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Synthesis and electrochemistry of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin (H_2tdcdmpp), [Co^{II}(tdcdmpp)] and [M(tdcdmpp)Cl] (M = Fe^{III} or Mn^{III})

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Four new highly chlorinated porphyrins, 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin (H_2tdcdmpp), [Co^{II}(tdcdmpp)] and [M(tdcdmpp)Cl] (M = Fe^{III} or Mn^{III}) have been prepared. The free base was synthesized by chlorination of H_2tdmpp [5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin] and metallated to give the complexes following published procedures. The same transition-metal derivatives of tdmpp were also prepared and all eight synthesized compounds were electrochemically investigated in benzonitrile or pyridine containing 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$. As expected the half-wave potentials of the tdcdmpp complexes are shifted towards positive values while those for oxidation or reduction of the tdmpp species are shifted negatively as compared with $E_{\frac{1}{2}}$ for oxidation or reduction of tetraphenylporphyrin (tpp) complexes having the same central metal ions. The magnitude of the anodic shifts in $E_{\frac{1}{2}}$ for reduction with respect to tpp is among the largest reported for chlorinated porphyrins and ranges between 590 and 860 mV depending upon the specific redox reaction and solvent. A smaller $\Delta E_{\frac{1}{2}}$ of 330–400 mV is seen for oxidation of the same compounds and these values can be compared to a negligible shift in $E_{\frac{1}{2}}$ upon going from planar M(tpp) to distorted M(obtpp) (obtpp = 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrinate) complexes of cobalt and iron where the effect of macrocycle ruffling is known to predominate over the electronic effects of added halide substituents. This result indicates that the core distortion cannot compensate totally for the electron-withdrawing effect of the Cl substituents. The macrocyclic distortion also induces a large red shift of the UV/VIS absorption bands and this shift in λ_{max} ranges up to 40 nm for the chlorinated compounds with respect to the tdmpp complexes.

A number of synthetic halogenated metalloporphyrins have been examined as catalysts for the oxidation of organic substrates.[1–4] The most well studied of the synthetic compounds have been either free-base tetraphenylporphyrins containing electron-withdrawing groups as substituents on the four phenyl rings or β-pyrrole positions of the macrocycle, or porphyrins with the same substitution and cobalt,[5–9] copper,[9–12] iron,[1,12–20] manganese,[1,13,15,19,21–24] or zinc[6,9,11,13–15] central metal ions. β-Halogenated derivatives of iron porphyrins have also been studied in suprabiotic catalysis.[16,17]

The robustness of a given porphyrin catalyst towards oxidative degradation is related to the compound's oxidation potentials in the absence of the substrate,[1] and this underscores the need for obtaining redox potentials of each newly synthesized catalyst. The half-wave potentials for oxidation or reduction of a given metalloporphyrin will depend upon the type of central metal ion,[18] the basicity of the porphyrin ring[18] and, in the case of oxidation, the planarity of the porphyrin macrocycle.[7,13,14,19–21] The introduction of four or more bulky halogen groups onto the eight β positions of the porphyrin macrocycle leads to a non-planar conformation of the ring and this will in turn affect both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).[9,13–15,22] The change in planarity affects mainly the HOMO[23–26] while inductive effects of the added halogenated groups will affect both the HOMO and LUMO, thus leading to a shift of $E_{\frac{1}{2}}$ for both oxidation and reduction with the magnitude of $\Delta E_{\frac{1}{2}}$ depending upon both the type and number of halogenated substituents.[7,11,19–21,23] The largest substituent effect on $E_{\frac{1}{2}}$ occurs when the halogens are placed directly on the β-pyrrole positions of the macrocycle with much smaller shifts being seen for addition of the same halogenated groups to the four *meso*-substituted phenyl rings of tetraphenylporphyrin derivatives.[11,20]

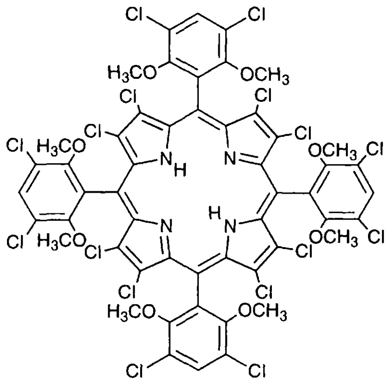
As part of our recent studies on the redox reactions of halogenated cobalt[7] and iron[19] porphyrins, we attempted to synthesize tdmpp[27] [the dianion of 5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin] derivatives containing halogen groups in each of the eight available β-pyrrole positions of the macrocycle. Surprisingly, the resulting isolated porphyrin was also chlorinated at the 3 and 5 positions of the four phenyl rings, thus giving as a final product 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin, H_2tdcdmpp.

In the present paper we report the synthetic procedures and electrochemical characterization of H_2tdcdmpp, as well as its iron, cobalt and manganese derivatives [M(tdcdmpp)Cl] (M = Fe or Mn) and [Co(tdcdmpp)]. The oxidation and reduction potentials of each compound were measured in both pyridine (py) and benzonitrile containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate and the resulting data are compared to values of $E_{\frac{1}{2}}$ for oxidation and reduction of both the non-substituted tetraphenylporphyrins on one hand and the non-chlorinated porphyrins, H_2tdmpp, [M(tdmpp)Cl] (M = Fe or Mn) and [Co(tdmpp)], on the other.

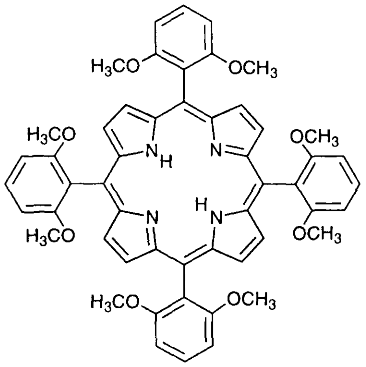
Experimental

Chemicals

Benzonitrile was obtained from Aldrich Chemical Co. and distilled over P_2O_5 under vacuum prior to use. Tetra-*n*-



H_2tdcdmpp



H_2tdmpp

butylammonium perchlorate (Sigma Chemical Co.) was recrystallized from ethanol and dried under vacuum at 40 °C for at least 1 week prior to use. 1,2-Dichloroethane and dichloromethane were distilled over P_2O_5 under nitrogen before use. Dry dimethylformamide (dmf) was obtained from Aldrich Chemical Co. *N*-Chlorosuccinimide was purified by literature methods.[28] All other reagents and solvents were of analytical grade used without further purification.

Instrumentation

Cyclic voltammetry was carried out with an EG&G model 173 potentiostat or an IBM model EC 225 voltammetric analyser. Current *vs.* voltage curves were recorded on an EG&G Princeton Applied Research model RE-0151 X-Y recorder. A three-electrode system was used, consisting of a glassy carbon or platinum-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. Proton NMR spectra were recorded as $CDCl_3$ solutions on a Bruker WP 80 SY and/or AM 400 instrument using tetramethylsilane as an internal standard, electronic absorption spectra of the initial compounds on a Philips PU 8730 UV/VIS spectrophotometer and FAB mass spectra on a VG Quattro spectrometer using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were carried out by the Microanalytical Laboratory at the University of Padova, Italy.

Syntheses

meso-5,10,15,20-Tetrakis(2,6-dimethoxyphenyl)porphyrin was synthesized according to literature procedures[27] and metal insertion carried out according to the method of Adler[29] in order to obtain its complexes of Zn^{II}, Co^{II}, Fe^{III} and Mn^{III}.

H_2tdcdmpp. Anhydrous $AlCl_3$ (20 mg) was added to Zn(tdmpp) (0.9 g) and *N*-chlorosuccinimide (3.3 g) dissolved in dry 1,2-dichloroethane (200 cm^3). The mixture was refluxed for 3 h while protecting from moisture with a $CaCl_2$ valve. After evaporation of the solvent, the zinc porphyrin was purified on a dry alumina column eluting with $CHCl_3$. The first green fraction was evaporated and the residue redissolved in trifluoroacetic acid (20 cm^3) and stirred under nitrogen for 10 h. The mixture was poured into ice–water and extracted with chloroform. The organic phase was then washed with a $NaHCO_3$ saturated solution, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was recrystallized from $CHCl_3$–diethyl ether to give 0.7 g (51%) of H_2tdcdmpp. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 457 (17 310), 553 (1340), 599 (690), 638 (400) and 706 (200). FAB mass spectrum: *m/z* 1406.6 $(M)^+$ (Found: C, 44.6; H, 2.35; N, 3.30. Calc. for $C_{52}H_{30}Cl_{16}N_4O_8$: C, 44.4; H, 2.15; N, 4.00%). ^1H NMR ($CDCl_3$): δ 7.85 (s, 4 H) and 3.37 (s, 24 H).

[Co(tdcdmpp)]. The compound H_2tdcdmpp (100 mg) was dissolved in dmf (50 cm^3) after which cobalt(II) acetate (100 mg) was added under nitrogen. The mixture was refluxed for 3 h and the solvent then evaporated under vacuum. The residue was chromatographed on Al_2O_3, eluting with $CHCl_3$. The first fraction eluted was recrystallized from $CHCl_3$–hexane to give [Co(tdcdmpp)] (yield 82%). UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 367 (sh) (20 400), 441 (135 500) and 560 (11 300). FAB mass spectrum: *m/z* 1461.8 $(M)^+$ (Found: C, 43.10; H, 1.85; N, 3.70. Calc. for $C_{52}H_{28}Cl_{16}CoN_4O_8$: C, 42.70; H, 1.95; N, 3.85%).

[Fe(tdcdmpp)Cl]. The compound H_2tdcdmpp (100 mg) was dissolved in dry argon-degassed dmf (100 cm^3) after which $FeBr_2$ (100 mg) was added and the solution refluxed under argon for 5 h. The solution was then evaporated under vacuum and the residue, redissolved in chloroform, was washed first with a 5% HCl solution, then with water, and finally dried over NaCl. Purification of the resulting iron(III) porphyrin followed the procedure given above for the cobalt(II) derivative. The pure compound was obtained in a 60% yield. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 400 (sh) (47 600), 448 (63 800), 583 (8600) and 625 (2900). FAB mass spectrum: *m/z* = 1458.6 $(M)^+$ (Found: C, 41.50; H, 2.00; N, 3.55. Calc. for $C_{52}H_{28}Cl_{17}FeN_4O_8$: C, 41.8; H, 1.90; N, 3.75%).

[Mn(tdcdmpp)Cl]. The compound H_2tdcdmpp (100 mg) was dissolved in dmf (50 cm^3) and $Mn(O_2CMe)_2 \cdot 4H_2O$ (50 mg) was added under nitrogen. The mixture was refluxed for 4 h, and the solvent then evaporated under vacuum. The residue was purified on acidic alumina (pH 6, Fluka), eluting first with $CHCl_3$ to remove the starting free base, then with $CHCl_3$–MeOH (96:4). The eluted fraction was first washed with 5% HCl, then with water and finally dried over NaCl to obtain the desired complex which was recrystallized from $CHCl_3$–MeOH. Yield 62%. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 390 (61 800), 506 (69 800), 610 (10 300) and 651 (6300) (Found: C, 41.0; H, 2.20; N, 3.65. Calc. for $C_{52}H_{28}Cl_{17}MnN_4O_8$: C, 41.8; H, 1.90; N, 3.75%).

Results and Discussion

Electrochemical studies were carried out both in pyridine and PhCN containing 0.1 mol dm^{-3} $NBu^n_4ClO_4$. Similar electrochemistry is seen in the two solvents but fewer redox reactions are observed in pyridine due to the smaller anodic potential window of this solvent (+0.8 V *vs.* SCE) as compared to PhCN (+1.8 V *vs.* SCE). Results in the two solvent systems are discussed below.

Electrochemistry in pyridine

Representative cyclic voltammograms are shown in Figs. 1 and 2 and a summary of the half-wave potentials is given in Table 1 which also includes $E_{\frac{1}{2}}$ values for the redox reactions of tetraphenylporphyrins with the same central metal ions.[30–32] The investigated compounds all undergo reversible reductions in this solvent. The same relative shifts in $E_{\frac{1}{2}}$ are seen for the iron, cobalt and manganese complexes upon going from tpp to tdmpp and then to tdcdmpp as a macrocycle.

Table 1 Half-wave potentials (V *vs.* SCE) for reduction in pyridine, 0.1 mol dm^{-3} $NBu^n_4ClO_4$ [a]

M[b]	Macrocycle	M^{III}-M^{II}	M^{II}-M^{I}	Ring
Fe	tpp[c]	+0.16	−1.51	−1.71
	tdmpp	−0.03	−1.71	
	tdcdmpp	+0.78	−0.99	−1.36
Co	tpp[d]	−0.21	−1.03	−1.93
	tdmpp	−0.40	−1.23	
	tdcdmpp	+0.28	−0.64	−1.33[e]
Mn	tpp[f]	−0.24		−1.31, −1.80
	tdmpp	−0.46		−1.57
	tdcdmpp	+0.26		−0.71, −1.11

[a] Assignments of metal oxidation state and site of electron transfer are made on the basis of spectroscopic results and literature data for tpp and related porphyrin derivatives containing the same central metal ions (see for example ref. 18). [b] Iron(III) and manganese(III) compounds exist as Cl^- salts. [c] Ref. 30. [d] Ref. 31. [e] At −50 °C. [f] Ref. 32.

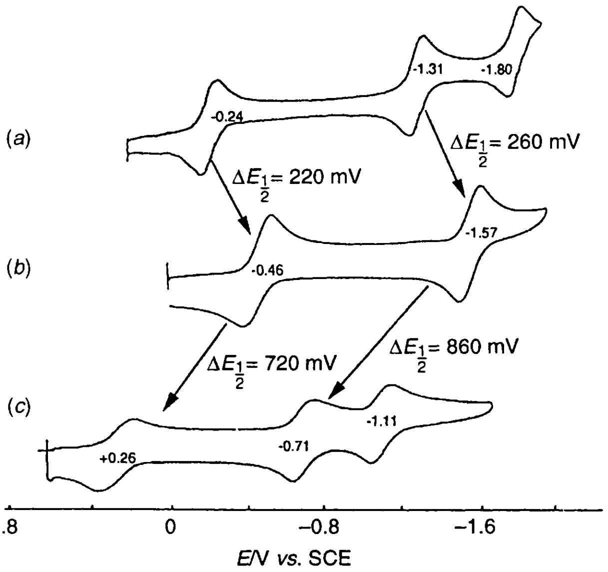


Fig. 1 Cyclic voltammograms of complexes [Mn(por)Cl] [por = (*a*) tpp = 5,10,15,20-tetraphenylporphyrin, (*b*) tdmpp or (*c*) tdcdmpp] in pyridine containing 0.1 mol dm^{-3} $NBu^n_4ClO_4$

The half-wave potentials for reduction of the three transition-metal tdmpp derivatives are all negatively shifted by 190 to 260 mV as compared to the $E_{\frac{1}{2}}$ values for the same redox reactions of the tpp complexes. This is expected, based on the electron-donating nature of the methoxy groups which increases the electron density at both the metal centre and macrocycle, thus leading to more difficult reductions in all cases. The magnitude of the shift in $E_{\frac{1}{2}}$ upon changing the macrocycle depends upon the specific electrode reaction (see values of $\Delta E_{\frac{1}{2}}$ in Figs. 1 and 2) with the largest value of $\Delta E_{\frac{1}{2}}$ being 260 mV for the second reduction of [Mn(tpp)Cl] and [Mn(tdmpp)Cl].

On the other hand, an anodic (positive) shift of all redox potentials is observed upon going from tdmpp to tdcdmpp as a macrocycle. In these cases the electron-withdrawing Cl groups decrease the electron density at both the metal centre and the conjugated porphyrin π-ring system and this leads to easier reductions. The positive shift of $E_{\frac{1}{2}}$ upon going from tdmpp to tdcdmpp is substantially larger in magnitude (and of a different sign) than that upon going from tpp to tdmpp and the values of $\Delta E_{\frac{1}{2}}$ in the former case range between 590 and 860 mV depending upon the specific electrode reaction. The largest $\Delta E_{\frac{1}{2}}$ (860 mV) is again observed for the second reduction of the manganese complexes.

Electrochemistry in PhCN

The results in PhCN parallel those in pyridine for reduction of the same series of compounds. A number of the redox processes in PhCN are irreversible as compared to the reversible reductions in pyridine, but it is still clear from the data that M^{III}–M^{II} and M^{II}–M^{I} reactions of the tdcdmpp complexes in this solvent occur at more positive potentials than for the tpp or tdmpp derivatives having the same central metal ions. The substituent effects in PhCN are similar to those in pyridine in that $E_{\frac{1}{2}}$ values for all four tdcdmpp derivatives are positively shifted compared to the oxidation or reduction potentials of the tpp compounds under the same experimental conditions (see Fig. 3 and Table 2).

Of some importance is the fact that the magnitude of the anodic shift in $E_{\frac{1}{2}}$ for oxidation of the chlorinated compounds is smaller than that for the reduction. For example, half-wave potentials for the M^{III}–M^{II} reactions of [Fe(tdcdmpp)Cl] and [Mn(tdcdmpp)Cl] are shifted by 450 and 500 mV, respectively, as compared to $E_{\frac{1}{2}}$ values for the same metal-centred reactions of the tpp complexes. In contrast, the first ring-centred oxidations of [Fe(tdcdmpp)Cl] ($E_{\frac{1}{2}}$ = 1.43 V) and [Fe(tpp)Cl] ($E_{\frac{1}{2}}$ = 1.20 V) differ from each other by only 230 mV, indicating that the ring-centred oxidation is affected only half as much as the metal-centred reduction ($\Delta E_{\frac{1}{2}}$ = 450 mV) upon introduction of the chloro substituents. This was also previously reported for other highly halogenated porphyrins.[7,13,15,19–21]

Finally it should be noted that the second oxidation of [Co(tdcdmpp)] involves a two-electron transfer and that the

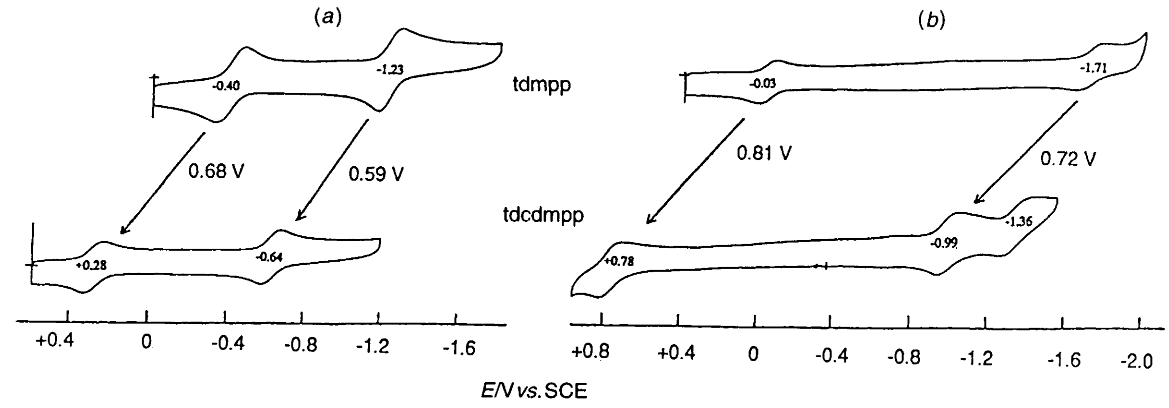


Fig. 2 Cyclic voltammograms of (*a*) [Co(por)] and (*b*) [Fe(por)Cl] complexes in pyridine containing 0.1 mol dm^{-3} $NBu^n_4ClO_4$

Table 2 Potentials (V *vs.* SCE) for reduction and oxidation of complexes in PhCN, 0.1 mol dm $^{-3}$ $NBu^n_4ClO_4$ [a]

M [b]	Compound	Ring oxidations	M^{III}–M^{II}, M^{II}–M^{I}	Ring reductions
H_2	tpp	+1.31, +1.06		−1.14, −1.53
	tdmpp	+1.35,[b] +0.88		−1.34, −1.68[c]
	tdcdmpp	+1.56,[d] +1.21		−0.48, −0.78
Fe	tpp	+1.52, +1.20	−0.29, −1.06	
	tdmpp	+1.43, +1.03	−0.47,[e] −1.22[e]	
	tdcdmpp	+1.43	+0.16, 0.90[c]	−1.15
Co	tpp	+1.20	+0.52,[d] −0.85	−1.97
	tdmpp	+1.37, +1.14	+0.39,[f] −1.02	−1.58[c]
	tdcdmpp	+1.64[g]	+1.15,[d] −0.28	−1.48[c,h]
Mn	tpp	+1.64, +1.28	−0.21	−1.47, −1.79[f]
	tdmpp	+1.54,[f] +1.02	−0.57[c]	−1.58
	tdcdmpp	+1.70,[d] +1.50[d]	+0.29	−0.89

[a] Assignments of metal oxidation state and site of electron transfer made on the basis of spectroscopic results and literature data for tpp and other porphyrin derivatives containing the same central metal ions (see for example ref. 18). [b] Iron(III) and manganese(III) compounds exist as Cl^- salts. [c] E_{pc} at scan rate of 0.1 V s $^{-1}$. [d] E_{pa} at scan rate of 0.1 V s $^{-1}$. [e] In presence of an excess of NBu^n_4Cl. [f] Quasi-reversible process. [g] Two-electron oxidation. [h] Irreversible multielectron process (see Fig. 3).

Table 3 The UV/VIS data (λ_{max}/nm) for tpp, tdmpp and tdcdmpp complexes in CH_2Cl_2

Compound	Macrocycle	Soret		Visible			
H_2por	tpp		411	508	542	585	642
	tdmpp		414	512	544	588	644
	tdcdmpp		457	553	599	638	706
[Fe^{III}(por)Cl]	tpp		410	502			
	tdmpp		417	507	580		
	tdcdmpp		448	583	625		
[Co^{II}(por)]	tpp		406	523			
	tdmpp		407	526			
	tdcdmpp		441	560			
[Mn^{III}(por)Cl]	tpp	370	471	578	618		
	tdmpp	374	477	582	615		
	tdcdmpp	390	506	610	651		

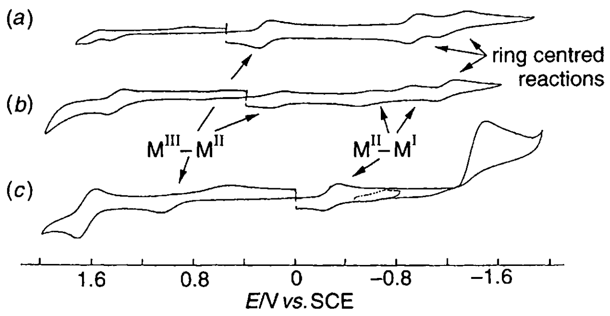


Fig. 3 Cyclic voltammograms of [M(por)Cl] [M = Mn (*a*) or Fe (*b*)] and [Co(por)] (*c*) (por = tdcdmpp) in PhCN containing 0.1 mol dm $^{-3}$ $NBu^n_4ClO_4$

second reduction of the same compound involves formation of an unstable cobalt(I) π-anion radical after which the Cl groups are lost in a reductive dehalogenation similar to what has been reported for brominated [Co(tpp)] under the same solution conditions.[7]

Effect of the chloro substituents on the redox potentials

The UV/VIS data for the eight investigated compounds are summarized in Table 3 which also gives spectral data for the related tpp complexes recorded in CH_2Cl_2. The red shift in wavelengths is small (3–4 nm) upon going from tpp to tdmpp but larger upon going from tdcdmpp to tdmpp where a red shift of 34 to 62 nm is observed in the visible region. This is consistent with the electrochemical data which indicate a significant decrease in the HOMO–LUMO gap upon addition of 16 chloro groups to the tdmpp complexes.[9,13,14]

The introduction of bulky substituents onto the porphyrin macrocycle affects the energy of the HOMO and LUMO of the compounds in two distinctive ways. The first involves the electron-donating or -withdrawing character of the substituents while the second involves a change in planarity of the macrocycle. The HOMO and LUMO levels are both destabilized upon introduction of electron-donating methoxy groups to the four phenyl rings of tpp while the addition of electron-withdrawing chloro substituents to the four phenyl rings and eight β positions of the macrocycle stabilizes the orbitals. As a consequence, a positive shift of the redox potentials is observed for the tdcdmpp species while a negative one is seen for the tdmpp complexes compared to the tpp compounds. The anodic potential shifts observed between the redox reactions of the tdcdmpp and tdmpp complexes are among the largest measured for halogenated porphyrins and contrast with results reported for brominated tpp complexes of Co^{II} [7] and $Fe^{III}Cl$ [19] under similar solution conditions.

The changes in porphyrin ring planarity which occur upon addition of more than four bulky substituents to the β positions of the macrocycle[19,21] also affect the $E_{\frac{1}{2}}$ for oxidation. The steric hindrance of the added groups leads to a saddle-shape core distortion. The HOMO but not the LUMO is destabilized[9,13,14] and thus the HOMO–LUMO energy gap decreases. A red shift of the electronic absorption bands is also observed.

As seen in Fig. 3 and Table 2, the potential difference ($\Delta E_{\frac{1}{2}}$) between the first oxidation of: (*i*) [Fe(tdcdmpp)Cl] and [Fe(tdmpp)Cl] (400 mV) or (*ii*) H_2tdcdmpp and H_2tdmpp (330 mV), are much more pronounced than the $\Delta E_{\frac{1}{2}}$ between the oxidation of [Fe(obtpp)Cl] (obtpp = 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrinate) and [Fe(tpp)Cl] (+10 mV),[19] H_2obtmp (2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetramesitylporphyrin) and H_2tmp (+80 mV)[21] or H_2octmp (2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetramesitylporphyrin) and H_2tmp (+140 mV).[21] This indicates that the electron-withdrawing effects of the chloride substituents on the tdcdmpp macrocycle are not totally offset by core distortion due to steric hindrance as in the case of the obtpp derivatives. This may be due to the fact that a maximum distortion is reached before total chlorination of the porphyrin, at which point the electronic effects of the substituents become predominant.

The first, metal-centred, reductions of [Co(tdcdmpp)] and [Fe(tdcdmpp)Cl] ($E_{\frac{1}{2}}$ = −0.28 and +0.16 V respectively in PhCN) are only slightly more positive than those measured for [Co(obtpp)][7] and [Fe(obtpp)Cl][19] (−0.35 and +0.10 V respectively) under the same solution conditions. The electronegativities of the Cl and Br substituents are comparable to each other[33] and the total substituent effects of the eight electron-withdrawing chloro groups on the *meso*-phenyl rings of the tdcdmpp derivatives are counterbalanced by the electron-

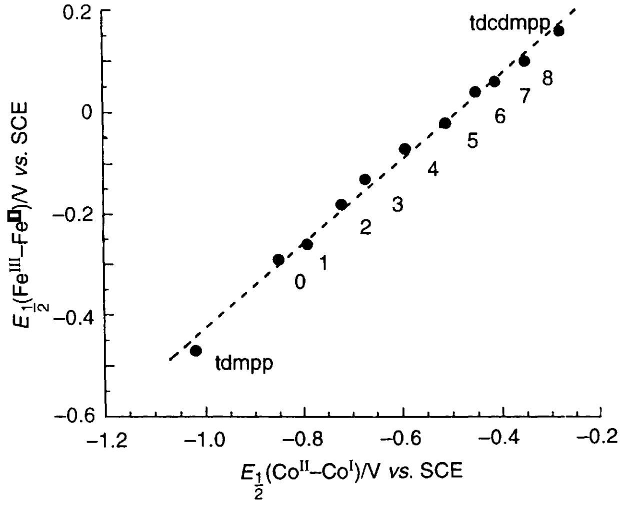


Fig. 4 Correlation between reversible half-wave potentials for the Fe^{III}–Fe^{II} and Co^{II}–Co^{I} processes of complexes of polybrominated tpp (number of Br is 0–8),[7,19] tdmpp and tdcdmpp in PhCN containing 0.1 mol dm^{-3} NBu$^{n}{}_4$ClO$_4$

donating effects of the eight methoxy groups. This is quantitated by the Hammett parameters which are almost identical in magnitude but of opposite sign, *i.e.* $\sigma_o = -0.39$ for OCH$_3$ and $\sigma_m = 0.37$ for Cl.[33] Thus, there is a negligible substituent effect from the groups on the four phenyl rings and the main shift in $E_{\frac{1}{2}}$ for the tdcdmpp complexes as a function of substituent is due only to the eight Cl groups at the β positions of the macrocycle.

Finally it should be pointed out that the $E_{\frac{1}{2}}$ for reduction of the brominated tpp complexes of Fe^{III}Cl[19] and Co^{II} (number of Br is 0–8)[7] varies linearly with the number of substituents. A linear relationship also exists between the first reduction potentials of these complexes as seen in Fig. 4 (correlation coefficient = 0.99) which also includes data for Fe^{III}–Fe^{II} and Co^{II}–Co^{I} reactions of the currently investigated tdmpp and tdcdmpp complexes. The slope of the line in Fig. 4 is 0.83 which is consistent with a larger substituent effect on the Co^{II}–Co^{I} reaction as compared to the Fe^{III}–Fe^{II} one. Finally, the fact that the four tdmpp and tdcdmpp complexes fit the same correlation between $E_{\frac{1}{2}}$ values as the β-brominated iron and cobalt porphyrins indicates that the relative effect of substituents on reduction potentials is constant over all 22 compounds in the iron and cobalt series.

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References

1 D. Mansuy, in *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, eds. D. H. R. Barton, A. E. Martell and D. T. Sawyer, Plenum, New York, 1993, pp. 347–358.
2 M. W. Grinstaff, M. G. Hill, J. A. Labinger and H. B. Gray, *Science*, 1994, **264**, 1311.
3 D. Mansuy, *Coord. Chem. Rev.*, 1993, **125**, 129.
4 J. F. Bartoli, O. Brigaud, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1991, 440.
5 A. Giraudeau, H. J. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Am. Chem. Soc.*, 1979, **101**, 3857.
6 S. A. Richert, P. K. S. Tsang and D. T. Sawyer, *Inorg. Chem.*, 1989, **28**, 2471.
7 F. D'Souza, A. Villard, E. Van Caemelbecke, M. Franzen, T. Boschi, P. Tagliatesta and K. M. Kadish, *Inorg. Chem.*, 1993, **32**, 4042; K. M. Kadish, E. Van Caemelbecke, J. Li, M. Autret and P. Tagliatesta, *Inorg. Chem.*, 1996, in the press.
8 X. Q. Lin, B. Boisselier-Cocolios and K. M. Kadish, *Inorg. Chem.*, 1986, **25**, 3242.
9 P. Bhyrappa and V. Krishnan, *Inorg. Chem.*, 1991, **30**, 239.
10 A. Giraudeau, I. Ezahr, M. Gross, H. J. Callot and J. Jordan, *Bioelectrochem. Bioenerg.*, 1976, **3**, 519.
11 A. Giraudeau, H. J. Callot and M. Gross, *Inorg. Chem.*, 1979, **18**, 201.
12 D. Reddy, M. Ravikanth and T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans.*, 1993, 3575.
13 T. Takeuchi, H. B. Gray and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1994, **116**, 9730.
14 O. Brigaud, P. Battioni, D. Mansuy and C. Giessner-Prettre, *Nouv. J. Chim.*, 1992, **16**, 1031.
15 J. A. Hodge, M. G. Hill and H. B. Gray, *Inorg. Chem.*, 1995, **34**, 809.
16 P. E. Ellis, jun., and J. E. Lyons, *Catal. Lett.*, 1989, **3**, 389.
17 J. E. Lyons and P. E. Ellis, jun., *Catal. Lett.*, 1991, **8**, 45.
18 K. M. Kadish, *Prog. Inorg. Chem.*, 1986, **34**, 435.
19 K. M. Kadish, F. D'Souza, A. Villard, M. Autret, E. Van Caemelbecke, P. Bianco, A. Antonini and P. Tagliatesta, *Inorg. Chem.*, 1994, **33**, 5169.
20 T. Wijesekera, A. Matsumoto, D. Dolphin and D. Lexa, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1028.
21 P. Ochsenbein, K. Ayougou, D. Mandon, J. Fischer, R. Weiss, R. N. Austin, K. Jayaraj, A. Gold, J. Terner and J. Fajer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 348.
22 H. Fujii, *J. Am. Chem. Soc.*, 1993, **115**, 4641.
23 K. M. Barkigia, L. Chantranupong, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1988, **110**, 7566.
24 K. M. Barkigia, M. W. Renner, L. R. Furenlid, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1993, **115**, 3627.
25 T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, 1987, **26**, 1338.
26 K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner and K. M. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 8851.
27 E. Tsuchida, T. Komatsu, E. Hasegawa and H. Nishide, *J. Chem. Soc., Dalton Trans.*, 1990, 2713.
28 D. D. Perrin, W. F. L. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 3rd edn., Pergamon, New York, 1988, p. 105.
29 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.
30 L. A. Bottomley and K. M. Kadish, *Inorg. Chem.*, 1981, **20**, 1348.
31 F. A. Walker, D. Beroiz and K. M. Kadish, *J. Am. Chem. Soc.*, 1976, **98**, 3484.
32 S. L. Kelly and K. M. Kadish, *Inorg. Chem.*, 1982, **21**, 3631.
33 P. Zuman, *Substituent Effects in Organic Polarography*, Plenum, New York, 1967.

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