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Metal Complexes with Tetrapyrrole Ligands. 67.[1] Synthesis and Spectroscopic Properties of Water-Soluble Cerium Bisporphyrinate Double-Decker Ions

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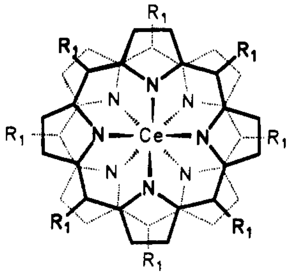
Reaction of cerium(III) acetylacetonate with lithiated tetrakis(4-pyridyl)porphyrin, tetrakis(4-(dimethylamino)-phenyl)porphyrin, and tetrakis (4-(methoxycarbonyl)phenyl)porphyrin in trichlorobenzene at 200 °C yields the corresponding neutral cerium(IV) bisporphyrinates Ce(TPyP)$_2$, Ce(TMAP)$_2$, and Ce(TMeCPP)$_2$, respectively. Quaternarization of the former two double deckers with methyl tosylate, 2-chloroethanol, or methyl iodide produces salts of the octaalkylated cations [Ce^{III}(TM$_4$PyP)$_2$]$^{7+}$, [Ce^{III}(TE$_4$PyP)$_2$]$^{7+}$, and [Ce^{IV}(TTM$_4$AP)$_2$]$^{8+}$, respectively. Ce^{III} in the two heptacations is oxidized to Ce^{IV} with bromine to obtain the corresponding octacations. The cations are isolated as halides or hexafluorophosphates. Saponification of the ester groups in Ce(TMeCPP)$_2$ with KOH gives the octacarboxylate [Ce^{IV}(TCPP)$_2$]$^{8-}$, which is hydrolyzed to a dianion and precipitated as a bis(triphenylphosphoranediyl)ammonium salt, (PPN)$_2$[Ce(TH$_3$CPP)$_2$]. The ionic Ce^{III} and Ce^{IV} porphyrin double deckers including [Ce^{IV}(TH$_4$PyP)$_2$]$^{8+}$, the octaprotonated form of Ce(TPyP)$_2$, are identified by UV/Vis and ^{1}H NMR spectra and gel electrophoresis at polyacrylamide or agarose gels in aqueous buffer solutions at pH 8.

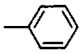
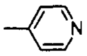
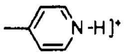
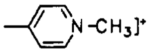
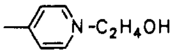
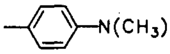
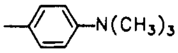
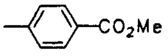
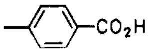
1. Introduction

The reaction center of bacterial photosynthesis bears a bacteriochlorophyll *b* dimer. This dimer is called "Special Pair".[2] Its photochemical oxidation is the first step of the light-induced decomposition of water. According to spectroscopic and electrochemical measurements and crystal structure analyses, sandwichlike bisporphyrinates of the lanthanoids[3] and the early transition metals zirconium and hafnium[4] may be regarded as structural and spectroscopic models of the Special Pair. So far, these bisporphyrinates are lipophilic, i.e. have just alkyl or aryl substituents in their periphery, as in the octaethylporphyrin derivative Ce(OEP)$_2$,[3e,5] tetraphenylporphyrin derivative Ce(TPP)$_2$[3f] (Chart 1), or Ce(OEP)(TPP)[3f] carrying two different porphyrin ligands.

Chart 1. Structural Formula and Specification of Porphyrinate Ligands of Cerium Bisporphyrinates Ce(P)$_2$ (Double Bonds Omitted)



Ce(P)$_2$

Substituents of the porphyrin ligands R$_1$	Abbrevation of the porphyrin ligands (P)$^{2-}$
	(TPP)$^{2-}$
	(TPyP)$^{2-}$
	(TH$_4$PyP)$^{2+}$
	(TM$_4$PyP)$^{2+}$
	(TE$_4$PyP)$^{2+}$
	(TMAP)$^{2-}$
	(TTMAP)$^{2+}$
	(TMeCPP)$^{2-}$
	(TH$_4$CPP)$^{2-}$

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(5) Additionally to the ones given in Scheme 1, the following abbreviations are used: (P)$^{2-}$, (OEP)$^{2-}$, (TTP)$^{2-}$, (TH$_4$CPP)$^{2-}$, (TH$_3$CPP)$^{3-}$, (TMe$_3$PyP)$^{+}$, (2-TMe$_4$PyP)$^{2+}$, and (TClP)$^{2-}$ for the species formed by deprotonation at the central N-atoms of a general porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, 5,10,15,20-tetrakis(4-methylphenyl)porphyrin, 5,10,15,20-tetrakis(4-(hydroxycarbonyl)phenyl)porphyrin, 5-(4-carboxyphenyl)-10,15,20-tris(4-(hydroxycarbonyl)phenyl)porphyrin, 5-(4-pyridyl)-10,15,20-tris(4-methylpyridinio)porphyrin, 5,10,15,20-tetrakis(2-methylpyridinio)porphyrin, and 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin, respectively; H(acac), acetylacetone; M, metal; PAA, polyacrylamide; PPN$^+$, bis(triphenylphosphoranediyl)ammonium cation; TCB, 1,2,4-trichlorobenzene; TosOMe, 4-(methoxysulfonyl)-1-methylbenzene; TSP, sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4.

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In order to evaluate these bisporphyrinates as functional models of the Special Pair, they must be aggregated with appropriate electron acceptors like quinones. This could be achieved by covalently linking hydrophobic double-decker entities to organic acceptors as is being done with a variety of monoporphyrin systems,[6] especially with zinc porphyrins.[7] However, an access to functionalized metal bisporphyrinates appears to be difficult.[1]

Under certain conditions, water-soluble porphyrins and metalloporphyrins form aggregates themselves.[8] This aggregation tendency should also be exhibited toward other multicharged aromatic acceptor molecules in solution. Therefore, the synthesis of water-soluble cerium(IV) bisporphyrinates seemed worth being done. In this paper, experiments directed toward the synthesis of the water-soluble cerium(IV) bisporphyrinate ions $[Ce(TH_4PyP)_2]^{8+}$, $[Ce(TM_4PyP)_2]^{8+}$, $[Ce(TE_4PyP)_2]^{8+}$, and $[Ce(TCPP)_2]^{8-}$ are described (see Chart 1). The redox chemistry and aggregation behavior of such ions will be described in forthcoming publications.

In a seminal paper,[9] complexes of water-soluble tetraarylporphyrins with transition metal ions have been described by Pasternack et al., along with a comparison of spectroscopic properties of cationic and anionic metal-free porphyrins in water at different pH values. pK_s values and aggregation states of water-soluble porphyrins have been discussed as well. Recently, their prospective application for industrial and medical purposes stimulated the interest in these substances. Manganese(III) tetrakis(*p*-sulfonatophenyl)porphyrinates have been used as oxidation catalysts for various purposes,[10] e.g. as ligninase models.[11] Paramagnetic water-soluble metalloporphyrins serve as contrast agents for NMR tomography.[12] Water-soluble porphyrins accumulate in tumors and help in photodynamic cancer therapy.[13] Boron-containing porphyrins are used in neutron-capture therapy of cancer.[14] Furthermore, the aggregation behavior of water-soluble porphyrins and phthalocyanines may become important for the creation of supramolecular assemblies.[15]

There is less knowledge about water-soluble lanthanoid porphyrinates. First, Horrocks et al.[16] have reported on the synthesis and properties of sulfonated lanthanoid monoporphyrinates that could be used as shift reagents for tomographic measurements. Recently, the aggregation between cationic, anionic, and neutral metal-free and samarium porphyrins has been studied.[17] The aggregate $[Sm(TMPyP)]^{5+}/[H_2(TMPyP)]^{4+}$ has the largest formation constant.

While this work was in progress, Machida and co-workers[18] have described the preparation of a cerium bisporphyrinate double decker, $Ce(TPyP)_2$, and its treatment with acid or methyl iodide giving a surprisingly stable octaprotonated cation $[Ce(TH_4PyP)_2]^{8+}$ or a salt with the alleged composition $[Ce(TM_4PyP)_2]I_8$.

2. Experimental Section

2.1. Instrumental Analysis. UV/Vis Spectra: Hewlett-Packard HP 8451 A (diode-array) and Bruins-Instruments Omega 10 spectrophotometers. Spectra were processed with SPECTRA CALC software (Galactic Industries Corp).

IR Spectra: Perkin-Elmer 397 (KBr pellets, 4000–400 cm^{-1}).

Mass Spectra: Varian MAT 311 A (field desorption mode). Molecular mass numbers, *m*/*z*, were calculated for ^{140}Ce; for masses above *m*/*z* 1500, only doubly charged ions were looked for.

^{1}H-NMR Spectra: Bruker WM-300 (300 MHz).

Elemental Analyses: Mikroanalytisches Laboratorium, Institut für Organische Chemie, TH Darmstadt, Germany (given at the end of the protocols), and Analytische Laboratorien Malissa & Reuter, D-51753 Engelskirchen, Germany (Table 6).

Electrophoresis: Horizontal slab gel system type Despahor HE 200 and vertical tube gel system Desaphor VC 135 (both Desaga/Heidelberg). Further details may be taken from previous publications.[19]

2.2. Materials. Chlorin-free tetraarylporphyrins[20] and cerium(III) acetylacetonate[21] were prepared according literature methods. The following chemicals were purchased from the companies indicated in parentheses: pyrrole and acetylacetone (both Merck, Darmstadt), 4-formylbenzoic acid methyl ester (Fluka), *N*,*N*-dimethylaminobenzaldehyde (Merck-Schuchardt), 4-formylpyridine (EGA-Chemie), cerium(III) chloride hydrate (Johnson-Matthey), *p*-toluenesulfonic acid methyl ester, propionic acid (99%), bis(triphenylphosphoranediyl)ammonium chloride (all Fluka), methyl iodide, *n*-butyllithium (1.6 M in *n*-hexane; both Merck), 2-chloroethanol (Riedel de Haën). Solvents: tetrahydrofuran and dichloromethane (both Merck) were purified by passing an alumina column (basic, super I). 1,2,4-Trichlorobenzene (TCB; Janssen Chimica), chloroform-d_1, dimethyl-d_6 sulfoxide, deuteriomethanol-d_4, and tetramethylsilane (all Merck), deuterium oxide containing 1% sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (TSP; Aldrich), and deionized water were used as received.

2.3. Stationary Phases: Alumina, type W 200, super I, basic (ICN Chemicals Woelm). Lower activity grades were generated by addition of water. Amberlite IRA (Fluka) in the chloride form was used as an anion exchanger to prepare chlorides from salts with other anions. Polyacrylamide gels (8%) were prepared by a literature method[22] using a mixture of acrylamide and 5% *N*,*N*′-methylenebis(acrylamide) (Fluka). Agarose (Fluka) was used as a 0.75% slurry in a tris/borate buffer pH 8 which was also used for all investigations with polyacrylamide gels.

2.4. Experimental Protocols. Protocol 1: Bis[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]cerium(IV), $Ce(TpyP)_2$. To a solution of 124 mg (0.2 mmol) of $H_2(TPyP)$ in 60 mL of TCB was added 1 mL of *n*-BuLi. The color of the solution turned from purple to green. After the solution was stirred under N_2 for 20 min at 20 °C, 270 mg (0.6 mmol) of $Ce(acac)_3 \cdot H_2O$ was added and the mixture was heated to reflux under N_2 for 5 h. After removal of the TCB in a high vacuum the resulting crude product A was dissolved in CH_2Cl_2 and chromatographed at an alumina column (grade III, basic, 4 × 20 cm). The following fractions were eluted: (1) a purple solution of unreacted $H_2(TPyP)$ with CH_2Cl_2/MeOH (95:5); (2) a purple solution of $H_2(TPyP)/Ce(TPyP)_2$; (3) a brown solution of $Ce(TPyP)_2$ with CH_2Cl_2/MeOH (4:1). Evaporation of fraction 3 yielded 73 mg (53%) of a brown-violet powder of $Ce(TPyP)_2$. IR (KBr): 3100, 3030 (m), 2960 (m), 1635 (m), 1600 (vs), 1440 (w), 1410 (s), 1330 (s), 1120 (vw), 980,800 (vs), 635 (m), 590 (m) cm^{-1}. MS, *m*/*z*: calcd 1372 for $[Ce(TPyP)_2]^+$, found 1374 (100%). Anal. Calcd for $C_{80}H_{48}N_{16}Ce$ (mol wt 1373.51): C, 69.96; H, 3.52; N, 16.32. Found: C, 67.77; H, 3.69; N, 14.24.

Protocol 2: Bis[5,10,15,20-tetrakis(*N*,*N*-dimethyl-4-aminophenyl)porphyrinato]cerium(IV), $Ce(TMAP)_2$. As described in protocol 1, an analogous crude product A was prepared from 157 mg (0.2 mmol) of $H_2(TMAP)$. The formation of $Ce(TMAP)_2$ was followed by thin-layer chromatography because the UV/Vis spectra of metal-free and metalated

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porphyrins do not differ significantly. After removal of the TCB in a high vacuum the resulting crude product A was dissolved in CH_2Cl_2, and the solution was chromatographed at an alumina column (grade III, basic, 4 × 20 cm). The following fractions were eluted: (a) brownish-green $Ce(TMAP)_2$ with CH_2Cl_2; (2) an olive-green mixture of $H_2(TMAP)/Ce(TMAP)_2$; at the top of the column remained $Ce^{III}H(TMAP)_2$. After evaporation of the first fraction, 57 mg (45%) of a brownish-black powder of $Ce(TMAP)_2$ was obtained. IR (KBr): 2940, 2800 (m, b), 1730 (m), 1610 (vs), 1520 (s, b), 1350 (s, vb), 1290 (m, b), 980, 950 (s), 730 (m) cm^{-1}. MS, *m/z*: calcd 855 for $[Ce(TMAP)_2]^{2+}$, found 855 (100%). Anal. Calcd for $C_{104}H_{96}N_{16}Ce$ (mol wt 1710.13): C, 73.04; H, 5.66; N, 13.10. Found: C, 70.70; H, 5.72; N, 10.62.

Protocol 3: Bis[5,10,15,20-tetrakis(4-(methoxycarbonyl)phenyl)porphyrinato]cerium(IV), $Ce(TMeCPP)_2$. As described in protocol 1, an analogous crude product A was prepared from 847 mg (1.0 mmol) of $H_2(TMeCPP)$. After removal of the TCB in a high vacuum product A was dissolved in CH_2Cl_2, and the solution was chromatographed at an alumina column (grade III, basic, 4 × 20 cm). The following fractions were eluted: (1) a purple fraction of $H_2(TMeCPP)$ with CH_2Cl_2; (2) a brown fraction of $Ce(TMeCPP)_2$ with CH_2Cl_2/MeOH (95:5) yielding 118 mg 68%) of a brownish-black powder of $Ce(TMeCPP)_2$ after evaporation of the solvent. IR (KBr): 2960 (m), 1725 (b), 1610 (s), 1570 (w), 1530 (vw), 1115–1110 (vs, vb), 740 (w) cm^{-1}. MS, *m/z*: calcd 914 for $[Ce(TMeCPP)_2]^{2+}$, found 914 (6%); calcd 846 for $H_2(TMeCPP)$, found 846 (100%). Anal. Calcd for $C_{104}H_{72}N_8O_{16}Ce$ (mol wt 1829.88): C, 68.26; H, 3.97; N, 6.12. Found: C, 65.05; H, 4.45; N, 4.75.

Protocol 4: Bis[5,10,15,20-tetrakis(4-pyridinio)porphyrinato]cerium(IV) Hexafluorophosphate, $[Ce^{IV}(TH_4PyP)_2](PF_6)_x$ (*x* unknown). A 10-mg sample of solid $Ce(TPyP)_2$ was layered with 2 mL of H_2O; while the mixture was shaken, 0.5 N HCl was added dropwise until a clear brown solution of the hydrochloride $[Ce^{IV}(TH_4PyP)_2]Cl_8$ was obtained. (Such solutions were used for electrophoreses and spectral measurements.) Then, an excess of a methanolic solution (5%) of NH_4PF_6 was added dropwise until opacity. The precipitate (13 mg) was centrifuged and dried at 40 °C. Analysis indicated decomposition of the sample on storage (see Table 6).

Protocol 5: Bis[5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrinato]cerium(III) Heptachloride, $[Ce^{III}(TM_4PyP)_2]Cl_7$. A 30-mg sample (0.02 mmol) of $Ce(TPyP)_2$ and 300 mg (1.6 mmol) of *p*-toluenesulfonic acid methyl ester were stirred 5 d at 100 °C. The cooled melt was dissolved in a mixture of 8 mL of CH_2Cl_2 and 8 mL of H_2O. Two phases were formed. The light-brown organic phase contained incompletely methylated material, and the clear dark brown aqueous phase the completely methylated product. After ion exchange of this phase on an Amberlite IRA column and evaporation, 37 mg (74%) of a black powder of $[Ce^{III}(TM_4PyP)_2]Cl_7\cdot 16H_2O$ was obtained. Anal. Calcd for $C_{88}H_{104}N_{16}O_{16}CeCl_7$ (mol wt 2030.18): C, 52.06; H, 5.16; N, 11.04; Cl, 12.22. Found: C, 51.89; H, 4.10; N, 11.13; Cl, 8.76.

Protocol 6: Bis[5,10,15,20-tetrakis(1-(hydroxyethyl)-4-pyridinio)porphyrinato]cerium(III) Heptachloride, $Ce^{III}(TE_4PyP)_2]Cl_7$. A 43-mg sample of $Ce(TPyP)_2$ was dissolved in 2 mL of 2-chloroethanol, and the solution was stirred 5 d at 100 °C. After removal of excess reagent at a high vacuum 41 mg (60%) of a black powder of $[Ce^{III}(TE_4PyP)_2]Cl_7\cdot 16H_2O$ remained. Anal. Calcd for $C_{96}H_{114}N_{16}O_{20}CeCl_7$ (mol wt 2200.34): C, 52.40; H, 5.22; N, 10.19; Cl, 11.28. Found: C, 51.37; H, 4.19; N, 9.99; Cl, 9.86.

Protocol 7: Bis[5,10,15,20-tetrakis(1-alkyl-4-pyridinio)porphyrinato]cerium(III) Hexafluorophosphates. A methanolic solution (5%) of NH_4PF_6 was added dropwise to an aqueous solution of 15 mg of the respective $[Ce^{III}(TR_4PyP)_2]Cl_8$ (R = methyl, 2′-hydroxyethyl) until the mixture became turbid, which then was kept 1 d at 4 °C. The precipitates (17–18 mg) were centrifuged and dried at 40 °C. For analyses, see Table 6.

Protocol 8: Bis[5,10,15,20-tetrakis(1-alkyl-4-pyridinio)porphyrinato]cerium(IV) Heptachloride Bromide, $[Ce^{IV}(TR_4PyP)_2]Cl_7Br$ (R = Methyl or 2′-Hydroxyethyl). A solution of bromine in CH_2Cl_2 (3 × 10^{-2} m) was added dropwise to an aqueous solution of $[Ce^{III}(TR_4PyP)_2]Cl_7$ (about 10^{-5} M for UV/Vis, about 10^{-3} M for NMR spectroscopy). The color of the mixture changed from greenish-brown due to the cerium(III) complex to red brown for the cerium(IV) species. The completeness of the oxidation was proven by UV/Vis spectroscopy. Solutions prepared like this were used for physical measurements directly.

Protocol 9: Bis[5,10,15,20-tetrakis(4-(trimethylammonio)phenyl)porphyrinato]cerium(IV) Octaiodide, $[Ce(TT_4MAP)_2]I_8$. A 0.5-mL portion (7.89 mmol) of CH_3I was added to a solution of 39 mg (0.023 mmol) of $Ce(TMAP)_2$ in 10 mL of $CHCl_3$/EtOH (8:2) and the mixture stirred for 2 h at 38 °C. The mixture was then kept 2 d at 20 °C. A 20-mL volume of 2 N aqueous NH_3 was added with shaking. The brown aqueous phase was separated and centrifuged. Small amounts (<5 mg) of a brown solid (incompletely methylated cerium bisporphyrinate) were separated. After evaporation, 42 mg (63%) of a brown powder of $[Ce(TTM_4AP)_2]I_8$ was obtained. Anal. Calcd for $C_{112}H_{120}N_{16}CeI_8$ (mol wt 2845.64): C, 47.27; H, 4.25; N, 7.88. Found: C, 50.74; H, 4.33; N, 8.76.

Protocol 10: Preparation of an Aqueous Solution of Octapotassium Bis[5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]cerium(IV), $K_8[Ce(TCPP)_2]$. To a solution of 50 mg (0.027 mmol) of $Ce(TMeCPP)_2$ in 50 mL of THF was added a mixture of 20 mL of MeOH and 8 mL of 1% KOH. After being stirred at 20 °C for 4 d, the organic phase slowly had lost its initially brown color. The aqueous phase had become dark brown due to $[Ce(TCPP)_2]^{8-}$, the product of the saponification. This aqueous solution (about 25 mL) was called "$K_8[Ce(TCPP)_2]$" and used for further experiments.

Protocol 11: Bis(triphenylphosphoranediyl)ammonium Bis[5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]cerium(IV), $(PPN)_8[Ce(TCPP)_2]$. A 2-mL volume of the aqueous solution of $K_8[Ce(TCPP)_2]$ described in protocol 10 was diluted with 2 mL of water in order to decrease the pH value of the solution to about 9 or 10, which later avoids the precipitation of the hydroxide (PPN)OH. Then, a solution of (PPN)Cl in MeOH (10%) was dropwise added until the mixture became turbid, which was kept at 4 °C. After 24 h the precipitate (about 8 mg) was centrifuged, washed twice with isopropanol, and dried. Anal. See Table 6.

3. Synthesis

The preparation of water-soluble cerium bisporphyrinates is done in two major steps: (1) Metalation of the free lipophilic (or hydrophobic) porphyrin carrying amine or ester functions; (2) transformation of the hydrophobic porphyrin ligands of neutral porphyrin complexes into hydrophilic ones by quaternarization of the amine functions or saponification of the ester groups, thus providing cationic or potentially anionic porphyrin complexes. The substituents of the porphyrin ligands used in this investigation are shown in Chart 1.

3.1. Lipophilic Complexes. The reaction of tetrakis(4-pyridyl)porphyrin, $H_2(TPyP)$, tetrakis(4-(dimethylamino)phenyl)porphyrin, $H_2(TMAP)$, and tetrakis(4-(methoxycarbonyl)phenyl)porphyrin, $H_2(TMeCPP)$, respectively, with cerium(III) acetylacetonate in trichlorobenzene, TCB, yielded the corresponding cerium bisporphyrinates.[3] Use of the lithiated porphyrins, $Li_2(P)$, increased the yield of $Ce(P)_2$ since they are far more active than the metal-free porphyrins $H_2(P)$ in many metalation reactions.[23] The essential steps are formulated in reactions 1–3. Application of this method lead to the lipophilic double deckers $Ce(TPyP)_2$, $Ce(TMAP)_2$, and $Ce(TMeCPP)_2$ (see protocols 1–3). These steps have also been discussed by Machida et al.[18c]

$$2H_2(P) + 4n\text{-BuLi} \rightarrow 2Li_2(P) + 4n\text{-Bu} \qquad (1)$$

$$2Li_2(P) + Ce(acac)_3 \rightarrow CeLi(P)_2 \qquad (2)$$

$$4CeLi(P)_2 + O_2 + 2H_2O \rightarrow 4Ce(P)_2 + 4LiOH \qquad (3)$$

The best yields were achieved by using *n*-butyllithium for eq 1. The period of refluxing should not pass 6 h. Attempts to increase the yield of cerium bisporphyrinates by increasing the duration of refluxing lead to an enhanced proportion of decomposed porphyrin. The lithium alkyls seemed to attack the porphyrins on heating and to act as reductants. Prolonged refluxing during the preparation of $Ce(TPyP)_2$ (protocol 1) shifted the Ce^{III}/Ce^{IV} relation toward the Ce^{III} species (reverse of step 3). The $Ce^{III}H(TPyP)_2$ thus obtained could not be eluted during the chromatographic purification but remained at the top of the column. Extraction of this top material with CH_2Cl_2/MeOH only partly released $Ce^{IV}(TPyP)_2$, thus reducing the yield. It is difficult to understand how Machida et al.[18c] obtained a yield of more than 60% after 48 h of refluxing in presence of *n*-BuLi.

During the preparation of $Ce(TMeCPP)_2$ (protocol 3) a third side reaction took place: Besides formation of $Ce^{III}H(P)_2$ and decomposition of the porphyrin, saponification of the carbomethoxy ester functions occurred when refluxing was extended for longer than 8 h. The resulting mixture of products could not be purified by column chromatography without great loss of material. Application of the strong, nonnucleophilic sterically hindered base lithium diisopropylamide in eq 1 decreased the proportion of saponification products but decomposition still occurred.

The lipophilic double deckers were identified by elemental analyses, IR, NMR, and mass spectra (for the data, see below or at the end of the protocols). Like $Ce(TPP)_2$, the double deckers $Ce(TMAP)_2$ and $Ce(TMeCPP)_2$ are disintegrated by dilute hydrochloric acid yielding $H_2(TMAP)$ and $H_2(TMeCPP)$,[5] respectively. Surprisingly, as already stated by Machida,[18] $Ce(TPyP)_2$ resists dilute hydrochloric acid, which seems to protonate all pyridine residues, yielding an octacation in reaction 4.

$$Ce(TPyP)_2 + 8HCl \rightarrow [Ce(TH_4PyP)_2]^{8+} + 8Cl^- \quad (4)$$

The special stability of complexes $M(TM_4PyP)^{8+}$ ($M^{2+} = Zn^{2+}$, Cd^{2+}, Hg^{2+}, Pb^{2+}) as compared with the corresponding complexes $M(TTM_4AP)^{4+}$ or $M(TPPS_4)^{4-}$ has already been stated by Hambright et al.[24] A stability order $(TM_4PyP)^{2+} > (TTM_4AP)^{2+} > (TPPS)^{6-}$ has been found for the respective porphyrin ligands. The reverse order is observed for the basicity at the central N-atoms of the porphyrins $H_2(TM_4PyP)^{4+} < H_2(TTM_4AP)^{4+} < H_2(TPPS)^{4-}$.[24]

3.2. Hydrophilic Complexes. The most simple procedure to get a water-soluble cerium(IV) bisporphyrinates was indeed the treatment of $Ce(TPyP)_2$ with acid according to reaction 4. While Machida[18a] mentions the existence of a hydrochloride derivative without detailed information about kind or concentration of the acid used, addition of 0.5 M HCl to $Ce(TPyP)_2$ in water (reaction 4, protocol 4) sufficed to obtain what appears to be an aqueous solution of $[Ce(TH_4PyP)_2]^{8+}$ by spectral and electrophoretic comparison to $[Ce(TM_4PyP)_2]^{8+}$ (see section 4.2). The cation was precipitated as a hexafluorophosphate with ammonium hexafluorophosphate dissolved in methanol (protocol 4). The resulting powder, however, decomposed on storing under evolution of HF as evidenced by the observed etching of the glass vessel (see also section 5). The octaprotonated cation seemd to act as a Brønsted acid in the solid state.

Quaternarization of the pyridine nitrogen atoms in $Ce(TPyP)_2$ with *p*-toluenesulfonic acid methyl ester,[25] TosOMe, yielded $[Ce^{III}(TPyP)_2](Tos)_7$ (protocol 5) with concomitant reduction of the Ce^{IV} ion according to reaction 5 as seen from the UV/vis spectrum. No attempts were made to identify the reducing agent involved. Obviously, the lower charge of Ce^{III} is more favorable in presence of the 8 positive charges at the pyridyl groups.

$$Ce^{IV}(TPyP)_2 + 8TosOMe + e^- + H^+ \rightarrow [Ce^{III}(TM_4PyP)]_2(Tos)_7 + TosOH \quad (5)$$

This tosylate was very hygroscopic and difficult to handle. Ion exchange at an Amberlite IRA column in the chloride form lead to water-soluble $[Ce^{III}(TM_4PyP)_2]Cl_7$. The methylation procedure given in the literature,[18c] methyl iodide, 20 °C, 20 h, did not yield any water-soluble material. Total methylation with methyl iodide required heating to 38 °C for about 3 d. The heptacation was isolated from the product after ion exchange as the chloride salt, $[Ce^{III}(TM_4PyP)_2]Cl_7$. Although Machida et al. address their methylation product as $[Ce^{IV}(TM_4PyP)_2]I_8$, it probably was a Ce^{III} derivative (see below).

2-Chloroethanol was used by Nadakyan and co-workers[26] to alkyllate copper and zinc complexes of tetrakis(3-methylpyridyl)porphyrin to obtain water-soluble complexes. Corresponding to this observation, treating $Ce(TPyP)_2$ with 2-chloroethanol yielded $[Ce^{III}(TE_4PyP)_2]Cl_7$, reaction 6 (protocol 6), also accompanied by reduction. $[Ce^{III}(TM_4PyP)_2]Cl_7$ and $[Ce^{III}(TE_4PyP)_2]Cl_7$ were

$$Ce^{IV}(TPyP)_2 + 8HOCH_2CH_2Cl + e^- + H^+ \rightarrow [Ce^{III}(TE_4PyP)]_2Cl_7 + HCl \quad (6)$$

soluble as well in water as in methanol. Because of the hydroxyethyl groups the solubility of $[Ce^{III}(TE_4PyP)_2]Cl_7$ in methanol was, as expected, higher than the solubility of the corresponding methylated derivative. From the aqueous solutions of the chlorides prepared according to the protocols 5 and 6, the corresponding hexafluorophosphates were precipitated (protocol 7). These salts did not contain the expected number of PF_6^- ions (see Table 6).

The cerium(IV) bisporphyrinate cations, $[Ce^{IV}(TM_4PyP)_2]^{8+}$ and $[Ce^{IV}(TE_4PyP)_2]^{8+}$, were obtained by oxidation of aqueous solutions of the corresponding cerium(III) bisporphyrinate chlorides with bromide (added as a $\sim 3 \times 10^{-2}$ M solution in CH_2Cl_2, protocol 8). This was evidenced by UV/vis spectroscopy and electrophoresis (see Tables 3 and 5).

Reaction of $Ce(TMAP)_2$ with methyl iodide cleanly lead to $[Ce(TTM_4AP)_2]I_8$; see reaction 7 (protocol 9). In this case,

$$Ce(TMAP)_2 + 8CH_3I \rightarrow [Ce(TTM_4AP)_2]I_8 \quad (7)$$

reduction to cerium(III) did not occur. The eight positive charges of the trimethylammonio groups are farther apart from the center of the double decker than those of the pyridinio groups and hence may exert a less repulsive interaction with a tetrapositive central ion like Ce^{IV}. Another example of the effect of an increased density of positive charge at the porphyrin center is the pair $[Fe(2\text{-}TM_4PyP)(OH)]^{4+}/[Fe(TM_4PyP)(OH)]^{4+}$.[5,27] The former Fe^{III} porphyrin bearing four 2-methylpyridinio groups has its positive charges in closer vicinity to the porphyrin center and hence is more easily reduced to the Fe^{II} state as compared with the 4-methylpyridinio derivative $[Fe(TM_4PyP)(OH)_2]^{4+}$.

$Ce(TMeCPP)_2$ was saponified by 1% aqueous KOH on addition of methanol (protocol 10) yielding a solution of the potassium salt $K_8[Ce^{IV}(TCPP)_2]$. Precipitaiton by acidification as used for monoporphyrinates was not possible for $[Ce(TCPP)_2]^{8-}$, because the fully protonated bisporphyrinate $Ce(TH_4CPP)_2$ was already demetalated below pH 9. Therefore, a solution of excess bis(triphenylphosphoranediyl)ammonium chloride ("(PPN)Cl") in methanol was added to the alkaline solution of the double-decker anion. A corresponding PPN salt was isolated according to reaction 8 (protocol 11). The molar cation/anion ratio of 2/1

$$[Ce(TCPP)_2]^{8-} + 2PPNCl + 6H_2O \rightarrow (PPN)_2[Ce(TH_3CPP)_2] + 2Cl^- + 6OH^- \quad (8)$$

shown in (8) was deduced from NMR data (see Table 3) and seems more plausible than higher ratios in view of crystal packing. The formation of a double-decker dianion $[Ce(TH_3CPP)_2]^{2-}$ [5] with three undissociated carboxy groups might stabilize the solid-state structure via creation of polynuclear bridged anions held

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Table 1. UV/Vis Data for Neutral Cerium Bisporphyrinates (in CH_2Cl_2; λ_{max} in nm, log ϵ in Italics)

		Ce(TPP)$_2$[a]			
338	396	486	540	630	
4.64	*5.32*	*4.12*	*4.00*	*3.46*	
		Ce(TPyP)$_2$			
334.4	392.8	486.2	538.9	636.8	720
4.64	*5.22*	*4.04*	*3.90*	*3.47*	*3.17*
c	394[b]	489[b]	539[b]	639[b]	*c*
		Ce(TMAP)$_2$			
323.6	414.1		549.3	602.2	703
4.76	*5.11*		*3.98*	*3.80*	*sh*[d]
		Ce(TMeCPP)$_2$			
336.8	398.5	487.0	542.8	645.6	718
4.48	*5.18*	*3.98*	*3.86*	*3.45*	*3.17*

[a] Data taken from ref 3f. [b] Data taken from ref 18b (no extinction coefficients given). [c] Not determined. [d] Shoulder.

Table 2. ^{1}H-NMR Data for Neutral Cerium Bisporphyrinates ($CDCl_3$, Internal TMS, 20 °C; δ in ppm; Signal Shape in Italics)[a]

complex	H_{peri}	$H_o/H_{o'}$	$H_m/H_{m'}$	p-CH_3
Ce(TTP)$_2$[b]	8.12 (*s*)	9.39 (*m*)/6.24 (*m*)	8.12 (*m*)/6.96 (*m*)	2.57 (*s*)
Ce(TpyP)$_2$	8.34 (*s*)	9.49 (*m*)/6.35 (*m*)	9.49 (*m*)/8.61 (*m*)	
Ce(TMAP)$_2$	8.31 (*s*)	9.48 (*m*)/6.33 (*m*)	7.51 (*m*)/6.63 (*m*)	3.25 (*s*)
Ce(TMeCPP)$_2$	8.31 (*s*)	9.48 (*m*)/6.34 (*m*)	7.50 (*m*)/6.63 (*m*)	3.25 (*s*)

[a] Key: *s* = singlet; *m* = broadened multiplet. [b] Data taken from ref 3a.

Table 3. UV/Vis Data for ionic Cerium Bisporphyrinates in Samples 1–12 (λ_{max} in nm, log ϵ in Italics; sh = shoulder)

			Sample 1: $[Ce^{IV}(TH_4PyP)_2]Cl_8$[a]			
340.5	394	491.5	539.5		649	718
5.32	*5.70*	*4.65*	*4.49*		*3.56*	*3.22*
			Sample 2: $[Ce^{III}(TM_4PyP)_2]Cl_7$[b]			
338.5	423.5		465.5		618	716
5.04	*5.52*		*4.30*		*4.11*	*3.53*
			Sample 3: $[Ce^{III}(TM_4PyP)_2](PF_6)_6HF_2$[c]			
339	427		567		621	724
4.62	*5.08*		*4.04*		*3.90*	*3.52*
			Sample 4: "$[Ce(TMPyP)_2]I_8$" [d]			
e	422	490 sh	564		619	*e*
			Sample 5: $[Ce^{IV}(TM_4PyP)_2]Cl_7Br$[b]			
343.5 sh	397.5	490	543	588	645	720
4.70	*5.05*	*4.08*	*3.83*	*3.52*	*3.40*	*3.23*
			Sample 6: $[Ce^{IV}(TM_4PyP)_2](PF_6)_6F_2$[c]			
339.5	400	490	541		643	719
4.31	*5.29*	*4.31*	*4.09*		*3.63*	*3.48*
			Sample 7: $[Ce^{III}(TE_4PyP)_2]Cl_7$[b]			
338	426		565		619	720
4.80	*5.29*		*4.05*		*3.85*	*3.25*
			Sample 8: $[Ce^{III}(Te_4PyP)_2](PF_6)_6HF_2$[c]			
339	429		567		620	715
4.65	*5.14*		*3.94*		*3.77*	*3.14*
			Sample 9: $[Ce^{IV}(TE_4PyP)_2]Cl_7Br$[b]			
340 sh	398	494	543	588	648	719
4.83	*5.21*	*4.21*	*3.93*	*3.63*	*3.52*	*3.27*
			Sample 10: $[Ce^{IV}(TE_4PyP)_2](PF_6)_6F_2$[c]			
345.5	400.5	494	542.5		646	720
3.74	*5.30*	*4.33*	*4.09*		*3.57*	*3.47*
			Sample 11: $[Ce(TTM_4AP)_2]I_8$[b]			
334.5	396	487 sh	541.5		645.5	719
4.61	5.08	4.11	3.96		3.64	3.39
			Sample 12: $(PPN)_2[Ce(TH_3CPP)_2]$[f]			
337	396	487	543		643.5	718
4.61	*5.32*	*4.12*	*4.02*		*3.48*	*3.15*

[a] In H_2O/HCl. [b] In H_2O. [c] In acetone. [d] Data taken from ref 18b. [e] Not measured. [f] In methanol.

together by carboxy-dimer entities. The PPN salt is well soluble in methanol.

4. Identification of the Neutral and Ionic Double Deckers

4.1. Neutral Double Deckers. The identification of the *neutral hydrophobic double deckers* Ce(TPyP)$_2$, Ce(TMAP)$_2$, and Ce(TMeCPP)$_2$ was straightforward. In their field ion desorption mass spectra, either the singly or the doubly-charged molecular ions were observed. Their IR, UV/vis, and NMR spectra were analogous to the known double deckers Ce(TTP)$_2$[3a] and Ce(TPP)$_2$.[34] The IR data are given in the Experimental Section, and the UV/vis and NMR data are compiled in Tables 1 and 2. NMR, IR, and UV/vis data for Ce(TPyP)$_2$ were consistent with the NMR, IR, and qualitative UV/vis data given by Machida et al.[18] for this compound.

Typical features of the double deckers[3] in these spectra are as follows: 1. There is the appearance of *additional bands* in the *visible region* besides the Q(0,0) and Q(1,0) bands which normally occur in metalloporphyrin spectra, e.g. for Ce(TTP)$_2$ near 590 (weak shoulder) and 550 nm. These extra bands are termed Q′ and Q″, have maxima at 640 and 485 nm, respectively, and originate from the strong π–π interaction between the two porphyrin rings.[28] 2. There are *large chemical shift differences* and *doubling* and the *broadening* of the *ortho*- and *meta*-phenyl (or pyridyl) proton resonance signals in the ^{1}H NMR spectra of the metal bis(tetraarylporphyrinates) which result from the mutual ring current effects of two porphyrin rings, the exo or endo position of these protons in the double decker, and the retarded rotation of the aryl groups about the C5-porphyrin–C1-aryl bond. These NMR features were first shown for Ce(TTP)$_2$.[3a] Both UV/vis and NMR features are reproduced in the new neutral double deckers (see Tables 1 and 2).

The UV/vis pattern of Ce(TPyP)$_2$ and Ce(TMeCPP)$_2$ contains the weak shoulders of the Q(0,0) band which are not listed in Table 1. Additional features to the spectra of Ce(TPP)$_2$ and Ce(TPP)$_2$ are small maxima appearing at about 720 nm in the spectra of the three double deckers carrying para-substituents at the phenyl groups (see Table 1). The reason for this is not clear. The UV/vis spectrum of Ce(TMAP)$_2$ is unusual with a Soret (B) band at 414 nm and only two bands in the visible region (Table 1). Similar spectral anomalies are described for the metal-free H_2(TMAP)[29] and "explained in terms of altered conjugation in the aromatic π-system" due to the p-dimethylamino groups.

Worth noting are the chemical shifts of the meta protons of the new double deckers. As compared with Ce(TTP)$_2$, they experience a small high-field shift in Ce(TMAP)$_2$ and Ce(TMeCPP)$_2$ but a large low-field shift in Ce(TPyP)$_2$. This indicates a special decrease in electron density in the tetrapyridylporphyrin system which is also observed in the ionic species (section 4.2). Machida and co-workers[18b] report of the pyrrole protons at 8.33 ppm of Ce(TPyP)$_2$ but of no further signals. The figure of the ^{1}H-NMR spectrum given[18b] corresponds with the one found here.

4.2. Ionic Double Deckers. The solid salts isolated of the cationic double deckers $[Ce^{III}(TM_4PyP)_2]^{7+}$, $[Ce^{III}(TE_4PyP)_2]^{7+}$, $[Ce^{IV}(TE_4PyP)_2]^{8+}$, and $[Ce(TTM_4AP)_2]^{8+}$, on one hand, and of the anionic double decker $[Ce(TCPP)_2]^{8-}$, on the other hand, were less well defined (see section 5). The products of the oxidation of the heptacations with bromine, $[Ce^{IV}(TM_4PyP)_2]^{8+}$ and $[Ce^{IV}(TE_4PyP)_2]^{8+}$, were reduced again to the heptacations on attempted isolation as solid salts. Therefore, the identification of the ionic double deckers was done in solution by UV/vis (Table 3) and ^{1}H NMR spectra (Table 4) and by gel electrophoresis (Table 5).

UV/Vis Spectra. The samples 1–10 listed in the center of Table 3 are derived from Ce(TPyP)$_2$ by protonation or alkylation.

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Table 4. ^{1}H-NMR Data for Cerium Bisporphyrinate Salts (20 °C, δ in ppm)

salt	H_{peri}	$H_o/H_{o'}$	$H_m/H_{m'}$	other
$[Ce(TD_4PyP)_2]Cl_8$[a]	8.50	9.84/7.03	9.45/8.60	
$[Ce(TM_4PyP)_2]Cl_8$[b]	8.71	9.95/7.20	9.60/8.70	4.60[c]
$[Ce(TE_4PyP)_2]Cl_8$[b]	8.76	10.02/7.20	9.72/8.76	5.07, 4.35[d]
$[Ce(TE_4PyP)_2]Cl_8$[e]	8.95	10.19/7.30	9.92/9.0	5.12, 4.41[d]
$[Ce(TTM_4AP)_2]I_8$[b]	8.42	9.69/6.57	8.69/7.45	3.31[c]
$(PPN)_2[Ce(TH_3CPP)_2]$[e]	8.31	9.63/6.50	8.72/7.95	7.35–7.51[f]

[a] Taken from $Ce(TPyP)_2$ dissolved in DCl/D_2O, internal TSP. [b] In D_2O, internal TSP. [c] Singlet of $N-CH_3$ groups. [d] Two tripletlike signals of the $N(CH_2)(CH_2)OH$ fragment. [e] In MeOD-d_4, internal TMS. [f] Cluster of signals of the PPN^+ cation.

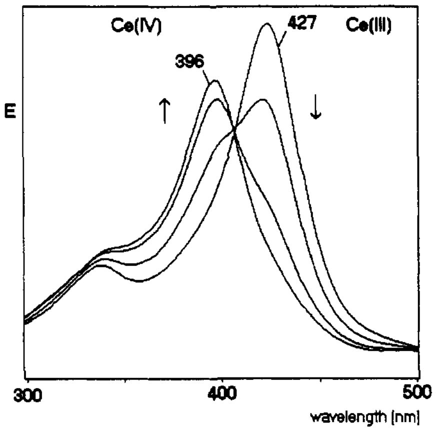

Figure 1. Spectrophotometric observation of the oxidation of $[Ce^{III}(TM_4PyP)_2]^{7+}$ (maximum at 427 nm) to $[Ce^{IV}(TM_4PyP)_2]^{8+}$ (maximum at 396 nm) with bromine in an aqueous solution. (For details, see protocol 8.)

The spectra of samples 1, 5, 6, 9, and 10 correspond well to those of $Ce(TPyP)_2$ (Table 1) and hence are easily assigned to Ce^{IV} double deckers. The Soret bands of samples 2, 3, 4, 7, and 8 appear between 422 and 427 nm. They are bathochromically shifted by about 20–30 nm as compared with $[Ce(TH_4PyP)_2]^{8+}$ in sample 1, and two strong bands in the visible appear at about 567 and 620 nm, indicating a notable alteration of the chromophore. Such a chromophore is assigned to a Ce^{III} double decker in analogy to the spectra of the Pr^{III} double-decker anion,[3a] $[Pr(TTP)_2]^-$, with maxima at 614, 562, and 410 nm or $[Ce(TClP)_2]^-$ with maxima at 610, 550, and 414 nm in their tetrabutylammonium salts.[30] Since there is no strong band at 614 nm in the N-protonated Pr^{III} double decker,[3a] $PrH(TTP)_2$, it is concluded that the ions $[Ce^{III}(TM_4PyP)_2]^{7+}$ and $[Ce^{III}(TE_4PyP)_2]^{7+}$ do not carry protons at the porphyrin N-atoms. This is plausible with respect to the high positive charge of these ions which would repel protons.

Samples 2, 4 (made by Machida et al.[18c]), and 7 were obtained by direct alkylation of $Ce(TPyP)_2$. Only with this double decker did this reduction of Ce^{IV} to Ce^{III} occur in the course of the alkylations, while in $Ce(TMAP)_2$ the Ce^{IV} ion remained unaffected. The Ce^{III} cations $[Ce(TM_4PyP)_2]^{7+}$ and $[Ce(TE_4PyP)_2]^{7+}$ were precipitated unchanged as hexafluorophosphates as was seen from the spectra of samples 3 and 8.

Addition of a dilute solution of bromine in CH_2Cl_2 to aqueous solutions of $[Ce^{III}(TM_4PyP)_2]^{7+}$ (prepared from samples 2 or 3) or $[Ce^{III}(TE_4PyP)_2]^{7+}$ (prepared from samples 7 and 8) and stirring led to formation of the Ce^{IV} cations $[Ce^{IV}(TM_4PyP)_2]^{8+}$ (samples 5 and 6) and $[Ce^{IV}(TE_4PyP)_2]^{8+}$ (samples 9 and 10), respectively. Dropwise addition effected a stepwise formation, e.g. of $[Ce^{IV}(TM_4PyP)_2]^{8+}$, as is demonstrated in Figure 1 by the stepwise growing-in of a new band at 396 nm at the expense of the band at 428 nm which ultimately vanished when only the Ce^{IV} double decker remained. A reasonable isosbestic point was seen. This clearly indicated that this double decker can exist with different oxidation states of the central ion and, hence, different net positive charges.[31] On standing in vessels open to air, the Ce^{IV} in these species slowly reverted to Ce^{III}.

Samples 11 and 12 of Table 3, $[Ce(TTM_4AP)_2]I_8$ and $(PPN)_2[Ce(TCH_3PP)_2]$, clearly were Ce^{IV} complexes, the Soret bands appearing at 396 nm with the typical stronger bands at about 487, 543, and 646 nm. The above peculiarities of the UV/vis spectrum of $Ce(TMAP)_2$ mentioned in Section 4.1 vanished on quaternarization of the dimethylamino groups; the resulting trimethylammonio groups then behave as "normal" *p*-phenyl substituents. All ionic double deckers have the characteristic small hump at about 720 nm in their spectra as well. The small feature due to the Q(0,0) transitions at about 590 nm is also seen in the spectra of the Ce^{IV} derivatives, as in those of the neutral species.

^{1}H-NMR Spectra. As is obvious by inspection of Table 4 and comaprison with Table 2, all samples containing double-decker ions gave NMR spectra with the signal pattern of the double-decker type with chemical shifts moved more or less downfield even for the anionic species in $(PPN)_2[Ce(TCH_3PP)_2]$, which was studied as a CD_3OD solution. Therefore, the spectra prove the complete formation of the ions indicated. All the cation-containing samples were measured in D_2O solutions. Thus, they were water soluble to a concentration of at least 10^{-3} mol/L. The tetrakis(pyridinio)porphyrin derivatives or $[Ce(TTM_4AP)_2]I_8$ had solubilities of at least 6×10^{-3} mol/L or 2×10^{-3} mol/L, respectively. These values are equivalent to about 12 mg/mL or 3 mg/mL, showing that the salts are indeed water soluble. $[Ce(TE_4PyP)_2]^{8+}$ was additionally measured in CD_3OD; this helped to show that chemical shifts are larger in this solvent than in D_2O.

A solution of $Ce(TPyP)_2$ in DCl/D_2O gave the spectrum of $[Ce(TH_4PyP)_2]^{8+}$. The solutions of $[Ce(TMe_4PyP)_2]^{8+}$ and $[Ce(TE_4PyP)_2]^{8+}$ were measured after oxidation with bromine of the corresponding Ce^{III} heptacations, which themselves gave only very broad signals in their spectra which could not be interpreted. This indicates the expected paramagnetism of the Ce^{III} heptacations. The similarity of the chemical shift pattern of $[Ce(TH_4PyP)_2]^{8+}$ and $[Ce(TMe_4PyP)_2]^{8+}$ is striking.

All porphyrin signals in the NMR spectra of the Ce^{IV} bis[tetrakis(4-pyridinio)porphyrinate] cations have lower chemical shifts as compared with the spectrum of the octacation $[Ce^{IV}(TTM_4AP)_2]^{8+}$ (see Table 4). This again demonstrates the large electron deficiency of the porphyrin center in the octacations derived from $Ce(TPyP)_2$, which on one hand stabilizes Ce^{III} in the center (section 3.1) and on the other hand prevents attack of protons to the central nitrogen atoms which would initiate demetalation (section 3.2).

The complete alkylation in $[Ce(TE_4PyP)_2]^{8+}$ is evident from the two unresolved triplets at 4.35 and 5.07 ppm which give the correct integral ratio to the pyrrole protons at 8.76 ppm (1:1:1). Similarly, full methylation is concluded from the appropriate integral ratios in the methylated compounds.

The 30 protons of the six phenyl groups belonging to the PPN cation generate a cluster of signals between 7.35 and 7.51 ppm in the ^{1}H-NMR spectra of PPN salts. This helped to determine the cation/anion ratio in $(PPN)_2[Ce(TCH_3PP)_2]$ with much more precision than elemental analysis (see below). For comparison, PPN salts of $[H_2(TCCP)]^{4-}$ and $[Zn(TPPS_4)]^{4-}$, i.e. zinc tetrakis(*p*-sulfonatophenyl)porphyrinate, were precipitated similarly to protocol 11 and NMR spectra were taken. A PPN/porphyrinate

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(30) Scharbert, B. Dissertation, Technische Hochschule Darmstadt, 1988.

(31) The formation of Ce^{III} complexes during the alkylation procedure seems to have been overlooked by Machida et al., their spectral data indicating the presence of a Ce^{III} species although a minute admixture of a Ce^{IV} species could be indicated by the small band at 490 nm.[18] However, larger amounts of this Ce^{IV} species ought to show up in the Soret region as well; see Figure 1.

Table 5. Electrophoresis of Ionic Cerium(IV) Double Deckers in Comparison to Ionic Copper or Metal-Free Monoporphyrins[a]

Cations[b]		
$[Cu(TM_4PyP]^{4+}$		0.11
$[H_2(TM_4PyP)]^{4+}$		0.39
$[Ce(TH_4PyP)_2]^{8+}$		0.86
$[Ce(TM_4PyP)_2]^{8+}$		0.86
$[Ce(TM_4PyP)_2]]^{7+}$		0.84
$[Ce(TE_4PyP)_2]^{8+}$		0.81
$[Ce(TE_4PyP)_2]^{7+}$		0.78
$[Ce(TTM_4AP)_2]^{8+}$		0.55
$[Cu(TTM_4AP)]^{4+}$		0.18
Anions[c]		
$[Ce(TCPP)_2]^{8-}$	0.78	0.79
$[H_2(TCPP)_2]^{4-}$	*d*	0.80

[a] R_f values measured at the front of the respective spot or zone. [b] Conditions: PAA flat bed gel, pH = 8, reference methyl green with R_f = 1.00; 150 or 300 V, 15 mA; 2–3 h. [c] Conditions: Agarose gel, pH = 8, reference potassium indigo tetrasulfonate with R_f = 1.00; left column, flat gel;[19] right column, tubular gels, tube diameter 4 mm, 2 mA per tube, 290 V. [d] Not determined.

ratio of 4:1 was clearly indicated from the integral ratio of the PPN cluster and the porphyrin signals. This ratio was found to be exactly 2:1 in $(PPN)_2[Ce(TCH_3PP)_2]$. Since this salt is only soluble in MeOH, the cationic $[Ce^{IV}(TE_4PyP)_2]Cl_8$ was also examined in deuteriomethanol in order to allow a direct comparison of chemical shifts. Signal of peri and ortho protons of the anionic species are approximately 0.6 ppm high-field-shifted compared to the cationic bisporphyrinate, as would be expected.

Electrophoresis. Horizontal gel electrophoresis of water-soluble, ionic porphyrins and their metal complexes proved to be a powerful tool to check the purity and the coordination behavior of certain samples.[19] Porphyrin tri- and tetraanions moved and separated in water at agarose gels; tri- and tetracations, at polyacrylamide (PAA) gels. Comparison with a colored reference ion (indigo tetrasulfonate for anions and methyl green, a dipositive triphenylmethane dye, for cations) allows one to assign R_f values to the colored spots observed on the gel, like in thin-layer chromatography. This method was applied to the double-decker ions described here. Results are presented in Table 5.

A variant of the flat bed technique developed by Künzel[19a] is the tube gel technique presented here. Commercial tubes (length about 15 cm, diameter 4 mm) are filled with the gel (length 12 cm) and placed vertically in an electrical field. Contrary to the flat bed technique, this system allows cooling, higher currents giving reduced migration times (about 15 min), and storage of prefilled tubes.

Figure 2 gives a comparison of cationic metal-free or copper(II) monoporphyrinates with different charges and cationic cerium(III) and cerium(IV) bisporphyrinates. Taking into account the different charges of the cations in the samples A–H, it can be seen that the gross charge alone does not determine the velocity of migration, the dication in A migrating faster than the octacation in H; therefore, the size, shape, and adsorptive properties of the cations are also important. However, species very similar in shape, but carrying different charges, can be discerned by their migration path lengths. These are compared in Table 5 for cations and anions, expressed in R_f values.

Samples B and C contained $H_2(TM_xPyP)$ (x = 3, 4) and the corresponding copper complexes, $Cu(TM_xPyP)$, with x indicating a mixture of 3- and 4-fold methylated product.[19b] The triply and quadruply charged species clearly form separate spots. The hepta- and octapositive cerium double deckers (samples D–H) have rather similar R_f values, but as regards pairs of Ce^{III} or Ce^{IV} cations containing otherwise equal porphyrin systems, the heptacations move distinctly slower than the octacations. The spots are sharp, indicating completeness of protonation or alkylation. The retardation of the hydroxyethyl octacation $[Ce(TE_4PyP)_2]^{8+}$ with respect to the methyl octacation $[Ce(TM_4PyP)_2]^{8+}$ may be caused by stronger interactions of its eight hydroxyl groups with the stationary phase. The even slower motion of $[Ce(TTM_4AP)_2]^{8+}$ is difficult to understand.

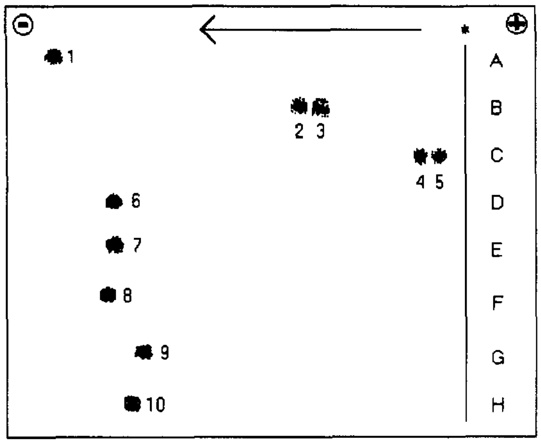

Figure 2. Flat gel electrophoresis of water-soluble, cationic porphyrins: PAA gel plate, 180 × 110 × 2 mm; tris/borate buffer, pH 8, 260 V, 3 h, asterisk marking the start line. Spots **1–10** are drawn according the eight samples A–H as follows: (A) Methyl green (R_f = 1,00), **1**; (B) mixture of $[H_2(TM_4PyP)]^{4+}$ and $[H_2(TM_3PyP)]^{3+}$, **2** and **3**; (C) mixture of $[Cu(TM_4PyP)]^{4+}$ and $[Cu(TM_3PyP)]^{3+}$, **4** and **5**; (D) $[Ce(TH_4PyP)_2]^{8+}$, **6**; (E) $[Ce^{III}(TM_4PyP)_2]^{7+}$, **7**; (F) $[Ce^{IV}(TM_4PyP)_2]^{8+}$, **8**; (G) $[Ce^{III}(TE_4PyP)_2]^{7+}$, **9**; (H) $[Ce^{IV}(TE_4PyP)_2]^{8+}$, **10**.

It seems plausible that the double-decker cations, e.g. $[Ce(TM_4PyP)_2]^{8+}$, have R_f values about two times larger than those of $[H_2(TM_4PyP)]^{4+}$. The slower migration of $[Cu(TM_4PyP)]^{4+}$ as compared with the former tetracation may be due to the basic centers of the stationary phase acting as ligands to the axial sites of the Cu^{II} ion. Similar effects were observed for anionic $[Zn(TPPS_4)]^{4-}$ and $[Mn(TPPS_4)H_2O]^{3-}$.[31b] Such interactions are not possible for $[H_2(TM_4PyP)]^{4+}$ or $[Ce(TM_4PyP)_2]^{8+}$. However, the octaanion $[Ce(TCPP)_2]^{8-}$ and the tetraanion $[H_2(TCPP)_2]^{4-}$ have practically the same mobility. It may be that the octaanion is hydrolyzed and the migrating species carries four undissociated carboxyl groups, as indicated by a formula $[Ce(TH_2CPP)_2]^{4-}$. The precipitation of $(PPN)_2[Ce(TCH_3PP)_2]$ is another hint to the importance of hydrolysis for these anions. Likewise, four K^+ ions could be complexed by one octaanion; however, such an entity should contain lots of coordinated water molecules and hence move rather slowly.

5. Characterization of the Solid Cerium Bisporphyrinate Salts

A general property of water-soluble porphyrin salts appears to be their low tendency to form crystals of well-defined composition. Therefore, only a few crystal structure determinations[32] of such salts exist, whereas hundreds of crystal structures of hydrophobic porphyrins and their metal complexes have been described.[33] Elemental analyses of water-soluble porphyrin salts found in the literature are frequently of low importance, the counterion and water content being adapted from C/H and N combustion analyses only. Despite numerous attempts, the salts described here also did not form well-defined crystals or even phases. Mostly they were isolated as powders.

Since the porphyrin ions themselves are clearly identified by their UV/vis and NMR spectra and their homogeneity proved by electrophoresis, it was not attempted to solve all the puzzles that were posed by the analytical figures obtained for the new compounds presented here, especially realizing the experience that the precision of combustion analyses of metalloporphyrins, and especially their salts, is low anyway because of the high combustion temperatures required. The elemental analyses of

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(32) (a) Ivanca, M. A.; Lappin, A. G.; Scheidt, W. R. *Inorg. Chem* .**1991**, *30*, 711–718. (b) Körber, F. C. F.; Lindsay Smith, J. R.; Prince, S.; Rizkallah, P.; Reynolds, C. D.; Shawcross, D. R. *J. Chem. Soc., Dalton Trans.* **1991**, 3291–3294.

(33) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1–70.

Table 6. Elemental Analyses of Salts Precipitated from Solutions of Cerium Bisporphyrinate Cations or Anions

	anal.: calcd (found)			
hexafluorophosphates	%C	%H	%N	%F
$Ce^{III}(TM_4PyP)_2](PF_6)_6(HF_2)6H_2O$ ($C_{88}H_{85}N_{16}CeF_{38}O_6P_6$ (2510.63))	42.10 (42.22)	3.41 (3.34)	8.93 (9.11)	28.75 (25.62)
$[Ce^{III}(TE_4PyP)_2](PF_6)_6(HF_2)\cdot 6H_2O$ ($C_{96}H_{101}N_{16}CeF_{38}O_{14}P_6$ (2750.84))	41.92 (40.32)	3.70 (3.30)	8.15 (8.18)	26.24 (27.86)
$[Ce^{IV}(TH_{3,5}PyP)_2](PF_6)_6(HF_2)\cdot 8H_2O$ ($C_{80}H_{72}N_{16}CeF_{38}O_8P_6$ (2433.44))	39.49 (38.18)	2.98 (2.83)	9.21 (8.98)	29.67 (17.63)

	anal.: calcd (found)			
"PPN" salts	%C	%H	%N	%P
$(PPN)_2[Ce^{IV}(TH_3CPP)_2]\cdot 4H_2O$ ($C_{168}H_{122}N_{10}CeO_{20}P_4$ (2864.88))	70.43 (68.30)	4.29 (4.25)	4.89 (4.48)	4.32 (7.66)
$(PPN)_4[Ce^{IV}(TH_2CPP)_2]\cdot 4H_2O$ ($C_{240}H_{180}N_{12}CeO_{20}P_8$ (3940.04))	73.16	4.60	4.27	6.29

the neutral hydrophobic double deckers $Ce(TMeCCP)_2$, $Ce(TPyP)_2$, and $Ce(TMAP)_2$ and of the chlorides or iodides obtained by alkylation of the latter two double deckers given at the end of the protocols are not very informative. The analytical figures obtained from the salts that were precipitated from aqueous solutions of the respective double-decker halides or potassium salts are listed in Table 6, together with calculated values.

Reasonable C/H and N values result only for inclusion of several water molecules in the formula. The hexafluorophosphates of $[Ce^{III}(TM_4PyP)_2]^{7+}$ and $[Ce^{III}(TE_4PyP)_2]^{7+}$ contained less fluorine than seven PF_6^- ions would require. Since the NH_4PF_6 used contained free fluoride, the formation and inclusion of HF_2^- ions was assumed and reasonable agreement of the figures achieved. For convenience, six PF_6^- and one HF_2^- where chosen likewise as counterions for the protonated $Ce(TPyP)_2$ derivative which then should carry seven protons, explaining the formula given in Table 6. The observed much lower fluoride content of the sample is due to the decomposition with loss of HF, the analytical figures proving nothing more than that a hexafluorophosphate has been precipitated. As regards the PPN salt of $[Ce(TCPP)_2]^{8-}$, the composition derived from the NMR integrals was chosen. It gives reasonable agreement for the C/H and N values when water is included, but the P value is much too high. Inclusion of more PPN (four PPN in Table 6) raises the C/H and N values exceeding the normal error limits of C/H and N determination; therefore doubts may be raised to the precision of the found P value. Certainly, only expensive and material-consuming total analyses of the samples would allow more definite conclusions.

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