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Synthesis, Characterization, and Electrochemistry of σ-Bonded Cobalt Corroles in High Oxidation States

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The synthesis, electrochemistry, spectroscopy, and structural characterization of two high-valent phenyl σ-bonded cobalt corroles containing a central cobalt ion in formal +IV and +V oxidation states is presented. The characterized compounds are represented as phenyl σ-bonded cobalt corroles, $(OEC)Co(C_6H_5)$ and $[(OEC)Co(C_6H_5)]ClO_4$, where OEC is the trianion of 2,3,7,8,12,13,17,18-octaethylcorrole. The electronic distribution in both molecules is discussed in terms of their NMR and EPR spectroscopic data, magnetic susceptibility, and electrochemistry.

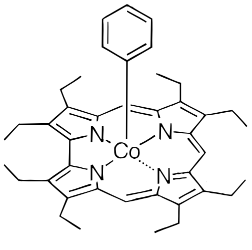
Introduction

The presence of a cobalt−carbon bond in coenzyme B_{12} has prompted the synthesis and chemical characterization of a variety of alkyl or aryl σ-bonded organocobalt complexes.[1] Our group has long been interested in the electrochemical reactivity of aryl σ-bonded porphyrins[2−4] including σ-bonded cobalt complexes.[5] The first oxidation of the latter compounds was initially proposed to involve the porphyrin π ring system followed by migration of the σ-bonded axial ligand.[6−8] However, more recent studies indicate that the chemically or electrochemically generated σ-bonded cobalt(III) porphyrin π cation radical is actually quite stable and that a migration will only occur after the initial formation of a transient σ-bonded Co(IV) derivative.[9]

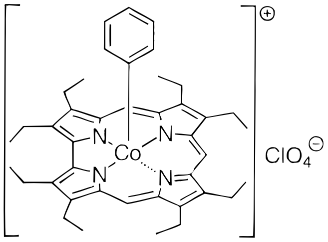
As part of our efforts to evaluate the chemistry of metal complexes in high oxidation states, the corrole ligand has been successfully utilized as a macrocycle to isolate and structurally characterize several neutral and oxidized σ-bonded tetrapyrrolic iron(IV) derivatives.[10,11] σ-Bonded cobalt(IV) complexes have yet to be characterized in the porphyrin series, and only a few non-porphyrin σ-bonded cobalt complexes have been reported in oxidation states higher than +III.[12,13] It was therefore of interest to know whether the corrole macrocycle could also stabilize a high-valent σ-bonded cobalt ion.

A number of Co(III) corroles with various axial ligands are known.[14−23] Cobalt corroles with an alkyl or aryl group in the axial position have not been reported in the literature, but the possible formation of a phenyl σ-bonded cobalt tetraethyltetramethyl substituted corrole was discussed and then rejected by Johnson and co-workers,[23] who, in the absence of structural data, suggested that the synthesized compound was best formulated as an *N*-phenyl cobalt(II) corrole.

In this paper, the synthesis, electrochemistry, spectroscopy, and structural characterization of two high-valent cobalt corroles in formal +IV and +V oxidation states is presented. The characterized compounds are represented as $(OEC)Co(C_6H_5)$ and $[(OEC)Co(C_6H_5)]ClO_4$ where OEC is the trianion of 2,3,7,8,12,13,17,18-octaethylcorrole.



$(OEC)Co(C_6H_5)$



$[(OEC)Co(C_6H_5)]ClO_4$

The electronic distribution in both molecules is discussed in terms of their NMR and EPR spectroscopic data, magnetic susceptibility, and electrochemistry.

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Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AP 300 NMR spectrometer at 300 and 75.5 MHz, respectively. The solvent signals were used as a standard at $\delta = 7.24$ ppm (^{1}H) or $\delta = 77.0$ ppm (^{13}C), and signal assignments were made by inverse $^{1}H-^{13}C$ correlation experiments.[24] Cyclic voltammetry was carried out with an EG&G Model 173 potentiostat or an IBM Model EC 225 voltammetric analyzer. A three-electrode system was used, consisting of a glassy carbon or platinum disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE. UV−visible spectroelectrochemical experiments were carried out with a Hewlett Packard Model 8452A diode array spectrophotometer. UV−visible spectra were recorded on a Perkin-Elmer Lambda 7 spectrophotometer, while IR measurements were performed with a Perkin-Elmer IR 283 or a Perkin-Elmer Series 1600 spectrometer. Mass spectra were obtained using a Finnigan MAT 212.

EPR spectra were recorded on an IBM ER 100D or on a Bruker ESP 380E spectrometer. The g values were measured with respect to diphenylpicrylhydrazyl ($g = 2.0036 \pm 0.0003$). Magnetic susceptibility was measured on powder samples using a Faraday balance. Data were corrected for diamagnetism, χ_{dia}, using a value of -300×10^{-6} cgsu. Elemental analyses were provided by Bayer AG (Leverkusen, Germany).

Chemicals. Benzonitrile (PhCN) was purchased from Aldrich Chemical Co. and distilled over P_2O_5 under vacuum prior to use. Absolute dichloromethane (CH_2Cl_2) was purchased from Aldrich Chemical Co. and used without further purification. $CDCl_3$, used for NMR measurements, was obtained from Aldrich Chemical Co. and used as received. Tetra-*n*-butylammonium perchlorate was purchased from Sigma Chemical Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least 1 week prior to use. (2,3,7,8,12,-13,17,18-Octaethylcorrolato)cobalt(III), (OEC)Co, was synthesized according to a literature procedure[19] but with the modification that the free base corrole was used instead of 1,19-dideoxyoctaethylbiladiene-*ac*.

(*σ*-Phenyl)(2,3,7,8,12,13,17,18-octaethylcorrolato)cobalt, (OEC)-Co(C_6H_5). To a 25 mL dichloromethane solution containing 579 mg (1 mmol) of (octaethylcorrolato)cobalt(III) was added 5 mmol of phenylmagnesium bromide in diethyl ether. The color of the solution changed from brown to red-brown, indicating formation of anionic $[(OEC)Co(C_6H_5)]^-$. The reaction mixture was then stirred for 15 min under air to completely oxidize $[(OEC)Co(C_6H_5)]^-$ to $(OEC)Co(C_6H_5)$. During this period, the color changed from red-brown to green. After water was added to the solution, the organic layer was dried over sodium sulfate and the volatile compounds were removed *in vacuo*. The residue was then purified by passing through a column of alumina (ICN, activity 2) using hexane/dichloromethane (2/1) as eluent. The first band contained the title compound. Recrystallization from hexane yielded the *σ*-phenyl compound (478 mg, 73 %) as black shiny rhombuses which decompose above 150 °C. ^{1}H NMR ($CDCl_3$): $\delta = 55, 41, 28$ (H-5, 15), 16.5, 11.0, 10.0, 7.0 (H-10), 6.0 (phenyl), 5.4 (phenyl), 5.3, 4.5, 2.9 (all broad singlets). MS (EI, 70 eV): *m/z* (%) 655 (34) M^{+}, 578 (100) $[M - Ph^{\bullet}]^{\bullet+}$, 563 (7) $[M - Ph^{\bullet} - CH_3^{\bullet}]^{+}$, 548 (16) $[M - Ph^{\bullet} - 2CH_3^{\bullet}]^{\bullet+}$, 533 (4) $[M - Ph^{\bullet} - 3CH_3^{\bullet}]^{+}$, 518 (8) $[M - Ph^{\bullet} - 4CH_3^{\bullet}]^{\bullet+}$, 503 (4) $[M - Ph^{\bullet} - 5CH_3^{\bullet}]^{+}$, 488 (5) $[M - Ph^{\bullet} - 6CH_3^{\bullet}]^{\bullet+}$, 327 (12) $M^{2\bullet+}$, 289 (15) $[M - Ph^{\bullet}]^{2+}$. IR (CsI): $\nu = 3045$ (ν_{C-H}, Ph), 2964, 2931, 2870, 1667, 1557 (ν_{C-C}, Ph), 1448, 1396, 1374, 1317, 1185, 1146, 1121, 1110, 1055, 1017, 1007, 990, 960, 821, 725, 638 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (ϵ, mol^{-1} L cm^{-1}) = 257 (28 100), 296 (21 200), 377 (68 900), 427 (17 000) sh, 616 (3700), 674 (7100). Magnetic moment: $\mu_{eff} = 1.15\ \mu_B$ (293 K); $\mu_{eff} = 0.54\ \mu_B$ (81 K). Anal. Calcd for $C_{41}H_{48}N_4Co$: C, 75.09; H, 7.38; N, 8.54. Found: C, 74.84; H, 7.27; N, 8.59.

Table 1. Crystallographic Data for $(OEC)Co(C_6H_5)$ and $[(OEC)Co(C_6H_5)]ClO_4{\cdot}CH_2Cl_2$

	$(OEC)Co(C_6H_5)$	$[(OEC)Co(C_6H_5)]ClO_4{\cdot}CH_2Cl_2$
empirical formula	$C_{41}H_{48}CoN_4$	$C_{42}H_{50}Cl_3CoN_4O_4$
fw	655.79	840.14
space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
Z	2	4
a, Å	11.898(3)	15.910(4)
b, Å	12.377(3)	20.165(5)
c, Å	15.070(4)	13.571(3)
α, deg	60.61(2)	90
β, deg	68.10(2)	101.42(3)
γ, deg	67.46(2)	90
V, Å^3	1738.1(8)	4268(2)
T, K	293(2)	293(2)
λ(Mo Kα), Å	0.710 69	0.710 69
d_{calcd}, g cm^{-3}	1.253	1.308
μ, mm^{-1}	0.528	0.634
no. of data: unique/obsd	7565/7425	8829/8498
no. of params	597	488
R1(F_o, $I > 2\sigma(I)$)[a]	0.0657	0.0902
wR2(F_o^2)[b]	0.2009	0.2521

[a] $R1 = [\sum||F_o| - |F_c||]/[\sum F_o|]$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

(*σ*-Phenyl)(2,3,7,8,12,13,17,18-octaethyl-*N*,*N*′-didehydrocorrolato)cobalt Perchlorate, $[(OEC)Co(C_6H_5)]ClO_4$. A 10 mL dichloromethane solution containing 130 mg (0.2 mmol) $(OEC)Co(C_6H_5)$ was stirred with a half-saturated aqueous solution of iron(III) perchlorate for 15 min. The organic layer was washed with 1 M perchloric acid, dried over sodium sulfate, and concentrated to a volume of 5 mL. After addition of 20 mL of benzene, the oxidized cobalt corrole crystallized as a benzene−dichloromethane solvate. This substance was dissolved in 5 mL of dichloromethane, and 25 mL of pentane was added dropwise while the solution was stirred. $[(OEC)Co(C_6H_5)]ClO_4$ was recovered as a brown powder with a yield of 105 mg (71%). ^{1}H NMR (300 MHz, $CDCl_3$, −20 °C): $\delta = 13.18$ (doublet, $^{3}J_{HH} = 7.8$ Hz; 2H; phenyl, *o*-H), 8.98 (multiplet; 2H; phenyl, *m*-H), 8.60 (triplet, $^{3}J_{HH} = 7.1$ Hz; 1H; phenyl, *p*-H), 2.63 (singlet, 1H; H-10), 1.67 (singlet, 2H; H-5,15), 0.98−0.51 (multiplets, 16H; H-2a,3a,7a,8a,12a,13a,17a,18a), 0.48 (triplet, 6H; H-8b,12b), 0.39 (triplet, 6H; H-7b,13b), 0.36 (triplet, 6H; H-2b,18b), 0.26 (triplet, 6H; H-3b,17b). ^{13}C NMR (75.5 MHz, $CDCl_3$, −20 °C): $\delta = 175.34$ (C-4,16), 161.91 (C-9,11), 159.21 (C-1,19), 155.05 (C-6,14), 153.03 (C-3,17), 147.04 (C-8,12), 143.24 (C-7,13), 142.60 (phenyl, C_{ipso}), 139.70 (phenyl, *o*-C, $^{1}J_{CH} = 161.2$ Hz), 138.22 (C-2,18), 131.56 (phenyl, *m*-C, $^{1}J_{CH} = 159.6$ Hz), 128.58 (phenyl, *p*-C, $^{1}J_{CH} = 159.5$ Hz), 109.72 (C-5,15, $^{1}J_{CH} = 165.5$ Hz), 102.98 (C-10, $^{1}J_{CH} = 161.7$ Hz), 16.49 (C-2a,18a), 16.17 (C-7a,13a), 16.10 (C-8a,-12a), 15.00 (C-3a,17a), 13.24 (C-7b,13b), 13.00 (C-2b,18b), 11.81 (C-8b,12b), 9.28 (C-3b,17b). IR (CsI): $\nu = 2969$, 2933, 2872, 1555, 1468, 1451, 1376, 1265, 1085 (ν_{ClO_4}), 1055, 1020, 1007, 983, 962, 910, 852, 732, 679, 632, 625 (ν_{ClO_4}) cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (ϵ, mol^{-1} l cm^{-1}) = 275 (23 300), 348 (69 400), 400 (11 800) sh. Anal. Calcd for $C_{41}H_{48}N_4CoClO_4$: C, 65.20; H, 6.41; N, 7.42; Cl, 4.69. Found: C, 64.93; H, 6.44; N, 7.47; Cl, 4.70.

Caution! Organic perchlorate salts can detonate spontaneously. Although no explosions were encountered in this work, precautions are warranted.

X-ray Structural Determination of $(OEC)Co(C_6H_5)$ and [(OEC)-Co(C_6H_5)]$ClO_4{\cdot}CH_2Cl_2$. X-ray data for both compounds were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation. Experimental conditions are given in Table 1. Cell parameters were determined by a least-squares refinement of 25 arbitrary reflections. The intensities of two standard reflections were checked during data collection every 2 h. The structures were solved by direct methods[25] and refined against F_o^2 for all observed reflections using the SHELXL-93 program package (non-

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hydrogen atoms with anisotropic temperature factors and hydrogen atoms with isotropic ones).[26]

Single crystals of (OEC)Co(C_6H_5) were grown from hot hexane. One methyl group (C(27)) was disordered and was found on two positions with equal occupancy factors. The final model shows no electron peaks and wholes larger than 0.804 and −0.481 e/Å^3, respectively.

Single crystals of [(OEC)Co(C_6H_5)]ClO_4·CH_2Cl_2 were obtained by diffusion of *n*-pentane into a concentrated dichloromethane solution of [(OEC)Co(C_6H_5)]ClO_4 at 4 °C. According to the observed density, d_{obsd} = 1.320 g cm^{-3}, the occupancy factor of the dichloromethane molecule was chosen as 1 (d_{calcd} = 1.308 g cm^{-3}). Hydrogen atoms of the ethyl substituents were refined with idealized parameters (C−H = 0.96 Å, H−C−H = 109.5°). The final model for [(OEC)Co(C_6H_5)]ClO_4·CH_2Cl_2 shows no electron peaks and holes larger than 0.742 and −0.491 e/Å^3, respectively.

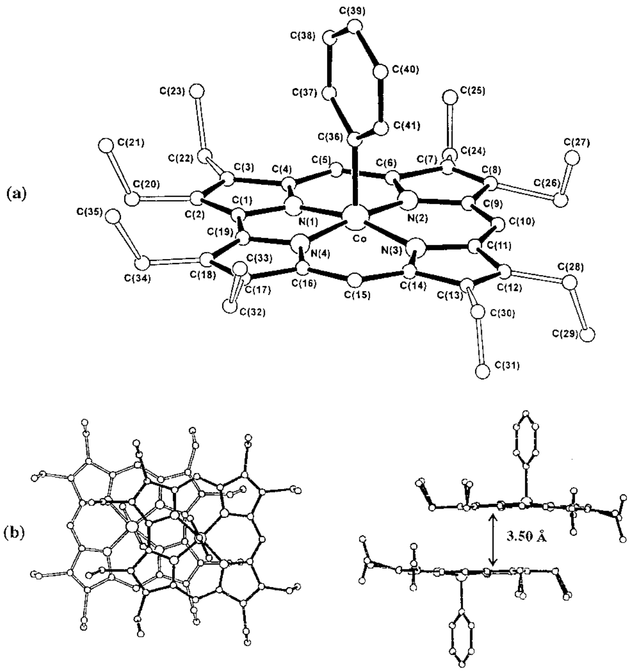

Figure 1. (a) ORTEP diagram of (OEC)Co(C_6H_5) (perspective view, hydrogen atoms omitted) displaying the atom-labeling scheme for the atoms used in Tables 3 and 4. Ellipsoids are contoured with arbitrary size. (b) Molecular structure of the π−π dimer of (OEC)Co(C_6H_5).

Table 2. Selected Bond Lengths and Distances (Å) for (OEC)Co(C_6H_5) and [(OEC)Co(C_6H_5)]ClO_4·CH_2Cl_2

	(OEC)Co(C_6H_5)	[(OEC)Co(C_6H_5)]ClO_4·CH_2Cl_2
Co−N[a]	1.856(3)	1.849(5)
Co−Ph	1.937(3)	1.970(7)
Δ(C,N)[b]	0.091(4)	0.062(6)
Δ(N_4)[c]	0.185(1)	0.165(3)
Co···Co[d]	5.33	4.13
mps[e]	3.50	3.45
ls[f]	3.58	1.66

[a] Average values. [b] Displacement of the cobalt atom with respect to the mean plane of the four nitrogen atoms. [c] Maximum distance of a C,N atom from the mean plane of the 23-atom corrole core. [d] Intermolecular cobalt−cobalt distance. [e] Mean plane separation of the corrole ligands in the π−π dimer. [f] Lateral shift of the corrole ligands in the π−π dimer.

Table 3. Selected Bond Lengths (Å) for (OEC)Co(C_6H_5)[a]

Co−N(4)	1.843(3)	C(3)−C(4)	1.453(5)
Co−N(1)	1.846(3)	C(4)−C(5)	1.395(6)
Co−N(3)	1.865(3)	C(5)−C(6)	1.361(6)
Co−N(2)	1.871(3)	C(6)−C(7)	1.458(6)
Co−C(36)	1.937(3)	C(7)−C(8)	1.320(8)
N(1)−C(4)	1.346(5)	C(8)−C(9)	1.448(6)
N(1)−C(1)	1.388(5)	C(9)−C(10)	1.370(6)
N(2)−C(9)	1.378(5)	C(10)−C(11)	1.369(6)
N(2)−C(6)	1.389(5)	C(11)−C(12)	1.452(6)
N(3)−C(11)	1.373(5)	C(12)−C(13)	1.331(7)
N(3)−C(14)	1.391(5)	C(13)−C(14)	1.449(6)
N(4)−C(16)	1.330(5)	C(14)−C(15)	1.382(6)
N(4)−C(19)	1.389(5)	C(15)−C(16)	1.389(6)
C(1)−C(2)	1.427(6)	C(16)−C(17)	1.466(6)
C(1)−C(19)	1.441(6)	C(17)−C(18)	1.354(7)
C(2)−C(3)	1.363(7)	C(18)−C(19)	1.425(6)

[a] Only values for the corrole framework are given. Numbers in parentheses are estimated standard deviations in the least significant digit.

Results and Discussion

Synthesis and Structural Characterization of (OEC)Co(C_6H_5). The reaction between cobalt(III) corroles and phenylmagnesium bromide was first described by the group of Johnson as giving a phenylated cobalt corrole.[23] The site of phenylation was not established with certainty at that time, but the product was suggested to be a cobalt(II) *N*-phenylcorrole, i.e., a species in which the phenyl group was bound to one of the four corrole nitrogens. As shown in the present paper, the actual reaction product is the phenyl σ-bonded cobalt corrole which, in the case of the octaethylcorrole macrocycle, is represented as (OEC)Co(C_6H_5). This σ-bonded compound is stable in the solid state for months when stored in a refrigerator and for at least several weeks at room temperature. However, it completely decomposes in solution within 2 days. A cleavage of the cobalt−carbon bond occurs upon heating of the solution to give (OEC)Co in high yield.

Crystallization of the σ-phenyl compound from hot hexane yielded single crystals suitable for an X-ray structure analysis (see Figure 1 and Tables 1−4). (OEC)Co(C_6H_5) is isomorphous with the previously reported (OEC)Fe(C_6H_5)[10] and exists in crystals as a π−π dimer with an average plane-to-plane separation of 3.50 Å and a lateral shift of 3.58 Å (Figure 1 and Table 2). The five-coordinate cobalt ion is located only 0.185 Å above the mean plane of the four nitrogen atoms. Due to the small metal displacement, the corrole ligand adopts a nearly planar conformation. The average cobalt−nitrogen distance is 1.856 Å while the Co−C bond length is 1.937 Å (Table 2) and both values are shorter than metal−nitrogen and metal−carbon bonds in (OEC)Fe(C_6H_5) (1.871 and 1.984 Å, respectively). The Co−N bonds in (OEC)Co(C_6H_5) are also shorter than those in the structurally related cobalamins (1.90−1.92 Å) which have a corrin macrocycle.[27]

Site of the Unpaired Electron in (OEC)Co(C_6H_5). Two extreme formulations are possible to describe the distribution of unpaired electron density in (OEC)Co(C_6H_5). The neutral complex might be formulated as a cobalt(IV) corrole, (OEC)Co^{IV}(C_6H_5), whose unpaired electron is localized on the metal center, or as a cobalt(III) corrole π cation radical, (OEC$^{•+}$)Co^{III}(C_6H_5), where the unpaired electron is delocalized over the corrole macrocycle.

The paramagnetic (OEC)Co(C_6H_5) complex shows a well-resolved EPR spectrum at 77 K in frozen CH_2Cl_2 or THF. The spectrum in CH_2Cl_2 is rhombic with $g_1 = 2.12$, $g_2 = 2.01$, and $g_3 = 1.94$ (see Figure 2). An eight-line hyperfine splitting is observed in the low-field (A_1 = 16 G) and high-field parts of the spectrum (A_3 = 18 G) due to the ^{59}Co nucleus ($I = {}^7/_2$). Virtually the same *g* values and hyperfine splittings are also obtained in frozen THF solutions at 77 K. Anisotropic spectra are observed at temperatures up to 140 K in frozen THF, CH$_2$-

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Table 4. Selected Bond Angles (deg) for (OEC)Co(C_6H_5)[a]

N(4)−Co−N(1)	81.49(14)	C(5)−C(4)−C(3)	130.7(4)
N(4)−Co−N(3)	91.60(13)	C(6)−C(5)−C(4)	124.5(4)
N(1)−Co−N(3)	165.51(13)	C(5)−C(6)−N(2)	123.9(3)
N(4)−Co−N(2)	168.54(13)	C(5)−C(6)−C(7)	127.2(4)
N(1)−Co−N(2)	91.26(13)	N(2)−C(6)−C(7)	108.8(4)
N(3)−Co−N(2)	93.42(13)	C(8)−C(7)−C(6)	107.7(4)
N(4)−Co−C(36)	93.94(13)	C(7)−C(8)−C(9)	108.0(4)
N(1)−Co−C(36)	95.86(13)	C(10)−C(9)−N(2)	123.5(4)
N(3)−Co−C(36)	97.31(13)	C(10)−C(9)−C(8)	127.1(4)
N(2)−Co−C(36)	95.62(13)	N(2)−C(9)−C(8)	109.4(4)
C(4)−N(1)−C(1)	108.7(3)	C(11)−C(10)−C(9)	124.7(4)
C(4)−N(1)−Co	131.8(3)	C(10)−C(11)−N(3)	124.1(4)
C(1)−N(1)−Co	119.2(3)	C(10)−C(11)−C(12)	126.2(4)
C(9)−N(2)−C(6)	106.1(3)	N(3)−C(11)−C(12)	109.7(4)
C(9)−N(2)−Co	126.9(3)	C(13)−C(12)−C(11)	107.3(4)
C(6)−N(2)−Co	126.9(2)	C(12)−C(13)−C(14)	107.9(4)
C(11)−N(3)−C(14)	106.1(3)	C(15)−C(14)−N(3)	123.2(4)
C(11)−N(3)−Co	126.7(3)	C(15)−C(14)−C(13)	127.8(4)
C(14)−N(3)−Co	126.9(3)	N(3)−C(14)−C(13)	109.0(4)
C(16)−N(4)−C(19)	109.9(3)	C(14)−C(15)−C(16)	124.3(4)
C(16)−N(4)−Co	131.9(3)	N(4)−C(16)−C(15)	121.2(3)
C(19)−N(4)−Co	118.1(3)	N(4)−C(16)−C(17)	107.2(4)
N(1)−C(1)−C(2)	108.0(4)	C(15)−C(16)−C(17)	131.5(4)
N(1)−C(1)−C(19)	109.4(3)	C(18)−C(17)−C(16)	107.8(4)
C(2)−C(1)−C(19)	142.5(4)	C(17)−C(18)−C(19)	107.3(4)
C(3)−C(2)−C(1)	107.8(3)	N(4)−C(19)−C(18)	107.7(4)
C(2)−C(3)−C(4)	106.9(4)	N(4)−C(19)−C(1)	111.3(3)
N(1)−C(4)−C(5)	120.7(3)	C(18)−C(19)−C(1)	140.8(4)
N(1)−C(4)−C(3)	108.6(4)		

[a] Only values for the corrole macrocycle are given. Numbers in parentheses are estimated standard deviations in the least significant digit.

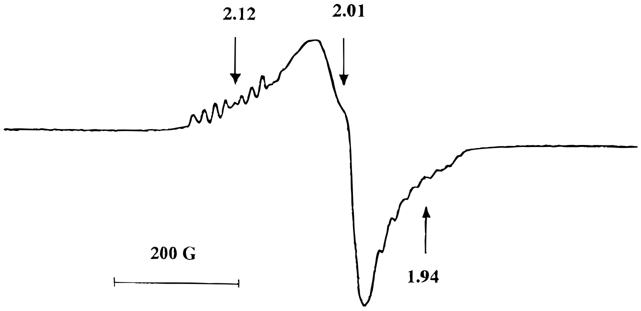

Figure 2. EPR spectrum of (OEC)Co(C_6H_5) in frozen CH_2Cl_2 at 77 K.

Cl_2, or PhCN solutions. However, a further increase in temperature results in a broadening of the hyperfine lines and the appearance of a broad isotropic spectrum ($g_{iso} = 2.02$ and $\Delta H = 170$ G) which can be observed even at room temperature in THF solutions.

The EPR spectra of (OEC)Co(C_6H_5) in frozen solutions are quite different from those of Co(III) porphyrin π cation radicals which exhibit sharp isotropic signals (line widths of 50−80 G) centered at $g \approx 2.00$ and have splittings on the cobalt nucleus on the order of 5−7 G under the same conditions.[28] However, the EPR spectra of (OEC)Co(C_6H_5) in frozen solutions are comparable with the spectra of several non-porphyrin Co(IV) complexes reported in the literature[12,13,29,30] and the spectrum of electrogenerated [(OMTPC)Co(PPh_3)]$^+$ (where OMTPC = trianion of octamethyltriphenylcorrole) which was proposed to contain a Co(IV) metal ion on the basis of its EPR spectrum (g = 2.14, 2.00, and 1.89 in frozen PhCN at 120 K).[22,31] Thus, the EPR data for (OEC)Co(C_6H_5) favor formulation of the neutral complex as containing a Co(IV) central ion.

The values of hyperfine splitting on the ^{59}Co nucleus of (OEC)Co(C_6H_5) are significantly smaller than the 100−200 G calculated for a free cobalt(IV) ion[12,13] but are comparable to values reported for other cobalt(IV) complexes (15−25 G[12,13,29,30] with the highest reported value being *ca.* 80 G[13]). The small hyperfine splittings for Co(IV) complexes as compared to a free Co(IV) ion could be explained by an admixture of the 4s and 4p orbitals with the 3d orbitals[13,14] or alternatively by a significant delocalization of the unpaired spin over the ligand.[13,30]

The EPR spectra of d^5 Co(IV) corroles can be compared with those of isoelectronic low-spin d^5 Fe(III) porphyrins which also show rhombic EPR spectra. In the case of the low-spin iron(III) porphyrins, the value $\sum g^2 = g_1^2 + g_2^2 + g_3^2$ will depend upon the ground state electronic configuration of the iron(III) ion and will range from $\sum g^2 = 12$ for a pure $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration to $\sum g^2 = 16$ for a $(d_{xy})^2(d_{xz},d_{yz})^3$ configuration.[32] An application of this theory to the EPR spectra of (OEC)Co(C_6H_5) and [(OMTPC)Co(PPh_3)]$^+$ gives $\sum g^2 = 12.15$ and 12.25, respectively. This suggests that both derivatives contain a low-spin d^5 cobalt(IV) ion with an almost pure $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration where the unpaired electron occupies a d_{xy} orbital located in the plane of the macrocycle.[33] A large spin delocalization throughout the π system of the porphyrin macrocycle is observed for iron(III) porphyrins having a $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration,[32] thus suggesting that these complexes possess a partial iron(II) porphyrin π cation radical character. A delocalization of the unpaired electron density over the macrocycle is also seen for (OEC)Co(C_6H_5), as evidenced by the NMR and magnetic susceptibility measurements discussed below.

The ^{1}H NMR spectrum of (OEC)Co(C_6H_5) exhibits extremely broadened resonances between $\delta = 55$ and 2.9 (see Figure 3a). A comparison of the (OEC)Co(C_6H_5) spectrum with that of the deuterated phenyl complex, (OEC)Co(C_6D_5), shows that the peaks at $\delta = 6.0$ and 5.4 can be assigned to the axial phenyl protons. There are a strong line broadening and a downfield shift of the ethyl hydrogen resonances, which suggest a significant delocalization of the unpaired electron over the π system of the corrole macrocycle. At the same time, the small hyperfine shifts of the axial ligand protons suggest that the unpaired electron is localized in an orbital which does not significantly overlap with the orbitals of the axial ligand. The ^{1}H NMR spectrum of (OEC)Co(C_6H_5) is significantly different from the spectra of isoelectronic d^5 low-spin iron(III) porphyrins containing a σ-bonded phenyl group. The latter complexes show smaller line widths for the signals of the macrocycle protons and strongly shifted resonances for the axial ligand protons.[34]

The magnetic moment of (OEC)Co(C_6H_5) was measured in the range 81−293 K on a polycrystalline sample and is strongly

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(33) We assume the same arrangement of axes for the corrole as for the porphyrin macrocycle, x and y axes being in the plane of the macrocycle and coming through the pyrrole nitrogens. Due to the lower symmetry of the corrole macrocycle (C_{2v}) compared to that of the porphyrin (D_{4h}), the coordinate system commonly adopted for corroles[19] differs from the system used for porphyrins in that the x axis is chosen as a C_{2v} axis which bisects the N−Co−N angle. As a result, the d_{xy} orbital of the central metal ion in a "porphyrin" coordinate system becomes the $d_{x^2-y^2}$ orbital in a "corrole" coordinate system.

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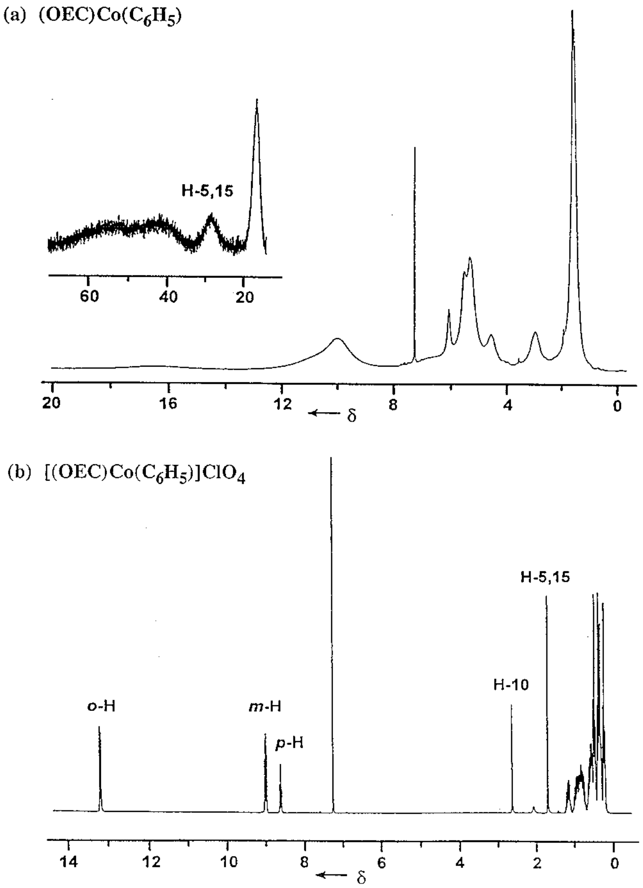

Figure 3. ^{1}H NMR spectra ($CDCl_3$) of (a) (OEC)Co(C_6H_5) at 25 °C and (b) [(OEC)Co(C_6H_5)]ClO_4 at −20 °C.

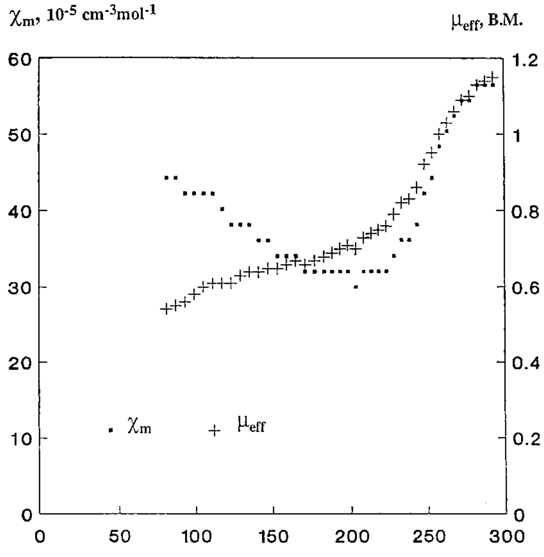

Figure 4. Plots of molar magnetic susceptibility, χ_m, and effective magnetic moment, μ_{eff}, versus temperature.

temperature dependent (see Figure 4). The value of μ_{eff} decreases from 1.15 μ_B at room temperature to 0.54 μ_B at 81 K. The room-temperature value of 1.15 μ_B is distinctly lower than the 1.73 μ_B expected for a compound with a single unpaired electron, and this behavior indicates a strong antiferromagnetic intermolecular spin−spin interaction in the solid state. This result is in agreement with (OEC)Co(C_6H_5) being dimeric in the solid state. The $\pi-\pi$ dimer possesses a singlet ground state as a whole unit, but the corresponding paramagnetic triplet state can be populated at higher temperatures. The magnetic exchange interaction between the two monomers of (OEC)Co(C_6H_5) is close to the thermal energy, which means that J is *ca.* 200 cm^{-1}.[35] This value can be compared to porphyrin π cation radical dimers which, in the solid state, have J values that range from ≈50 cm^{-1} for $[(TPP)Zn]_2^{2+}$ to > 1000 cm^{-1} for $[(OEP)Zn]_2^{2+}$,[36] perhaps indicating that the unpaired electron in (OEC)Co(C_6H_5) is located to a large extent on the macrocycle.

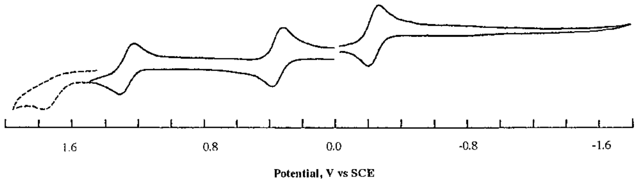

Figure 5. Cyclic voltammogram of (OEC)Co(C_6H_5) in PhCN, 0.2 M TBAP. Scan rate = 0.1 V/s.

A strong delocalization of the unpaired electron over the corrole macrocycle of (OEC)Co(C_6H_5) would give a partial π cation radical character to this formal cobalt(IV) complex. Therefore, on the basis of the combined magnetic susceptibility, EPR, and NMR data, (OEC)Co(C_6H_5) can best be represented as a resonance hybrid between a cobalt(III) π cation radical and a cobalt(IV) corrole:

$$(\mathrm{OEC})\mathrm{Co}^{\mathrm{IV}}(\mathrm{C_6H_5}) \leftrightarrow (\mathrm{OEC}^{\bullet+})\mathrm{Co}^{\mathrm{III}}(\mathrm{C_6H_5}) \tag{1}$$

Electrochemistry and Spectroelectrochemistry. (OEC)Co(C_6H_5) undergoes three reversible one-electron transfers in PhCN, 0.2 M TBAP. Two are oxidations (at $E_{1/2}$ = 0.36 and 1.23 V) and one is a reduction (at $E_{1/2}$ = −0.23 V). A third oxidation, associated with an irreversible chemical reaction, can also be observed at E_{pa} = 1.77 V (see dashed line in Figure 5).

The UV−visible spectrum of (OEC)Co(C_6H_5) in PhCN exhibits a Soret-like band at 377 nm and another band in the visible region at 674 nm. This spectrum is similar to spectra of $[(OMC)Co(PPh_3)]^+$ (OMC = trianion of octamethylcorrole) and $[(OMTPC)Co(PPh_3)]^+$ (OMTPC = trianion of octamethyltriphenylcorrole), which also have a visible band at around 650 nm.[21,22] The band between 600 and 700 nm in Figure 6 might be compared with the near-IR bands often observed for metalloporphyrin π cation radicals.[37] However, in the case of the corroles, this band is observed only for the oxidized cobalt and rhodium derivatives[21,22] which could contain the metal ion in a +IV oxidation state. A weak band around 610 nm is also seen for the iron(III) corrole π cation radical $[(OEC)Fe^{III}(NO)]^{\bullet+}$,[38] but no such band is observed in the case of $[(OEC)Fe^{IV}(C_6H_5)]^{\bullet+}$ or $[(OEC)Fe^{IV}Cl]^{\bullet+}$, both of which have been assigned as iron(IV) corrole π cation radicals.[11]

The one-electron reduction of (OEC)Co(C_6H_5) leads to $[(OEC)Co^{III}(C_6H_5)]^-$ whose spectrum has a Soret band at 402 nm and a broad band between 500 and 550 nm (Figure 6a). This spectrum is similar to UV−visible spectra of previously studied cobalt(III) corroles.[16−23] No further reductions of

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(35) Assuming the presence of magnetic dimers in (OEC)Co(C_6H_5) and a spin Hamilton operator $H = 2J{\cdot}S_1{\cdot}S_2$ ($S_1 = S_2 = {}^1/_2$), the room temperature susceptibility of 565 × 10^{-6} cgsu corresponds to a coupling constant, J, of 184 cm^{-1}. The coupling constant will depend strongly on the contribution of the diamagnetic susceptibility whose exact value is unknown for (OEC)Co(C_6H_5).

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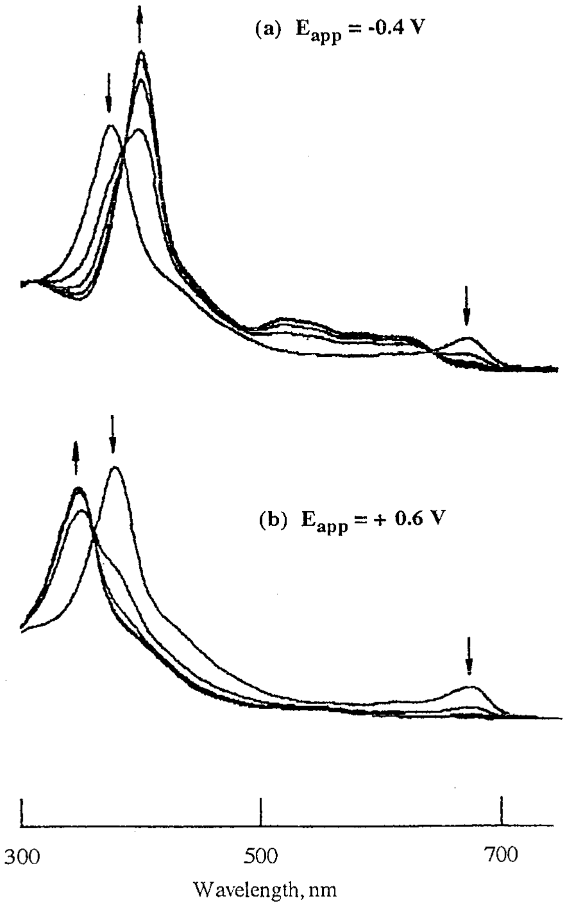

Figure 6. UV−visible spectral changes obtained during (a) reduction and (b) oxidation of (OEC)Co(C_6H_5) in PhCN, 0.2 M TBAP.

(OEC)Co^{III}(C_6H_5) are seen up to a potential of −2.0 V vs SCE. This contrasts with previously characterized cobalt(III) corroles, all of which undergo a facile Co(III)/Co(II) reduction[16−23] but do not possess an additional negative charge as is the case for the electrogenerated [(OEC)Co^{III}(C_6H_5)]$^-$.

The spectral changes which occur upon the first oxidation of (OEC)Co(C_6H_5) are shown in Figure 6b and resemble those seen upon the *second* oxidation of (OMC)Co(PPh_3).[21] The UV−visible spectrum of [(OEC)Co(C_6H_5)]$^+$ also resembles spectra obtained for the Fe(IV) octaethylcorrole π cation radicals [(OEC)Fe^{IV}(C_6H_5)]$^{\bullet+}$ and [(OEC)Fe^{IV}Cl]$^{\bullet+}$.[11] Although the spectral changes in Figure 6b suggest that an electron is abstracted from the conjugated macrocycle of (OEC)Co(C_6H_5), additional information is needed to confirm the actual site of electron transfer. The product of the second oxidation, [(OEC)Co(C_6H_5)]$^{2+}$, is stable only on the cyclic voltammetry time scale, and this species could not be spectrally characterized.

Synthesis and Characterization of [(OEC)Co(C_6H_5)]ClO_4. The singly oxidized cobalt corrole [(OEC)Co(C_6H_5)]ClO_4 is easily obtained by treatment of (OEC)Co(C_6H_5) in dichloromethane with aqueous iron(III) perchlorate followed by precipitation of the oxidized compound with pentane (see Experimental Section). The resulting cationic complex [(OEC)Co(C_6H_5)]ClO_4 is more stable than the neutral complex and shows no tendency for decomposition in the solid state. This is not the case in solution, where decomposition is observed within a few hours at room temperature.

The ^{1}H NMR spectrum of [(OEC)Co(C_6H_5)]ClO_4 exhibits resonances with small line widths, indicating a diamagnetic species (see Figure 3b). However, these resonances are seen in a region of the spectrum which is quite uncommon for diamagnetic metalloporphyrins.[39] The *meso*-protons give rise to singlets at δ = 2.63 (H-10) and 1.67 (H-5,15) while peaks of the ethyl groups are detected at δ = 0.98−0.51 (CH_2) and δ = 0.48−0.26 (CH_3). The protons of the phenyl ligand resonate at δ = 13.18, 9.98 and 8.60, respectively (*o*-H, *m*-H, and *p*-H). The experimentally observed shifts—upfield for the corrole protons and downfield for the phenyl protons—lead to the conclusion that a pronounced paramagnetic ring current is present in [(OEC)Co(C_6H_5)]ClO_4. For this reason, the oxidation product cannot be formulated as a cobalt(V) corrole for which a diamagnetic ring current would be expected due to the 18-π-electron main conjugation path.

Paratropic behavior, as is seen for [(OEC)Co(C_6H_5)]ClO_4, is a characteristic feature of cyclic π systems with 4*n* π electrons.[40] The NMR data thus suggest that [(OEC)Co(C_6H_5)]ClO_4 contains a doubly oxidized corrole ligand and a low-spin Co(III) center. Such a macrocyclic ligand would possess 16 π electrons in its inner main conjugation path and would be derived from the so far unknown *N,N′*-didehydrocorrole. A formulation of (OEC)Co(C_6H_5)]ClO_4 as a Co(IV) corrole π cation radical with a strong antiferromagnetic coupling between the unpaired electrons of the macrocycle and the metal center is also a possibility, but this is less likely, since a ring current effect is not expected in this case due to the 17-π-electron system for such a compound.

The ^{13}C NMR spectrum of [(OEC)Co(C_6H_5)]ClO_4 in $CDCl_3$ reveals only resonances of the phenyl group since absorptions of the corrole macrocycle are extremely broadened due to rapid electron exchange with a small amount of unoxidized (OEC)Co(C_6H_5) which is still present in solution. However, after addition of trace bromine to convert all of the neutral compound to its oxidized form, 18 sharp resonances of the macrocycle are observed in the range δ = 175.33−102.98 according to the effective C_s symmetry of the complex. In contrast with the case of diamagnetic metallocorroles,[10,38] there is a striking deshielding of the core carbon atoms, reflecting a decrease of π-electron density on the oxidized corrole macrocycle.

A doubly oxidized corrole ligand in [(OEC)Co(C_6H_5)]ClO_4 would be related to porphyrin dications[37a,41] in that both are two oxidation levels above the neutral unoxidized ligand. Although the NMR features of doubly oxidized porphyrins with diamagnetic metal ions are unknown, the similarity between the UV−vis spectra of [(OEC)Co(C_6H_5)]ClO_4 and porphyrin dications with Mg(II) or Zn(II) central metal ions indicates that both types of compounds have similar electronic structures.

Very little structural information is available about porphyrin dications or porphyrinoids showing paratropic behavior,[42] and it was therefore of general interest to also characterize [(OEC)Co(C_6H_5)]ClO_4 by X-ray crystallography. [(OEC)Co(C_6H_5)]ClO_4·CH_2Cl_2 exists as a pair of cationic cobalt corrole moieties with a mean separation between the two corrole planes of 3.45 Å and a lateral shift of 1.66 Å (see Table 2 and Figure 7b). Due to the arrangement of the molecules in the crystals, the cobalt ion is five-coordinate and does not contain a

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Table 5. Selected Bond Lengths (Å) for $[(OEC)Co(C_6H_5)]ClO_4{\cdot}CH_2Cl_2$[a]

Co−N(4)	1.829(4)	C(3)−C(4)	1.470(8)
Co−N(1)	1.838(5)	C(4)−C(5)	1.414(8)
Co−N(3)	1.857(5)	C(5)−C(6)	1.364(8)
Co−N(2)	1.873(5)	C(6)−C(7)	1.467(8)
Co−C(36)	1.970(7)	C(7)−C(8)	1.319(9)
N(1)−C(4)	1.321(7)	C(8)−C(9)	1.461(8)
N(1)−C(1)	1.427(7)	C(9)−C(10)	1.375(8)
N(2)−C(9)	1.362(7)	C(10)−C(11)	1.391(9)
N(2)−C(6)	1.404(7)	C(11)−C(12)	1.462(8)
N(3)−C(11)	1.368(7)	C(12)−C(13)	1.342(9)
N(3)−C(14)	1.423(7)	C(13)−C(14)	1.459(8)
N(4)−C(16)	1.327(7)	C(14)−C(15)	1.365(8)
N(4)−C(19)	1.431(7)	C(15)−C(16)	1.424(8)
C(1)−C(19)	1.375(8)	C(16)−C(17)	1.461(8)
C(1)−C(2)	1.441(8)	C(17)−C(18)	1.356(8)
C(2)−C(3)	1.353(9)	C(18)−C(19)	1.454(8)

[a] Only values for the macrocyclic ligand are given. Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 6. Selected Bond Angles (deg) for $[(OEC)Co(C_6H_5)]ClO_4{\cdot}CH_2Cl_2$[a]

N(4)−Co−N(1)	81.0(2)	C(5)−C(4)−C(3)	130.0(6)
N(4)−Co−N(3)	92.0(2)	C(6)−C(5)−C(4)	123.7(5)
N(1)−Co−N(3)	169.2(2)	C(5)−C(6)−N(2)	123.6(5)
N(4)−Co−N(2)	166.5(2)	C(5)−C(6)−C(7)	128.4(6)
N(1)−Co−N(2)	91.2(2)	N(2)−C(6)−C(7)	108.0(5)
N(3)−Co−N(2)	94.1(2)	C(8)−C(7)−C(6)	107.5(5)
N(4)−Co−C(36)	94.0(2)	C(7)−C(8)−C(9)	108.5(5)
N(1)−Co−C(36)	93.1(2)	N(2)−C(9)−C(10)	124.9(6)
N(3)−Co−C(36)	95.6(2)	N(2)−C(9)−C(8)	108.9(5)
N(2)−Co−C(36)	97.4(2)	C(10)−C(9)−C(8)	126.2(6)
C(4)−N(1)−C(1)	108.8(5)	C(9)−C(10)−C(11)	124.5(5)
C(4)−N(1)−Co	132.7(4)	N(3)−C(11)−C(10)	122.5(5)
C(1)−N(1)−Co	118.3(4)	N(3)−C(11)−C(12)	110.3(5)
C(9)−N(2)−C(6)	107.1(5)	C(10)−C(11)−C(12)	127.2(6)
C(9)−N(2)−Co	125.6(4)	C(13)−C(12)−C(11)	107.5(5)
C(6)−N(2)−Co	126.9(4)	C(12)−C(13)−C(14)	107.8(5)
C(11)−N(3)−C(14)	105.9(5)	C(15)−C(14)−N(3)	123.8(5)
C(11)−N(3)−Co	127.6(4)	C(15)−C(14)−C(13)	127.6(6)
C(14)−N(3)−Co	126.1(4)	N(3)−C(14)−C(13)	108.5(5)
C(16)−N(4)−C(19)	107.7(5)	C(14)−C(15)−C(16)	123.4(5)
C(16)−N(4)−Co	133.0(4)	N(4)−C(16)−C(15)	120.6(5)
C(19)−N(4)−Co	118.8(4)	N(4)−C(16)−C(17)	110.0(5)
C(19)−C(1)−N(1)	110.9(5)	C(15)−C(16)−C(17)	129.4(5)
C(19)−C(1)−C(2)	142.0(6)	C(18)−C(17)−C(16)	107.6(5)
N(1)−C(1)−C(2)	107.1(5)	C(17)−C(18)−C(19)	107.2(5)
C(3)−C(2)−C(1)	107.6(5)	C(1)−C(19)−N(4)	110.3(5)
C(2)−C(3)−C(4)	107.7(5)	C(1)−C(19)−C(18)	142.2(6)
N(1)−C(4)−C(5)	121.2(5)	N(4)−C(19)−C(18)	107.5(5)
N(1)−C(4)−C(3)	108.8(5)		

[a] Only values for the corrole macrocycle are given. Numbers in parentheses are estimated standard deviations in the least significant digit.

perchlorate anion in its coordination sphere. The tetrapyrrole macrocycle in $[(OEC)Co(C_6H_5)]ClO_4$ adopts a nearly planar conformation. The one-electron oxidation of $(OEC)Co(C_6H_5)$ results in a slight shortening of the Co−N bonds and a decreased displacement of the cobalt atom from the macrocyclic plane (see Table 2). Surprisingly, the Co−phenyl bond in $[(OEC)Co(C_6H_5)]ClO_4$ is longer than that in $(OEC)Co(C_6H_5)$ (1.937 vs 1.970 Å).

Finally, it is of interest to compare the structure of the macrocyclic ligand in $[(OEC)Co(C_6H_5)]ClO_4$ with that of unoxidized or singly oxidized corrole ligands. One recently characterized corrole π cation radical, $[(OEC)Fe(C_6H_5)]ClO_4$,[11] showed a pattern of short and long bonds in the inner 15-membered ring, and this is also the case for the macrocyclic ligand of $[(OEC)Co(C_6H_5)]ClO_4$. However, the bond alternations are more pronounced in $[(OEC)Co(C_6H_5)]ClO_4$ than in $[(OEC)Fe(C_6H_5)]ClO_4$.[11] The bipyrrolic substructure of $[(OEC)Co(C_6H_5)]ClO_4$ contains exceptionally long and short C−N bonds, indicating a strong tendency for π-bond localization in this unit. Alternating bond lengths are seen for many other [4*n*]-annulenes[43] according to theory which predicts that structures with localized π-bonds stabilize the singlet state.[44] The structural features of $[(OEC)Co(C_6H_5)]ClO_4$ are thus in agreement with formation of a 4*n* π electron system upon oxidation of $(OEC)Co(C_6H_5)$.

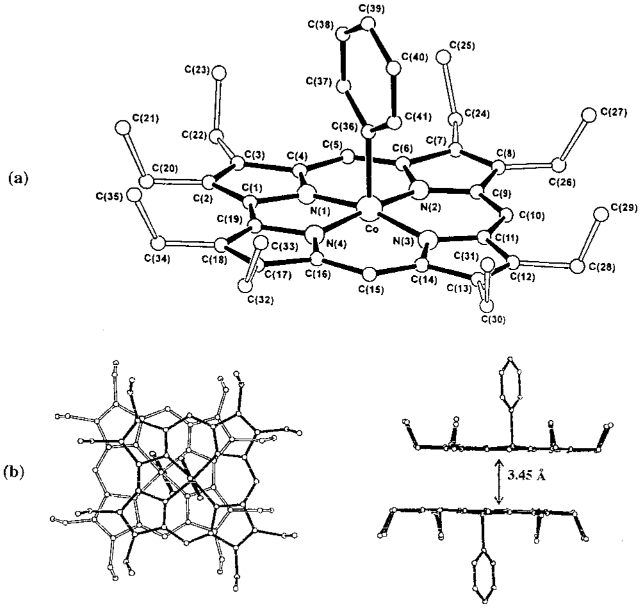

Figure 7. (a) ORTEP diagram of $[(OEC)Co(C_6H_5)]^+$ (perspective view, hydrogen atoms omitted) displaying the atom-labeling scheme for the atoms used in Tables 5 and 6. Ellipsoids are contoured with arbitrary size. (b) Molecular structure of the π−π dimer of $[(OEC)Co(C_6H_5)]^+$.

In conclusion, $(OEC)Co(C_6H_5)$ represents the only isolated cobalt tetrapyrrole complex to exhibit a strong cobalt(IV) character. This feature of the cobalt corrole differs from that of cobalt porphyrins, where a stable cobalt(IV) oxidation state is not accessible, and once again points out that the corrole macrocycle is capable of stabilizing central metal ions in high oxidation states.

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Supporting Information Available: Tables containing details of data acquisition and refinement, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters (23 pages). Ordering information is given on any current masthead page.

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