Cerium(IV) Bis(octaethylporphyrinate) and Dicerium(III) Tris(octaethylporphyrinate): Parents of a New Family of Lanthanoid Double-Decker and Triple-Decker Molecules[1]

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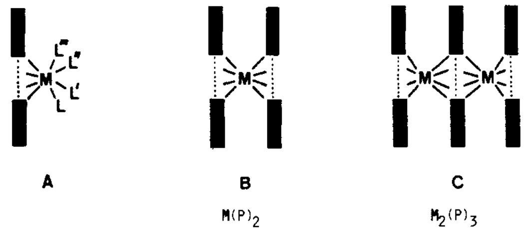
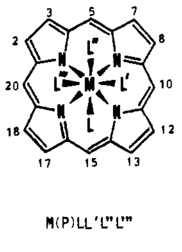
Contribution of the Institut für Anorganische Chemie and the Institut für Physikalische Chemie, Technische Hochschule, Darmstadt, D-6100 Darmstadt, Germany (F.R.), and the Laboratoire de Chimie des Métaux de Transition et de Catalyse associé au CNRS, Université Louis Pasteur, F-67008 Strasburg, France. *Received November 13, 1985*

Abstract: The synthesis, spectral characterization, and crystal structure determination of novel lanthanoid porphyrins, i.e., cerium(IV) bis(octaethylporphyrinate) (Ce(OEP)$_2$) and dicerium(III) tris(octaethylporphyrinate) (Ce$_2$(OEP)$_3$), are described. Synthesis is achieved by prolonged boiling of cerium(III) acetylacetonate (Ce(acac)$_3$) and octaethylporphyrin (H$_2$(OEP)) in 1,2,4-trichlorobenzene, $C_6H_3Cl_3$, followed by chromatography on basic alumina. Solutions of reddish-brown, diamagnetic Ce(OEP)$_2$ slowly decompose, depositing scarcely soluble, brown paramagnetic Ce$_2$(OEP)$_3$. The solution structures are deduced from ^{1}H resonance spectra, and the solid-state structures are proved by X-ray crystallography of monoclinic Ce(OEP)$_2$ ($P2_1/n$) and monoclinic ($P2_1/c$) or tetragonal ($I\bar{4}$) modifications of bis(trichlorobenzene) or tetrakis(benzene) solvates of Ce$_2$(OEP)$_3$. The bisporphyrinate is a double-decker while the trisporphyrinates are triple-decker molecules. The cerium ions appear in an approximate square-antiprismatic geometry with Ce–N distances of 2.48 Å for the Ce^{IV} and of about 2.50 Å (external porphyrinate) and 2.75 Å (internal porphyrinate) for the Ce^{III} sandwich systems. The external porphyrinates are bent away from the cerium ions in a saucer-like shape, whereas the internal porphyrinate is planar. The two mean planes of the 24 core atoms of the individual porphyrin rings lie 3.40 or 3.54 Å away from each other in the double-decker or triple-decker, respectively.

Coordination compounds of the type M(P)$_2$[3] in which two tetrapyrrole ligands (P) encompass a large metal ion M in a sandwich-like fashion have been known since 1936 when Linstead et al.[4] described the blue stannic bisphthalocyaninate, Sn(Pc)$_2$ (**1a**). The sandwich nature (see Scheme I, B) of this compound was proven by X-ray crystallography[5] after the discovery of the actinoid phthalocyanines, e.g., Th(Pc)$_2$ (**1b**) and U(Pc)$_2$ (**1c**) by Lux et al.[6] **1b** and **1c** have a sandwich structure as well.[7] While the tetrapositive central ions in **1a**–**1c** neatly coordinate to the two dinegative phthalocyanine anions in an approximate square antiprismatic geometry, difficulties are encountered in understanding the structures of the series of lanthanoid hydrogen bisphthalocyaninates LnH(Pc)$_2$ (**1d**)[8,9] first prepared by Moskalev and Kirin.[10] The molecular shape of the neodymium(III) derivative obtained by X-ray crystallography[11] did not reveal any obvious binding site for the acidic hydrogen, and recent evidence on Lu(Pc)$_2$ (**1e**)[12,13] suggests that all the green lanthanoid sandwiches have instead the composition Ln(Pc)$_2$ consisting of a Ln^{III} ion neutralized by a (Pc)$^{2-}$ and a (Pc)$^{1-}$ radical ion. Since the first observations made by Moskalev and Kirin[14,15] these complexes are being studied intensively because of their electrical conductivity and their electrochromic properties.[16-20]

Scheme I. Constitution M(P)LL′L″L‴ of Monotetrapyrroles and Configurations **A**, **B**, and **C** of Monotetrapyrroles, Bistetrapyrroles M(P)$_2$, and Tristetrapyrroles M$_2$(P)$_3$[3] and Specification of Formulas **1a**–**3b**





Specification of Important Formulae[3]

No.	M	(P)	L	L'	L''	L'''
1a	Sn	(Pc)	----------(Pc)----------			
1b	Th	(Pc)	----------(Pc)----------			
1c	U	(Pc)	----------(Pc)----------			
1d	Ln,H	(Pc)	----------(Pc)----------			
1e	Lu	(Pc)	----------(Pc)----------			
2a	Hf	(OEP)	--(OAc)-		--(OAc)---	
2b	Ce	(OEP)	----------(OEP)----------			
2c	Ce	(OEP)	--- (OEP)Ce(OEP) -------			
2d	Hf	(OEP)	-(acac)-		-acac)---	
2e	La	(OEP)	--- (OEP)La(OEP) -------			
3a	Ce	(TTP)	----------(TTP)----------			
3b	Pr,H	(TTP)	----------(TTP)----------			

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[3] Abbreviations used: (P)$^{2-}$, (Pc)$^{2-}$, (TPP)$^{2-}$, (TTP)$^{2-}$, (OEP)$^{2-}$, dianions of a general porphyrin, phthalocyanine, 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetra(*p*-tolyl)porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, respectively; M, metal; Ln, lanthanoid metal; H(acac), acetylacetone; HOAc, acetic acid; TCB, 1,2,4-trichlorobenzene; TLC, thin-layer chromatography; Me$_4$Si, tetramethylsilane; DEDE, diethyleneglycol diethyl ether.

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As metalloporphyrins are generally more soluble than their metallophthalocyanine counterparts, we thought it worthwhile to look for sandwich-like rare-earth porphyrins which might lend themselves more easily to a growth of single crystals suitable for structural studies, to a location of an acidic hydrogen atom, and to an investigation of the mechanism of the electrochromic effects. More than a decade ago, Smith et al.[21] described trinuclear mercury octaalkylporphyrins, e.g., of the composition $Hg_3(OAc)_2(OEP)_2$, in which according to ^1H resonance spectra, two terminal (acetato)mercury(II) porphyrin anions sandwich a third bridging mercury(II) ion. The previous efforts in the synthesis of lanthanoid and actinoid porphyrins,[22-25] especially of Horrocks et al.,[22,23] had only produced monoporphyrinates which were, inter alia, formulated as hexacoordinated species Ln(TPP)(acac). However, in view of the size of the lanthanoid ions and by analogy to more recent crystal structure determinations of rare-earth monophthalocyaninates,[13,26] these complexes should be regarded rather as octacoordinated species $Ln(TPP)(acac)(H_2O)_2$ representing coordination type A (Scheme I). This type is related to the square antiprismatic geometry and has been exemplified for the first time in porphyrin chemistry by the zirconium(IV) and hafnium(IV) porphyrins, e.g., $Hf(OAc)_2(OEP)$ (**2a**).[27]

On repeating the procedure of Horrocks with prolonged heating of the corresponding lanthanoid(III) acetylacetonates with tetra(*p*-tolyl)porphyrin in 1,2,4-trichlorobenzene ("TCB"), we had obtained a diamagnetic cerium(IV) bisporphyrinate, $Ce(TTP)_2$ (**3a**) and the hydrogenpraseodymium(III) bisporphyrinate, $PrH(TTP)_2$ (**3b**).[28] The hydrogen atom in **3b** can be detected by a specific NH vibration in the IR spectrum and may be removed by base to yield the symmetrical anion, $\langle Pr(TTP)_2\rangle^-$, which was characterized as the tetra(*n*-butyl)ammonium or tetraphenylarsonium salts. However, all attempts to obtain crystals suitable for an X-ray diffraction analysis have failed so far. Therefore, we have begun a study of the corresponding octaethylporphyrin derivatives, $Ln(OEP)_2$.[29] To our great surprise, the aforementioned metal insertion procedure not only produced the entire series of double-deckers $Ln(OEP)_2$ (Scheme I, coordination type B, M = Ln = La···Lu apart from Pm), but additionally the novel triple-deckers $Ln_2(OEP)_3$ (Scheme I, coordination type C, M = Ln = La···Gd apart from Pm). Some properties of $Ln(OEP)_2$ and $Ln_2(OEP)_3$ (Ln = Ce, Pr, Eu) have already been communicated.[30] This paper reports the synthesis and the structure determination of the cerium(IV) double-decker, $Ce(OEP)_2$ (**2b**), and the biscerium(III) triple-decker, $Ce_2(OEP)_3$ (**2c**). **2b** and **2c** may be regarded as the parents of the whole family of novel lanthanoid octaethylporphyrins.

Experimental Section

A. Materials. Octaethylporphyrin was purchased from Strem Chemicals, acetylacetone and 1,2,4-trichlorobenzene (TCB) from Aldrich, and alumina (super I, basic) from Woelm-ICN-Biomedicals. $Ce(acac)_3 \cdot 3H_2O$ was prepared from $Ce(SO_4)_2 \cdot 4H_2O$ (99%, Fluka).[31] TCB was dried by passing an alumina column (basic, super I).

Table I. Crystallographic Data of $Ce(OEP)_2$, **2b**, and $Ce_2(OEP)_3$ as the Bis-TCB Solvate, **2c**·2TCB

crystals	**2b**	**2c**·2TCB
formula	$C_{72}H_{88}N_8Ce$	$C_{120}H_{138}N_{12}Cl_6Ce_2$
Mol wt	1205.68	2241.48
Cryst syst	monoclnc	monoclnc
a(Å)	15.514 (4)	13.937 (4)
b (Å)	15.206 (4)	22.758 (8)
c (Å)	26.141 (8)	18.506 (6)
β (deg)	93.04 (2)	110.25 (1)
U (Å^3)	6158	5507
Z	4	2
densty (calcd)	1.30	1.35
μ (cm^{-1})	62.07	10.27
space group	$P2_1/n$	$P2_1/c$
radiatn	Cu	Mo
Cryst size (mm)	0.14 × 0.24 × 0.28	0.17 × 0.30 × 0.30
diffrctmtr	PW 1100/16	Siemens/Stoe
temp (°C)	−100	23
scan mode	$\theta/2\theta$ flying^a	$2\theta:\omega = 1:3$
$\Delta\theta$ (deg)	$1 + 0.14 \tan(\theta)$	$1.65 + 0.35 \tan(\theta)$
step width (deg)	0.05	0.03
scan speed (deg/s)	0.024	0.1/0.3^b
θ limits (deg)	4/57	2/20
octants	$+h, +k \pm l$	$\pm h, +k + l$
no. of measd data	8892	6908
no. of obsd data	6969	4042
abs. min and max	1.14/1.42	1.15/1.38
R_1	0.048	0.037
R_2	0.053	0.047
ERRFIT	1.26	1.71

^{a} Flying step scan. ^{b} Depending on intensity.

B. Methods. Spectra were obtained with the following instruments: mass spectra, Varian MAT 311 A with data system SS 100 MS (direct insertion, ion source at 250 °C, field ion desorption); infrared spectra, Perkin-Elmer 397, KBr pellets; UV-Vis spectra, Hewlett Packard HP 8451 A; ^1H NMR spectra, Bruker WM 300 (300 MHz, Me_4Si as internal reference, room temperature). Magnetic measurements were performed with a vibrating reed magnetometer in the Institut für Festkörperphysik, Technische Hochschule Darmstadt, elemental analyses by Analytische Laboratorien Malissa & Reuter, D-5251 Elbach.

C. Synthesis of Bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)cerium(IV), $Ce(OEP)_2$ (2b), and Tris(2,3,7,8,12,13,17,18-octaethylporphyrinato)dicerium(III), $Ce_2(OEP)_3$ (2c). A solution of 300 mg (0.566 mmol) of $H_2(OEP)$ and 1 g (2.28 mmol) of $Ce(acac)_3 \cdot 3H_2O$ in 50 mL of TCB is refluxed under a slow stream of nitrogen ("reinst"/99.99%; $O_2 < 50$ vpm). After 1 h, the color of the initially red-violet solution changes to yellow-brown. After another 19 h, the TCB is removed in a high vacuum at a bath temperature of 50 °C. The dark blue residue is chromatographed at an alumina column (grade I, basic, 3.5 × 7 cm). A dark reddish-brown, first fraction (I) is eluted with toluene, a dark brown second fraction (II) with toluene/methanol (100:1). I contained mainly **2c** besides some **2b**, II preponderantly **2b** besides some **2c**. After combining I and II, vacuum evaporation of the solvents, and recrystallization of the residue from benzene/TCB (5:1) small compact dark blue crystals of a bis(TCB) solvate of **2c** appear while **2b** remains in the solution. The crystals of **2c**·2TCB (42 mg, 12%) are separated by filtration and washed with benzene in which they are insoluble. The filtrate was taken to dryness in vacuo, and the crude **2b** was chromatographed at an alumina column (grade I, basic, 3.5 × 5 cm) with toluene. Pure **2b** (264 mg, 78%) is obtained by crystallization from *n*-decane.

Note: when the cerium insertion is run in a stream of argon (99.9999%), fraction I of the first chromatography contains pure **2c**, fraction II consists of pure **2b**. However, during the subsequent manipulations **2b** is to some extent transformed into **2c** which is separated by filtration. In this case, the total yields of combined crops are **2b**, 185 mg (55%), and **2c**·2TCB, 118 mg (35%).

Anal. Calcd for $C_{72}H_{88}N_8Ce$ (**2b**): C, 71.73; H, 7.36; N, 9.29; Ce, 11.62. Found: C 71.64; H, 7.23; N, 9.19; Ce, 11.94 (difference to 100%). Calcd for $C_{120}H_{138}N_{12}Ce_2Cl_6$ $\langle Ce_2(OEP)_3 \cdot 2TCB$, bis(TCB) solvate of **2c**): C, 64.30; H, 6.21; N, 7.50; Ce, 12.50; Cl, 9.49. Found: C, 64.87; H, 6.34; N, 7.61; Ce, 12.73 (difference to 100%); Cl, 8.45. Infrared spectra: **2b**, single band at 841 cm^{-1}; **2c**, double band at 832 and 841

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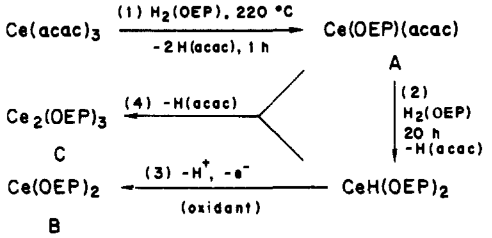
Scheme II. Formation of Double-Decker and Triple-Decker Porphyrins, Type B and C (Scheme I) from Monoporphyrins A, Exemplified with Cerium Derivatives



cm^{-1}. Mass spectrum: **2b**, A = 1204 (^{140}Ce isotope); **2c** did not give any ions.

D. X-ray Crystallography. Crystals of **2b** suitable for X-ray diffraction were obtained by slow evaporation of a *n*-decane solution. A crystal of **2c**·2TCB was picked from the deposit of the fraction I of the first chromatography and was the bis(TCB) solvate according to the elemental analysis and the X-ray data. A second crystalline modification of **2c** appeared on attempted recrystallization of **2b** from benzene, showing that the transformation **2b** → **2c** was still going on to some extent. This crystal had the composition $Ce_2(OEP)_3{\cdot}4C_6H_6$ as shown by X-ray crystallography.[32]

For the crystals of **2b**, the diffraction data were collected at -100 °C on a Philips PW1100/16 automated diffractometer equipped with a low-temperature device built in Strasbourg. For **2c**·2TCB, these data were collected in Darmstadt at room temperature on a Siemens/Stoe automated diffractometer (a low-temperature device was not available for this instrument). Crystal data and data collection parameters are displayed in Table I. For **2b**, orientation matrices and unit-cell parameters were obtained from 25 machine-centered reflections. For **2c**·2TCB, the orientation matrix was determined from 16 reflections; final cell dimensions were obtained from the 2θ values of 64 reflections, measured at positive and negative 2θ to minimize experimental errors. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize background counts without loss of net peak intensity at the 2σ level.

Three standard reflections were measured every hour; **2b** showed no decay and **2c**·2TCB standards dropped by 15% over the duration of the data collection. No equivalent reflections were recorded for **2b**; 6908 reflections of **2c** were collected which yielded 5111 unique reflections (internal R: 0.023). The raw step-scan data of **2b** were converted to intensities by using the Lehmann-Larsen method.[33] For both complexes, Lorentz, polarization, and absorption corrections were applied (computed by numerical integration for **2c**·2TCB and by the empirical method of Walker and Stuart[34] for **2b**).

The structures were solved by using the heavy atom method (**2b**) or direct methods (**2c**). After isotropic refinements of the heavy atoms, difference-Fourier maps revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors B(H) = 1 + Beqv (C) Å^2. Hydrogen atom parameters were not allowed to vary during the full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was $w = [(\sigma_{\text{counts}})^2 + (pI)^2]^{-1}$ with p = 0.08 (**2b**) and p = 0.04 (**2c**·2TCB). The scattering factors and anomalous dispersion coefficients were taken from the literature.[35,36] For all computations, the Enraf-Nonius SDP package was used[37] on a PDP 11/60 computer with the exception of local data reduction programs.

Results and Discussion

(a) Chemistry. The formation of the novel cerium(IV) bisporphyrinate ($Ce(OEP)_2$, **2b**) and the dicerium(III) trisporphyrinate ($Ce_2(OEP)_3$, **2c**) is explained according to Scheme II. The original protocol developed by Horrocks, Jr.[22] does not seem to provide an easy access to a cerium monoporphyrin. Wong mentions a complex $Ce(TPP)(acac)_2$ the isolation of which could not be reproduced by the checker.[24] In our extension of this protocol, we always find double-deckers like $Ce(TTP)_2$[28] or $Ce(TPP)_2$[38] while monoporphyrins are not observed. However, with the majority of other lanthanoid insertions, Horrocks and ourselves have isolated lanthanoid(III) monoporphyrins of the coordination type A (Scheme II, reaction 1) which seem to have the general formula Ln(P)LL′L″L‴ (see Scheme I, A) where L–L′ is a rather firmly bound (acac) residue while L″ and L‴ are solvent or water molecules.[24,29] They appear especially after 1–4 h of refluxing of the reaction mixture but are converted into double-deckers or triple-deckers on prolonged boiling. As we start from $Ce(acac)_3$, it then seems reasonable to assume that also in this case, a Ce^{III} monoporphyrin Ce(OEP)(acac) is formed which then is partially converted to the Ce^{III} double-decker $CeH(OEP)_2$ by reaction with uncomplexed $H_2(OEP)$ (Scheme II, reaction 2). Such a hydrogen lanthanoid(III) bisporphyrinate has been isolated in the case of $PrH(TTP)_2$[28] but never in the case of cerium; therefore, it seems likely that the hydrogen cerium(III) bisporphyrinates are easily autoxidized under the reaction conditions to yield cerium(IV) bisporphyrinates, e.g., **2b** (Scheme II, reaction 3).

Apart from autoxidation, there is another reaction path for the consumption of the postulated species $CeH(OEP)_2$: it may undergo the condensation reaction 4 (Scheme II) with the monoporphyrin, Ce(OEP)(acac), to yield the triple-decker, $Ce_2(OEP)_3$ (**2c**). Obviously, the condensation and the autoxidation compete with each other. Thus, a more thorough exclusion of oxygen considerably increases the yield of the triple-decker from 12 to 35% at the expense of the yield of the double-decker which drops from 78 to 55%. Within the yield limits given, the procedure is fully reproducible. However, no attempts were made to avoid the formation of the double-decker completely because the latter seemed to be a more useful compound; presently we are investigating its oxidation to a paramagnetic salt, $\langle Ce(OEP_2)\rangle\langle SbCl_6\rangle$[39] which resembles the neutral species like $Eu(OEP)_2$.[30] Anyway, the monoporphyrin Ce(OEP)(acac) and the bisporphyrin $CeH(OEP)_2$ appear to be plausible intermediates to explain the formation of both **2b** and **2c**.

$Ce(OEP)_2$ (**2b**) and $Ce_2(OEP)_3$ (**2c**) have very different solubilities. **2b** is rather soluble even in alkanes, while **2c** is practically insoluble in most solvents used in metalloporphyrin chemistry, e.g., dichloromethane or toluene, as soon as it has crystallized. Nevertheless, **2c** is sufficiently soluble in tetrachloromethane for the measurement of a NMR spectrum. The separation of the two species is impeded by a slow transformation of **2b** into **2c** according to reaction 5.

$$2Ce(OEP)_2 + 2H^+ + 2e^- \rightarrow Ce_2(OEP)_3 + H_2(OEP) \quad (5)$$

The nature of the required reducing agent in this reaction is not clear. The sparingly soluble **2c** slowly crystallizes from solutions of **2b**. This was rather confusing in the beginning of the work: crystals having deposited from benzene/TCB solutions of apparently pure **2b** which was fully characterized spectrally (see next paragraph) surprisingly then consisted of $Ce_2(OEP)_3{\cdot}2TCB$ (**2c**·2TCB) as shown by X-ray crystallography (see later) and elemental analysis. A second attempt to grow crystals of **2b** from benzene resulted in the deposition of crystals of $Ce_2(OEP)_3{\cdot}4C_6H_6$.[32] The octaethylporphyrin remaining in the solution was identified by TLC (thin-layer chromatography) and UV–vis spectra. The reactions 1–5 seem to be general for lanthanoid

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[32] Crystallographic data: $C_{132}H_{156}N_{12}Ce_2$ (2191.04), tetragonal, a = 13.889 Å, b = 13.889 Å, c = 29.195 Å, β = 90°, Z = 2, d = 1.29 g/cm^3, space group $I\bar{4}$, Cu radiation, crystal size 0.12 × 0.18 × 0.24 mm, diffractometer PW 1100/16, T = -100 °C; number of data: measd 2982, obsd: 1870; R_1: 0.053, R_2: 0.077. The data were recorded, and the structure was solved as given for **2b**. Due to a large mosaic spread of the crystal the peak widths at half-height were 0.7° in θ. Preliminary tests in the ω scan mode did not improve the situation. Therefore, only qualitative bond lengths and angles can be derived from this structure (see footnote 52).

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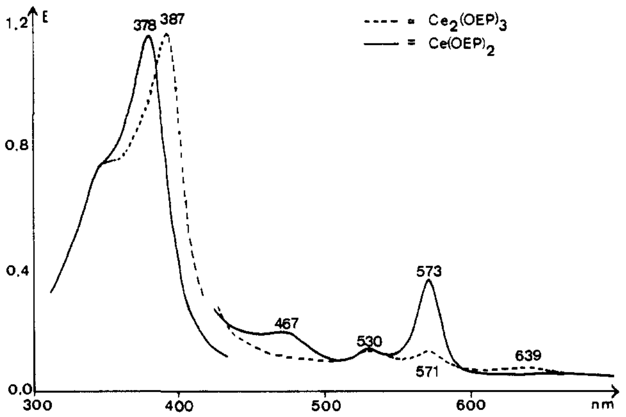

Figure 1. UV–vis spectra of $Ce(OEP)_2$ (**2b**) (solid line; in cyclohexane) and $Ce_2(OEP)_3$ (**2c**) (dashed line; in DEDE[3]). $\lambda < 430$ nm: 1-mm cuvette, $\lambda > 430$ nm: same solution, 10-mm cuvette.

octaethylporphyrins for Ln = La···Gd.[29,30] Heating the compounds above 50 °C should be avoided, because sometimes decomposition (mostly demetalation) may occur. Therefore, traces of solvents have been left within the samples, and no attempts of thorough drying were made.

(b) Identification. $Ce(OEP)_2$ (**2b**) and $Ce_2(OEP)_3$ (**2c**) are identified by elemental analyses, their TLC R_f values (**2b**, 0.79 in toluene; **2c**, 0.19 in tetrachloromethane), infrared spectra showing all the typical bands of octaethylporphyrin complexes lacking axial ligands, magnetic measurements, and their optical spectra (see Figure 1). **2b** gave a molecular ion in the field ion desorption mass spectrum. From **2c**, no ions could be obtained. In the IR spectrum, **2c**·2TCB shows an additional band at 832 cm^{-1} and slightly different relative intensities of the other bands as compared with **2b**; an additional band at 1475 cm^{-1} appearing in **2b** is missing in **2c**. **2b** is diamagnetic, whereas **2c** is paramagnetic with $\mu_{eff} = 2.2\ \mu_B$ (per Ce^{III}) independent of temperature; for an undisturbed Ce^{III} ion, 2.54 μ_B would be expected. Thus, there does not seem to exist an antiferromagnetic interaction between the two Ce^{III} ions in **2c**.

On first glance, the double-decker **2b** has a "normal" UV–vis spectrum of a metalloporphyrin as would be expected for a lanthanoid porphyrin.[40] There are strong B ("Soret"), Q(0,1), and Q(0,0) bands at 378, 530, and 573 nm, respectively (see Figure 1). The Soret band, however, is hypsochromically shifted as compared with a lanthanoid monoporphyrin, e.g., the europium(III) octaethylporphyrinate described by Srivastava,[25] or other octacoordinated d^0 monoporphyrinates, e.g., $Hf(OEP)(acac)_2$ (**2d**); in the latter, the Soret band is found at 400 nm.[41] Such a hypsochromic shift is typical for several μ-oxo complexes, e.g., (μ-oxo)bis[(octaethylporphyrinato)scandium(III)] systems like $[Sc(OEP)_2]_2O$[42] or $[RuOMe(OEP)]_2O$,[43] and the metal–metal bonded bismetalloporphyrins, e.g., $Rh_2(OEP)_2$[44] or $Mo_2(OEP)_2$,[45] in which two porphyrin systems are brought together in a face-to-face arrangement. Exciton interactions may be responsible for an extra band in the visible region at 661 nm and a broad tail extending into the near infrared region. Another extra band appears at 467 nm. A similar band has been found in $Ce(TTP)_2$ (**3a**).[28] This band may be due to a porphyrin-to-cerium(IV) charge-transfer transition; such transitions have been observed as very broad features in cerium(IV) acetylacetonate, $Ce(acac)_4$, at about 400–500 nm.[46]

Table II. ¹H NMR Data of the Double-Decker $Ce(OEP)_2$ as Compared with the Data of Several Binuclear or Trinuclear Metalloporphyrins with Two Cofacial Porphyrin Ligands

		chemical shift[d]				
complex	solv	CH=	CH_2 exo	CH_2 endo	CH_3	ref
$Ce(OEP)_2$ (**2b**)	*a*	9.11	4.20	3.86	1.68	1
$[Sc(OEP)]_2O$	*b*	9.55	3.98	3.94	1.65	42a
$[RuOMe(OEP)]_2O$	*c*	9.40	4.37	3.99	1.86	43a
$[OsOMe(OEP)]_2O$	*b*	9.22	4.4	3.9	1.82	47
$Hg_3(OAc)_2(OEP)_2$	*b*	9.0	4.2	3.8	1.7	21
$Rh_2(OEP)_2$	*c*	9.23	4.41	3.92	1.68	44
$Mo_2(OEP)_2$	*c*	9.20	4.33	3.91	1.78	45

[a] Toluene-d_8. [b] Chloroform-d_1. [c] Benzene-d_6. [d] δ, ppm vs. int. Me_4Si

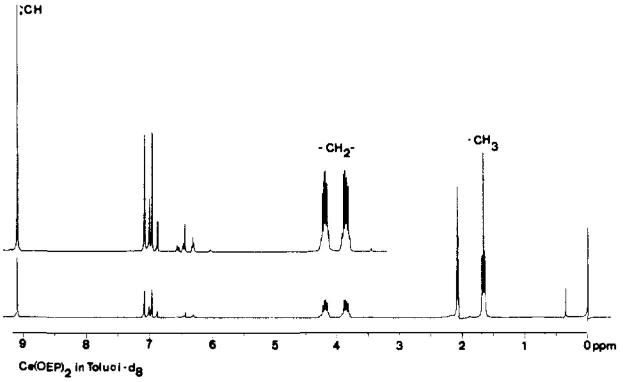

Figure 2. ¹H NMR spectrum of $Ce(OEP)_2$ (**2b**) in toluene-d_8. (The peaks at about 2.1 ppm or 6.3–7.2 ppm are due to toluene or TCB.)

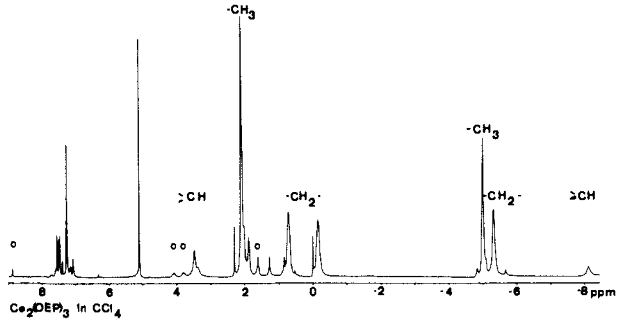

Figure 3. ¹H NMR spectrum of $Ce_2(OEP)_3$ (**2c**) in tetrachloromethane (solvent peaks as in Figure 2; additional peaks marked with an o are due to a minute amount of **2b** contained in **2c**).

Similar phenomena are found with the triple-decker $Ce_2(OEP)_3$ (**2c**). The Soret band is hypsochromically shifted to 387 nm, and extra bands occur at 755 and 639 nm. No band is found between 450 and 500 nm. If the band found at 467 nm in **2b** is a porphyrin-to-cerium(IV) charge-transfer band, there should not be such a band in **2c** because **2c** contains two cerium(III) ions which certainly have a lower oxidation potential than cerium(IV). As a whole, the spectra of the double-decker and triple-deckers then are of the "hyper" type.[40]

(c) Structures in Solution. The double-decker or triple-decker structures for $Ce(OEP)_2$ (**2b**) or $Ce_2(OEP)_3$ (**2c**), respectively, could be deduced from the ¹H NMR spectra of their solutions in perdeuteriotoluene or carbon tetrachloride (see Figures 2 and 3 and Tables II and III). Apart from the peaks due to solvents which were not removed because of the lability of the complexes, **2b** and **2c** showed patterns of methyl (CH_3), methylene (CH_2), and methine (CH=) proton signals that could be accommodated with the structures found in the solid state (see below) both by

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Table III. ^{1}H NMR Data of the Triple-Decker Complexes, $Ce_2(OEP)_3$ (**2c**) and $La_2(OEP)_3$ (**2e**)[a]

complex	chemical shifts[b]						
				CH_2(e)			
no.	CH═(e)	CH═(i)	CH_2(i)	1	2	CH_3(i)	CH_3(e)
2e	8.19	8.13	4.09	3.72	3.37	2.59	0.95
2c	3.47	−8.12	−5.33	0.72	−0.15	−5.00	2.08
2c	−4.72	−16.25	−9.42	−2.82	−3.69	−7.59	+1.13

[a] The bottom line gives the isotropic shifts $\delta_{iso} = \delta - \delta_{ref} = \delta(\mathbf{2c}) - \delta(\mathbf{2e})$; high field shifts are given negative values; the two CH_2(e) signals (1) and (2) are not assigned to individual positions; hence, the corresponding isotropic shifts of **2c** refer to the mean value of these protons in **2e**, i.e., 3.54 ppm. [b] δ in ppm, int. Me_4Si, solvent CCl_4 + 0.1 mL benzene-d_6.

consideration of the chemical shifts and the integrated intensity ratios.

2b shows a single triplet for the methyl groups, two partially superimposed double quartets for the two diastereotopic protons of the methylene groups, and a singlet for the methine protons. The pattern of signals found with **2b** is very similar to the patterns found in the trimercury bis(octaethylporphyrinate), $Hg_3(OAc)_2(OEP)_2$,[21] in the μ-oxo complexes $[Sc(OEP)]_2O$,[42a] $[RuOMe(OEP)]_2O$,[43a] and $[OsOMe(OEP)]_2O$,[47] respectively, and in the diamagnetic dimers $Rh_2(OEP)_2$[44] or $Mo_2(OEP)_2$[45] (see Table II). Double resonance experiments disclose the geminal coupling of the diastereotopic methylene protons: on irradiation of the methyl signal at 1.68 ppm, the two double quartets at 3.86 and 4.20 ppm both collapse to two doublets with a coupling constant J = 14 Hz. Irradiation of the quartet at 4.20 ppm reduces the methyl signal to a doublet (J = 7 Hz) and the other quartet partially to a doublet, showing that all three of these signals are dependent on each other.

In mononuclear octaethylporphyrin complexes, the methyl, methylene, and methine proton signals appear in the ranges of 1.8–2.0, 4.1–4.4, and 9.6–10.6 ppm.[48] As has been noted before, in the binuclear derivatives and in $Ce(OEP)_2$ (**2b**) shown in Table II, the methyl and methine resonances experience a high field shift as compared with the mononuclear species. This shift is due to the mutual influence of each of the two ring current effects of one porphyrin system on the other. At least with the methine protons, the effect is much stronger in **2b** than in the μ-oxo complex, $[Sc(OEP)]_2O$, and comparable to the metalloporphyrin dimers, $M_2(OEP)_2$ (see Table II). This means that the porphyrin rings come very close together both in the doubledecker and the dimers. The pyrrole protons in $Ce(TTP)_2$ (**3a**) also experience a high field shift relative to a corresponding monoporphyrin.[28]

As regards the diastereotopic methylene resonances, the signal appearing at 4.20 ppm could be attributed to the exo situation because its chemical shift is close to the values found with mononuclear porphyrin complexes. Hence, the other signal at 3.86 ppm should be due to the endo situation.

From the relative intensities of the proton resonances of $Ce_2(OEP)_3$ (**2c**) (see Figure 3 and Table III), the triple-decker structure with an internal, bridging porphyrin ligand and two external, terminal porphyrin ligands becomes obvious. There are sets of broad, unresolved methyl, methylene, and methine proton signals in a 1:2 ratio belonging either to the internal (i) or the two external (e) porphyrin systems. The broad, structureless signals indicate paramagnetism of the complex which is also evident from the unusual chemical shifts of the various signals. However, not only isotropic shifts caused by the two paramagnetic cerium(III) ions but also the mutual ring current effects of three adjacent porphyrin ligands contribute to these unusual chemical shifts.

The ring current effects are evident from the data of the diamagnetic lanthanum(III) triple-decker[29] $La_2(OEP)_3$ (**2e**) (see Table III). The multiplet pattern of the spectrum of **2e** can be explained by superimposing a spectrum of the $Ce(OEP)_2$ type for the external porphyrin rings with two double quartets caused by the diastereotopic methylene protons and a spectrum of an axially symmetrical monoporphyrin for the internal porphyrin ring with a single methylene quartet. The assignments of the various signals to the internal or external rings of **2e** are given in Table III and have been checked by double resonance experiments; however, the assignment of the exo or endo methylene protons remains arbitrary. As compared with the above mentioned ranges of proton resonances of mononuclear octaethylporphyrin complexes, only the internal methyl resonance, CH_3(i), has experienced a small low field shift; all the other resonances are more or less shifted to high field. The magnitude of the high field shift increases in the series CH_2(i) < CH_2(e-exo) < CH_2(e-endo) < CH_3(e) < CH(e) < CH(i). The ethyl signals of the internal ring are shifted to higher field to a lesser degree than those of the external rings. In the NMR spectrum of a three-ring silicon phthalocyanine oligomer,[49] the very peripheral 4,5 protons of the fused benzene part in the internal ring experience a small low field shift as compared with the single-ring compound, while the 3,6 protons show the opposite behavior. Therefore, it is not surprising that the protons of the internal ring in the triple-decker **2e** which are most remote from the ring axis, i.e., CH_3(i), appear shifted to low field and the others to high field.

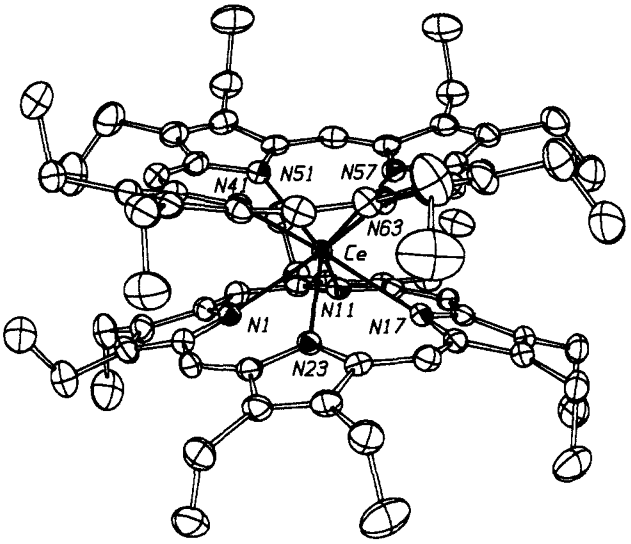

Figure 4. Ortep plot of one molecule of $Ce(OEP)_2$ (**2b**). Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted. The numbering of the CeN_8 coordination group is given.

Replacing the two diamagnetic La^{III} ions by two paramagnetic Ce^{III} ions wipes out the multiplets and causes the isotropic shifts displayed in Table III, but the principal pattern of two sets of signals due to the protons of one internal and two external porphyrin systems remains. The data of Table III indicate larger isotropic shifts for all proton resonances of the internal ring as compared with their external counterparts; this seems plausible if one realizes that the internal ring experiences the magnetic influence of two coordinated Ce^{III} ions, whereas the external rings are influenced by only one of these cations. Only the external methyl protons experience a positive shift, all others show negative shifts which have also been found for the methine protons of

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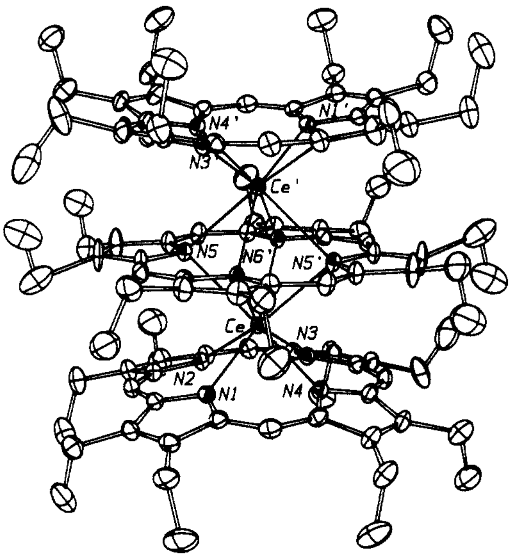

Figure 5. Ortep plot of the complete triple-decker Ce$_2$(OEP)$_3$ in **2c**·2TCB. Ellipsoids are scaled to enclose 50% of the electronic density. The numbering of the Ce$_2$N$_{12}$ coordination group is given. Primed atoms refer to their crystallographically equivalent unprimed counterparts.

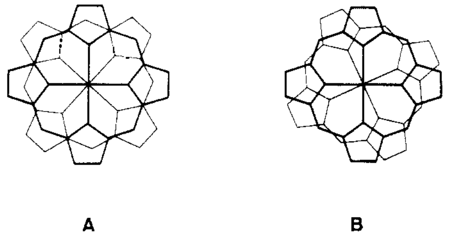

Figure 6. Stick bond model projections of Ce(OEP)$_2$ (**2b**; *A*: along the Ct–Ct′ axis) and Ce$_2$(OEP)$_3$ in **2c**·2TCB (*B*: along the Ce–Ce′ axis) showing the respective rotations of the two macrocycles in **2c** (the two external macrocycles of **2c** are superimposed; ethyl groups are omitted throughout).

various cerium(III) complexes with organic ligands, e.g., cyclopentadienide or tropolonate.[50]

(d) Crystal Structures. Table IV shows significant geometrical data for both complexes.

In the crystalline state, **2b** consists of discrete Ce(OEP)$_2$ sandwich molecules linked solely by van der Waals contacts; there are no unusually short intermolecular contacts. Figure 4 shows an Ortep plot of a single Ce(OEP)$_2$ sandwich. The Ce^{IV} ion is surrounded by the eight nitrogen atoms of the two porphyrin rings, and its coordination polyhedron is nearly a square antiprism: the porphyrin rings (henceforth, specified by their nitrogen atom with the lowest count, i.e., "N1" or "N41", see Figure 4) are rotated by an angle of 41.8° (mean value) with respect to their eclipsed position (see Figure 6a). Thus, this polyhedron is very similar to those found in the bisphthalocyaninates such as Sn(Pc)$_2$,[5] U(Pc)$_2$,[7] Nd(Pc)$_2$,[11] and Lu(Pc)$_2$.[13] The four pyrrole nitrogen atoms (henceforth, designated as 4N$_p$) of each of the macrocycles are coplanar within experimental error. The two mean planes formed by N1/N11/N17/N23 and N41/N51/N57/N63 are almost parallel, their dihedral angle being only 0.5°.

The cerium ion lies at 1.375 or 1.377 Å from the 4N$_p$ mean planes of ring "N1" or ring "N41", respectively. The separation of the two 4N$_p$ mean planes then nearly amounts to 2.752 Å. The eight Ce–N$_p$ bond lengths do not significantly differ from each other and have a mean value of 2.475 (1) Å (see Table IV).

Both macrocycles are convex and severely distorted from planarity as seen from Figure 7 (A and B). The four pyrrole mean planes of ring "N1" make dihedral angles with its 4N$_p$ mean plane of 14.8, 11.7, 17.7, and 15.4°, respectively. For ring "N41", these dihedral angles equal 13.2, 19.0, 14.3, and 17.6°, respectively. Thus, the two macrocycles are domed as seen from Figure 7 (A and B). The distances between the 4N$_p$ mean planes and the mean planes of the 24 C and N atoms of the cores (henceforth, "core atoms") are equal to 0.315 and 0.339 Å, respectively. Thus, the two mean planes of the core atoms of the individual macrocycles are about 3.40 Å apart from each other. Ring "N41" is somewhat more deformed than ring "N1", the mean displacement of the core atoms from their respective mean plane being 0.186 Å for ring "N41" and 0.177 Å for ring "N1".

Table IV. Mean Values of Selected Bond lengths (Å), Bond Angles (deg), and Individual Values of the Ce–N Bond Distances with Their Standard Deviations of **2b** and **2c**[a]

		Bonds	
2b		**2c**	
Ce–N1	2.476 (3)	Ce–N1	2.496 (4)
Ce–N11	2.474 (3)	Ce–N2	2.523 (4)
Ce–N17	2.467 (3)	Ce–No	2.504 (4)
Ce–N23	2.475 (3)	Ce–N4	2.481 (4)
Ce–N41	2.478 (3)	Ce–N5	2.751 (4)
Ce–N51	2.483 (3)	Ce–N5′	2.766 (4)
Ce–N57	2.474 (3)	Ce–N6	2.768 (4)
Ce–N63	2.484 (3)	Ce–N6′	2.745 (4)
		Mean Values	
Ce–N1/63	2.475 (1)	Ce–N1/4	2.501 (2)
		Ce–N5/6	2.758 (2)
		Core Bond Lengths	
N–C$_\alpha$	1.375 (1)		1.375 (2)
C$_\alpha$–C$_\beta$	1.449 (1)		1.442 (2)
C$_\beta$–C$_\beta$	1.358 (2)		1.349 (3)
C$_\alpha$–C$_m$	1.384 (1)		1.384 (2)
C$_\beta$–C$_\alpha$(Et)	1.503 (1)		1.523 (2)
C$_\alpha$(Et)–C$_\beta$(Et)	1.507 (1)		1.435 (3)
		Core Bond Angles	
C$_\alpha$–N–C$_\alpha$	105.6 (1)		106.0 (2)
N–C$_\alpha$–C$_\beta$	110.4 (1)		109.8 (1)
C$_\alpha$–C$_\beta$–C$_\beta$	106.7 (1)		107.1 (1)
C$_\alpha$–C$_m$–C$_\alpha$	127.7 (1)		128.8 (2)
N–C$_\alpha$–C$_m$	124.8 (1)		124.1 (1)
C$_\beta$–C$_\alpha$–C$_m$	124.4 (1)		125.8 (1)

[a] C$_\alpha$, C$_\beta$, 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.

The individual pyrrole rings are planar within experimental error. The mean values of the principal bond lengths and angles are normal[51] and given in Table IV. As seen from Figure 4, five ethyl groups of ring "N1" and three of ring "N41" point away from the sandwich, whereas the remaining eight point inwards to the opposite macrocycle.

The crystal structure of **2c**·2TCB consists of discrete Ce$_2$(OEP)$_3$ and TCB molecules which are linked by van der Waals interactions and do not show any unusual intermolecular contacts. For each Ce$_2$(OEP)$_3$ entity there are two TCB solvent molecules in the crystal. Each Ce$_2$(OEP)$_3$ molecule lies on a crystallographically imposed inversion center located between the two Ce^{III} ions. Figure 5 shows an Ortep plot of such an entity. The molecule may be described as a small stack of three octaethylporphyrinate dianions which are separated by two Ce^{III} ions. Thus, the molecule is neutral and has the shape of a triple-decker. The benzene solvate of **2c**[32] shows essentially the same molecular structure.[52]

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(52) Despite the insufficient quality of the data of the benzene solvate of **2c**, significant conclusions may be drawn from these. The overall geometry of the Ce$_2$(OEP)$_3$ moiety is similar to that found in **2c**·2TCB. In contrast to this modification, where the Ce$_2$(OEP)$_3$ molecule lies on a crystallographic inversion center, in the benzene solvate, the molecule is found on a crystallographic twofold axis. The Ce–Ce distance equals 3.74 Å, the Ce–N$_p$ distances are 2.47 and 2.51 Å for the external and 2.75 and 2.76 Å for the internal macrocycles. The internal ring is rotated from the eclipsed position by 40° with respect to the outer rings.

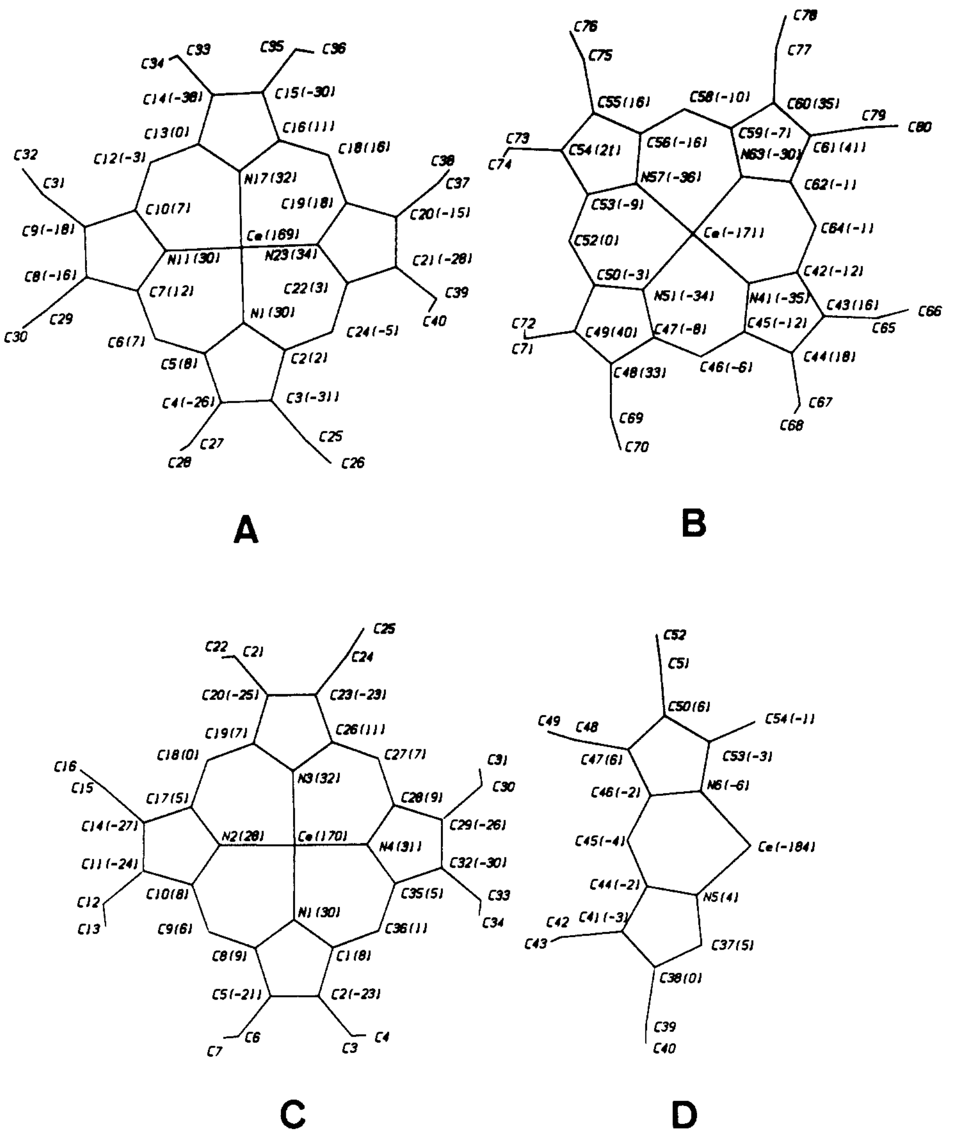

Figure 7. Stick bond model projections of Ce(OEP)$_2$ (**2b**; *A*, *B*: along the Ct–Ce and Ce–Ct′ axes; Ct and Ct′ are the centroids of the 4N$_p$ atoms) and Ce$_2$(OEP)$_3$ in **2c**·2TCB (C, D: along the Ce–Ce′ axis) with the labeling scheme of the crystallographically independent porphyrin atoms. Also shown are the deviations of the porphyrin core atoms (in 0.01 Å units) from their respective mean planes.

Due to the presence of the inversion center, the two external rings have exactly the same orientation with respect to the internal macrocycle. As in **2b**, the lanthanoid ions are surrounded by eight nitrogen atoms, four of which belong to the internal and four to the external porphyrinate ring. However, in this case, the coordination polyhedron is more distorted from the ideal square antiprism than in **2b**, the rotational angle of the two macrocycles being now 24.5° (mean value; see Figure 6, B). Furthermore, the Ce^{III} ions are not equidistant from their neighboring macrocycles: their displacements from the 4N$_p$ mean planes of the external rings and the internal rings amounting to 1.394 and 1.876 Å, respectively. The larger distance to the internal ring reflects the fact that this ring is shared between two metal ions and hence cannot be as firmly bound as the external rings. The dihedral angle between the two 4N$_p$ mean planes is 1.1° leading to a 4N$_p$ mean-plane separation of approximately 3.27 Å.

Consequently, the Ce–N$_p$ distances fall in two classes: those concerning the pyrrole nitrogen atoms of the external rings, mean value 2.501 (2) Å, slightly lengthened compared to those found in **2b**, and those concerning the pyrrole atoms of the internal ring, with a mean value of 2.758 (2) Å (see Table IV). The mean value of all Ce–N distances is 2.63 Å and is considerably larger than the corresponding value in Ce(OEP)$_2$, reflecting the fact that the former molecule contains two Ce^{III} ions whereas the latter one encompasses the smaller Ce^{IV} ion. The Ce–Ce distance in Ce$_2$(OEP)$_3$ is 3.7522 (1) Å; the observed temperature independence of the magnetic moment does not invoke any magnetic interactions between the two Ce^{III} ions.

As in **2b**, the external macrocyclic ligands of **2c** are convex and severely distorted from planarity (see Figure 7, C). The four mean planes of their pyrrole rings make dihedral angles of 13.2, 13.8, 14.8, and 15.7° with the 4N$_p$ mean plane. The external macrocycles are domed as seen from Figure 7, C. The distance between the mean planes of the 4N$_p$ atoms and the 24 core atoms equals 0.305 Å. The mean displacement of the individual core atoms with respect to their mean plane is 0.167 Å.

In contrast, and quite logically, due to the symmetrical environment of the internal macrocycle, the dihedral angles of the mean planes of the two crystallographically independent pyrrole systems with the 4N$_p$ mean plane are equal to 2.3 and 5.9°, respectively. The mean planes of the 4N$_p$ atoms and the independent 12 core atoms of the internal porphyrin half (see Figure 7, D) are quasicoincident leading to separations of approximately 3.54 Å between the mean planes of the 24 core atoms of the external ring and the 12 core atoms of the internal ring. The mean displacement of the 12 individual core atoms of the internal ring with respect to their mean plane equals 0.036 Å.

The individual pyrrole rings are planar within experimental error. The mean bond distances and angles are within the range of those generally found with complexed octaethylporphyrinates (see Table IV).[51] At each of the external rings, two ethyl groups point toward the internal ring, the other six show an outward orientation; at the internal ring, four C_2H_5 moieites of two adjacent pyrrole rings are directed to the first, the other four of the two other pyrrole rings to the second external macrocycle. The phenyl rings of the TCB solvates are planar within experimental error with C–C and C–Cl mean bond lengths of 1.358 (5) and 1.715 (5) Å, respectively, and C–C–C bond angles of 119.9 (4)°.

Conclusion. Besides a variety of phthalocyanine double-decker complexes $M(Pc)_2$, the lanthanoid derivative $Ce(OEP)_2$ (**2b**) is the first crystallographically identified porphyrin sandwich. Although Moskalev and Kirin[53] have already mentioned a phthalocyanine derivative of the molecular formula $Nd_2(Pc)_3$, they have suggested an ionic composition $Nd(Pc)^+Nd(Pc)_2^-$ for this material which may as well have been a triple-decker. Nonetheless, the triple-decker $Ce_2(OEP)_3$ (**2c**) seems to be the first of its kind which is fully characterized and its structure proven by crystal structure analysis. The chemistry and physics of the whole family of lanthanoid porphyrin double-decker and triple-decker systems is presently being explored in our laboratories.

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Registry No. 2b, 96383-13-0; **2c**, 96383-16-3; **2c**·2TCB, 96383-17-4; **2c**·$4C_6H_6$, 102233-38-5; **2e**, 102233-39-6; $Ce(acac)_3$, 15653-01-7.

Supplementary Material Available: Tables V and VI: positional and equivalent isotropic thermal parameters of all non-hydrogen atoms of **2b** and **2c**, respectively; Tables VII and VIII: anisotropic temperature factors for **2b** and **2c**; Tables IX and X: hydrogen atom coordinates for **2b** and **2c**; Tables XI and XII: complete sets of bond lengths for **2b** and **2c**; Tables XIII and XIV: complete sets of bond angles for **2b** and **2c**; Tables XV and XVI: observed and calculated structure factor amplitudes for **2b** (×10) and **2c** (78 pages). Ordering information is given on any current masthead page.

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Reactivity of Rhodium and Iridium Octaethylporphyrin Hydrides Toward Carbon Monoxide: Thermodynamic Studies of the Rhodium Formyl and Iridium Hydrido Carbonyl Complexes

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Abstract: Iridium octaethylporphyrin hydride, Ir(OEP)(H), reacts with carbon monoxide to form the carbonyl complex Ir(OEP)(H)(CO) at the same conditions where Rh(OEP)(H) reacts with CO to produce the metalloformyl complex Rh(OEP)(CHO). Thermodynamic studies for these reactions are reported and discussed in terms of differences in the M–H and M–C bond energies and the acceptor properties of the five-coordinate metalloporphyrin hydride complexes.

Metalloformyl species are important intermediates in the reactions of H_2 with CO to form organic oxygenates.[1] Formyl complexes are best known as kinetic products from reactions of metal carbonyls with hydride reducing agents.[2-6] Several metallohydrides are now known to react with CO to produce both η^1- and η^2-formyl species. Rhodium porphyrin hydrides[7-9] and $(\eta^5\text{-}C_5(CH_3)_5)_2V(H)$[10] react with CO to form carbon bonded η^1-formyl complexes, and $(\eta^5\text{-}C_5(CH_3)_5)_2Th(H)(OR)$ complexes produce compounds formulated as η^2-formyl species.[11] Rhodium

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