Metal Complexes with Tetrapyrrole Ligands, LIV[1)]

Synthesis, Spectra, Structure, and Redox Properties of Cerium(IV) Bisporphyrinates with Identical and Different Porphyrin Rings in the Sandwich System

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Further symmetrical cerium(IV) bisporphyrinates are prepared from cerium(III) acetylacetonate and tetraphenylporphyrin, tetra-*p*-chlorophenylporphyrin, and hexadecahydrotetrabenzporphyrin. In the latter case, a biscerium(III) triple-decker is also found which is the only product in the case of octamethylporphyrin. From a mixture of two different porphyrins, namely octaethylporphyrin [$H_2(OEP)$] and either tetraphenylporphyrin [$H_2(TPP)$] or tetra-*p*-chlorophenylporphyrin [$H_2(TClP)$], besides the symmetrical species $Ce(OEP)_2$ and $Ce(TPP)_2$, the unsymmetrical ("mixed") double-deckers Ce(OEP)(TPP) or Ce(OEP)(TClP) are obtained which have different porphyrin rings in the sandwich system and can be separated by chromatography. The crystal structure analysis of Ce(OEP)(TPP) shows Ce^{IV} in a square-antiprismatic geometry of the pyrrole N atoms of the porphyrin rings. While the IR and NMR spectra of the unsymmetrical double-deckers are superpositions of the spectra of the individual rings, their UV/VIS spectra and cyclic voltammograms indicate that the two porphyrin rings behave as a common π-electron system. The preparation of the π-cation radical salts $[Ce(OEP)_2]ClO_4$ and $[Ce(OEP)(TPP)]SbCl_6$ is also described. In the latter, the defect electron seems to reside preferentially in the OEP ring.

Metallkomplexe mit Tetrapyrrol-Liganden, LIV[1)]. – Synthese, Spektren, Struktur und Redox-Chemie von Cer(IV)-Bisporphyrinaten mit gleichen und verschiedenen Porphyrin-Ringen im Sandwich-System

Weitere symmetrische Cer(IV)-Bisporphyrinate werden aus Cer(III)-acetylacetonat und Tetraphenylporphyrin, Tetra-*p*-chlorphenylporphyrin, und Hexadecahydrotetrabenzporphyrin hergestellt. Aus dem letzteren Porphyrin entsteht auch ein Biscer(III)-Tripeldecker; ein solcher bildet sich als einziges Produkt aus Octamethylporphyrin. Aus einem Gemisch zweier verschiedener Porphyrine, nämlich Octaethylporphyrin [$H_2(OEP)$], und Tetraphenylporphyrin [$H_2(TPP)$] oder Tetra-*p*-chlorphenylporphyrin [$H_2(TClP)$] erhält man neben den symmetrischen Spezies $Ce(OEP)_2$ und $Ce(TPP)_2$ die unsymmetrischen („gemischten") Doppeldecker Ce(OEP)(TPP) oder Ce(OEP)(TClP), die verschiedene Porphyrin-Ringe im Sandwich-System haben und sich trennen lassen. Die Kristallstrukturanalyse von Ce(OEP)(TPP) zeigt Ce^{IV} in quadratisch-antiprismatischer Umgebung der Pyrrol-N-Atome der Porphyrin-Ringe. Während die IR- und NMR-Spektren der unsymmetrischen Doppeldecker-Überlagerungen der Spektren der einzelnen Ringe darstellen, zeigen ihre UV/VIS-Spektren und die cyclischen Voltammogramme, daß die zwei unterschiedlichen Porphyrin-Ringe sich wie ein gemeinsames π-Elektronensystem verhalten. Die Darstellung der π-Kation-Radikal-Salze $[Ce(OEP)_2]ClO_4$ und $[Ce(OEP)(TPP)]SbCl_6$ wird ebenfalls beschrieben. In letzterem scheint sich das Defektelektron bevorzugt im OEP-Ring aufzuhalten.

While sandwich-like metal(IV) bis(tetrapyrroles) with square-antiprismatic geometry are known for a long time in the phthalocyanine series, e. g. $Sn(Pc)_2$[3)] or $Th(Pc)_2$[4)], papers on the preparation of Ce^{IV}[5)] or Th^{IV} and U^{IV} bisporphyrinates[6)] have not appeared before 1983 when the synthesis of the cerium(IV) bis(tetra-*p*-tolylporphyrinate) double-decker, $Ce(TTP)_2$ (**1B**, see Scheme 1), was described[7)]. Since these sandwich systems can be regarded as structural and spectroscopic models[5d–f,6b)] of the special pair of bacteriochlorophyll molecules in the reaction centre of bacterial photosynthesis[8)], the photophysical properties[9)] and resonance Raman spectra[10)] have been measured; these studies were also promoted by the idea that these sandwich systems might serve as molecular metals[10)] or intrinsic semiconductors[11)] when one of the rings is oxidized to a radical as, e. g., in $Lu(Pc)_2$[12)]. Therefore, a somewhat broader variation of these molecules seems appropriate. These variations may include incorporation of two different kinds of tetrapyrrole ligands as was achieved for the first time with the triple-decker $Nd_2(Pc)_2(TAP)$[13)]. Likewise, the mixed system Ce(OEP)(TTP)

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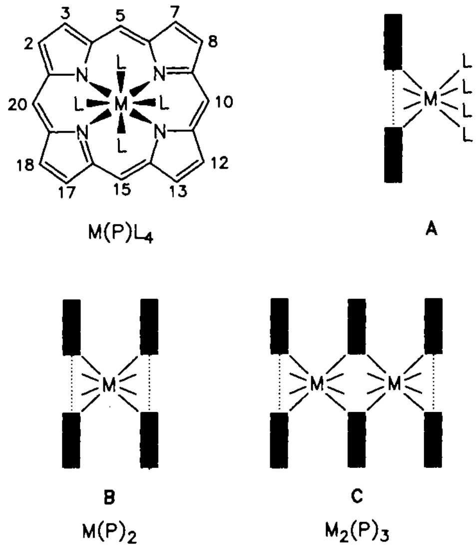
has been studied[14]. Here, the synthesis and properties of some further symmetrical cerium(IV) bisporphyrinate double-deckers Ce(P)$_2$ and their unsymmetrical counterparts Ce(P)(P′) are described[2].

Scheme 1. Constitution M(P)L$_4$ of octacoordinated metal monotetrapyrroles and configurations **A**, **B**, and **C** of monotetrapyrroles, bistetrapyrroles M(P)$_2$, and tristetrapyrroles M$_2$(P)$_3$; M = Ce if not otherwise stated; numbering of porphyrins



Specification of porphyrins[a)]

No.	P in M(P)L$_4$[2)]	R in positions 2–20
1	TTP	pCH$_3$C$_6$H$_4$ in 5,10,15,20
2	OEP	C$_2$H$_5$ in 2,3,7,8,12,13,17,18
3	TPP	C$_6$H$_5$ in 5,10,15,20
4	TClP	pClC$_6$H$_4$ in 5,10,15,20
5	HBP	(CH$_2$)$_4$ in 2/3, 7/8, 12/13, 17/18
6	OMP	CH$_3$ in 2,3,7,8,12,13,17,18
7	TAP	pCH$_3$OC$_6$H$_4$ in 5,10,15,20

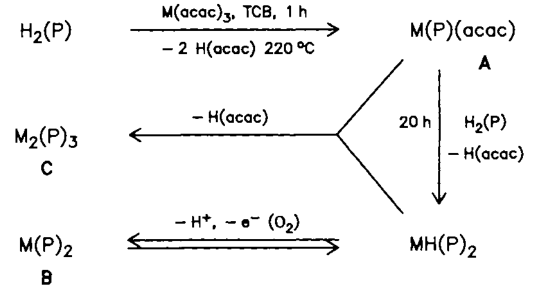
[a)] Numbers indicate porphyrin ligands present, capital letters the coordination type; "mixed" double-deckers and triple-deckers are specified as follows: **2B3** for Ce(OEP)(TPP), **2C4C2** for (OEP)-Ce(TClP)Ce(OEP), etc.

Synthesis of Symmetrical and Unsymmetrical Cerium(IV) Bisporphyrinates

Previous work on the synthesis of symmetrical metal porphyrin double-deckers M(P)$_2$ (**B**) and triple-deckers M$_2$(P)$_3$ (**C**) is summarized in Scheme 2 which has been discussed in detail for Ce(OEP)$_2$ (**2B**)[5a,c)]. The monoporphyrins **A** [M(P)L$_4$ where M = Ce^{III}, 2 L = (acac)$^-$, 2 L = H$_2$O or H(acac)] are never observed when Ce^{IV} porphyrins are made from Ce(acac)$_3$, but can be isolated after shorter periods of refluxing with a variety of Ln^{III} ions[15,16)]. Although not observed in the initial work on M(P)$_2$ with M = Eu[17)] or Ce[5a,c,7)], the Ln^{III} intermediate MH(P)$_2$ can be isolated for M = Pr[18)] and may be seen by UV/VIS spectroscopy in fresh reaction mixtures after the insertion of cerium with Ce(acac)$_3$[19)].

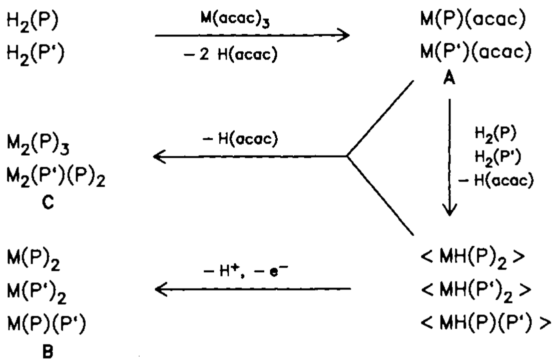
In this work, the cerium(IV) double-deckers, Ce(TPP)$_2$[10)] (**3B**), Ce(TClP)$_2$ (**4B**), and Ce(HBP)$_2$ (**5B**) were prepared according to Scheme 1. **5B** was accompanied by Ce$_2$(HBP)$_3$ (**5C**). In the case of octamethylporphyrin, a double-decker was not found, and only the triple-decker Ce$_2$(OMP)$_3$ (**6C**) was isolated. The gain in solubility that was found when going from a monoporphyrin **A** to a double-decker **B** in the OEP series was not observed in the HBP or OMP series, therefore, these systems were not further studied.

Scheme 2. Formation of monoporphyrins **A**, symmetrical double-deckers **B**, and symmetrical triple-deckers **C**



A: M = La...Lu (except Ce)
B: M = La...Tb (OEP), ...Gd (TPP) (except Pm)
C: M = La...Gd (only for octaalkylporphyrins) (except Pm)

Scheme 3. Formation of monoporphyrins **A**, double-deckers **B**, and triple-deckers **C** (M = Ce) starting from two different porphyrins, H$_2$(P) and H$_2$(P′)



A rational synthesis of double-deckers with mixed porphyrin rings would be achieved by treating a monoporphyrin Ln(P)(acac)L$_2$ (**A**) with the lithium salt of a different porphyrin, Li$_2$(P′)[16)], yielding Li[Ln(P)(P′)] which on oxidation could produce Ln(P)(P′). This was indeed attempted for Ln = Eu[20)], but due to scrambling of the porphyrin ligands at the high reaction temperatures, besides the desired Eu(OEP)(TPP), the symmetrical double-deckers Eu(OEP)$_2$ and Eu(TPP)$_2$ were obtained. Therefore, and because Ce^{III} monoporphyrins **A** are not yet known, the only access to unsymmetrical Ce^{IV} double-deckers is the extension of Scheme 2 to a mixture of two different porphyrins as depicted in Scheme 3. For the isolation of Ce(OEP)(TPP) (**2B3**; P = OEP, P′ = TPP), at least 6 components had to be separated by tedious, repeated chromatographic procedures during workup of the metal insertion mixtures: the residual starting materials octaethylporphyrin, $H_2(OEP)$, and tetraphenylporphyrin, $H_2(TPP)$, the known triple-decker $Ce_2(OEP)_3$[5a,c], the two symmetrical double-deckers and the desired unsymmetrical double-decker. This procedure was also applied to $H_2(OEP)$ and tetrakis(*p*-chlorophenyl)porphyrin, $H_2(TClP)$. In this case, the mixed double-decker Ce(OEP)(TClP) (**2B4**, P = OEP, P′ = TClP) was obtained, and a trace of a mixed triple-decker, $Ce_2(OEP)_2(TClP)$, found besides $Ce_2(OEP)_3$.

Analytical and Spectral Characterization of the Cerium(IV) Complexes

All new complexes gave correct microanalyses and molecular ions in the mass spectra. The individual porphyrin systems both in the symmetrical and unsymmetrical double-deckers can be identified by both the IR and ^{1}H-NMR spectra. The former show the characteristic C−H and skeletal vibrations of the ligands (see Experimental), and the latter all the typical proton signals (see Tables 1 and 2).

Table 1. ^{1}H-NMR data of cerium(IV)-bisporphyrinates $Ce(TPP)_2$, Ce(OEP)(TPP), $Ce(OEP)_2$, Ce(OEP)(TClP), and $Ce(TClP)_2$ [δ in ppm, TMS, 300 MHz]

Complex	No.	Solvent	Specification, Signals, Multiplicity					
			H(pyrr)	*o*-H		*m*-H		*p*-H
$Ce(TPP)_2$	**3B**	$CDCl_3$	8.32	9.61	6.38	8.11	7.10	7.66
			s	m	m	m	m	t
(TPP)			8.18	9.68	6.40	8.25	7.25	7.72
Ce	**2B3**	$CDCl_3$						
(OEP			9.05	4.24	3.88	1.36		
			CH=	CH_2	CH_2	CH_3		
$Ce(OEP)_2$	**2B**	$[D_8]$Toluene	9.11	4.20	3.88	1.68		
			s	dq	dq	t		
(OEP)			9.04	4.20	3.89	1.35		
Ce	**2B4**	$CDCl_3$						
(TClP)			8.26	9.61	6.34	8.16	7.26	
			s	m	m	m	m	
$Ce(TClP)_2$	**4B**	$CDCl_3$	8.15	9.47	6.30	8.26	7.19	
			H(pyrr)	*o*-H		*m*-H		

Table 2. ^{1}H-NMR spectra of Zn(HBP), $Ce(HBP)_2$ (**5B**), $Ce_2(HBP)_3$ (**5C**) [δ in ppm, TMS, multiplicity or half width in Hz]

Complex	No.	Solvent	CH	α-CH_2		β-CH_2	
Zn(HBP)	–	$CDCl_3$	9.90 (s)	4.14 (10)		2.35 (10)	
$Ce(HBP)_2$	**5B**	C_5D_5N	9.09 (s)	4.73 (30)	3.63 (30)	2.96 (24)	2.32 (24)
$Ce_2(HBP)_3$	**5C**	$CDCl_3$	2.80 −8.27	−0.68 −4.85	−0.98 −5.24	1.76 −3.14[b]	1.20[a]

[a] External ring. — [b] Internal ring.

The only notable feature in the NMR spectra of Ce(OEP)(TPP) and Ce(OEP)(TClP) is the high-field shift (ca. 0.3 ppm, Table 1) of the methyl proton signals of the peripheral ethyl groups as compared with $Ce(OEP)_2$, which may be attributed to a ring-current effect of the phenyl groups of the tetraarylporphyrin ring; these phenyl groups are in close proximity to the methyl groups (see below). The NMR data of the hexadecahydrotetrabenzoporphyrin complexes **5B** and **5C** are compared with the data of the corresponding zinc porphyrin Zn(HBP) which was prepared for this purpose. The spectra of **2B** and **5B** display similar chemical shifts for the methyne and methylene signals; the methyl signal of **2B** is replaced by the two signals of the remote methylene groups. Due to the sandwich structure, the two methylene signals of the cyclohexene rings in Zn(HBP) are split into four signals (an "internal" and an "external" pair) and broadened due to flipping motions of these rings; such broad signals have been previously observed in the spectrum of $H_2(HBP)$[21]. The high-field shift of the methyne signals of **5B** as compared with Zn(HBP) is typical for the double-decker structure[5c]. The chemical shifts and line widths of the signals of the triple-decker **5C** indicate the presence of paramagnetic Ce^{III} ions and are comparable to the values of **2C**[5c].

The optical spectra of the double- and triple-deckers are compiled in Table 3. The symmetrical octaalkyl- and tetraarylporphyrin species display significant differences: the octaalkyl species have a prominent α band near 575 nm, a Soret band at about 380 nm, and at least 5 discernible bands in the region covered, whereas the tetraaryl species show only 4 bands, a Soret band above 390 nm, and no α band[9]. Small or missing α bands are typical for many tetraarylporphyrin complexes[22].

Table 3. UV/VIS/NIR spectra of the cerium sandwich complexes

Complex	Solvent[a]	λ_{max} [nm] (lg ε)
$Ce(TPP)_2$ (**3B**)	1	396 (5.32), 486 (4.12), 540 (4.00), 630 (3.46)
Ce(OEP)(TPP) (**2B3**)	2	390 (5.26), 490 (4.15), 540 (4.05), 652 (3.38)
$Ce(OEP)_2$ (**2B**)[5b]	3	378 (5.08), 467 (3.92), 530 (3.77), 573 (4.24), 661 (3.16)
Ce(OEP)(TClP) (**2B4**)	2	394 (5.22), 494 (4.08), 542 (4.00), 656 (3.24)
$Ce(TClP)_2$ (**4B**)	4	398 (5.40), 488 (4.20), 542 (4.09), 634 (3.55)
$Ce(HBP)_2$ (**5B**)	2	354 (5.01 sh), 380 (5.15), 482 (4.04), 540 (3.83), 580 (4.28), 704 (3.20)
$Ce_2(HBP)_3$ (**5C**)	4	352 (5.15), 388 (5.20), 538 (3.96), 580 (3.90), 648 (3.53)
$Ce_2(OEP)_2(TClP)$	2	394 (I), 550 (II) (relative intensities I ≫ II)
$[Ce(OEP)_2]ClO_4$	1	362 (4.97), 502 (3.84), 1280 (3.74)
$[Ce(OEP)(TPP)][SbCl_6]$	1	366 (4.97), 538 (3.88), 1194 (3.68)

[a] Solvents: 1, dichloromethane; 2, toluene; 3, cyclohexane; 4, chloroform.

Table 3 and Figure 1 demonstrate that the optical spectra of the unsymmetrical double-deckers **2B3** and **2B4** are not simply superpositions of the individual spectra of the porphyrin rings, but rather represent electronic states that are much more similar to the pure tetraarylporphyrin double-deckers. This is reflected in the number of bands, in the wavelength of the Soret band, and in the lack of an α band. Only the band of **2B3** at 652 nm is more comparable with that of $Ce(OEP)_2$. Therefore, the UV/VIS spectra of the unsymmetrical double-deckers suggest that all double-deckers have an individual, new chromophore in which the two π-electron systems of the rings have penetrated each other, the tetraaryl system governing the properties in the mixed systems.

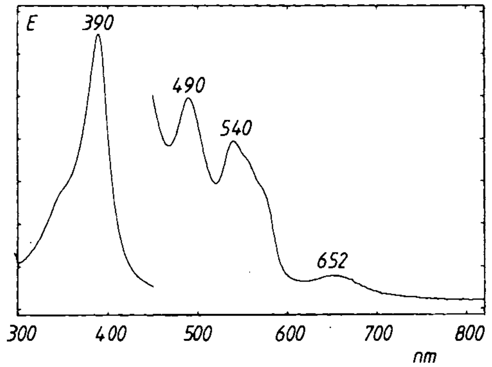


Figure 1. Optical spectrum of the unsymmetrical double-decker Ce(OEP)(TPP) (**2B3**) (see Table 1)

The oxidation/reduction potentials were determined by cyclic voltammetry (see Table 4) as described previously for the double-deckers $M(OEP)_2$ (M = Y, La, Ce···Lu)[5f]. The half-wave potentials E_1 to E_3 were measured in dichloromethane, E_3 and E_4 in *N,N*-dimethylformamide, and associated with the electron-transfer reactions in eq. (1) and (2) in the case of cerium(IV)[5f,19].

$$[Ce(P)_2]^{+} \underset{-e^-}{\overset{E_1}{\rightleftarrows}} [Ce(P)_2]^{+} \underset{-e^-}{\overset{E_2}{\rightleftarrows}} Ce(P)_2 \underset{-e^-}{\overset{E_3}{\rightleftarrows}} [Ce(P)_2]^{-} \qquad (1)$$

$$Ce(P)_2 \underset{-e^-}{\overset{E_3}{\rightleftarrows}} [Ce(P)_2]^{-} \underset{-e^-}{\overset{E_4}{\rightleftarrows}} [Ce(P)_2]^{2-} \qquad (2)$$

Oxidations of $Ce(P)_2$ beyond E_1 and E_2 produce π-cation radicals and π-dication diradicals, i.e. oxidation occurs at the two porphyrin rings, reduction beyond E_3 generates a Ce^{III} double-decker anion, and beyond E_4, a π-radical anion is formed. The half-wave potentials increase as alkyl side chains are replaced by aryl substituents. According to solvent and nature of the alkyl groups, the most important potential E_2 for the first ring oxidation varies between +0.16 and +0.33 V. For the aryl groups, E_2 increases from 0.62 to 0.85 V according Hammett's constant 4σ applied for the *p* substituents of the aryl groups[19]. The difference E_2(TPP) − E_2(OEP) amounts to 505 mV, a rather large value compared to the general statement that OEP complexes are oxidized at potentials being about 160 to 250 mV lower than those of the corresponding TPP complexes[23]. The corresponding E_1 and E_3 differences are much smaller (250 to 300 mV). E_4 was only determined for octaalkylporphyrin derivatives, since the tetraarylporphyrin derivatives show only limited solubility in DMF.

In the case of the unsymmetrical double-deckers, the shape of the cyclic voltammograms (see Figure 2) is very similar to those published previously for the symmetrical species[5d]. The number of redox steps is not affected by introducing different porphyrin ligands, but the values are shifted and appear roughly at the average of the values for the corresponding symmetrical double-deckers (see Table 4). Obviously the redox reactions affect the whole electron system of the double-decker, and not individual porphyrin rings, and the redox potentials reflect a balance of properties between the rings.

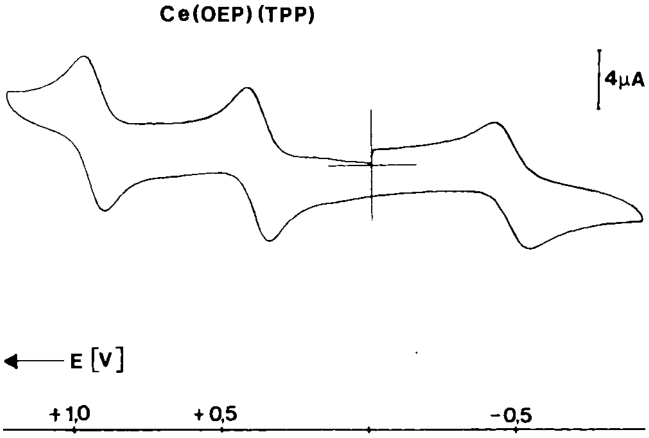


Figure 2. Cyclic voltammogram of Ce(OEP)(TPP); CH_2Cl_2, NBu_4PF_6, scan rate 0.1 V/s, SCE

Table 4. Redox potentials of cerium(IV) double-deckers[19], ordered according to increasing E_2 [V], vs. SCE; NBu_4PF_6, CH_2Cl_2, if not otherwise stated

Complex	No.	E_1	E_2	E_3	E_4
$Ce(HBP)_2$	**5B**	+0.685	+0.160	−0.520	
				−0.46[a]	−1.905[a]
$Ce(OEP)_2$	**2B**	+0.745	+0.170	−0.580	
				−0.47[a]	−1.935[a]
Ce(OEP)(TPP)	**2B3**	+0.968	+0.402	−0.436	
Ce(OEP)(TClP)	**2B4**	+1.043	+0.510		
$Ce(TAP)_2$	**7B**	+0.970	+0.620	−0.300	
$Ce(TTP)_2$	**1B**	+1.000	+0.620	−0.290	
$Ce(TPP)_2$	**3B**	+1.075	+0.675	−0.270	
				−0.04[a]	
$Ce(TClP)_2$	**4B**	+1.210	+0.850	−0.110	

[a] Solvent DMF.

A more careful inspection, however, shows that E_1 and E_2 lie by about +45 to +58 mV and −10 to −20 mV, respectively, off the mean value, i.e., E_2 is slightly more determined by the OEP ring, and E_1 considerably more determined by the TPP ring. This is plausible, when the lower oxidation potential of OEP derivatives is taken into account. Ce(OEP)(TPP) should then be oxidized first at the OEP ring. This is indeed the case as taken from the IR spectrum of $[Ce(OEP)(TPP)]^+$, see below. Subsequent oxidation then should occur at the TPP ring at potentials more positive than the average, as is the case.

Cerium(IV) Double-Decker Radical Cations

The cerium(IV) bisporphyrinate radical cations $[Ce(P)_2]^+$ may not only be observed by cyclovoltammetry and spectroelectrochemistry, but also isolated as salts with characteristical NIR absorptions (given in parentheses), e. g. $[Ce(OEP)_2]SbCl_6$ (1270 nm)[5d], $[Ce(OEP)_2]ClO_4$ (1280 nm)[10,22], $[Ce(TTP)_2]PF_6$ (1350 nm)[5d], $[Ce(TPP)_2]ClO_4$[10], and $[Ce(TPP)_2]SbCl_6$ (1350 nm)[5d]. Here, we present our electrochemical preparation of $[Ce(OEP)_2]ClO_4$ and the oxidation of Ce(OEP)(TPP) according to eq. (3) with the radical salt $[C_{12}H_8SO]SbCl_6$ prepared from phenoxathiin, $C_{12}H_8SO$[24].

$$\mathrm{Ce(OEP)(TPP)} \xrightarrow[-C_{12}H_8SO]{+\,[C_{12}H_8SO]SbCl_6} \mathrm{[Ce(OEP)(TPP)]SbCl_6} \quad (3)$$

Both $[Ce(OEP)_2]ClO_4$ and $[Ce(OEP)(TPP)]SbCl_6$ do not show ^{1}H-NMR spectra, indicating paramagnetism, which is corroborated for the former by an ESR spectrum which shows a single broad absorption at $g = 1.9924$ in dichloromethane at room temperature, as observed before[10]. The visible spectra are very similar (see Table 4). However, the NIR band of the unsymmetrical cation $[Ce(OEP)(TPP)]^+$ occurs at 1194 nm, i. e. at a notably shorter wavelength than the NIR bands of both the symmetrical counterparts (see above).

The π-radical nature of certain double-deckers $M(P)_2$ or $[M(P)_2]^+$ can be detected[5a,b,d,16b–18] by so-called "oxidation state marker" bands which have been found and assigned in the IR spectra of various metal-monoporphyrin π radicals[25]. They occur for TPP derivatives between 1270 and 1300 cm^{-1}, for OEP derivatives round about 1550 cm^{-1}, i.e. in $[Ce(TTP)_2]SbCl_6$ at 1270 cm^{-1}, and in $[Ce(OEP)_2]ClO_4$ at 1525 cm^{-1}.

Most notably, the oxidation state marker appears in the unsymmetrical $[Ce(OEP)(TPP)]SbCl_6$ at 1530 cm^{-1}, along with other features at 1440 and 1310 cm^{-1}. However, no features typical for a TPP radical are seen. The same comparison can be made in the series $Eu(TPP)_2/Eu(OEP)_2/Eu(OEP)(TPP)$[20]. This suggests that in a mixed OEP-TPP-sandwich π radical, the hole is preferentially localized in the OEP system, i.e. in that ring in which a positive charge experiences a better stabilization by inductive effects of the ethyl groups.

Table 5. Crystallographic data of Ce(OEP)(TPP) · 1.5 C_5H_5N

$C_{87.5}H_{79.5}N_{9.5}Ce$, molecular mass 1402.8
Crystal system triclinic, space group $P\bar{1}$
$a = 1317.9(4)$, $b = 2649.2(7)$, $c = 1067.5(3)$ pm
$V = 3483.10^6$ pm^3
$\alpha = 95.37(2)$, $\beta = 109.78(2)$, $\gamma = 91.85(2)°$
$Z = 2$, d(calcd.) = 1.337 g/cm^3
Crystal size 0.24 × 0.20 × 0.16 mm
Diffractometer PW 1100/16
Cu-K_α radiation, graphite monochromator
$\mu = 55.68$ cm^{-1}, temperature 173 K
Θ/2Θ flying-step scan, ΔΘ = 1 + 0.14 tan(Θ)°, step width 0.05°
Scan speed 0.024°/sec, Θ limits 3/51°, octants $\pm h \pm kl$
Number of measured data 7452
Number of observed data 6777
Absorption min. and max. 0.88/1.14
Lorentz, polarization, and empirical absorption corrections[a]
Solution of the structure by the heavy atom method
Number of variables refined 901
Residual electron density not exceding 0.2 e/Å
$R_1 = 0.028$, $R_2 = 0.045$, ERRFIT = 1.077

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[a] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A,* **389** (1983) 158.

Molecular Structure of a "Mixed Porphyrin" Cerium(IV) Double-Decker

Crystals of Ce(OEP)(TPP) (**2B3**) were grown from a pyridine/toluene solution. Details of the structure determination are collected in Table 5[26]. Fractional atomic coordinates and thermal parameters are listed in Table 6. The numbering of the essential carbon and nitrogen atoms is displayed in Figure 3. The asymmetrical unit contains one discrete double-decker molecule, which is shown in Figure 4, and one and a half pyridine molecule. One of the pyridine molecules lies on a crystallographic inversion centre and consequently is disordered. The 8 N atoms of the two porphyrin rings set up an approximately square antiprism

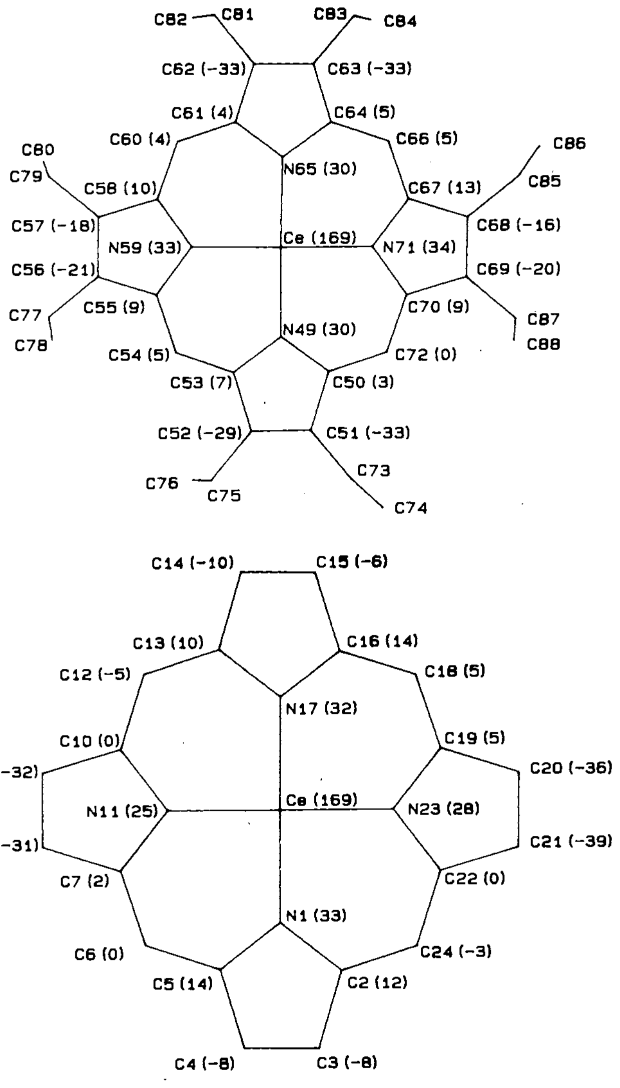

Figure 3. Stick bond model projection of Ce(OEP)(TPP) (**A**, **B**: along the Ce–Ct and Ce–Ct′ axes; Ct and Ct′ are the centroids of the 4 N_P atoms). **A** gives the labeling scheme of all but the hydrogen atoms of the OEP ring, **B** the labeling scheme of the 24 core atoms of the TPP ring. Also shown are the deviations [pm] of the porphyrin core atoms from their respective mean planes

about the Ce^{IV} ion which is depicted in Figure 5. Mean values of selected bond lengths and bond angles of the porphyrinato core and values of the Ce-N bond distances of the coordination polyhedron are given in Table 7.

Table 6. Fractional atomic coordinates[a,b] and equivalent thermal parameters[c] for Ce(OEP)(TPP)

Atom	X	Y	Z	B(Å^2)
Ce	0.1393	0.2693	0.1591	1.649(4)
N1	0.0477(2)	0.3094(1)	-0.0451(3)	1.83(6)
C2	-0.0559(3)	0.3266(1)	-0.0797(3)	2.01(8)
C3	-0.0633(3)	0.3685(1)	-0.1573(4)	2.46(8)
C4	0.0316(3)	0.3748(1)	-0.1770(4)	2.50(9)
C5	0.0998(3)	0.3376(1)	-0.1097(3)	1.97(8)
C6	0.1989(3)	0.3276(1)	-0.1254(3)	2.03(8)
C7	0.2613(3)	0.2869(1)	-0.0771(3)	2.06(8)
C8	0.3540(3)	0.2734(2)	-0.1100(4)	2.64(9)
C9	0.3853(3)	0.2296(2)	-0.0584(4)	2.71(9)
C10	0.3103(3)	0.2153(1)	0.0070(3)	2.12(8)
N11	0.2366(2)	0.2519(1)	-0.0016(3)	2.10(7)
C12	0.3105(3)	0.1690(1)	0.0608(3)	2.17(8)
C13	0.2321(3)	0.1512(1)	0.1119(3)	2.04(8)
C14	0.2274(3)	0.1013(1)	0.1518(4)	2.50(9)
C15	0.1337(3)	0.0951(1)	0.1761(4)	2.53(9)
C16	0.0781(3)	0.1406(1)	0.1477(3)	2.34(8)
M17	0.1419(2)	0.1761(1)	0.1156(3)	1.87(6)
C18	-0.0282(3)	0.1463(1)	0.1411(3)	1.94(8)
C19	-0.0892(3)	0.1874(1)	0.0956(3)	2.09(8)
C20	-0.2041(3)	0.1866(1)	0.0601(4)	2.36(8)
C21	-0.2360(3)	0.2296(1)	0.0043(3)	2.20(8)
C22	-0.1409(3)	0.2578(1)	0.0046(3)	2.05(8)
N23	-0.0508(2)	0.2316(1)	0.0619(3)	1.85(6)
C24	-0.1440(3)	0.3026(1)	-0.0574(3)	1.89(8)
C25	0.2340(3)	0.3591(1)	-0.2154(3)	2.29(8)
C26	0.2840(3)	0.4076(2)	-0.1712(4)	3.05(9)
C27	0.3099(3)	0.4372(2)	-0.2572(4)	3.6(1)
C28	0.2852(3)	0.4185(2)	-0.3905(4)	3.5(1)
C29	0.2375(3)	0.3709(2)	-0.4343(4)	3.9(1)
C30	0.2129(3)	0.3408(2)	-0.3479(4)	3.3(1)
C31	0.3927(3)	0.1332(1)	0.0495(4)	2.31(8)
C32	0.4725(3)	0.1198(2)	0.1611(4)	3.2(1)
C33	0.5493(3)	0.0870(2)	0.1480(5)	4.2(1)
C34	0.5468(4)	0.0674(2)	0.0232(5)	4.5(1)
C35	0.4671(4)	0.0794(2)	-0.0875(4)	4.7(1)
C36	0.3905(3)	0.1122(2)	-0.0749(4)	3.7(1)
C37	-0.0889(3)	0.1007(1)	0.1644(3)	2.14(8)
C38	-0.1175(3)	0.0577(2)	0.0717(4)	3.05(9)
C39	-0.1735(3)	0.0165(2)	0.0925(4)	3.7(1)
C40	-0.2012(3)	0.0167(2)	0.2049(4)	3.7(1)
C41	-0.1724(3)	0.0588(2)	0.2978(4)	3.6(1)
C42	-0.1173(3)	0.1006(2)	0.2769(4)	3.20(9)
C43	-0.2521(3)	0.3229(1)	-0.1193(3)	2.08(8)
C44	-0.3089(3)	0.3449(2)	-0.0428(4)	3.4(1)
C45	-0.4087(3)	0.3623(2)	-0.1016(4)	4.0(1)
C46	-0.4575(3)	0.3577(2)	-0.2385(4)	3.2(1)
C47	-0.4031(3)	0.3356(2)	-0.3158(4)	3.2(1)
C48	-0.3012(3)	0.3181(1)	-0.2572(4)	2.75(9)
N49	0.1164(2)	0.2423(1)	0.3632(3)	1.75(6)
C50	0.1732(3)	0.2063(1)	0.4378(3)	2.10(8)
C51	0.1138(3)	0.1854(1)	0.5143(3)	2.25(8)
C52	0.0201(3)	0.2093(1)	0.4865(3)	2.08(8)
C53	0.0243(3)	0.2456(1)	0.3952(3)	1.85(8)
C54	-0.0492(3)	0.2824(1)	0.3567(3)	2.01(8)
C55	-0.0388(3)	0.3251(1)	0.2948(3)	1.85(8)
C56	-0.1070(3)	0.3673(1)	0.2827(3)	2.23(8)
C57	-0.0635(3)	0.4030(1)	0.2274(4)	2.51(9)
C58	0.0318(3)	0.3831(1)	0.2104(3)	2.25(8)
N59	0.0436(2)	0.3346(1)	0.2461(3)	1.85(6)
C60	0.1070(3)	0.4107(1)	0.1742(3)	2.15(8)
C61	0.2097(3)	0.3978(1)	0.1812(3)	2.11(8)
C62	0.2927(3)	0.4330(1)	0.1720(3)	2.28(8)
C63	0.3839(3)	0.4076(1)	0.1959(3)	2.31(8)
C64	0.3572(3)	0.3568(1)	0.2197(3)	1.98(8)
N65	0.2496(2)	0.3512(1)	0.2075(3)	2.01(6)
C66	0.4313(3)	0.3206(1)	0.2593(3)	2.00(8)
C67	0.4180(3)	0.2756(1)	0.3106(3)	2.02(8)
C68	0.5045(3)	0.2451(1)	0.3773(3)	2.05(8)
C69	0.4608(3)	0.2099(1)	0.4328(3)	2.43(8)
C70	0.3471(3)	0.2186(1)	0.3974(3)	2.03(8)
N71	0.3212(2)	0.2576(1)	0.3183(3)	1.82(6)
C72	0.2770(3)	0.1939(1)	0.4471(3)	2.23(8)
C73	0.1536(3)	0.1465(2)	0.6113(4)	3.22(9)
C74	0.1465(4)	0.0925(2)	0.5436(5)	4.5(1)
C75	-0.0685(3)	0.2030(1)	0.5431(4)	2.47(8)
C76	-0.0523(3)	0.2400(2)	0.6669(4)	3.8(1)
C77	-0.2010(3)	0.3709(2)	0.3297(4)	2.65(9)
C78	-0.1686(3)	0.3837(2)	0.4811(4)	3.7(1)
C79	-0.1028(3)	0.4543(2)	0.1957(5)	3.9(1)
C80	-0.0568(5)	0.4943(2)	0.3119(6)	6.9(2)
C81	0.2783(3)	0.4877(2)	0.1473(4)	3.4(1)
C82	0.2872(4)	0.5232(2)	0.2710(5)	5.0(1)
C83	0.4951(3)	0.4282(2)	0.2100(4)	2.87(9)
C84	0.5618(3)	0.4478(2)	0.3548(4)	3.7(1)
C85	0.6200(3)	0.2531(2)	0.3856(4)	2.66(9)
C86	0.6371(3)	0.2374(2)	0.2535(4)	3.7(1)
C87	0.5174(3)	0.1707(2)	0.5208(4)	2.91(9)

Table 6 (*Continued*)

Atom	X	Y	Z	B(Å^2)
C88	0.5421(4)	0.1863(2)	0.6700(4)	4.3(1)
N90	0.1685(4)	0.9577(2)	0.3455(5)	4.8(1)
C91	0.2176(4)	0.9171(2)	0.3220(6)	6.1(2)
C92	0.1649(4)	0.8742(2)	0.2432(4)	4.4(1)
C93	0.0543(4)	0.8727(2)	0.1876(4)	4.4(1)
C94	0.0019(4)	0.9145(2)	0.2103(4)	4.1(1)
C95	0.0634(4)	0.9561(2)	0.2899(5)	5.3(1)
C96	0.40701(1)	0.02148(1)	0.44505(2)	7.9(2)
C97	0.4737(6)	0.0106(3)	0.3773(6)	8.1(2)
C98	0.5647(5)	-0.0109(3)	0.4269(7)	8.1(2)

[a] Figure 3 displays the numbering of all nonhydrogen atoms other than C25···C48 (phenyl groups of the TPP ring, see Figure 4), N90···C95 (ordered pyridine molecule), C96···C98 (half of the disordered pyridine molecule). — [b] The estimated standard deviations of the last significant digits are given in parentheses. — [c] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot \beta(1,1) + b^2 \cdot \beta(2,2) + c^2 \cdot \beta(3,3) + ab(\cos\gamma) \cdot \beta(1,2) + ac(\cos\beta) \cdot \beta(1,3) + bc(\cos\alpha) \cdot \beta(2,3)]$.

Table 7. Selected bond lengths [pm], bond angles [°] and individual values of the Ce–N bond distances with their standard deviations of the (OEP) and (TPP) fragments of Ce(OEP)(TPP) (**2B3**); data of Ce(OEP)$_2$[5c] (**2B**) for comparison

Bonds	**2B**	**2B3**-(OEP)	**2B3**-(TPP)
Ce–N		246.5(3)	246.3(3)
		246.5(3)	248.5(3)
		248.1(3)	247.5(3)
		247.3(3)	249.8(3)
Ce–N mean values		247.1(1)	248.0(1)
	247.5(1)	247.6(1)	
Core bond lengths[a]	Ce(OEP)$_2$	Ce(OEP)	Ce(TPP)
$N-C_\alpha$	137.5(1)	137.5(1)	138.4(1)
$C_\alpha-C_\beta$	144.9(1)	143.4(2)	144.4(2)
$C_\alpha-C_\beta$	135.8(2)	136.1(3)	134.8(3)
$C_\alpha-C_m$	138.4(1)	139.7(2)	140.2(2)
$C_\beta-C_\alpha(Et)$	150.3(1)	150.1(2)	150.0(2)[b,c]
$C_\alpha(Et)-C_\beta(Et)$	150.7(1)	152.0(2)	137.8(1)[c,d]
Core bond angles	Ce(OEP)$_2$	Ce(OEP)	Ce(TPP)
$C_\alpha-N-C_\alpha$	105.6(1)	105.2(1)	105.3(1)
$N-C_\alpha-C_\beta$	110.4(1)	110.7(1)	109.0(1)
$C_\alpha-C_\beta-C_\beta$	106.7(1)	106.6(1)	107.3(1)
$C_\alpha-C_m-C_\alpha$	127.7(1)	127.6(1)	125.4(1)
$N-C_\alpha-C_m$	124.8(1)	124.6(1)	125.7(1)
$C_\beta-C_\alpha-C_m$	124.4(1)	124.3(1)	123.9(1)
$C_{phe}-C_{phe}-C_{phe}$			120.0(1)

[a] C_α, C_β, C_m, $C_\alpha(Et)$, and $C_\beta(Et)$ denote the α and β carbon atoms of the pyrrole ring, the methine carbon atom, and the two carbon atoms of the ethyl group, respectively. — [b] C_m-C_{phe}. — [c] C_{phe} is an adjacent phenyl carbon. — [d] $C_{phe}-C_{phe}$.

The mean Ce–N(OEP) bond distance (247.1 pm) is just slightly smaller than the Ce–N(TPP) distance (248.0 pm) and in the same order of magnitude as Ce–N(OEP)$_2$ (**2B**, 247.5 pm[5c]). Likewise, the distances of the mean planes of the porphyrinato cores (henceforth "$C_{20}N_4$ mean planes") and of the four nitrogen atoms ("N_4 mean planes") amount to 338.3 and 276.8 pm, respectively, and are comparable with

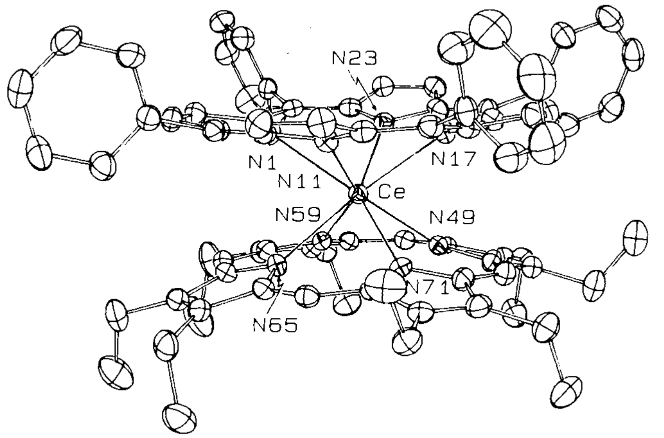

Figure 4. ORTEP plot of a Ce(OEP)(TPP) molecule as it exists in the crystal. Ellipsoids are scaled to enclose 50% of the electronic density. The numbering of the atoms is given in part. Hydrogen atoms are omitted

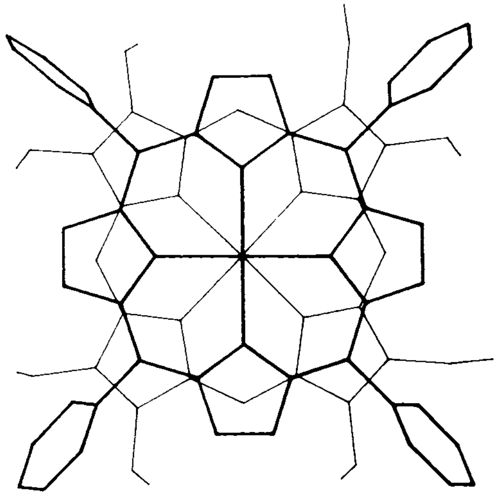

Figure 5. Stick bond model projection of Ce(OEP)(TPP) along the Ct−Ct′ axis showing the respective rotations of the two macrocycles; Ct and Ct′ are the centroids of the 4 N_p atoms

the values observed in **2B**[5c]. Both porphyrin rings are "domed" and at the same time saucer-like deformed. The distance d_{CN} of the $C_{20}N_4$ mean plane and the N_4 mean plane of a porphyrin ring is a measure of the doming, which is generally observed in porphyrin complexes with metal ions more or less protruding from the porphyrinato plane[27]. Since $d_{CN} = 32$ pm for the (OEP) part is larger than $d_{CN} = 29.5$ pm for the (TPP) part, the (OEP) ring is somewhat more deformed. This saucer-like deformation is also expressed by the dihedral angles δ of the individual pyrrole rings with respect to the corresponding $C_{20}N_4$ mean plane. Individual inclinations δ of the pyrrole rings (specified by their N atoms) are as follows: (TPP) part, N1/10.3(4)°, N11/14.0(3)°, N17/9.8(3)°, N23/18.0(2)°, average 13.0°; (OEP) part, N49/16.0(2)°, N59/13.1(3)°, N65/16.3(2)°, N71/13.6(3)°, average 14.8°. These figures corroborate the stronger doming of the (OEP) ring.

Although the CeN bond distances and the doming parameters d_{CN} and δ show only small differences for the (OEP) and the (TPP) ring, they altogether indicate a somewhat stronger covalent, and hence more directional, interaction of the OEP ligand with the central ion as compared with the TPP ligand. The smaller Ce−N distance and the larger doming in the Ce(OEP) part of **2B3** clearly point in this direction and seem to indicate that the $(OEP)^{2-}$ ligand is more basic than the $(TPP)^{2-}$ ligand. This seems plausible when the octaalkyl substitution pattern of the former is compared with the tetraaryl pattern of the latter. Direct measurements of the basicities of the porphyrin dianions are not available[28].

Bond angles and distances of the porphyrinato cores (see Table 7) are very close to the values that are generally found in metal porphyrins[29]. The planes of the phenyl rings occupy a nearly orthogonal orientation to the $C_{20}N_4$ plane of the TPP ring. Individual inclinations of the phenyl ring planes (specified by the porphyrin C atoms to which they are connected) are as follows: C6/83(1)°, C12/109.4(1)°, C18/71.9(1)°, C24/112.5(1)°. Surprisingly, they are situated just above the ethyl groups of the OEP ring as was already taken from the high-field shift of the methyl protons in **2B3** (see Table 1). A geometry with smaller steric interactions should result if the phenyl groups were located above the methyne groups of the OEP ring, but this would require the less frequent cubic coordination at the metal.

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Experimental

Mass spectra: Varian MAT 311 A with data system SS 100 MS (direct insertion, ion source at 150°C, field-ion desorption). − Infrared spectra: Perkin-Elmer 397, KBr pellets. − UV/VIS spectra: Hewlett-Packard HP 8451 A. − ^{1}H-NMR spectra: Bruker WM 300 (300 MHz). − ESR spectrum: Varian X-band, E-line spectrometer, 9.25 GHz, diphenylpicrylhydrazyl as calibrant (courtesy of Prof. *B. Elschner*, Institut für Festkörperphysik). − Elemental analyses: Mr. *F. Roth* (microanalytical laboratory of the Institut für Organische Chemie und Biochemie der TH Darmstadt) or Analytische Laboratorien Malissa & Reuter, D-5250 Engelskirchen. Precision is sometimes reduced below standards, because the combustion of high-melting metalloporphyrins is difficult. − The electrochemical equipment and techniques are described elsewhere[5f,18]. The diffraction data were collected with a Philips PW 1100/16 automated diffractometer equipped with a low-temperature device built in Strasbourg. Details of the procedure of structure determination can be taken from Table 5 and previous papers[5c,17].

The following chemicals were purchased from the companies indicated in parentheses: Octaethylporphyrin [H_2(OEP)] (Strem Chemicals); acetylacetone (Aldrich); [D_1]chloroform, [D_2]dichloromethan, [D_8]toluene (Merck); alumina, type W 200 basic super I (Woelm-ICN-Biomedicals). Trichlorobenzene (TCB) was a gift of the Bayer AG, Leverkusen, and dried by passing an alumina column (basic, super I). Propylene carbonate [PC], p. A. (Merck) was stored over molecular sieve and dried with alumina (super I, basic). The tetraarylporphyrins H_2(TPP) and H_2(TClP)[30,31], hexadecatetrahydrotetrabenzporphyrin[21] [H_2(HBP)], phenoxathiinylium hexachloroantimonate[24] from phenoxathiin ("dibenzo-1,4-oxthiin", Eastman Kodak), and Ce(acac)$_3$ · H_2O[32] from $CeCl_3$ (Johnson-Matthey) were prepared by literature methods. Octamethylporphyrin [H_2(OMP)] was a gift from Prof. *R. Guilard*. Chloroform and dichloromethane were distilled and passed through an alumina column (super I, basic) prior to use. – All the metal insertion procedures are run under nitrogen.

Bis(5,10,15,20-tetraphenylporphyrinato)cerium(IV), Ce(TPP)$_2$ (**3B**): 322 mg (0.54 mmol) of H_2(TPP) and 1000 mg (2.30 mmol) of Ce(acac)$_3$ · H_2O are heated to reflux under N_2 in 50 ml of TCB for 18 h. The colour of the red solution slowly turns to brown. TCB is removed in vacuo and the residue chromatographed on alumina (I, basic, 3.5 × 7 cm) with warm toluene whereby a first brown fraction containing **3B** is eluted. A reddish second fraction, a mixture of H_2(TPP) and **3B**, is obtained with toluene/chloroform (10:1) and has to be repeatedly rechromatographed with toluene/chloroform (10:3) until pure **3B** results as the first brown fraction, and H_2(TPP) as the red last fraction. The combined brown fractions yield 134 mg (36%) of **3B** after evaporation of the solvent and recrystallization from chloroform[33].

$C_{88}H_{56}CeN_8$ (1365.6) Calcd. C 77.40 H 4.14 N 8.20
Found C 77.66 H 4.36 N 7.76

Bis[5,10,15,20-tetrakis(p-chlorophenyl)porphyrinato]cerium(IV), Ce(TClP)$_2$ (**4B**): 350 mg (0.54 mmol) of H_2(TClP) and 1000 mg (2.30 mmol) of Ce(acac)$_3$ · H_2O are heated to reflux under N_2 in 60 ml of TCB for 18 h. After removal of TCB in vacuo at 60°C in a water bath the dark blue residue is chromatographed on alumina (I, basic, 3.5 × 8 cm) with toluene/chloroform (5:1). The first reddish fraction containing a mixture of H_2(TClP) and **4B** is eluted with toluene/chloroform (5:1) and discarded. The second brown fraction is eluted with a gradient of toluene/chloroform from 5:1 to 1:10 from which the product, 260 mg (59%) of **4B**, is obtained as a blue powder after evaporation of the solvent and recrystallization from dichloromethane/toluene (1:1).

$C_{88}H_{48}CeCl_8N_8$ (1641.2) Calcd. C 64.40 H 2.95 N 6.83
Found C 63.85 H 3.09 N 6.07

(1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecahydrotetrabenzo[b,g,l,q]porphyrinato)zinc(II), Zn(HBP): To a solution of 105 mg (0.2 mmol) of H_2(HBP) in hot glacial acetic acid (25 ml) under N_2 is added 110 mg (0.5 mmol) of finely powdered Zn(OAc)$_2$ · 2H_2O. After 2 h heating to 110°C the colour of the solution changes from red-violet to dark red. On cooling and adding 25 ml of methanol, a red solid separates which is washed with methanol, dissolved in chloroform and chromatographed on silica gel (II, neutral, 3 × 10 cm). The first red fraction is eluted with chloroform and yields 82.7 mg (70%) of Zn(HBP) after evaporation of the solvent and recrystallization from chloroform/methanol. – UV/VIS ($CHCl_3$): λ_{max} (lg ε) = 568 nm (4.25), 532 (4.07), 400 (5.33). – MS (FD): Calcd. *m/z* = 588 [M^+; ^{64}Zn], found *m/z* = 588. A small second, dichroic reddish-green fraction of unknown composition is eluted with chloroform/methanol (20:1).

$C_{36}H_{36}N_4Zn$ (590.1) Calcd. C 73.28 H 6.15 N 9.49
Found C 73.03 H 6.17 N 8.91

Bis(1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecahydrotetrabenzo[b,g,l,q]porphyrinato)cerium(IV), Ce(HBP)$_2$ (**5B**), *and Tris(1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecahydrotetrabenzo[b,g,l,q]porphyrinato)dicerium(III), Ce$_2$(HBP)$_3$* (**5C**): 300 mg (0.56 mmol) of H_2(HBP) and 1000 mg (2.30 mmol) of Ce(acac)$_3$ · H_2O are heated to reflux in 60 ml of TCB for 6 h. After cooling the solvent is removed in vacuo and the residue extracted with toluene and filtered. The red-brown solution is chromatographed on alumina (I, basic, 4 × 5 cm) with toluene and finally with toluene/methanol (300:1) yielding a dilute, red-brown solution which is evaporated to dryness and recrystallized from chloroform/toluene giving black crystals of **5B** (50 mg, 15%). – IR: $\tilde{\nu}$ = 2810 cm^{-1}, 2730, 1440, 1210, 1075, 1025, 890, 835. – MS (FD): Calcd. *m/z* = 1188.5 [M^+; ^{140}Ce]; found *m/z* = 1189 [M^+].

$C_{72}H_{72}CeN_8$ (1189.6) Calcd. C 72.70 H 6.11 N 9.42
Found C 72.28 H 6.13 N 9.01

On top of the column remains a black material which cannot be eluted. The residue of the first filtration with toluene is placed into a Soxhlet extractor and treated with 200 ml of boiling dichloromethane for 48 h. From the red-brown extract a large part of the product precipitates. After removal of the solvent in vacuo 220 mg (64%) of **5C** is obtained as a black powder. The grey-brown residue remaining in the extractor does not contain a porphyrin. – UV/VIS ($CHCl_3$): λ_{max} (lg ε) = 352 nm (5.15), 388 (5.20), 538 (3.96), 580 (3.90), 648 (3.53). – IR: $\tilde{\nu}$ = 835 cm^{-1}, 825 (split methyne-CH out-of-plane vibration). – MS: Calcd. *m/z* = 1852.7, 926 [M^+, M^{2+}; ^{140}Ce]; found *m/z* = 927 [M^{2+}].

$C_{108}H_{108}Ce_2N_{12}$ (1854.5) Calcd. C 69.95 H 5.87 N 9.06
Found C 68.77 H 5.70 N 8.10

Tris(2,3,7,8,12,13,17,18-octamethylporphyrinato)dicerium(III), Ce$_2$(OMP)$_3$ (**6C**): 250 mg (0.59 mmol) of H_2(OMP) are extracted from a thimble of a Soxhlet apparatus to 1000 mg (2.30 mmol) of Ce(acac)$_3$ · H_2O in 80 ml of boiling TCB. After 20 h the H_2(OMP) has completely reacted. The TCB is removed in vacuo, the residue washed with methanol and extracted from a thimble with chloroform. The solvent is removed from the dark brown extract. 92 mg (30%) of **6C** remain in form of a black powder. – UV/VIS ($CHCl_3$): λ_{max} (lg ε) = 350 nm (4.92), 392 (5.12), 534 (3.85), 574 (3.74), 656 (3.50), 796 (2.92). – IR: $\tilde{\nu}$ = 2860 cm^{-1}, 2810, 1660, 1440, 1380, 1210, 1140, 920, 830, 725, 710. – MS: Calcd. *m/z* = 1540.5, 770 [M^+, M^{2+}; ^{140}Ce]; found *m/z* = 770 [M^{2+}].

$C_{84}H_{84}Ce_2N_{12}$ (1542.0) Calcd. C 65.43 H 5.49 N 10.90
Found C 66.12 H 5.56 N 9.94

(2,3,7,8,12,13,17,18-Octaethylporphyrinato)(5,10,15,20-tetraphenylporphyrinato)cerium(IV), Ce(OEP)(TPP) (**2B3**): A solution of 900 mg (2000 μmol) of Ce(acac)$_3$ · H_2O, 137 mg (250 μmol) of H_2(OEP) and 158 mg (250 μmol) of H_2(TPP) in 60 ml of TCB is heated to reflux for 18 h. After cooling and removal of the solvent at 60°C in vacuo the violet residue is extracted with 40 ml of toluene and filtered (solution A). The residue is extracted with chloroform from which remain 20 mg (15 μmol) of Ce(TPP)$_2$ after evaporation. Solution A is chromatographed with toluene on alumina (I, basic, 4 × 15 cm). The fractions 1 to 4 are obtained by elution with toluene, again toluene, dichloromethane, and toluene/methanol (200:1), respectively. Fraction 1 is a brown-red solution of a mixture of **2C** and **2B**, fraction 2 contains **2B3** besides traces of **2B**, H_2(OEP), and H_2(TPP), fraction 3 contains H_2(OEP) and H_2(TPP), and fraction 4 contains again **2B**. Fraction 2 is rechromatographed twice with toluene, producing further crops of fractions 1–4. The combined fractions 1 and 4 are chromatographed with toluene on alumina (I, basic, 4 × 10 cm), thus producing fractions 1.1 containing 10 mg (5 μmol) of **2C** and 1.2 on further elution with toluene/methanol containing 65 mg (54 μmol) of **2B**. During this elu-

tion, the concentration of methanol is slowly increased, starting with a ratio of 1:200 (v/v). The rechromatographed fraction 2 on evaporation of the solvent in vacuo yields a red-brown solid which is recrystallized from pyridine/toluene as glittering black prisms of **2B3** (140 mg, 44%). – IR: characteristic bands of the OEP ligand: $\tilde{\nu}$ = 2960 cm^{-1}, 2910, 2860, 1460, 1055, 950, 840; of the TPP ligand: $\tilde{\nu}$ = 3050 cm^{-1}, 1595, 1435, 975, 800, 755, 700. – MS (FD): Calcd. m/z = 1284.5 [M$^+$; ^{140}Ce]; found m/z = 1284 [M$^+$].

$C_{80}H_{72}CeN_8$ (1285.7) Calcd. C 74.74 H 5.65 N 8.71
Found C 75.04 H 5.71 N 8.81

(2,3,7,8,12,13,17,18-Octaethylporphyrinato)(5,10,15,20-tetraphenylporphyrinato)cerium(IV) Hexachloroantimonate, [Ce(OEP)(TPP)][SbCl$_6$]: A solution of 25 mg (0.02 mmol) of Ce(OEP)(TPP) in 10 ml of CH_2Cl_2 is oxidized by dropwise addition of a solution of phenoxathiinylium hexachloroantimonate in CH_2Cl_2. The process is accompanied by a colour change from red to yellow-brown and followed by UV/VIS/NIR spectra. After completion of the reaction the solvent is removed by distillation, the residue washed several times with n-hexane, dissolved in CH_2Cl_2 and filtered. After distillation of the solvent a blue-violet solid of [Ce(OEP)(TPP)][SbCl$_6$] (23 mg, 71%) remains. – UV/VIS/NIR (CH_2Cl_2): λ_{max} (lg ε) = 366 nm (4.97), 538 (3.88), 1194 (3.68). – IR: $\tilde{\nu}$ = 1530 cm^{-1}, 1440, 1310 ("oxidation state marker" bands of the OEP ligand). – ^{1}H-NMR (CD_2Cl_2): no signals.

$C_{80}H_{72}CeCl_6N_8Sb$ (1620.2) Calcd. C 59.31 H 4.48 N 6.92
Found C 58.74 H 4.26 N 6.08

(2,3,7,8,12,13,17,18-Octaethylporphyrinato)[5,10,15,20-tetrakis(p-chlorophenyl)porphyrinato]cerium(IV), Ce(OEP)(TClP) (**2B4**), *and Bis(2,3,7,8,12,13,17,18-Octaethylporphyrinato)μ-[5,10,15,20-tetrakis(p-chlorophenyl)porphyrinato]dicerium(III), Ce$_2$(OEP)$_2$(TClP)* (**2C4C2**): 680 mg (1500 μmol) of Ce(acac)$_3$ · H_2O, 188 mg (250 μmol) of H_2(TClP) and 133 mg (250 μmol) of H_2(OEP) are heated to reflux for 20 h in 50 ml of TCB. After removal of the TCB in vacuo the residue is extracted with cold toluene ("solution A") and filtered. The residue is extracted with cold chloroform ("solution B") and filtered again. Solution B contains CeH(TClP)$_2$ [UV/VIS: λ_{max} = 414 nm (I), 510 (II), 550 (III); relative intensities I ≫ III > II]. Removal of the solvent from solution B in vacuo yields 20 mg of **4B** which is contaminated with H_2(TClP); during this procedure, CeH(TClP)$_2$ is dehydrogenated. The isolation of **2B4** requires the three chromatographic steps 1 – 3. – Chromatography 1: Solution A is chromatographed on alumina (I, basic, 4 × 10 cm). The following fractions 1.1 – 1.3 are eluted with toluene, 1.4 with a toluene/methanol gradient (200:1 to 10:1), and 1.5 with chloroform/methanol (10:1). Fraction 1.1 contains a trace of the mixed triple-decker, **2C4C2**, 1.2 the triple-decker Ce$_2$(OEP)$_3$, 1.3 the mixed double-decker **2B4**, 1.4 a mixture of double-deckers **2B4**, **2B**, and **4B**, and 1.5 the double-decker **4B** and traces of H_2(OEP) and H_2(TClP). – Chromatography 2: After removal of the solvent, fraction 1.4 is chromatographed on alumina (I, basic, 2 × 20 cm) with dichloromethane, yielding fraction 2.1 containing **2B4** and some **4B**, and then with dichloromethane/methanol (10:1), yielding fraction 2.2 containing **2B** and some **4B**. Fraction 2.1 is combined with fraction 1.3, the solvent removed in vacuo, and the residue extracted with toluene and filtered. **4B** remains undissolved, the filtrate is further purified as fraction 2.3. – Chromatography 3: Fraction 2.3 is chromatographed on alumina (I, basic, 4 × 15 cm) with toluene. Fraction 3.1 is a dilute solution of **4B**, fraction 3.2 contains pure **2B4** which remains as a black powder (75 mg, 21%). – MS (FD): Calcd. m/z = 1420.4 [M$^+$; ^{140}Ce, ^{35}Cl]; found m/z = 1420 [M$^+$]. – IR: Characteristical bands of the OEP ligand: $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 2860, 1450, 1060, 950, 910, 845; of the TClP ligand: $\tilde{\nu}$ = 1480 cm^{-1}, 1325, 1090, 980, 800, 725, 500.

$C_{80}H_{68}CeCl_4N_8$ (1423.4) Calcd. C 67.51 H 4.82 N 7.87
Found C 67.33 H 4.74 N 7.16

2C4C2: MS (FD): Calcd. m/z = 2092.6 [M$^+$; C^{140}Ce, ^{35}Cl], 1046.3 [M^{2+}]; found m/z = 1046 [M^{2+}]. – UV/VIS: λ_{max} = 394 nm (I), 550 (II); relative intensities I ≫ II.

Bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)cerium(IV) Perchlorate, [Ce(OEP)$_2$][ClO$_4$]: 32 mg (27 μmol) of **2B** are electrolyzed in 100 ml of a 0.1 M solution of LiClO$_4$ in propylene carbonate (PC) on a sonicated platinum gauze electrode at +0.45 V. After 1 h the current drops from 1.2 mA to 0.5 mA, indicating a charge transport of 2.97 C (formally 1.2 F/mol). As soon as a rise in current is observed, the electrolysis is terminated, the solvent removed in vacuo at 50°C, and the resultant oily liquid dissolved in dichloromethane and filtered. A violet substance (39 mg, 99%) crystallizes from the filtrate. – MS (FAB): Calcd. m/z = 1204 [M$^+$ for the cation [Ce(OEP)$_2$]$^+$; ^{140}Ce]; found m/z = 1206 [M$^+$]. – IR: $\tilde{\nu}$ = 1525 cm^{-1} (oxidation state marker), 620 ($\tilde{\nu}_{Cl-O}$). – ESR (CH_2Cl_2): g = 1.9924. – ^{1}H NMR (CD_2Cl_2): δ = 3.3 (very broad signal).

$C_{72}H_{88}CeClN_8O_4 \cdot C_4H_6O_3 \cdot 0.75\ CH_2Cl_2$ (1470.9)
Calcd. C 62.67 H 6.54 Cl 6.03 N 7.62
Found C 63.81 H 6.53 Cl 6.32 N 7.22

CAS Registry Numbers

1B: 88667-89-4 / **2B**: 96383-13-0 / **2B3**: 122723-07-3 / **2B3** · 1.5 C_5H_5N: 122844-40-0 / **2B4**: 122723-10-8 / **2C4C2**: 122723-11-9 / **3B**: 101200-31-1 / **4B**: 122723-03-9 / **5B**: 122873-93-2 / **5C**: 122723-05-1 / **6C**: 122723-06-2 / **7B**: 122760-96-7 / Zn(HBP): 122723-04-0 / [Ce(OEP)(TPP)][SbCl$_6$]: 122723-09-5 / CeH(TClP)$_2$: 122723-12-0 / [Ce(OEP)$_2$][ClO$_4$]: 122723-13-1 / Ce(acac)$_3$: 15653-01-7 / [POT][SbCl$_6$]: 84071-05-6

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[1] Part LIII: J. W. Buchler, M. Kihn-Botulinski, J. Löffler, M. Wicholas, *Inorg. Chem.* in the press.

[2] Abbreviations used: (P)$^{2-}$ [or (P′)$^{2-}$], (Pc)$^{2-}$, (TTP)$^{2-}$, (TAP)$^{2-}$, (OEP)$^{2-}$, (TPP)$^{2-}$, (TClP)$^{2-}$, (HBP)$^{2-}$, (OMP)$^{2-}$: dianions of a general porphyrin, phthalocyanine, 5,10,15,20-tetra(p-tolyl)porphyrin, 5,10,15,20-tetra(p-anisyl)porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetra(p-chlorophenyl)porphyrin, 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecahyrotetrabenzo[*b,g,l,q*]porphyrin, 2,3,7,8,12,13,17,18-octamethylporphyrin, respectively; BChl, bacteriochlorophyll b; M, metal; Ln: lanthanoid metal; H(acac), acetylacetone; DMF, *N,N*-dimethylformamide; NIR, near infrared; PC, propylene carbonate; SCE, saturated calomel electrode; TCB, 1,2,4-trichlorobenzene; THF, tetrahydrofuran.

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