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Synthesis and Electrochemical Reactivity of σ-Bonded and N-Substituted Cobalt Porphycenes

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The first synthesis and characterization of σ-bonded and N-substituted cobalt porphycenes is reported. The investigated compounds are represented as (Pc)Co(R) and (N-CH_3OEPc)CoCl, where R is CH_3 or C_6H_5, Pc is the dianion of 2,3,6,7,12,13,16,17-octaethylporphycene (OEPc), 2,7,12,17-tetrapropylporphycene (TPrPc), or 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycene (EtioPc), N-CH_3OEPc is the monoanion of N-methyl-2,3,6,7,12,13,16,17-octaethylporphycene. Each σ-bonded (Pc)Co(R) derivative can be reversibly reduced or oxidized by two electrons, but a slow migration of the σ-bonded R group occurs following electrogeneration of $[(Pc)Co(R)]^{+\bullet}$ leading, as a final product, to an N-substituted cobalt(II) porphycene which is also electroactive and undergoes two reductions in PhCN. The singly reduced product of this reaction is formulated as a Co(II) π-anion radical which undergoes a slow "back-migration" of the CH_3 group to regenerate (OEPc)Co(CH_3).

Introduction

σ-Bonded cobalt(III) porphyrins[1−3] along with other organocobalt complexes[4−9] have been used as model compounds to study the release of adenosyl or methyl radicals by homolysis of the cobalt−carbon bond of adenosylcobalamin (coenzyme B_{12}, AdoB_{12}) or methylcobalamin (MeB_{12}).[10,11] Cobalt porphyrins have also been studied as precursors in the synthesis of new conducting materials or in the synthesis of complexes possessing metal−metal interactions that can be used as catalysts for the reduction of dioxygen such as the face-to-face diporphyrin complexes.[12−15] Interestingly, some organocobalt porphyrin complexes were also recently found to efficiently initiate the polymerization of acrylates by homolysis of the cobalt−carbon bond.[16]

Porphycenes,[17,18] like their parent porphyrin isomers, can coordinate a variety of metal ions in different oxidation states.[17−23] A number of spectral and electrochemical studies

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have been carried out on metalloporphycenes,[21−23] but only two derivatives containing a cobalt central metal ion have, to date, been described in the literature.[21a,h,23i] These are (OEPc)Co^{II} and (TPrPc)Co^{II}, where OEPc and TPrPc are the dianions of 2,3,6,7,12,13,16,17-octaethylporphycene and 2,7,12,17-tetrapropylporphycene, respectively. This present paper reports the first synthesis and electrochemical characterization of cobalt porphycenes with metal−carbon and nitrogen−carbon bonds. The investigated compounds are represented by (Pc)Co(R) and (*N*-CH$_3$OEPc)CoCl, where Pc is the dianion of 2,3,6,7,12,13,-16,17-octaethylporphycene (OEPc), 2,7,12,17-tetrapropylporphycene (TPrPc), or 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycene (EtioPc), R is CH$_3$ or C$_6$H$_5$, and *N*-CH$_3$OEPc is the monoanion of *N*-methyl-2,3,6,7,12,13,16,17-octaethylporphycene.

A great deal of effort has been directed toward understanding how the nonplanarity of a given tetrapyrrole macrocyclic compounds can be related to their chemical and physical properties[24−31] and especially their redox properties.[24a,28−31] The porphycenes and their metal complexes are generally quite planar,[19,21] and they thus represent compounds whose electrochemical behavior can be compared to that of the less planar porphyrin macrocycles. This study of (Pc)Co(R) and [(*N*-ROEPc)Co]$^+$ thus provides an opportunity to investigate how differences in the physicochemical properties of σ-bonded and cobalt N-alkylated or arylated porphycenes and porphyrins can be related to each other and also to their porphyrin analogues. It was of special interest to determine if the cobalt−carbon bond is affected during reduction or oxidation of the σ-bonded cobalt porphycene and specifically if a cleavage of the cobalt−carbon bond and migration of the axial ligand occur after oxidation to give the corresponding N-arylated or N-alkylated cobalt(II) compound.[1,32−34] It was also of interest to investigate the reduction of [(*N*-ROEPc)Co]$^+$ since, in the case of porphyrins, the singly reduced N-substituted Co(II) porphyrin is unstable and undergoes a "back-migration" to re-form the initial σ-bonded complex.[32,34a,b,35,36] *N*-substituted porphyrins are able to stabilize metal ions in low oxidation states[35,37−40] but porphycenes do not show such ability due, in large part, to the smaller size of the central cavity. Thus, it was also of interest to monitor the site of electron transfer along with the possible electrochemically initiated migration of (*N*-CH$_3$OEPc)-CoCl to (OEPc)Co(CH$_3$).

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Experimental Section.

All common solvents were purified in an appropriate manner and distilled under argon prior to use. Pyridine, for the electrochemical studies, was of the highest available purity (Aldrich Chemical Co., packaged under nitrogen in Sure/Seal bottles) and was used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP) (Eastman Kodak Co.) was recrystallized from ethanol and then dried under reduced pressure at 40 °C prior to use. Tetra-*n*-butylammonium chloride (TBACl) (Eastman Kodak Co.) was used as received.

(OEPc)CoCl. (OEPc)Co was synthesized as described in the literature.[21a] To a suspension of (OEPc)Co (120 mg, 0.2 mmol) in methanol (140 mL) was added 4.8 mL of concentrated HCl. After vigorous stirring for 15 h, the solution was filtered and concentrated to about 30 mL by vacuum. CH_2Cl_2 (100 mL) was added and the resulting solution washed twice with water and then dried over Na_2SO_4 before removal of the solvent by vacuum. The residue was dissolved in CH_2Cl_2 and hexane added which led to precipitation of a black powder. Yield: 60 mg (48%). Mp: >300 °C (CH_2Cl_2/hexane). ^1H NMR (CD_3OD): $\delta = 10.25$ (s, 4H, H-9, 10, 19, 20), 4.45 (q, 8H, H-3a, 6a, 13a, 16a), 4.32 (q, 8H, H-2a, 7a, 12a, 17a), 1.98 (t, 12H, H-2b, 7b, 12b, 17b), 1.90 (t, 12H, H-3b, 6b, 13b, 16b). ^{13}C NMR (CD_3OD): $\delta = 153.8$, 149.3, 147.7, 141.3, 108.2, 22.2, 21.5, 19.5, 19.3. MS [m/z (%)]: 626 (11) [M^+], 591 (100) [M-Cl]. IR: $\nu = 2967$, 2931, 2871, 1508, 1450, 1406, 1375, 1302, 1056, 1012, 948 cm^{-1}. UV−vis (CH_2Cl_2) [λ, nm (ϵ)]: 391 (62 000), 582^{sh} (9900), 618 (23 100).

(OEPc)Co(CH_3). Methylmagnesium iodide in diethyl ether was added dropwise to a solution of (OEPc)CoCl (60 mg, 0.1 mmol) in 12 mL of absolute 1,2-dimethoxyethane under an argon atmosphere at 0 °C. The progress of the reaction was monitored by thin-layer chromatography. After no more starting material could be detected, the solution was then poured into a cold mixture containing 50 mL of CH_2Cl_2 and 10 mL of saturated NH_4Cl. The organic phase was separated, washed three times with water (20 mL), and then dried over Na_2SO_4. The solvent was removed under vacuum and the residue crystallized twice from CH_2Cl_2/hexane to yield violet prisms. Yield: 28 mg (45%). Mp: 178−179 °C (dec, CH_2Cl_2/hexane). ^1H NMR (C_6D_6): $\delta = 9.34$ (s, 4H, H-9, 10, 19, 20), 3.96 (m, 8H, H-3a, 6a, 13a, 16a), 3.79 (q, 8H, H-2a, 7a, 12a, 17a), 1.74 (t, 12H, H-2b, 7b, 12b, 17b), 1.68 (t, 12H, H-3b, 6b, 13b, 16b), −4.29 (s, 3H, H-methyl). ^{13}C NMR (C_6D_6): $\delta = 149.5$, 148.1, 146.8, 137.5, 106.9, 21.3, 20.5, 18.8, 18.3. MS [m/z (%)]: 606 (28) [M^+], 591 (100) [$M - CH_3$]. IR: $\nu = 2964$, 2931, 2869, 1510, 1300, 1135, 1057, 1013, 952, 760 cm^{-1}. UV−vis ($CHCl_3$) [λ (ϵ)]: 296 (32 100), 364^{sh} (39 500), 389 (81 000), 566^{sh} (18 000), 596 (33 700), 6712^{sh} nm (28 600). Anal. Calcd for $C_{37}H_{47}N_4Co$: C, 73.25; H, 7.81; N, 9.23. Found: C, 73.09; H, 7.52; N, 9.20.

(TPrPc)Co(CH_3). Methylmagnesium iodide in diethyl ether was added dropwise to a solution containing 60 mg (0.1 mM) of (2,7,12,-17- tetrapropylporphycenato)cobalt(III) chloride[18,21b] in 12 mL of absolute 1,2- dimethoxyethane under argon atmosphere at 0 °C. The progress of the reaction was monitored via TLC (alumina, dichloromethane). After the starting material could no longer be detected, the solution was poured into a mixture of 50 mL of dichloromethane and 10 mL of saturated aqueous ammonium chloride. The organic layer was washed twice with water, dried over sodium sulfate, and then evaporated by vacuum. The residue was crystallized twice from CH_2Cl_2/hexane to give violet prisms. Yield: 28 mg (50%). Mp: dec, 178−179 °C. ^1H NMR ($CDCl_3$): $\delta = 9.44$ (s, 4H, H-3, 6, 13, 16), 9.09 (s, 4H, H-9, 10, 19, 20), 3.99 (m, 8H, α-CH_2), 2.38 (m, 8H, β-CH_2), 1.35 (t, 12H, CH_3), −4.90 (s, 3H, Co−CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 151.4$, 149.1, 146.1, 121.0, 106.9, 31.2, 25.0, 14.6, −20.1. MS [m/z (%)]: 550 (70) [M^+], 535 (100) [$M - CH_3^+$]. IR: $\nu = 2954$, 2925, 2867, 1864, 1608, 1553, 1528, 1485, 1455, 1376, 1307, 1238, 1134, 1101, 1049, 970, 931, 913, 809, 738, 529, 436, 362, 321 cm^{-1}. UV−vis (CH_2Cl_2) [λ (ϵ)]: 289 (29 100), 365^{sh} (53 700), 385 (91 900), 560^{sh} (18 000), 592 (40 400), 610^{sh} nm (3700). Anal. Calcd for $C_{33}H_{31}N_4Co$: C, 71.98; H, 7.14; N, 10.18. Found: C, 71.60; H, 7.14; N, 9.98.

(OEPc)Co(C_6H_5). The phenylcobalt(III) complex was synthesized from (OEPc)CoCl and phenylmagnesium iodide in diethyl ether using a procedure similar to the one reported above for (OEPc)Co(CH_3). After workup, the title compound was crystallized twice from CH_2Cl_2/hexane to give violet lustrous needles. Yield: 34 mg (50%). Mp: 274−275 °C (dec, CH_2Cl_2/hexane). ^1H NMR ($CDCl_3$): $\delta = 9.47$ (s, 4H, H-9, 10, 19, 20), 5.17 (t, 1H, para-H-phenyl)), 4.57 (m, 2H, meta-H-phenyl), 3.97 (m, 8H, H-3a, 6a, 13a, 16a), 3.91 (m, 8H, H-2a, 7a, 12a, 17a), 1.67 (t, 12H, H-3b, 6b, 13b, 16b), 1.77 (t, 12H, H-2b, 7b, 12b, 17b), 0.05 (d of d, 2H, ortho-H-phenyl). ^{13}C NMR ($CDCl_3$): $\delta = 149.8$, 147.3, 146.3, 137.8, 133.3, 121.9, 120.7, 107.0, 21.0, 20.3, 18.5, 18.1. MS [m/z (%)]: 668 (43) [M^+], 591 (100) [$M - C_6H_5$]. IR: $\nu = 3052$, 2964, 2930, 2870, 1509, 1467, 1302, 1063, 1013, 952, 728 cm^{-1}. UV−vis (CH_2Cl_2) [λ, nm (ϵ)]: 302 (26 000), 361^{sh} (37 000), 390 (71 000), 591 (31 300), 612^{sh} (19 900).

(*N*-CH_3OEPc)CoCl. A 10 mL chloroform solution containing 53 mg (0.1 mM) of (OEPc)H_2, 0.5 g of sodium formate, and 0.5 mL (8 mM) of iodomethane was refluxed for 15 h. After evaporation of the solvent, the residue was dissolved in chloroform, washed with water, and chromatographed on aluminum oxide (activity III, chloroform). The second fraction was collected and diluted with chloroform to a volume of 20 mL. Cobalt(II) chloride hexahydrate was added and the mixture refluxed for 3 h. The organic layer was then washed twice with water and chromatographed on silica (3:1 chloroform/ethyl acetate). Crystallization from 1:1 chloroform/hexane yields 42.6 mg (71%) of green needles. Mp: 194−196 °C. MS [m/z (%)]: 641 (5) [M^+], 606 (30) $[M - Cl]^+$, 591 (100) $[M - CH_3 - Co - Cl]^+$. IR: $\nu = 2966$, 2933, 2873, 1488, 1453, 1128, 1014, 1002, 952, 304 cm^{-1}. UV−vis (CH_2Cl_2) [λ (ϵ)]: 243^{sh} (17 000), 335^{sh} (20 000), 402 (39 100), 625^{sh} (14 300), 666 nm (19 900).

(*N*-CH_3OEPc)$H_2^+ClO_4^-$. A 10 mL chloroform solution containing 53 mg (0.1 mM) of (OEPc)H_2, 0.5 g of sodium formate, and 0.5 mL (8 mM) of methyl iodide was refluxed for 15 h. The solvent was then removed by vacuum and the residue dissolved in chloroform, washed with water, and chromatographed on basic alumina with chloroform. The second, blue fraction was collected and shaken twice with 10% perchloric acid. Crystallization from CH_2Cl_2/hexane yielded 51.4 mg (80%) of blue needles. Mp: 165−167 °C (dec). ^1H NMR ($CDCl_3$): $\delta = 9.72$ (d, 1H, H-19), 9.68−9.61 (m, 2H, H-8, 10), 9.61 (d, 1H, H-20), 4.11−3.67 (m, 12H, H-6a, 12a, 13a, 16a, 17a), 3.45−3.09 (m, 4H, H-2a, 3a), 1.98 (br s, 1H, NH), 1.81−1.35 (m, 18H, H-6b, 7b, 12b, 13b, 16b, 17b), 1.31−1.18 (m, 6H, H-2b, 3b), −3.57 (s, 3H, *N*-CH_3), −3.32 (br, s, 1H, NH). ^{13}C NMR ($CDCl_3$): $\delta = 153.66$, 151.14, 150.68, 147.41, 146.95, 141.62, 141.14, 140.62, 140.27, 139.92, 136.44, 136.13, 134.19, 132.44, 132.14, 130.78, 116.58, 115.51, 115.03, 111.73, 30.39, 21.22, 21.04, 20.87, 20.49, 19.95, 19.71, 19.63, 17.98, 17.75, 17.70, 17.50, 17.41, 16.06, 15.27. MS [m/z (%)]: 549 (100) $[M]^+$, 550 (100) M^+H^+. IR: $\nu = 2975$, 2937, 2877, 1539, 1492, 1455, 1297, 1241, 1112, 1057, 1017, 996, 957, 915, 662, 458 cm^{-1}. UV−vis [λ, nm (ϵ)] = 274 (9900), 327^{sh} (15 700), 394 (82 400), 421^{sh} (39 700), 608 (19 700), 683 (25 000).

(EtioPc)Co(C_6H_5). The synthesis of (EtioPc)Co(C_6H_5) paralleled the procedure given above for (OEPc)Co(C_6H_5) and was carried out using (EtioPc)CoCl and phenylmagnesium bromide in THF. After conventional workup, the target compound was crystallized from a mixture of dichloromethane and heptane to give violet needles (yield 50%). Mp: 282 °C. ^1H NMR ($CDCl_3$): $\delta = 9.64$ (s, 4H, H-9, 10, 19, 20), 5.17 (dd, 1H, para-H-phenyl), 4.54 (t, 1H, meta-H-phenyl), 3.93 (m, 4H, CH_2-2,7,12,17), 3.54 (s, 4H, CH_3-3,6,13,16), 1.75 (t, 4H, CH_3-2,7,12,17), −0.29 (d, 1H, ortho-H-phenyl). ^{13}C NMR ($CDCl_3$): $\delta = 151.2$, 147.8, 146.0, 138.1, 134.1, 123.0, 121.3, 107.4, 22.0, 18.2, 17.8. MS [m/z (%)]: 612 (40) (M), 535 (100) ($M - C_6H_5$). IR: $\nu = 2977$, 2938, 2877, 1541, 1490, 1450, 1296, 1240, 1110, 1056, 998, 956, 916, 660, 460 cm^{-1}. UV−vis [λ, nm (ϵ)]: 328 (26 000), 387 (73 000), 557 (17 000), 595 (31 000).

Instrumentation. Cyclic voltammetry was carried out with a Princeton Applied Research model 173 potentiostat coupled to a model 175 universal programmer, a model EC 225 2A voltammetric analyzer (IBM Instruments Inc), or a BAS-100 electrochemical analyzer (Bioanalytical Systems). Current−voltage curves were recorded on a model RE0151 X-Y recorder or a DMP-40 digital plotter (Houston Instruments). A three-electrode system was used and consisted of a platinum button or a glassy carbon disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as reference. All potentials listed in this manuscript are given as V vs SCE. The

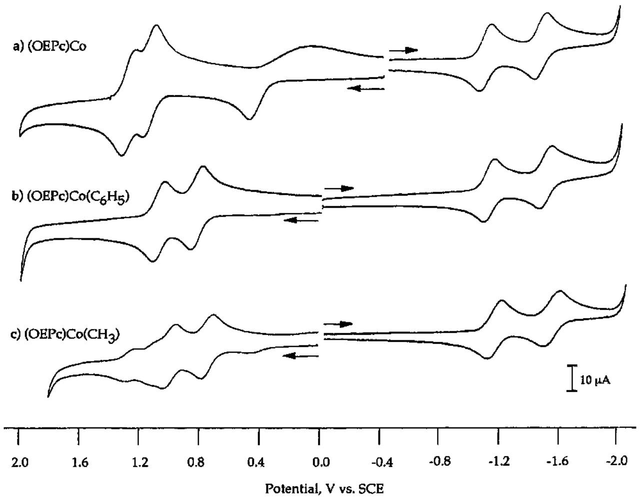

Figure 1. Cyclic voltammograms showing the reduction and oxidation of (a) (OEPc)Co, (b) (OEPc)Co(C_6H_5) and (c) (OEPc)Co(CH_3) in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent and supporting electrolyte. Solutions were deoxygenated by nitrogen purging.

Spectroelectrochemical experiments and thin-layer coulometry were performed at a platinum mesh thin-layer electrode.[41] Potentials were monitored with a Princeton Applied Research model 173 potentiostat coupled to a model 175 universal programmer. Time-resolved UV–visible spectra were recorded with a Tracor Northern model TN-6500 rapid scan spectrophotometer/multichannel analyzer. UV–visible spectra of the neutral complexes were recorded with an IBM Instruments Inc. model 9430 UV–visible spectrophotometer.

Results and Discussion

Sensitivity of (Pc)Co(R) toward Light and Oxygen. All spectroscopic and electrochemical studies on σ-bonded cobalt porphycenes were carried out under an N_2 atmosphere since the presence of oxygen and ambient light may lead to decomposition of the σ-bonded complexes by photolysis of the metal–carbon bond.[42–44] Two types of decomposition pathways are known to occur. One is via insertion of dioxygen into the metal–carbon bond,[42,43] while the other involves a cleavage of the cobalt–carbon bond leading to a cobalt(II) complex.[44] Both types of photochemical reactions were examined as to their possible occurrence with (Pc)Co(R) under oxygen. To evaluate the light and oxygen sensitivity of the σ-bonded cobalt porphycenes, a solution of (OEPc)Co(CH_3) was exposed to air under ambient light and its UV–visible spectrum recorded at regular intervals of time. No spectral changes were observed for more than 2 h suggesting that a photodecomposition of the (OEPc)Co(R) derivatives does not occur during the time scale of the electrochemical and spectroscopic measurements.

Electrochemistry of (Pc)Co(R). Cyclic voltammograms illustrating the reduction and oxidation of (OEPc)Co(CH_3) and (OEPc)Co(C_6H_5) in PhCN, 0.1 M TBAP are shown in Figure 1, which also displays, for comparison, the reduction and oxidation of (OEPc)Co under the same solution conditions. All three OEPc derivatives undergo two reversible one-electron reductions at almost identical potentials (see Table 1). The four-coordinate (OEPc)Co^{II} species is reduced at −1.07 and −1.43 V, while the two (OEPc)Co(R) complexes are reduced at −1.09 and −1.46 V (R = C_6H_5) or −1.13 and −1.51 V (R = CH_3). Previous studies of (OEPc)Co have shown that electroreduction leads to formation of a porphycene π-anion radical and dianion,[21a,h,23i] and this is also the case for the σ-bonded complexes investigated in the present study, all of which show separations between half-wave potentials of 360–380 mV that are diagnostic of electron addition to the conjugated porphycene macrocycle.[21a,23i]

Table 1. Half-Wave Potentials (V vs SCE) for the Reversible Electrode Reactions of Cobalt Porphycenes in PhCN, 0.1 M TBAP

		oxidn			redn	
macrocycle	R	2nd	1st	M(III)/M(II)	2nd	1st
OEPc	none	1.26	1.13	0.47[a]	−1.07	−1.43
	C_6H_5[b]	1.05	0.81		−1.09	−1.46
	CH_3[b]	0.99	0.75		−1.13	−1.51
EtioPc	C_6H_5	1.09	0.80		−1.13	−1.46
TPrPc	none	1.22	0.99	0.67[a]	−0.99	−1.36
	CH_3[b]	1.14	0.83		−1.08	−1.44

[a] E_{pa} at 0.1 V/s. [b] Additional redox processes are observed following migration of the axial ligand. See text for details.

Distinctly different redox behavior is seen for the oxidation of (OEPc)Co, (OEPc)Co(CH_3), and (OEPc)Co(C_6H_5). The (OEPc)Co complex undergoes an irreversible Co(II)/Co(III) process in PhCN which is located at E_p = 0.47 V for a scan rate of 0.1 V/s, and this is followed by two reversible one-electron macrocycle oxidations located at $E_{1/2}$ = 1.13 and 1.26 V.[21a,h,23i] Two reversible one-electron oxidations are also seen for (OEPc)Co(C_6H_5) and (OEP)Co(CH_3) at potential scan rates higher than 50 mV/s. These processes are located at $E_{1/2}$ = 0.81 and 1.05 V for (OEPc)Co(C_6H_5) and at $E_{1/2}$ = 0.75 and 0.99 V for (OEPc)Co(CH_3). Similar redox behavior is seen for (EtioPc)Co(C_6H_5) and (TPrPc)Co(C_6H_5), and a summary of the reversible half-wave potentials for these compounds is given in Table 1.

The absolute potential difference between the two oxidations of (OEPc)Co(R) ($\Delta E_{1/2}$) is 240 mV for both σ-bonded derivatives, while the $\Delta E_{1/2}$ values between the two oxidations of (EtioPc)Co(C_6H_5) and (TPrPc)Co(CH_3) are 290 and 310 mV, respectively. These $\Delta E_{1/2}$ values obtained for the two successive oxidations compare with a 130 mV potential difference between the two ring-centered oxidations of (OEPc)Co. Also, the potential separation between the first oxidation and first reduction of the four investigated σ-bonded compounds (see Table 1) agrees well with the HOMO–LUMO gap of 1.88–1.90 V reported for the free-base and zinc metal complexes of OEPc or TPrPc macrocycles.[21a,h] These results clearly suggest that all oxidations and reductions of these compounds are located at sites involving the conjugated macrocycle.

The singly and doubly reduced (OEPc)Co(R) species are stable on the cyclic voltammetry time scale, and solutions of these anionic porphycenes could also be prepared by controlled potential electrolysis. This is not the case for singly oxidized (OEPc)Co(CH_3), which undergoes, in a matter of minutes, a chemical reaction that leads to formation of new electroactive species. This chemical transformation is proposed to involve a migration of the CH_3 group from the cobalt center to one of the four nitrogens of the porphycene ring to give (*N*-CH_3OEPc)-CoClO_4 as a final product of the combined electrochemical/chemical process. Evidence for this assignment is given in following sections of this article.

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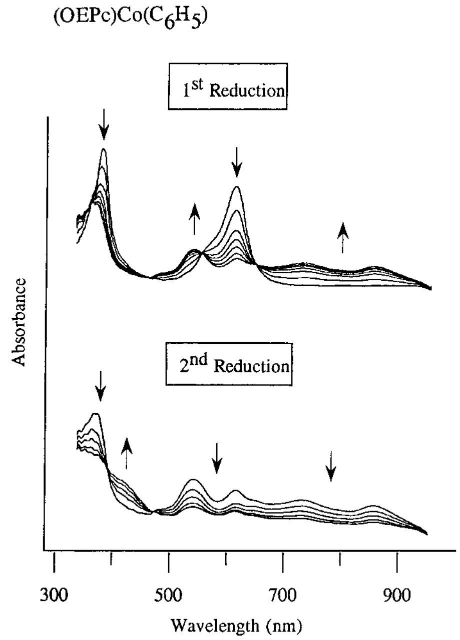

Figure 2. Thin-layer spectral changes observed during the first and second controlled-potential reductions of (OEPc)Co(C_6H_5) in THF containing 0.2 M TBAP. The applied potentials were −1.3 and −1.7 V, respectively, for the two reductions.

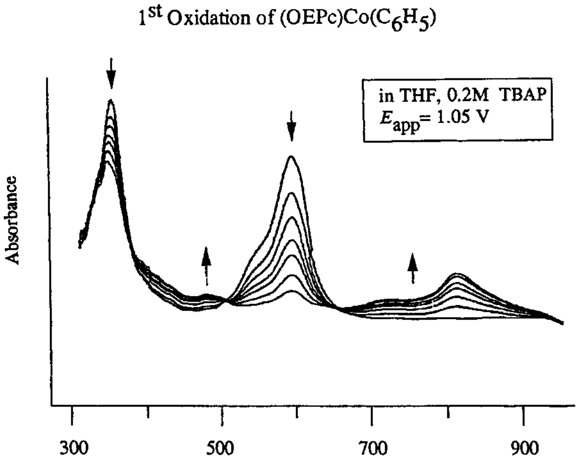

Figure 3. Thin-layer spectral changes observed during the first controlled potential oxidation of (OEPc)Co(C_6H_5) in THF containing 0.2 M TBAP.

Spectral Characterization of [(OEPc)Co(R)]^n ($n = -2$ to $+2$). The reduction and oxidation of each porphycene was investigated by thin-layer UV−visible spectroelectrochemistry in both PhCN and THF, and examples of the resulting data in THF are given in Figures 2 and 3 for (OEPc)Co(C_6H_5). The UV−visible spectrum of neutral (OEPc)Co(C_6H_5) in PhCN is similar to that of other non-σ-bonded metalloporphycenes containing a M(II) central metal ion.[18,20,21a,b,e−g,22,23i] The compound before reduction has four absorption bands located at 361, 395, 593, and 618 nm, while the singly reduced compound in PhCN, 0.2 M TBAP has absorption bands at 352, 381, 550, 738, and 872 nm. The 550 nm band is characteristic of a porphycene π-anion radical as are the two broad bands at 738 and 872 nm.[21a,c,i,23i] These spectral data are given in Table 2, which also summarizes the UV−visible spectral properties of each electrogenerated [(OEPc)Co(C_6H_5)]^n ($n = -2$ to $+2$) complex in PhCN.

The second electroreduction of (OEPc)Co(C_6H_5) leads to a bleaching of all absorption bands in the UV region of the spectrum and, by comparison with results previously reported,[21a,23i] suggests formation of a porphycene dianion, i.e., a ring-centered electroreduction. Similar types of spectral changes are observed during the first and second reductions of (OEPc)Co(CH_3), suggesting similar sites of electron transfer during reduction of both σ-bonded derivatives.

The products of (OEPc)Co(C_6H_5) oxidation are sufficiently stable on the spectroelectrochemical time scale (10−30 s) so that the UV−visible spectrum of [(OEPc)Co(C_6H_5)]$^{\bullet+}$ (Figure 3) and [(OEPc)Co(C_6H_5)]$^{2+}$ (not shown) could be obtained in THF just after their electrogeneration in the thin-layer cell. These spectra are characteristic of a porphycene π-cation radical and dication, respectively,[21a] and indicate the absence of a metal-centered reaction under these experimental conditions. Unfortunately, similar assignments could not be made in the case of (OEPc)Co(CH_3) due to the fact that the methyl migration rate is too rapid to spectrally observe the singly oxidized porphycene in the absence of a final migration product (see following section).

Axial Ligand Migration. A migration of the σ-bonded axial ligand in [(OEPc)Co(CH_3)]$^+$ and [(OEPc)Co(C_6H_5)]$^{\bullet+}$ was electrochemically and spectrally monitored, and the electrochemical results for (OEPc)Co(CH_3) are shown in Figure 4. Two new reversible reductions are observed at −0.52 and −0.94 V during a cathodic potential scan which was made after holding the applied potential for 60 or more seconds at a value more positive than $E_{1/2}$ for the first oxidation in PhCN, 0.1 M TBAP (see Figure 4a). These new redox processes compare well with processes observed in the cyclic voltammogram of (N-CH_3-OEPc)CoClO_4 ($E_{1/2} = -0.54$ and −0.94 V) which was recorded in the same solvent (Figure 4b) and lend strong support to the migration process schematically shown in Scheme 1.

The migration of the methyl group in singly oxidized (OEPc)-Co(CH_3) is qualitatively faster than that of the phenyl group in singly oxidized (OEPc)Co(C_6H_5) (as easily ascertained by the cyclic voltammetric data), and this agrees with quantitative results in the tetraphenylporphyrin (TPP) series where first-order migration rate constants vary by 1 full order of magnitude upon going from singly oxidized (TPP)Co(CH_3) ($k_{mig} = 1.4 \times 10^{-2}$ s^{-1}) to singly oxidized (TPP)Co(C_6H_5) ($k_{mig} = 1.3 \times 10^{-3}$ s^{-1}).[45] In a similar manner, Dolphin et al.[32] have shown that electrochemically generated [(TPP)Co(C_2H_5)]$^{\bullet+}$ is unstable in CH_2Cl_2 at room temperature and rapidly undergoes a metal to nitrogen migration of the C_2H_5 group, whereas [(TPP)Co-($COOC_2H_5$)]$^{\bullet+}$ is relatively stable under the same experimental conditions. The differences in stability of the singly oxidized species might simply be interpreted in terms of differences in the electron-donating ability of the axial ligand. The more electron donating the axial ligand, the weaker will be the cobalt−carbon bond and the faster will be the migration. However, as earlier demonstrated,[45] the rates of migration also relate directly to the degree of Co(IV) character in the singly oxidized species and this would imply a greater Co(IV) character in the case of [(OEPc)Co(CH_3)]$^+$.

The ^{1}H NMR chemical shifts of the protons located on the ethylenic bridge of the porphycene macrocycle (H-ethylenic) can, in theory, be used to probe the electron-donating capacity of the σ-bonded alkyl or aryl groups because of the through-

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Table 2. UV−Visible Data for $[(OEPc)Co(R)]^n$ (n = 0, −1, −2, +1, +2) in PhCN, 0.2 M TBAP, Where R = CH_3 and C_6H_5[a]

complex	λ_{max} ($10^{-5}\epsilon$)						
$(OEPc)Co(C_6H_5)$	361^{sh} (0.52)	395 (1.03)		593 (0.45)	618 (0.41)		
$[(OEPc)Co(C_6H_5)]^{\bullet-}$	352 (0.62)	380 (0.67)	549 (0.22)			737^{bb} (0.21)	862^{bb} (0.15)
$[(OEPc)Co(C_6H_5)]^{2-}$	346 (0.48)	390 (0.39)	545^{sh} (0.05)	593 (0.03)			
$[(OEPc)Co(C_6H_5)]^{\bullet+}$		390 (0.79)	516^{sh} (0.09)	596^{bb} (0.10)		742^{bb} (0.12)	825 (0.16)
$[(OEPc)Co(C_6H_5)]^{2+}$	352 (0.52)	381 (0.41)	427^{sh} (0.26)	597^{bb} (0.07)	645^{sh} (0.05)		
$(OEPc)Co(CH_3)$		394 (1.21)	563^{sh} (0.26)	610 (0.60)			
$[(OEPc)Co(CH_3)]^{\bullet-}$	375 (0.88)		496^{sh} (0.13)	549 (0.30)	673^{sh} (0.17)	737 (0.23)	850 (0.17)
$[(OEPc)Co(CH_3)]^{2-}$		413 (0.41)					

[a] sh = shoulder; bb = broad band.

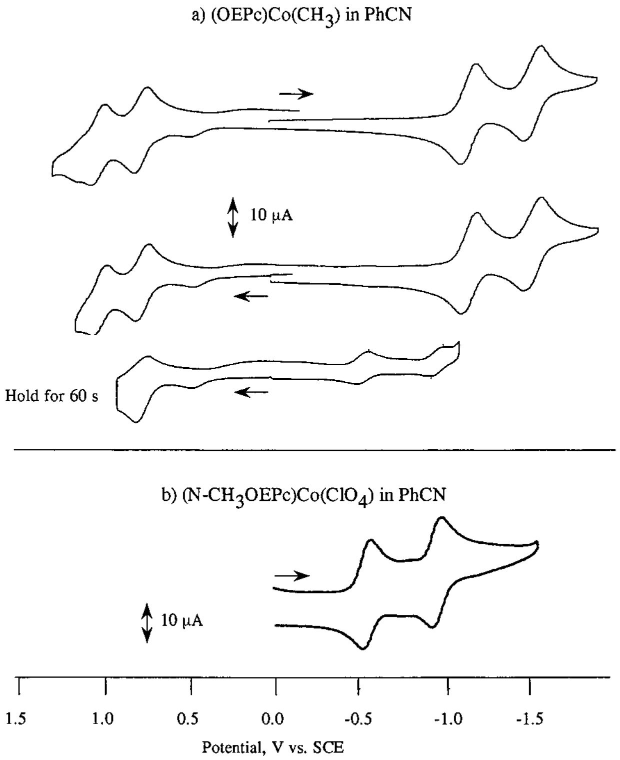
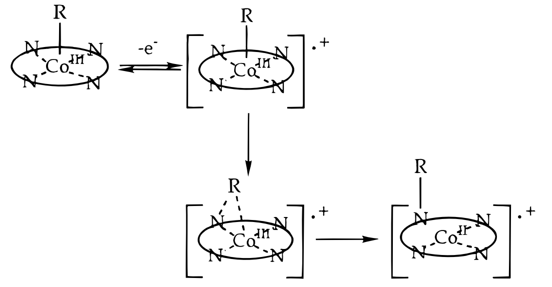


Figure 4. Cyclic voltammograms of (a) $(OEPc)Co(CH_3)$ and (b) (N-$CH_3OEPc)CoClO_4$ in PhCN 0.1 M TBAP.

Scheme 1



metal interaction between the axial ligand and the macrocycle, as has been described in the literature for porphyrin derivatives. The more electron donating the axial ligand, the higher the field at which the H-ethylenic resonances appear. In the case of $(OEPc)Co(CH_3)$, the ethylenic proton resonances appear at 9.34 ppm, whereas, in the case of $(OEPc)Co(C_6H_5)$, they appear at 9.47 ppm. This indicates a higher electron-donating ability of the methyl than the phenyl axial ligand and is consistent with the higher reactivity observed for the one-electron oxidized product of $(OEPc)Co(CH_3)$.

Electrochemistry of (N-$CH_3OEPc)CoCl$. (N-CH_3OEPc)-CoCl exhibits four reductions in PhCN, two of which are associated with the original compound and two of which are due to (N-$CH_3OEPc)CoClO_4$ which is generated by the exchange of Cl^- with ClO_4^- from the supporting electrolyte as shown in eq 1.

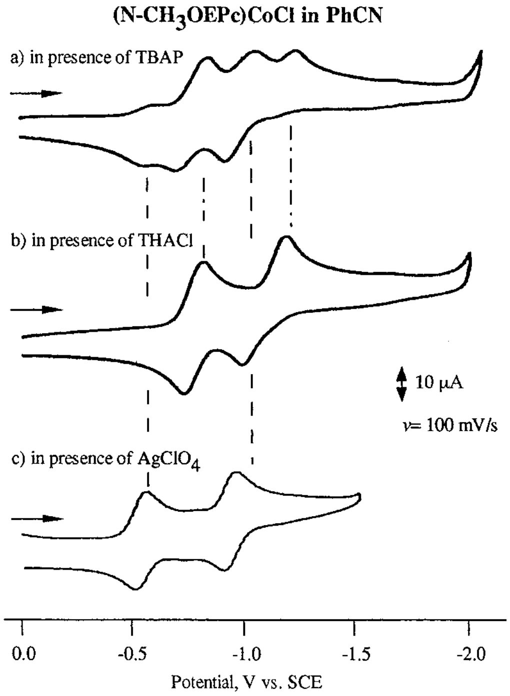


Figure 5. Cyclic voltammograms of (a) (N-$CH_3OEPc)CoCl$ in PhCN containing 0.1 M TBAP, b) (N-$CH_3OEPc)CoCl$ containing 0.1 M (THA)Cl, and (c) (N-$CH_3OEP)CoCl$ containing 0.1 M TBAP and $AgClO_4$ (1.5 equiv). Scan rate = 0.1 V/s.

$$(N\text{-}CH_3OEPc)CoCl + ClO_4^- \rightleftarrows (N\text{-}CH_3OEPc)CoClO_4 + Cl^- \quad (1)$$

The above ligand exchange reaction was confirmed by cyclic voltammetric measurements made before and after addition of 0.1 M tetrahexylammonium chloride ((THA)Cl) or silver perchlorate to solutions of (N-$CH_3OEPc)CoCl$ in PhCN, 0.1 M TBAP. The addition of a Cl^- salt generates (N-CH_3OEPc)-CoCl by shifting the equilibrium to the left, while the addition of ClO_4^- in the form of $AgClO_4$ next shifts the equilibrium to the right and leads to the formation of (N-$CH_3OEPc)CoClO_4$.

Voltammograms under the above three experimental conditions are shown in Figure 5 and indicate that (N-CH_3OEPc)-CoCl is reduced via two one-electron-transfer steps, the first of which is reversible and located at $E_{1/2} = -0.76$ V. The second reduction is quasireversible and located at $E_{pc} = -1.20$ V and $E_{pa} = -0.97$ V for a potential scan rate of 0.1 V/s. (N-CH_3-$OEPc)CoClO_4$ is also reduced by two successive one-electron reductions, both of which are reversible and located at $E_{1/2}$ =

Table 3. Half-Wave Potentials (V vs SCE) for Reduction of (*N*-RPc)CoX Complexes in PhCN, 0.1 M TBAP

Pc	R	X	redn	
			1st	2nd
OEPc	CH$_3$	Cl$^-$	−0.76	−1.20^a
		ClO$_4^-$	−0.54	−0.94
	C$_6$H$_5$^{b}	ClO$_4^-$	−0.49	−0.73^c
TPrPc	CH$_3$	ClO$_4^-$	−0.52	−0.92

[a] E_{pc} at 0.1 V/s. [b] Electrogenerated species after oxidation of (OEPc)Co(C$_6$H$_5$) in PhCN, 0.1 M TBAP. [c] E_{pc} at 0.1 V/s.

−0.54 and −0.94 V in PhCN (see Figure 5c). These data are summarized in Table 3.

The porphycene species electrogenerated after electroreduction of (*N*-CH$_3$OEPc)CoCl or (*N*-CH$_3$OEPc)CoClO$_4$ in PhCN are stable on the cyclic voltammetric time scale but not under bulk electrolysis conditions where the first reduction of (*N*-CH$_3$OEPc)CoCl leads to formation of a new species which is reduced in two reversible one-electron transfers located at $E_{1/2} = -1.14$ and -1.49 V. No demetalation of (*N*-CH$_3$OEPc)CoCl occurs, as ascertained by the fact that reductions associated with free-base (*N*-CH$_3$OEPc)H$_2$+ClO$_4^-$ are not detected (these electrode reactions occur at $E_{1/2} = 0.20$ and -0.20 V). Two additional porphycene species can also be generated in the bulk electroreduction of (*N*-CH$_3$OEPc)CoCl. The first is (OEPc)Co, and the second, (OEPc)Co(CH$_3$). A (OEPc)Co product would result from cleavage of the nitrogen−carbon bond on (*N*-CH$_3$OEPc)CoCl while (OEPc)Co(CH$_3$) could be formed in a "reverse migration", as in the case of chemically or electrochemically reduced *N*-alkyl- or arylcobalt porphyrins.[32,34a,b,35,36,45] The similarity of reduction potentials for (OEPc)Co and (OEPc)Co(CH$_3$) in PhCN does not allow for a differentiation of these two possible chemical products based solely on the cathodic electrochemistry. However, the anodic electrochemistry of the [(*N*-CH$_3$OEPc)CoCl]$^-$ "decomposition product" is uniquely consistent with the formation of (OEPc)Co(CH$_3$) since the oxidation potentials and spectra (see following section) match up perfectly and no process is seen at E_p close to 0.47 V, a potential where the Co(II)/Co(III) reaction of (OEPc)Co is known to occur (see Figure 1 and Table 1).

Spectral Characterization of [(*N*-CH$_3$OEPc)CoCl]^n, Where $n = 0, -1,$ and -2. The UV−vis spectrum of (*N*-CH$_3$OEPc)CoCl in PhCN containing 0.2 M Ph$_4$PCl shows strong absorption bands at 421 and 669 nm and two weaker bands that appear as shoulders at ca. 400 and ca. 620 nm. All four absorption bands decrease in intensity and two new broad bands appear at 550 and 870 nm during the first reduction (see Figure 6). The 550 nm band is the key marker band for a porphycene π anion radical, and the data in Figure 6 thus suggest that the electroreduction of (*N*-CH$_3$OEPc)CoCl occurs at the conjugated macrocycle rather than at the metal center.

The second reduction of (*N*-CH$_3$OEPc)CoCl is associated with an overall reduction of intensity in the absorption bands, and the final spectrum of the doubly reduced species can be assigned to a Co(II) *N*-CH$_3$ porphycene dianion. However, as mentioned above, [(*N*-CH$_3$OEPc)CoCl]$^{\bullet-}$ undergoes a chemical transformation to give (OEPc)Co(CH$_3$) on longer time scales under an applied potential, and the resulting spectral changes which lend support to this assignment are shown in Figure 7. The results in Figure 7 are consistent with the electrochemical data and demonstrate that the CH$_3$ group migrates from the porphycene core of electrogenerated [(*N*-CH$_3$OEPc)Co]$^{\bullet-}$ to give, as a final porphycene product, the σ-bonded Co(III) derivative, (OEPc)Co(CH$_3$).

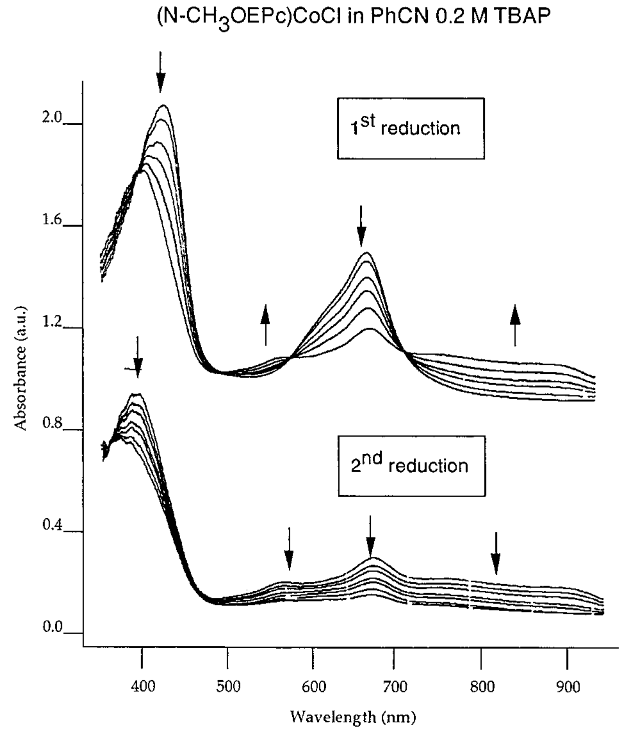


Figure 6. Thin-layer spectral changes seen during the first and second controlled-potential reductions of (*N*-CH$_3$OEPc)CoCl in PhCN, 0.2 M Ph$_4$PCl. The applied potentials were −0.85 and −1.25 V, respectively.

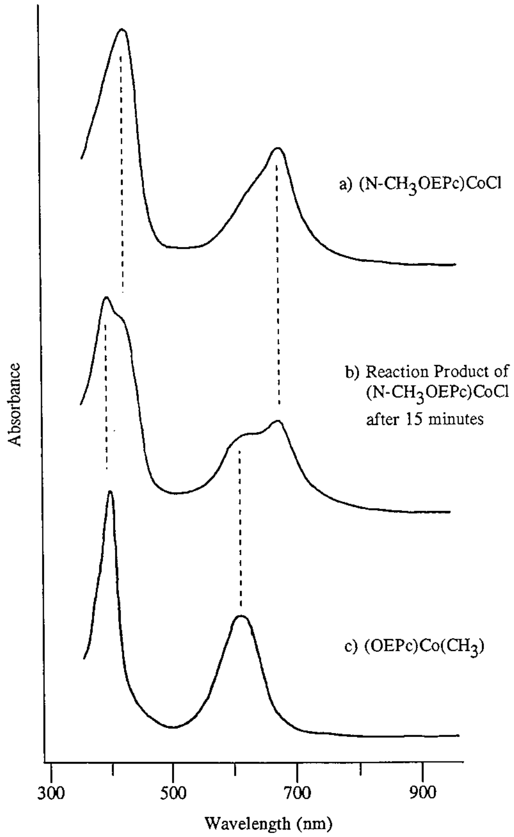


Figure 7. UV−visible spectra of (*N*-CH$_3$OEPc)CoCl in PhCN, 0.2 M TBAP (top), the mixture of species generated when the potential is held for 15 min after the first reduction of (*N*-CH$_3$OEPc)CoCl and stepped back to 0 V (middle), and (OEPc)Co(CH$_3$) (bottom).

Conclusion. The electrochemical and spectroelectrochemical results lead to the conclusion that the first oxidations of (OEPc)Co(C$_6$H$_5$) and (OEPc)Co(CH$_3$) are followed by an axial ligand migration to ultimately generate an N-substituted cobalt(II) porphycene. A similar electrochemically initiated migration of the axial ligand is known in the case of σ-bonded cobalt porphyrins, (P)Co(R),[1,32−34] but the reaction qualitatively appears to be much slower in the case of porphycenes. The singly and doubly reduced (OEPc)Co(R) complexes are stable, which is not the case for many related (Por)Co(R) complexes where a reduction by one electron is often followed by a cleavage of the cobalt−carbon bond.[12a,34a,43,46,47] This suggests a stronger cobalt−carbon bond for the σ-bonded cobalt porphycenes than for the σ-bonded porphyrin derivatives.

The first and second reductions of (N-CH$_3$OEPc)CoCl are ring centered as shown by UV−visible spectroelectrochemistry and thus do not lead to formation of a cobalt(I) complex. This contrasts markedly with results for N-substituted metalloporphyrins that are known to stabilize metal ions in their low oxidation states.[35,37−40] For example, electrogenerated N-methyl copper(I)[38] and cobalt(I)[35,37,40] porphyrins are stable but a metal-centered Co(II)/Co(I) reaction seems not to occur in the porphycene series.

Surprisingly, despite the difference in electrochemical behavior between (N-CH$_3$OEPc)CoCl and N-substituted Co(II) metalloporphyrins, both types of complexes undergo a migration of the N-substituent from the pyrrole nitrogen to the metal ion after reduction by one electron. To our knowledge, there are only two cases where a nitrogen to metal migration occurs after reduction of an N-alkyl porphyrin at the conjugated π-ring system of the macrocycle. These involve the cobalt(II) and nickel(II) complexes of N-methyltetrakis(4-sulfonatophenyl)-porphyrins.[48]

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