$.

$C_{72}H_{88}HfN_8$ (1244.0)
Calcd. C 69.51 H 7.13 N 9.01
Found C 69.55 H 7.12 N 8.81 (AL)

Bis(5,10,15,20-tetraphenylporphyrinato)zirconium(IV), Zr(TPP)$_2$: 1.6 mmol of butyllithium in 1 ml of hexane is added to a solution of 307 mg (0.50 mmol) of H_2(TPP) in 50 ml of TCB under argon. After stirring at room temp. for 15 min, 148 mg (0.51 mmol) of $ZrCp_2Cl_2$ is added and the green solution heated to reflux for 7 h. After evaporation of the TCB in vacuo the brown residue is extracted with MeOH to remove lithium salts and with hexane to remove some decomposition compounds. A mixture of Zr(TPP)$_2$ and H_2(TPP) remains which is dissolved in CH_2Cl_2. Some toluene is added and the solution is slowly concentrated. Thin red plates of Zr(TPP)$_2$ are obtained besides amorphous H_2(TPP) which can be removed by careful washing with toluene. Repeating this procedure several times yields 104 mg (32%) of thin transparent reddish-brown plates of Zr(TPP)$_2$. — IR (KBr), most intense bands: $\tilde{\nu}$ = 3060 cm^{-1}, 1600, 1440, 1335, 1075, 1000, 980, 805, 755, 700. — MS: *m/z* = 1314 $[^{90}Zr(TPP)_2^+]$.

$C_{88}H_{56}N_8Zr$ (1316.7)
Calcd. C 80.27 H 4.29 N 8.51
Found C 79.72 H 4.08 N 8.20

Bis(5,10,15,20-tetraphenylporphyrinato)hafnium(IV), Hf(TPP)$_2$: As described for Zr(TPP)$_2$ with 309 mg (0.50 mmol) of H_2(TPP) and 187 mg (0.49 mmol) of $HfCp_2Cl_2$; yield 103 mg (29%) of transparent reddish-brown plates of Hf(TPP)$_2$. — IR (KBr), most intense bands: $\tilde{\nu}$ = 3055 cm^{-1}, 1600, 1495, 1445, 1340, 980, 805, 755, 725, 705. — MS: *m/z* = 1404 $[^{180}Hf(TPP)_2^+]$.

$C_{88}H_{56}HfN_8$ (1404.0)
Calcd. C 75.28 H 4.02 N 7.98
Found C 75.43 H 4.03 N 7.64

CAS Registry Numbers

Zr(OEP)$_2$: 132017-20-0 / $ZrCp_2Cl_2$: 1291-32-3 / Hf(OEP)$_2$: 132017-18-6 / $HfCp_2Cl_2$: 12116-66-4 / Zr(TPP)$_2 \cdot 4\,H_2O$: 131618-89-8 / Hf(TPP)$_2$: 131618-88-7 / Zr(OEP)$_2^+$: 132017-21-1 / Hf(OEP)$_2^+$: 132017-19-7 / Ce(OEP)$_2^+$: 101200-27-5 / Hf(TPP)$_2^+$: 131635-39-7 / Zr(TPP)$_2^+$: 131618-87-6 / Ce(TPP)$_2^+$: 101200-29-7 / Zr(OEP)$_2^{2+}$: 131618-86-5 / Hf(OEP)$_2^{2+}$: 131618-85-4 / Ce(OEP)$_2^{2+}$: 115731-19-6 / Hf(TPP)$_2^{2+}$: 131618-84-3 / Zr(TPP)$_2^{2+}$: 131618-83-2 / Ce(TPP)$_2^{2+}$: 115677-93-5 / Zr(OEP)$_2^-$: 131618-82-1 / Hf(OEP)$_2^-$: 131618-81-0 / Zr(TPP)$_2^-$: 131618-80-9 / Hf(TPP)$_2^-$: 131618-79-6 / Zr(TPP)$_2^{2-}$: 131618-78-5 / Hf(TPP)$_2^{2-}$: 131618-77-4

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[2] Short formulae of porphyrins and their metal complexes are defined in Scheme 1.

[3] Abbreviations used: M = metal; H(acac) = acetylacetone; HOAc = acetic acid; H(Cp) = cyclopentadiene; TCB = 1,2,4-trichlorobenzene.

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[16] *Note added in proof* (March 6, 1990): After submission of this paper we became aware of the fact that K. Kim, W. S. Lee, and S. Cho had succeeded in obtaining Zr(TPP)$_2$ by the diethylamide method [*65th Annual Meeting of the Korean Chemical Society*, Program and Abstracts, Sogang University, Seoul (Korea), April 13–14, 1990]. – S.-H. Cho, G. S. Girolami, P. A. Gorlin, H.-J. Kim, K. Kim, W. Lee, and K. S. Suslick (*Inorg. Chem.*, in press) obtained M(P)$_2$ (M = Zr, Hf; P = TPP, OEP) by using M(NEt$_2$)$_4$. — Our results were, inter alia, presented at the *International Symposium on Applied Bioinorganic Chemistry*, Huashong University of Science and Technology, Wuhan (China), April 23–26, 1990 (Abstracts, p. 18).

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[372/90]