Electrooxidation of Cobalt(II) β-Brominated-Pyrrole Tetraphenylporphyrins in CH$_2$Cl$_2$ under an N$_2$ or a CO Atmosphere

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The electrochemical behavior of (TPPBr$_x$)Co (TPPBr$_x$ = the dianion of β-brominated-pyrrole tetraphenylporphyrin and $x = 0-8$) is reported under an N$_2$ or a CO atmosphere in dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Each investigated compound undergoes three reversible one-electron oxidations within the potential window of the solvent, and this results in the ultimate formation of a cobalt(III) dication as the final three-electron-oxidation product under both an N$_2$ and a CO atmosphere. The initial one-electron abstraction from (TPPBr$_x$)Co involves the central metal ion for derivatives with $x \leq 5$ and the conjugated porphyrin π ring system for derivatives with six, seven, or eight Br groups. Thin-layer infrared spectroelectrochemical measurements were performed during the first oxidation of (TPPBr$_x$)Co in dichloromethane and indicate that *in situ* generated [(TPPBr$_x$)Co]$^+$ forms mono- and bis(carbon monoxide) adducts for complexes with zero to five Br groups but that no CO molecule binds to the singly oxidized derivatives with six, seven, or eight Br groups, all of which exist as Co(II) π cation radicals.

Introduction

Metalloporphyrins containing halogenated substituents at the pyrrole β positions of the macrocycle are of current interest since they show a high catalytic efficiency for the oxidation of organic substrates.[1−20] The same types of metalloporphyrins might also be used in conjunction with hydrogen peroxide and KHSO$_5$ for treatment of wastewater[13,21a] or as catalysts for molecular dioxygen reduction.[21b,c]

The high number of turnovers which are reached during catalytic epoxidation and other oxygen insertion reactions of organic substrates by β-halogenated-pyrrole porphyrins has been, in large part, attributed to the electron-withdrawing halogen substituents on the macrocycle.[4,5,9,20,22−25] Increasing the number of halogens at the pyrrole β positions of tetraphenylporphyrin type derivatives should, in principle, lead to harder oxidations and easier reductions due to inductive effects of the electron-withdrawing substituents. However, this is not the case for oxidation, as has been documented for several types of metalloporphyrins,[26−29] in particular for compounds in the series (TPPBr$_x$)FeCl, (TPPBr$_x$)H$_2$, and (TPPBr$_x$)Cu where TPPBr$_x$ = the dianion of β-brominated-pyrrole tetraphenylporphyrin and $x = 0-8$.

The most detailed electrochemical studies of TPPBr$_x$ derivatives have been carried out for (TPPBr$_x$)FeCl.[28,29] The $E_{1/2}$ for the two reversible oxidations of these compounds depends upon both the inductive effects of the added halogen groups and the increased distortion of the macrocycle which is known to occur for these types of compounds with increase in the number of bulky halogen substituents at the pyrrole β positions of the tetraphenylporphyrin macrocycle.[30−33] The effect of macrocycle

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distortion becomes predominant upon going from (TPPBr$_3$)-FeCl to (TPPBr$_8$)FeCl, and this not only affects the $E_{1/2}$ for the first oxidation of each compound in the series but also leads to an increased potential separation between the first two oxidations, both of which involve the conjugated porphyrin macrocycle.[29]

On the other hand, cobalt porphyrins with the same set of brominated TPPBr$_x$ macrocycles, (TPPBr$_x$)Co, seem to show an opposite effect of the halide substituents as compared to the same compounds in the (TPPBr$_x$)FeCl series. The absolute potential separation between the two ring-centered oxidations *decreases* rather than *increases* with increase in nonplanarity of the macrocycle,[34] i.e., upon going from (TPP)Co to (TPP-Br$_8$)Co. It was suggested that the distance between the metal and the porphyrin ring nitrogen might be a key factor influencing the potential separation between the ring-centered oxidations of nonplanar porphyrins,[29] but this suggestion has yet to be explored in detail.

Another question not addressed in previous studies of (TPP-Br$_x$)Co, (TPPBr$_x$)FeCl, and (TPPBr$_x$)H$_2$ is the role of macrocycle distortion on the site of electron transfer. Free-base brominated tetraphenylporphyrins can only be oxidized at the porphyrin π ring system due to the absence of a central metal ion, but this is not the case for (TPPBr$_x$)Co,[34] (TPPBr$_x$)FeCl,[29] and (OETPP)-FeCl[35] (OETPP = the dianion of octaethyltetraphenylporphyrin) where either metal- or ring-centered oxidations can occur, with the exact site of electron transfer being directly or indirectly affected by distortion of the macrocycle.

It has long been known that the site of oxidation in cobalt-(II) porphyrins is intimately connected to the solution conditions and related axial coordination.[36] Thus, the (TPPBr$_x$)Co derivatives ($x = 0-8$) appear to be the ideal candidates for studying how systematic changes in planarity of the porphyrin macrocycle might be related to systematic changes in the site of electron transfer. We know that (TPPBr$_x$)Co, where $x = 0$, 6, 7, or 8 is oxidized at the metal center in PhCN containing tetra-n-butylammonium perchlorate (TBAP) as supporting electrolylte,[34] but this may not be the case in nonbonding solvents containing weakly coordinating anions where [(TPPBr$_x$)Co]$^+$ may exist as a Co(II) porphyrin π cation radical.[36-38]

In order to investigate this point and, at the same time, to remove the "complicating" factor of PhCN and ClO$_4^-$ coordination to singly oxidized [(TPPBr$_x$)Co]$^+$, we have now investigated the electrochemistry and spectroelectrochemistry of (TPPBr$_x$)Co in a noncoordinating solvent, CH$_2$Cl$_2$, containing weakly coordinating tetra-n-butylammonium hexafluorophosphate, (TBA)-PF$_6$, as supporting electrolyte. We have also examined the interaction of CO with singly oxidized [(TPPBr$_x$)Co]$^+$, since

Table 1. FAB Mass Spectral Data for (TPPBr$_x$)Co

compd	m/z found	m/z calcd	compd	m/z found	m/z calcd
(TPPBr$_1$)Co	751	750.6	(TPPBr$_5$)Co	1067	1066.1
(TPPBr$_2$)Co	831	829.5	(TPPBr$_6$)Co	1145	1145.0
(TPPBr$_3$)Co	910	908.4	(TPPBr$_7$)Co	1225	1223.9
(TPPBr$_4$)Co	987	987.3	(TPPBr$_8$)Co	1304	1302.8

Table 2. Elemental Analyses of Newly Synthesized (TPPBr$_x$)Co Complexes Where $x = 1-5$[a]

compd	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
(TPPBr$_1$)Co·CH$_2$Cl$_2$	64.69	3.50	6.71	64.50	3.47	6.66
(TPPBr$_2$)Co	63.71	3.16	6.75	63.59	3.32	6.82
(TPPBr$_3$)Co	58.18	2.77	6.17	58.32	2.65	6.04
(TPPBr$_4$)Co	53.53	2.45	5.67	53.14	2.55	5.77
(TPPBr$_5$)Co	49.57	2.17	5.26	50.12	2.37	5.49

[a] Elemental analyses of compounds with $x = 6-8$ are given in ref 34.

[(TPP)Co)]$^+$ and [(OEP)Co]$^+$ are both known to bind carbon monoxide.[39-41] In this regard, it was of special interest to examine how the increasing nonplanarity of the (TPPBr$_x$)Co macrocycle with increasing number of Br groups would affect the binding of CO by *in situ* generated [(TPPBr$_x$)Co]$^+$

Experimental Section

Chemicals. Absolute dichloromethane (CH$_2$Cl$_2$) over molecular sieves, tetra-n-butylammonium perchlorate (TBAP), and tetra-n-butylammonium hexafluorophosphate ((TBA)PF$_6$) were obtained from Fluka Chemical Co. TBAP and (TBA)PF$_6$ were recrytallized from ethyl alcohol and ethyl acetate, respectively, while CH$_2$Cl$_2$ was used as received. Both salts were used as supporting electrolytes and were dried under vacuum at 40 °C for at least 1 week prior to use. All other reagents were of analytical grade, purchased from Aldrich, and used without further purification unless otherwise indicated. Nitrogen gas of "ultrahigh purity" was purchased from Trigas while CP grade carbon monoxide (CO) gas was obtained from Union Carbide Corp., Linde Division.

Synthesis. The free-base brominated complexes, (TPPBr$_x$)H$_2$, were synthesized according to literature procedures.[29] The cobalt derivatives with one to four Br groups, (TPPBr$_x$)Co ($x = 1-4$) were synthesized by following a method described by Callot,[42] while those with six, seven, or eight Br groups were synthesized as we earlier reported in the literature.[34] The synthesis of (TPPBr$_5$)Co is described below. Mass spectral and elemental analysis data for each investigated compound are given in Tables 1 and 2.

(TPPBr$_5$)Co. A 100 mg amount of (TPPBr$_5$)H$_2$ was dissolved in 50 mL of DMF, and 100 mg of (CH$_3$COO)$_2$Co was added under nitrogen. The solution was refluxed for 4 h, after which it was evaporated under vacuum. The residue was redissolved in chloroform, washed with water, and dried with anhydrous Na$_2$SO$_4$. The solvent was evaporated and the residue chromatographed on silica gel using a CHCl$_3$/n-hexane (1:1) mixture as eluent. The fraction containing the complex was evaporated and the residue crystallized from a CH$_2$Cl$_2$/n-hexane (1:2) mixture. (TPPBr$_5$)Co was obtained in an 85% yield.

Instrumentation. Mass spectra were obtained on a VG-4 mass spectrometer using m-nitrobenzyl alcohol (NBA) as the matrix. Elemental analyses were carried out at the Microanalysis Laboratory of the University of Padova, Italy.

Cyclic voltammograms were obtained with an EG&G Model 173 potentiostat. Current−voltage curves were recorded on an EG&G Princeton Applied Research Model RE-0151 X-Y recorder. A three-electrode system was used and consisted of a glassy carbon or platinum

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Table 3. Half-Wave Potentials ($E_{1/2}$, V vs SCE) for Oxidation of $(TPPBr_x)Co$ in CH_2Cl_2, 0.2 M $(TBA)PF_6$ under an N_2 or a CO Atmosphere

compd	1st ox			2nd ox			3rd ox		
	N_2	CO	Δ_{CO-N_2}	N_2	CO	Δ_{CO-N_2}	N_2	CO	Δ_{CO-N_2}
(TPP)Co	0.90	0.76	−0.14	1.10	1.20	0.10	1.30	1.30	0.00
$(TPPBr_1)Co$	0.91	0.79	−0.12	1.12	1.22	0.10	1.31	1.31	0.00
$(TPPBr_2)Co$	0.92	0.80	−0.12	1.14	1.22	0.08	1.33	1.33	0.00
$(TPPBr_3)Co$	0.94	0.85	−0.09	1.15	1.23	0.08	1.33	1.33	0.00
$(TPPBr_4)Co$	0.95	0.86	−0.09	1.20	1.24	0.04	1.36	1.36	0.00
$(TPPBr_5)Co$	0.99	0.93	−0.06	1.22	1.26	0.04	1.37	1.37	0.00
$(TPPBr_6)Co$	0.99	0.95	−0.04	1.27	1.28	0.01	1.40	1.39	−0.01
$(TPPBr_7)Co$	0.97	0.97	0.00	1.32	1.32	0.00	1.44	1.43	−0.01
$(TPPBr_8)Co$	0.98	0.97	−0.01	1.33	1.34	0.01	1.47	1.47	0.00

button working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). This reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

A Matheson Model 8250 modular Dyna-Blender with a flowmeter was used to deliver carbon monoxide/nitrogen gas mixtures that contained preset N_2/CO mixtures where the CO percentage varied from 0 to 100%.

UV−visible spectroelectrochemical experiments were performed with an optically transparent platinum thin-layer electrode of the type described in the literature.[43] Potentials for oxidation of each compound were applied with an EG&G Model 173 potentiostat. Time-resolved UV−visible spectra were recorded with a Hewlett Packard Model 8453 diode array rapid-scanning spectrophotometer.
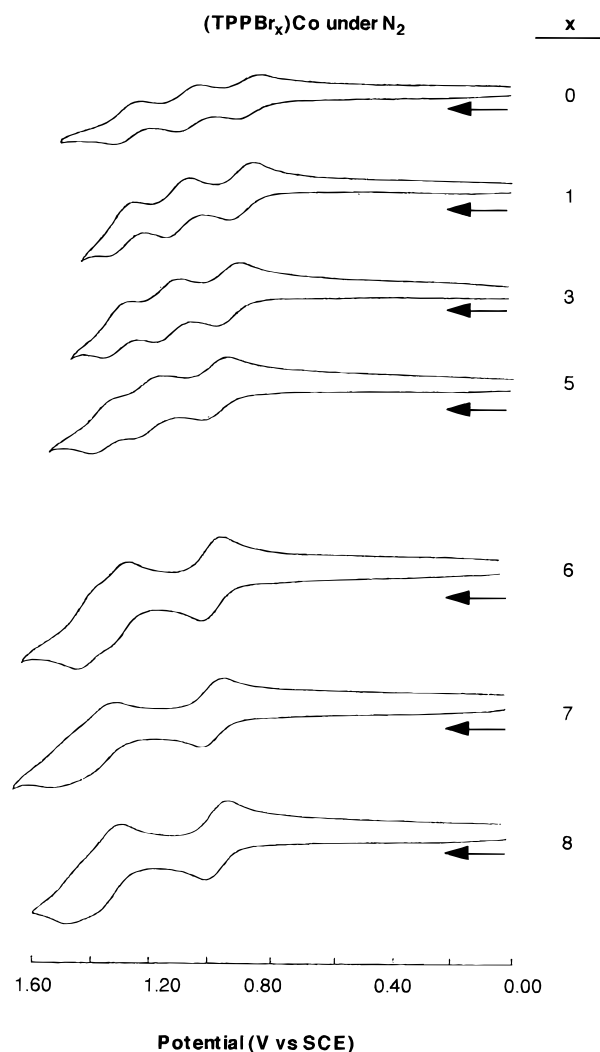
Infrared spectroelectrochemical measurements were made with an FTIR Nicolet Magna-IR 550 spectrometer using a specially constructed light-transparent three-electrode cell.[44] The background was obtained by recording the IR spectrum of $(TPPBr_x)Co$ in dichloromethane under a CO atmosphere in the absence of an applied potential. The IR spectrum of the electrooxidized compound under CO was obtained after bubbling CO through the spectroelectrochemical cell for 5−15 min prior to applying a potential, and a blanket of CO was maintained above the solution during the measurement.

Results and Discussion

Electrooxidation under a Nitrogen Atmosphere. Cyclic voltammograms for seven of the investigated $(TPPBr_x)Co$ derivatives in CH_2Cl_2 containing 0.2 M $(TBA)PF_6$ under a nitrogen atmosphere are illustrated in Figure 1, and half-wave potentials of each redox process under these experimental conditions are listed in Table 3. (TPP)Co is converted to $[(TPP)Co^{III}]^{3+}$ in three one-electron transfer steps.[36] The initial oxidation can occur either at the central metal ion or at the porphyrin macrocycle, with the exact site of electron transfer depending upon the strength of the counteranion and/or the presence of any coordinating ligands in solution.[36−38,45,46]

The brominated $(TPPBr_x)Co$ derivatives also undergo three one-electron oxidations within the positive potential limit of the solvent. The electrochemistry of $(TPPBr_x)Co$ ($x = 6$, 7, or 8) in PhCN containing 0.1 m TBAP has previously been reported.[34] The first oxidation of these porphyrins involves the central metal ion, while the second and third involve the porphyrin macrocycle to give Co(III) porphyrin π cation radicals and dications, respectively.

A plot of $E_{1/2}$ versus the number of Br groups on the macrocycle is illustrated in Figure 2 for all three oxidations of $(TPPBr_x)Co$. The first oxidation shifts linearly in a positive direction for compounds with $x = 0-5$ but shifts slightly in a negative direction for compounds with six, seven, or eight Br

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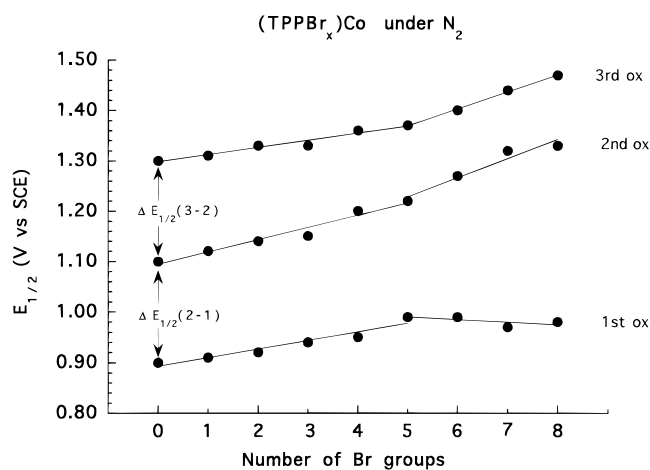(46) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1984**, *23*, 382.

Figure 1. Cyclic voltammograms of $(TPPBr_x)Co$ derivatives in CH_2Cl_2 containing 0.2 M $(TBA)PF_6$ under N_2.

groups. The second and third oxidations both shift in a positive direction as the number of Br groups on the macrocycle is increased but show an increased effect of substituent for compounds with six to eight Br groups. Consequently, the absolute potential difference between the first two oxidations, $\Delta E_{1/2}(2-1)$, remains virtually the same upon going from (TPP)-Co to $(TPPBr_5)Co$ but increases by 120 mV upon going from $(TPPBr_5)Co$ ($\Delta E_{1/2} = 230$ mV) to $(TPPBr_8)Co$ ($\Delta E_{1/2} = 350$ mV). Likewise the potential separation between the second and third oxidations of $(TPPBr_x)Co$, $\Delta E_{1/2}(3-2)$, decreases from 200 mV in the case of (TPP)Co to 140 mV in the case of (TPP-Br_8)Co.

A comparison between data for the first oxidation of (TPP-Br_x)Co and previously characterized $(TPPBr_x)FeCl^{28,29}$ is given in Figure 3. Linear relationships are seen between $E_{1/2}$ and the

Figure 2. Plots of $E_{1/2}$ versus the number Br groups on the macrocycle for the first, second, and third oxidations of (TPPBr$_x$)Co under N$_2$.
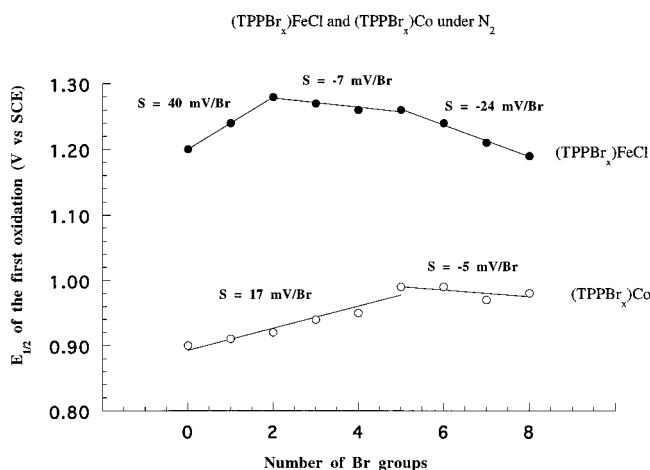

Figure 3. Plots of $E_{1/2}$ versus the number of Br groups on the macrocycle for the first oxidation of (TPPBr$_x$)Co in CH$_2$Cl$_2$, 0.2 M (TBA)PF$_6$ and (TPPBr$_x$)FeCl in PhCN, 0.1 M TBAP. Data for the Fe complexes are taken from ref 29.

$$(TPPBr_x)Co \rightleftharpoons [(TPPBr_x)Co]^+ + e$$

Figure 4. Time-resolved UV−visible spectral changes during the first oxidation of (TPPBr$_x$)Co ($x = 3, 5, 6, 8$) in CH$_2$Cl$_2$ containing 0.2 M (TBA)PF$_6$ under N$_2$.

number of Br groups for brominated cobalt porphyrins with $x \leq 5$ and for brominated iron porphyrins with $x \leq 2$. However, the different initial slopes in the two plots of $\Delta E_{1/2}/\Delta$Br (40 mV per Br group in the case of the iron porphyrins and 17 mV per Br group in the case of the cobalt porphyrins) are consistent with different sites of electron transfer in the two series of compounds. Ring-centered electrode reactions are generally more sensitive to the electronic effects of the substituents at the porphyrin macrocycle than are metal-centered electrode reactions,[36] and since the (TPPBr$_x$)FeCl complexes all undergo an initial oxidation at the porphyrin macrocycle,[29] the much smaller slope in the $\Delta E_{1/2}/\Delta$Br plot for (TPPBr$_x$)Co suggests that the cobalt derivatives with $x \leq 5$ are all oxidized at the central metal ion. This is indeed the case, as discussed in the following sections.

The data in Figure 3 also shows that the slope of $\Delta E_{1/2}/\Delta$Br decreases from +17 mV per Br group for (TPPBr$_x$)Co when $0 \leq x \leq 5$ to −5 mV per Br group when $x = 6-8$. One explanation for this change is that the investigated cobalt porphyrins are all oxidized at the metal center but that the increasing nonplanarity of the macrocycle which is induced by the presence of increasing numbers of bulky substituents at the pyrrole β positions strongly predominates over the inductive effect of the electron-withdrawing Br substituents, thus resulting in a nonlinear relationship between $E_{1/2}$ and the overall number of Br groups. An alternative explanation is that cobalt porphyrins with more than five Br groups are oxidized at the
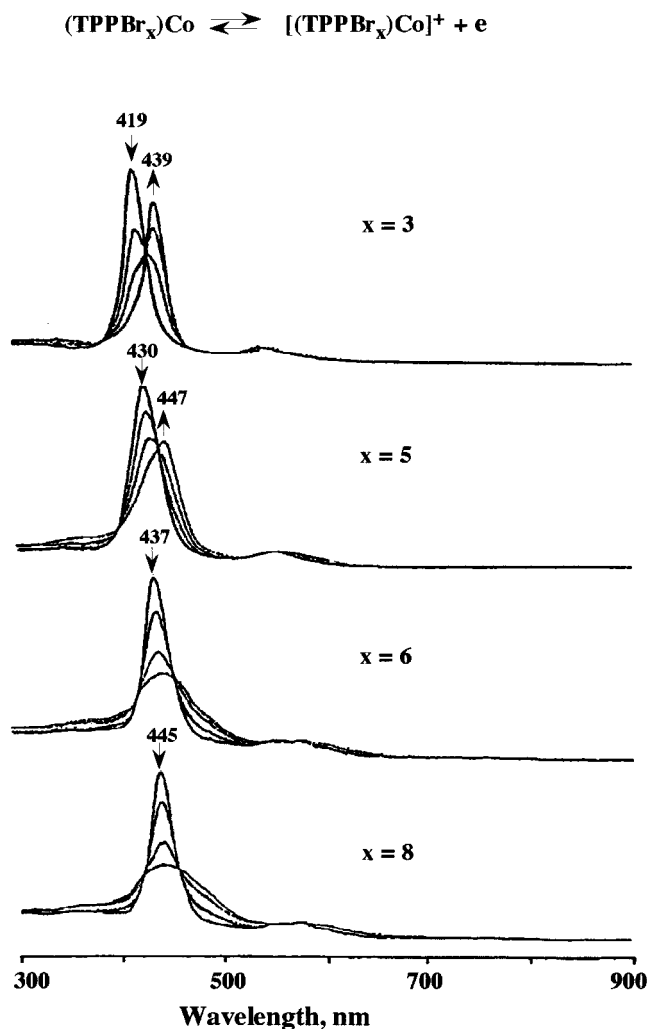
porphyrin π ring system, and hence the same substituent effect is observed for oxidation of (TPPBr$_x$)FeCl with $x = 2-5$ and (TPPBr$_x$)Co with $x = 6-8$.

In order to determine the exact formulation of [(TPPBr$_x$)-Co]$^+$ ($x = 0-8$), i.e., as a Co(III) species or as a Co(II) π cation radical, UV−visible spectra of the singly electrooxidized products were recorded using thin-layer spectroelectrochemistry. The results of these studies are described in the following section.

UV−Visible Spectroelectrochemistry under a Nitrogen Atmosphere. The time-resolved UV−visible spectral changes which occur during the first oxidation of (TPPBr$_x$)Co ($x = 3$, 5, 6, or 8) in CH$_2$Cl$_2$, 0.2 M (TBA)PF$_6$ are shown in Figure 4, and a summary of spectral data is given in Table 4. Each (TPP-Br$_x$)Co derivative has a Soret band at 410−445 nm and a single visible band between 527 and 560 nm. Each singly oxidized [(TPPBr$_x$)Co]$^+$ derivative has a Soret band at 427−477 nm and a single visible band between 540 and 586 nm. The positions of the absorption bands of (TPPBr$_x$)Co and [(TPPBr$_x$)Co]$^+$ are all red-shifted with increase in the number of Br groups on the macrocycle, and this has been interpreted in terms of configurational interactions.[32b,34]

Two types of spectral changes are observed in Figure 4. The first is seen for compounds with three and five Br groups and is diagnostic of a Co(II)/Co(III) transition in that the Soret and visible bands of the singly oxidized products are well-defined and red-shifted with respect to those of their neutral counter-

Table 4. UV−Visible Spectral Data for Neutral and Singly Oxidized (TPPBr$_x$)Co in CH$_2$Cl$_2$, 0.2 M (TPA)PF$_6$ under N$_2$

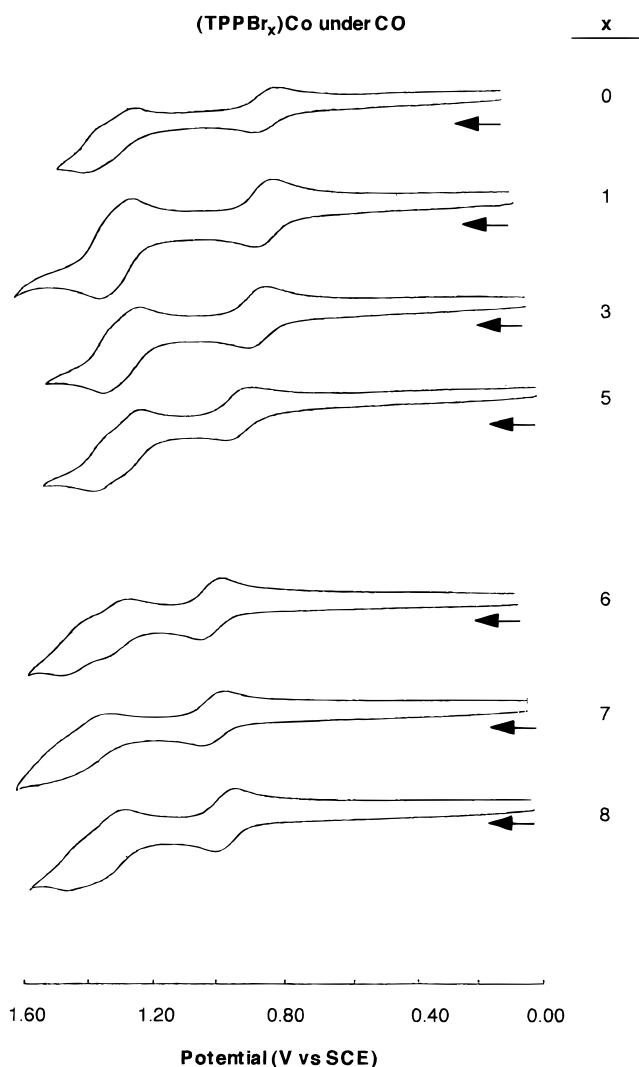|	λ_{max}, nm ($10^{-4}\epsilon$)			
	neutral		singly oxidized	
compd				
(TPP)Co	410 (19.5)	527 (1.2)	427 (12.1)	540 (1.0)
(TPPBr$_1$)Co	413 (17.4)	532 (1.1)	433 (13.8)	546 (1.1)
(TPPBr$_2$)Co	415 (19.2)	533 (1.3)	434 (23.0)	547 (1.7)
(TPPBr$_3$)Co	419 (17.9)	542 (1.3)	439 (14.7)	553 (1.3)
(TPPBr$_4$)Co	426 (15.4)	548 (1.4)	443 (14.7)	557 (1.2)
(TPPBr$_5$)Co	430 (11.6)	549 (1.0)	447 (8.0)	558 (1.0)
(TPPBr$_6$)Co	437 (16.2)	556 (1.3)	443 (7.3)	576 (1.2)
(TPPBr$_7$)Co	441 (15.4)	555 (1.2)	446 (6.3)	585 (1.1)
(TPPBr$_8$)Co	445 (15.5)	560 (1.3)	447 (6.7)	586 (1.0)

parts.[34,44,47] The second is seen for compounds with $x = 6$ and 8 and is diagnostic of Co(II) porphyrin π cation radical formation in that the spectra of the singly oxidized products exhibit broad, low-intensity Soret bands along with broad visible bands.[40,45,48] It should also be pointed out that the spectra of singly oxidized (TPPBr$_x$)Co ($x = 6-8$) in CH$_2$Cl$_2$ containing 0.2 M (TBA)PF$_6$ differ from spectra previously reported for the same singly oxidized compounds in PhCN containing 0.1 M TBAP.[34] The latter spectra show sharp Soret bands with well-defined visible bands and have been assigned as representing the spectra of a cobalt(III) complex with an uncharged porphyrin ring[34] rather than a Co(II) porphyrin π cation radical. The difference between the two sets of experimental conditions for compounds with $x = 6-8$ is that both the solvent and supporting electrolyte anion in the present study, CH$_2$Cl$_2$ and PF$_6^-$, are less strongly coordinating than those used in the previous study, which was carried out in PhCN containing ClO$_4^-$. This could explain the apparent change of electron transfer site from the metal under one set of solution conditions to the macrocycle under another.

The spectral and electrochemical data are thus self-consistent and suggest that the initial site of electron transfer in CH$_2$Cl$_2$ containing 0.2 M (TBA)PF$_6$ shifts from the central metal to the macrocycle as x is increased above 5. Such an effect of the halogenated substituents does not occur for (TPPBr$_x$)FeCl ($x = 0-8$), where the initial site of electron transfer remains the same along the complete series of compounds.[29]

Electrooxidation under a Carbon Monoxide Atmosphere. The electrooxidations of (TPP)Co and (OEP)Co have both been examined in CH$_2$Cl$_2$ containing 0.1 M TBAP under a CO atmosphere.[39,40] On the basis of the electrochemical and spectroscopic data, it was shown that one CO molecule, rather than two, binds to the singly oxidized species and that neither the neutral form of the Co(II) complex nor the doubly or triply oxidized form of the Co(II) derivative contains a bound CO molecule. As a result, the first oxidation of the porphyrin under CO is shifted negatively by about 100 mV with respect to $E_{1/2}$ for the first oxidation under N$_2$, while $E_{1/2}$ for the second oxidation is shifted positively by about the same amount upon going from 1.0 atm of N$_2$ to 1.0 atm of CO.

Cyclic voltammograms of (TPPBr$_x$)Co in CH$_2$Cl$_2$ containing 0.2 M (TBA)PF$_6$ under a CO atmosphere are shown in Figure 5 and reveal an electrochemical behavior similar to that of previously investigated (TPP)Co and (OEP)Co.[39,40] Each investigated (TPPBr$_x$)Co derivative undergoes three one-electron oxidations under a CO atmosphere, and as is the case for both (TPP)Co and (OEP)Co, the $E_{1/2}$ values for the first two oxidations of (TPPBr$_x$)Co are shifted upon going from an N$_2$

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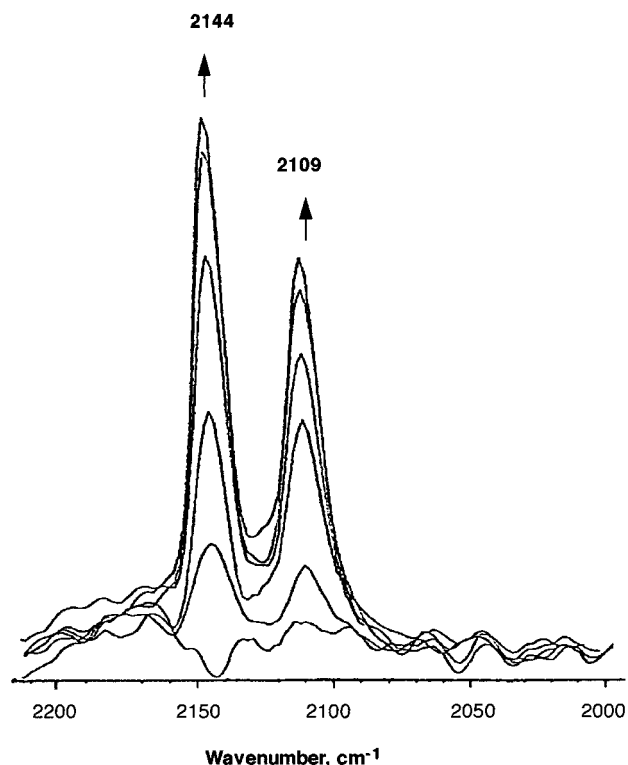
Figure 5. Cyclic voltammograms of (TPPBr$_x$)Co in CH$_2$Cl$_2$ containing 0.2 M (TBA) PF$_6$ under CO.

to a CO atmosphere, whereas the $E_{1/2}$ values for the third oxidation are independent of the gas above the solution.

The magnitude of the potential shift upon going from $E_{1/2}$ of a given oxidation under N$_2$ to $E_{1/2}$ of the same electrode reaction under CO is expressed in Table 3 by the quantity Δ_{CO-N_2} for each (TPPBr$_x$)Co derivative. The Δ_{CO-N_2} values for the first and second oxidations of the (TPPBr$_x$)Co derivatives with zero to three Br groups are similar in magnitude but opposite in sign (see Table 3), and this is as expected when CO binds only to the singly oxidized form of (TPPBr$_x$)Co.[39,40] This result is also consistent with the fact that Δ_{CO-N_2} is equal to zero fo the third oxidation of each compound. The magnitude of $|\Delta_{CO-N_2}|$ decreases with increase in the number of Br groups above 3 (see Table 3) and approaches zero for the first and second oxidations of the (TPPBr$_x$)Co complexes with more than five Br groups. This indicates that the singly oxidized forms of these nonplanar porphyrins either very weakly interact with CO or do not bind CO at all.

The data in Table 3 show unambiguously that CO interacts with singly oxidized [(TPPBr$_x$)Co]$^+$ ($0 \leq x < 6$), but it provides no information as to the number of CO molecules bound to the singly oxidized species under a carbon monoxide atmosphere. Only mono(carbon monoxide) adducts were generated upon the first oxidation of (TPP)Co or (OEP)Co in CH$_2$Cl$_2$ containing TBAP,[39,40] but as will be shown in the following sections, both mono- and bis(carbon monoxide) adducts of [(TPPBr$_x$)Co]$^+$

Figure 6. Time-resolved spectral FTIR changes recorded during the first oxidation of (TPP)Co in CH_2Cl_2 containing 0.2 M (TBA)PF_6 under CO.

Figure 7. UV−visible spectra of [(TPP)Co]$^+$ in (a) CH_2Cl_2 containing 0.2 M (TBA) PF_6 under different CO/N_2 mixtures and (b) CH_2Cl_2 containing 0.2 M (TBA)PF_6 and 0−50 equiv of TBAP under CO.

can be electrogenerated in the nonbonding CH_2Cl_2 solvent containing the more weakly coordinating supporting electrolyte, (TBA)PF_6.

FTIR Spectroelectrochemistry under a Carbon Monoxide Atmosphere. Figure 6 illustrates the time-resolved FTIR spectral changes which occur during the first oxidation of (TPP)-Co in CH_2Cl_2 containing 0.2 M (TBA)PF_6 under a CO atmosphere. As the electrolysis proceeds, two well-defined bands appear at 2144 and 2109 cm^{-1}. The first band ($\nu_{CO} = $ 2144 cm^{-1}) is assigned to the bis(carbon monoxide) adduct, [(TPP)Co(CO)$_2$]$^+$, and the second ($\nu_{CO} = $ 2109 cm^{-1}), to the mono(carbon monoxide) adduct, [(TPP)Co(CO)]$^+$. These assignments are based on the fact that ν_{CO} values of a bis(carbon monoxide) adduct are usually higher than those of a mono-(carbon monoxide) adduct.[49,50] Indeed, one would expect that the binding of a second CO molecule to [(TPP)Co(CO)]$^+$ would attenuate the degree of π back-bonding from the metal to CO, thus shifting the ν_{CO} of [(TPP)Co(CO)$_2$]$^+$ toward a value characteristic of the "free" CO molecule ($\nu_{CO} = $ 2155 cm^{-1}).[51] A similar trend of the CO stretching frequency has earlier been observed for [(OEP)Co^{III}(CO)]ClO$_4$ and [(OEP)Co^{III}(CO)$_2$]ClO$_4$. The mono(carbon monoxide) adducts shows a CO vibration at 2110 cm^{-1}, while the bis(carbon monoxide) adduct exhibits a CO vibration at 2137 cm^{-1}.[41]

It should be also noted that the $\Delta\nu_{CO}$ between [(TPP)Co-(CO)]$^+$ and [(TPP)Co(CO)$_2$]$^+$ (35 cm^{-1}) is similar to that $\Delta\nu_{CO}$ between [(OEP)Co^{III}(CO)]ClO$_4$ and [(OEP)Co^{III}(CO)$_2$]ClO$_4$ (27 cm^{-1}) but smaller than the $\Delta\nu_{CO}$ between (TPP)Fe(CO) and (TPP)Fe(CO)$_2$ (69 cm^{-1}).[49] The difference of magnitude in $\Delta\nu_{CO}$ between the iron and cobalt derivatives can be accounted
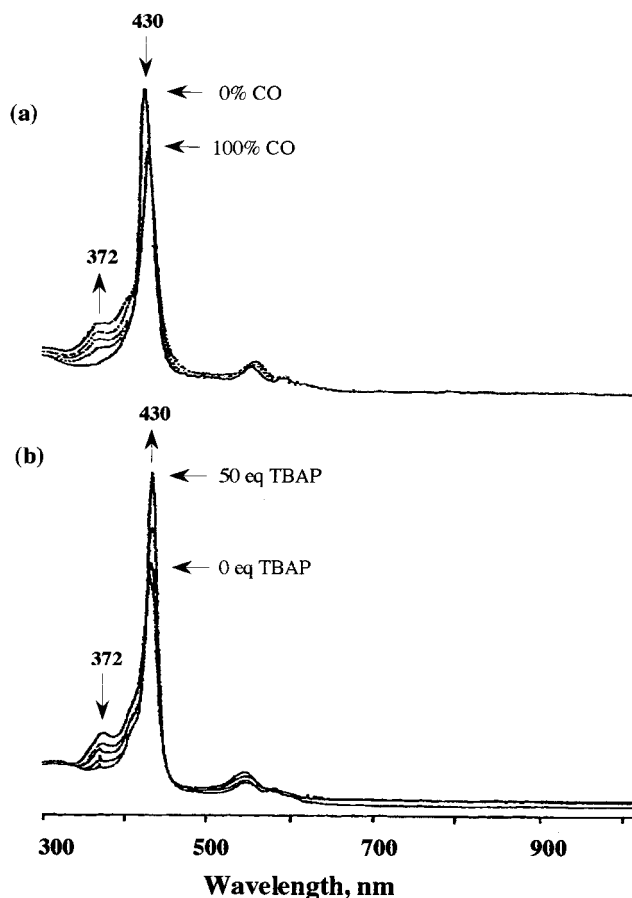
for by the fact that the π-back-bonding effect of the iron(II) compounds is stronger than that of the cobalt(III) derivatives, which have less electron density on their d orbitals.

The fact that mono- and bis(carbon monoxide) adducts of [(TPP)Co]$^+$ are both electrogenerated when (TBA)PF_6 is used as a supporting electrolyte suggests that either the PhCN solvent or the ClO$_4^-$ anion, which was used in previous electrochemical studies, was coordinated to the cobalt metal ion of [(TPP)Co]$^+$, thus preventing the binding of a second CO molecule to [(TPP)-Co(CO)(PhCN)]$^+$ or [(TPP)Co(CO)]$^+$ClO$_4^-$ in PhCN containing 0.1 M TBAP. This point was examined in the present study by measuring the UV−visible spectra of [(TPP)Co]$^+$ in CH_2Cl_2 containing 0.2 M (TBA)PF_6 under different percentages of CO as well as in CH_2Cl_2 containing (TBA)PF_6/TBAP mixtures under 100% CO.

The UV−visible spectra of [(TPP)Co]$^+$ in CH_2Cl_2 containing 0.2 M (TBA)PF_6 under different percentages of CO are shown in Figure 7a. As the percentage of CO is increased from 0 to 100%, the Soret band decreases in intensity while a new band appears at 372 nm. Similar UV−visible spectral changes are seen when 0−50 equiv of TBAP is added to a CH_2Cl_2 solution containing [(TPP)Co]$^+$ and 0.2 M (TBA)PF_6 under 100% CO (see Figure 7b). As the concentration of TBAP in solution is increased from 0 to 50 equiv, the Soret band at 430 nm increases in intensity while the absorption band at 372 nm decreases. The band at 372 nm is tentatively assigned to the bis(carbon monoxide) adduct, [(TPP)Co(CO)$_2$]$^+$, a species which is not detected in CH_2Cl_2 containing 0.2 M (TBA)PF_6, under a low percentage of CO, or in CH_2Cl_2, containing 0.2 M (TBA)-PF_6 and more than 50 equiv of TBAP under 100% CO. The assignment of the 372 nm band to [(TPP)Co(CO)$_2$]$^+$ is also

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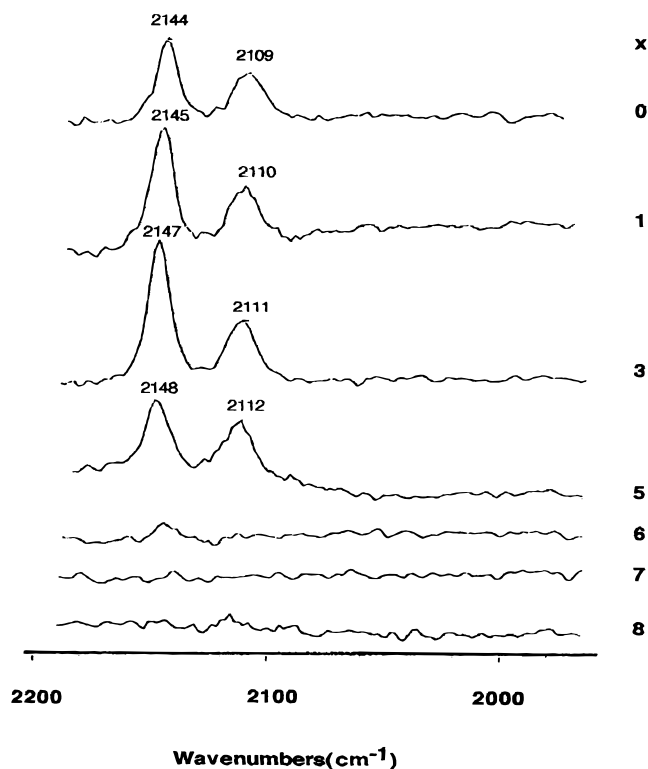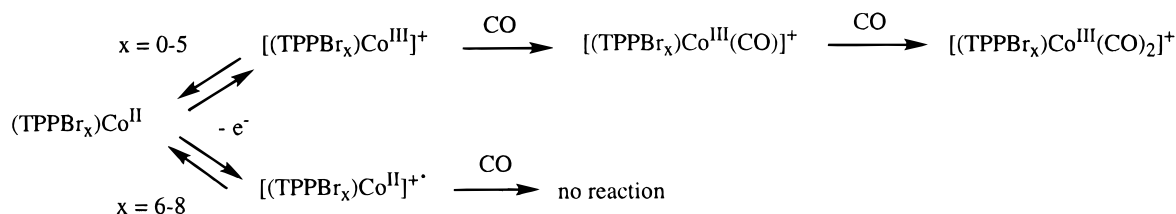
Scheme 1

Figure 8. FTIR spectra of $[(TPPBr_x)Co]^+$ in CH_2Cl_2 containing 0.2 M $(TBA)PF_6$ under CO.

consistent with the fact that a similar band is not seen in the UV−visible spectrum of electrogenerated $[(TPP)Co]^+$ in CH_2Cl_2 containing 0.1 M TBAP under a CO atmosphere.[39]

FTIR spectra of the other singly oxidized $(TPPBr_x)Co$ derivatives in CH_2Cl_2 containing 0.2 M $(TBA)PF_6$ under a CO atmosphere are shown in Figure 8. The derivatives with zero to five Br groups on the macrocycle show two IR bands in the ranges $2144-2148$ and $2109-2112$ cm^{-1}, respectively. The band at $2144-2148$ cm^{-1} is assigned to the bis(carbon monoxide) adduct, $[(TPPBr_x)Co(CO)_2]^+$, and that at $2109-2112$ cm^{-1} is assigned to the mono(carbon monoxide) adduct, $[(TPPBr_x)Co(CO)]^+$. The data are consistent with the IR

spectrum of $[(TPP)Co]^+$ in CH_2Cl_2 containing 0.2 M TBAP under CO and show that the ν_{CO} of $(TPPBr_x)Co$ varies only slightly with the number of Br groups, a result which contrasts with what has been observed for compounds in the $(TPPBr_x)$-FeCl series.[29] The difference between the two series of compounds might be explained by a weaker $d\pi$−ligand π^* back-bonding resulting from the oxidation of Co(II) to Co(III).[41]

The $[(TPPBr_x)Co]^+$ derivatives having six, seven, or eight Br groups show no IR bands between 2100 and 2200 cm^{-1}. This agrees with the electrochemical data, which indicates the absence of any CO binding to the singly oxidized porphyrin products and suggest the mechanism shown in Scheme 1.

Summary. It has been shown that the HOMO level of β-brominated-pyrrole porphyrins will rise upon increased distortion of the porphyrin macrocycle.[28,33] One might suggest that the metal d orbitals decrease in energy upon addition of Br groups to the porphyrin macrocycle, as evidenced by a positive shift in $E_{1/2}$ for the first oxidation, but that the π ring orbitals rise in energy due to an increase in the nonplanarity of the porphyrin ring and thus lie above the d orbitals for compounds with six to eight Br groups. The data in Figure 3 show that the distortion of the macrocycle compensates for the electronic effect of the substituents after the addition of only two Br groups in the case of $(TPPBr_x)FeCl$ but at least five Br groups are required to produce a similar effect in the case of $(TPPBr_x)Co$. It is not clear whether this difference in behavior is due to the different sizes of the metal ions (0.72 Å for Co(II) and 0.64 Å for Fe-(III)), differences in axial coordination (five-coordinate for iron and four-coordinate for cobalt), differences in the site of electron transfer (metal for cobalt vs ring for iron), or a combination of all three factors. The data also show that the CO binding ability of $[(TPPBr_x)Co]^+$ decreases upon going from compounds with zero to five Br groups to those with six, seven, and eight Br groups, and this is accounted for by a decreased basicity of the porphyrin macrocycle owing to an increase in number of electron-withdrawing substituents at the porphyrin periphery.