Cyanoporphyrins. Co-ordinating and Electrochemical Properties

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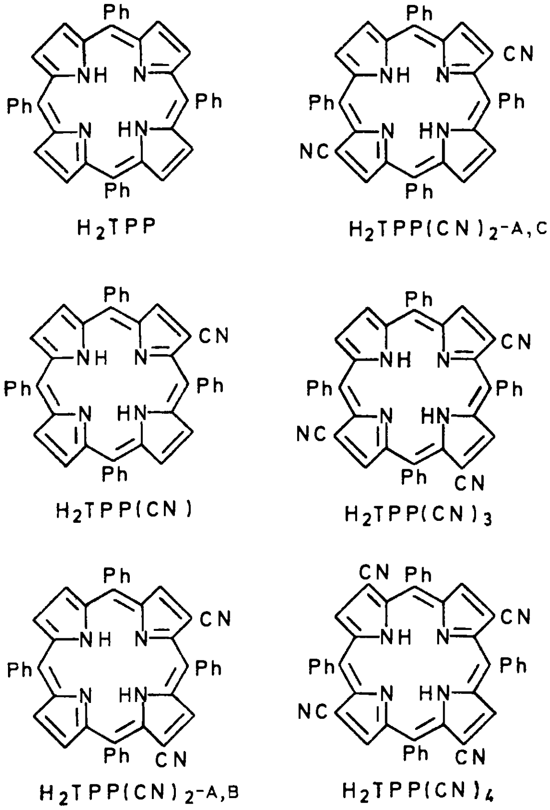
Successive substitutions in the pyrrole rings of tetraphenylporphyrin by up to four cyano-groups lead to large additive anodic shifts of the redox potentials. These shifts are larger than those observed with other electron-withdrawing substituents. The stoicheiometry and stability of the complexes formed from metallotetracyanoporphyrins (Cu, Ni, Ag) and nitrogenous bases (pyridine. piperidine) are determined. A novel five-co-ordinate silver(II) porphyrin is reported.

A SUBJECT of some interest in the chemistry of porphyrins (P) and metalloporphyrins (MP) is the influence of electron-withdrawing groups on the porphyrin nucleus. Certain natural porphyrins (haem a, chlorophyll b) fall into this category in that they have formyl replacing the methyl groups on the nucleus. Several porphyrins have been synthesized in order to study this effect including modified deuteroporphyrins (acetyl, formyl, cyano, nitro),[1] or *p*-substituted tetraphenylporphyrins.[2] Recently, we have demonstrated the regiospecific introduction of up to four electron-withdrawing cyano-groups into the tetraphenylporphyrin (TPP) nucleus.[3] We now report two aspects of the reactivity of cyanoporphyrins and their metal complexes, that of electrochemical reduction, with emphasis on the additive effect of increasing number of cyano-groups and their particular isomers, and that of the stability of the metallotetracyanoporphyrin–nitrogenous base complexes.



H_2TPP $H_2TPP(CN)_2$-A,C

$H_2TPP(CN)$ $H_2TPP(CN)_3$

$H_2TPP(CN)_2$-A,B $H_2TPP(CN)_4$

The central hydrogen atoms may be replaced by a divalent cation

EXPERIMENTAL

(a) *Preparation of Substituted Porphyrin Derivatives.*—The polycyanotetraphenylporphyrins [$H_2TPP(CN)_x$] and their respective Cu^{II} and Ni^{II} complexes were prepared as previously described.[3] The complexes Ag^{II}- and Pd^{II}-$TPP(CN)_4$ were synthesized by the method of Adler *et al.*,[4] involving reflux of $H_2TPP(CN)_4$ with silver acetate or palladium dichloride for a short time in dimethylformamide (DMF) followed by evaporation. The complexes were purified by column chromatography on alumina with chloroform elution, the product appearing as a green band. The complexes were precipitated as violet crystals from chloroform by addition of methanol. The product was shown to be pure by t.l.c. and mass and visible spectrometry. H_2(*p*-Cyanophenyl)$_4$P was synthesized by known methods.[5]

(b) *Electrochemical Determinations.*—DMF (Merck; puriss) was dried over calcium hydride, redistilled under reduced pressure, and stored over Linde molecular sieves (4 Å) under dry argon prior to use. The electrolyte, tetraethylammonium perchlorate (TEAP) (Eastman Kodak), was recrystallized from methanol and vacuum desiccated at 80°. The electrochemical device was from Solea–Tacussel, and all measurements were performed under argon or nitrogen. The potentials are referred to the standard calomel electrode in saturated aqueous KCl (s.c.e.). The electrical junction between s.c.e. and the cell was made *via* a bridge of 0.1M-TEAP in DMF; hence the given potentials include a constant liquid junction potential.

Polarography. The first two reduction waves were studied for the cyanoporphyrins $H_2TPP(CN)_x$ and Cu-$TPP(CN)_x$ (x = 0—4), $NiTPP(CN)_x$ (x = 0, 3, or 4), and $PdTPP(CN)_x$ (x = 0 or 4). In each case the first two waves were well defined, the limiting currents being proportional to the concentration of porphyrin and the square root of the corrected mercury height above the tip of the capillary ($47 < h_{cm} < 117$). Thus the limiting currents were diffusion controlled, and the Illkovic's equation holds. Kinetically, logarithmic analysis of these waves demonstrated the polarographic reversibility of all the reductions. The values of the half-wave potentials $U_{\frac{1}{2}}$ are given in Tables 1—3.

Potentiostatic coulometry. We examined the first two reduction steps of $H_2TPP(CN)_x$ and $Cu^{II}TPP(CN)_x$ (x =

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0—4) at a potential 200 mV more cathodic than the corresponding half-wave potential. In all cases only one electron per reduction step was given to the porphyrin rings. The *I–t* responses gave a series of exponential curves as anticipated for a pure electron transfer process without kinetic complications.

TABLE 1

Half-wave potentials of porphyrin free bases

	$U_{\frac{1}{2}}$ (I)/mV *versus* s.c.e.*	$U_{\frac{1}{2}}$ (II)/mV *versus* s.c.e.†	$\Delta = \lvert U_{\frac{1}{2}}$ (II) = $U_{\frac{1}{2}}$ (I)$\rvert$/mV
H_2TPP	−1 080	−1 460	380
$H_2TPP(CN)$	−840	−1 200	360
$H_2TPP(CN)_2$-A, B	−600	−940	340
$H_2TPP(CN)_2$-A, C	−510	−910	400
$H_2TPP(CN)_3$	−330	−640	310
$H_2TPP(CN)_4$	−120	−470	350

* First polarographic wave. † Second wave.

TABLE 2

Half-wave potentials of copper porphyrins

	$U_{\frac{1}{2}}$ (I)/mV *versus* s.c.e.*	$U_{\frac{1}{2}}$ (II)/mV *versus* s.c.e.†	$\Delta = \lvert U_{\frac{1}{2}}$ (II) − $U_{\frac{1}{2}}$ (I)$\rvert$/mV
CuTPP	−1 200	−1 680	480
CuTPP(CN)	−940	−1 440	500
$CuTPP(CN)_2$-A, B	−700	−1 190	490
$CuTPP(CN)_2$-A, C	−660	−1 150	490
$CuTPP(CN)_3$	−500	−930	430
$CuTPP(CN)_4$	−230	−670	440

* First polarographic wave. † Second wave.

TABLE 3

Half-wave potentials of other porphyrins

	$U_{\frac{1}{2}}$ (I)/mV *versus* s.c.e.*	$U_{\frac{1}{2}}$ (II)/mV *versus* s.c.e.†	$\Delta = \lvert U_{\frac{1}{2}}$ (II) − $U_{\frac{1}{2}}$ (I)$\rvert$/mV
PdTPP	−1 179	−1 642	463
$PdTPP(CN)_4$	−240	−693	453
NiTPP	−1 190	−1 725	535
$NiTPP(CN)_3$	−530	−1 005	475
$NiTPP(CN)_4$	−330	−785	455
$H_2(p\text{-}CNC_6H_4)_4P$	−910	−1 257	347

* First polarographic wave. † Second wave.

Cyclic voltammetry. The compounds examined by this method were those described in the polarography section. In each case two anodic and two cathodic peaks were observed, corresponding to the two first reduction steps. At low sweep rates ($v < 0.1$ V s^{-1}) the potential differences between the corresponding anodic and cathodic peaks were constant, confirming the polarographic reversibility and transfer of one electron of these steps. At higher sweep rates ($0.2 < v < 100$) the potential difference between the corresponding anodic and cathodic peaks increased as a function of v. From these results the apparent rate constant for the electrochemical reduction of $H_2TPP(CN)_x$ and $CuTPP(CN)_x$ (x = 0—4) was calculated as $k_s{}^0$ = 0.4—1 cm s^{-1}, independent of the value of x.

(c) *Axial Co-ordination of Nitrogenous Bases to* $M^{II}TPP(CN)_4$.—To study the axial co-ordination of nitrogenous bases to the metallotetracyanoporphyrins, spectrophotometric methods were employed. The complexes were formed by the addition of pyridine or piperidine in portions to chloroform solutions of metalloporphyrins (5×10^{-6}M) directly in the spectrophotometer cell (glass stoppered cell; 1 cm path; 20 ± 0.5°). In each case the starting material exhibited a large long wavelength band as well as a Soret band, whilst the complexes had two intense absorption bands at long wavelength and a shifted Soret band (Table 4). The longest wavelength absorption band of the complex appeared in a region which was transparent for the starting material, facilitating identification. In the case of a strong interaction between $M^{II}TPP(CN)_4$ and the ligand L (*e.g.* with Ni) the value of ε for the longest wavelength absorption of the product was calculated by extrapolation to $[L]^{-1} = 0$ and both K $\{= [M^{II}TPP(CN)_4L_n]/[M^{II}TPP(CN)_4][L]^n\}$ and n were determined graphically (Table 5).

TABLE 4

Visible spectra [λ/nm (10^{-3} ε)] of metalloporphyrins and complexes

Porphyrins	Soret	Major long wavelength bands
$NiTPP(CN)_4$	439 * (193)	633 * (52)
Piperidine complex	466 (177)	663 (22.5), 698 (26.5)
Pyridine complex	466 (174)	633 (21.5), 695 (24)
$PdTPP(CN)_4$	435 (193)	617 (65)
$CuTPP(CN)_4$	436 (224)	638 (52)
Piperidine complex	460	652, 680
Pyridine complex	455	650, 675
$AgTPP(CN)_4$	440 (210)	637 (41)
Piperidine complex	460	650, 680

* Erroneously indicated as 456 and 651 nm in ref. 3.

TABLE 5

Values of n and log K for formation of complexes of metalloporphyrins

Porphyrin	Added ligand	n (±0.1)	log K
$NiTPP(CN)_4$	Piperidine	1.3	1.6 ± 0.05
$NiTPP(CN)_4$	Pyridine	1.6	1.3 ± 0.05
$CuTPP(CN)_4$	Piperidine	0.9	0.3 ± 0.1
$CuTPP(CN)_4$	Pyridine	1.1	0.0 ± 0.1
$AgTPP(CN)_4$	Piperidine	1.0	−0.6 ± 0.15

For weaker interaction (*e.g.* with Cu or Ag) the decrease of the longest wavelength absorption peak of the starting material was measured and K and n were determined (Table 5), although with less accuracy. Similar measurements on the Soret band furnished comparable results.

DISCUSSION

(a) *Electrochemical Results*.—In cellular metabolism, the role of porphyrins is related to their electron-transfer ability, and hence there have been many reports of electrochemical studies associated with both natural and synthetic model porphyrins.[1,6-19] Electro-

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chemically, this participation of porphyrins is governed by their electron-transfer kinetic parameters, such as rate constant, and thermodynamic parameters, such as redox potentials. Previous observations [1] have demonstrated the effect of ring substituents on redox potentials. Electron-withdrawing groups reduce the basicity of the nucleus and cause an anodic displacement of the redox potential; [20] values of up to +100 mV have been observed in model systems.

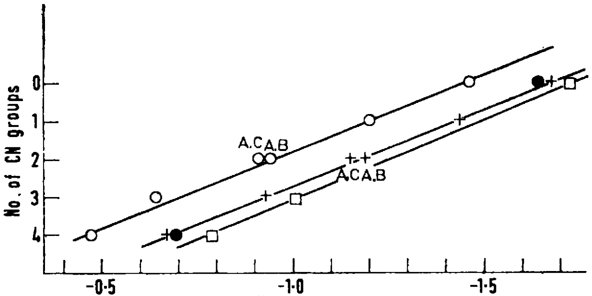

FIGURE 1 Relation between half-wave potentials and number of cyano-groups (first wave: 0.1M-TEAP in DMF; porphyrin concentration *ca.* 5 × 10^{-4}M): ○, $H_2TPP(CN)_x$, $x = 0$—4; +, $CuTPP(CN)_x$, $x = 0$—4; ●, $PdTPP(CN)_4$ and PdTPP; □, $NiTPP(CN)_x$ (x = 0, 3, and 4)

Our electrochemical data on ring substituted free porphyrin bases $H_2TPP(CN)_x$ ($x = 0$—4) indicated a substantial anodic displacement in the redox potentials as x increases (Table 1). This is qualitatively expected on the basis of the increased electron-withdrawing effect due to an increasing number of cyano-groups.*

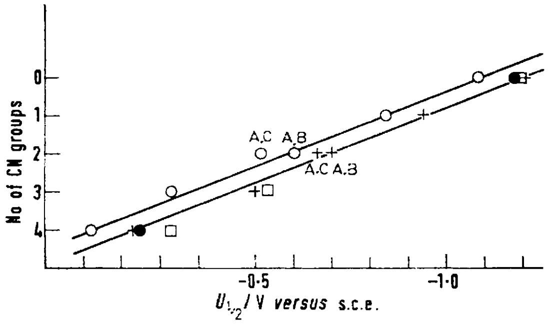

FIGURE 2 Relation between half-wave potentials and number of cyano-groups (second wave) ○, $H_2TPP(CN)_x$, $x = 0$—4; +, $CuTPP(CN)_x$, $x = 0$—4; ●, $PdTPP(CN)_4$ and PdTPP; □, $NiTPP(CN)_x$ (x = 0, 3, and 4)

Quantitatively, this anodic displacement of the half-wave potentials $U_{\frac{1}{2}}$ increased linearly with the number of cyano-groups with a relationship 0.23—0.24 V per CN for the first reduction (Figure 1) and 0.26 V per CN for the second (Figure 2). This indicated an essentially polar effect by the cyano-groups. Table 1 and Figures 1 and 2 show that the additive effects did not explain the behaviour of the A,C-isomer of $H_2TPP(CN)_2$ in which the anodic displacement of $U_{\frac{1}{2}}$ with respect to that of H_2TPPCN is greater than that of the A,B-isomer. This ' reinforcement ' effect of the second A,C-cyano-group may be explained in terms of mesomeric interaction between the two substituents. Indeed a parallel effect exhibited by the A,C-disubstituted $H_2TPP(CN)_2$ compound was observed in the visible light absorption peaks: the bathochromic displacement was regular along the series $x = 0$—4 except in the A,C-disubstituted isomer, where the displacement observed was greater than that of the A,B-isomer.[3]

In the case of the metalloporphyrins $M^{II}TPP(CN)_x$ (M = Cu, Ni, or Pd) the effect of the cyano-substituents on the redox potentials was analogous to that observed in the $H_2TPP(CN)_x$ series, and again additive (Tables 2 and 3, Figures 1 and 2). Thus the known cathodic shifts in the half-wave potentials due to the complexing of metals in the porphyrin nucleus [21,22] was not affected by the progressive substitution of hydrogen atoms by cyano-groups.

These results lead to the conclusion that the mechanism of reduction of the studied porphyrins and metalloporphyrins is essentially the same in both the first and second steps, two electrons being successively fixed onto the porphyrin nucleus.

To confirm the polar nature of the interaction between the cyano-groups and the ring, a comparison made between the polarographic behaviour of H_2(*p*-cyanophenyl)$_4$P and $H_2TPP(CN)_4$ (Table 3) shows that the anodic shifts in $U_{\frac{1}{2}}$ for the first two waves (+170 and +203 mV respectively) of the former compound were less than those of the latter (+960 and 990 mV respectively). This was due to the non-coplanarity of the phenyl groups of *meso*-TPP and confirms a recent observation [2] concerning partial transmission of the electron-withdrawing effect across the phenyl groups. It also confirms the greater ' efficiency ' of a cyano-group attached directly to the porphyrin nucleus.

By applying the Hammett equation [23,24] $\Delta U_{\frac{1}{2}} = \rho_\pi \sigma$ the reaction constant ρ_π for the first and second reductions may be calculated from the known value of $\Delta U_{\frac{1}{2}}$ and σ of the cyano-group: [25] ρ_π +0.38 (±0.03) (first reduction) and +0.42 (±0.03) (second reduction), the positive sign confirming the diminution in the electron density around the porphyrin ring.[26]

(b) *Axial Co-ordination on* $M^{II}TPP(CN)_4$.—In metalloporphyrins, many metal ions are able to add one or

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* These being rapid systems, the standard redox potentials (U_0) are identical to $U_{\frac{1}{2}}$, without taking into account the differences between the diffusion and activity coefficients of the oxidized and reduced species.

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two Lewis base ligands to form five or six co-ordinated complexes.[27] Studies [28] on nickel(II) porphyrins showed that the stability of such complexes is enhanced by an *increase in* basicity of the nitrogenous bases used and the presence of one or several electron-withdrawing groups on the porphyrin nucleus. This effect of substituents and its relation with the Hammett constants was clearly demonstrated using a series of deuteroporphyrins,[29] and more recently using *para*-substituted tetraphenylporphyrins.[2] The stoicheiometry of the species present in solution is still controversial: whilst most examples favour 1 : 2 complexes,[2,28,30] other determinations led to lower values [31] or to a 1 : 1 composition.[32] The complexes between copper(II) porphyrins and nitrogenous bases are of much lower stability, and therefore determination of thermodynamic data is less accurate. However a 1 : 1 complex was detected,[29,30] thus involving five-co-ordination on copper.

Stability of the $M^{II}TPP(CN)_4L_n$ *Complexes*.—The influence of the cyano-groups is particularly striking when compared to the very weak complexation (Ni^{II}) or the quasi-absence of interaction (Cu^{II}) earlier observed [33-35] using unsubstituted tetraphenylporphyrin complexes. This effect allowed us to determine the stability constant for $Ag^{II}TPP(CN)_4$–piperidine although, by contrast, the corresponding $Pd^{II}TPP(CN)_4$ did not show any interaction with piperidine or pyridine. The results illustrate the known similarity between the Cu^{II} and Ag^{II} complexes, and also the very low tendency of Pd^{II} to form octahedral complexes, in contrast to the extensive chemistry of six-co-ordinate Ni^{II}.[36]

Geometry of the $M^{II}TPP(CN)_4L_n$ *Complexes*.—The metalloporphyrin–nitrogenous base complexes formed from Cu^{II}– and Ag^{II}–$TPP(CN)_4$ are 1 : 1 species and are thus five-co-ordinate. In both cases we observed a family of isosbestic points. This confirms the already known [29,31] 1 : 1 stoicheiometry determined for Cu^{II} porphyrin complexes.

The formation of complexes from Ni^{II} porphyrin is less clearly understood. Various authors favour 1 : 2 complexes,[28,31] although the presence of electron-attracting groups attached to the porphyrin nucleus appears to lower the value of n. For example Ni diacetyl- and Ni diformyl-deuteroporphyrins [28] led to an n value of 1.7, whilst Ni αβ-dinitrodeuteroporphyrin did not show isosbestic points in the presence of pyridine.[31] An n.m.r. study [32] of Ni^{II} mesoporphyrin in the presence of piperidine favoured a 1 : 1 complex.

For $NiTPP(CN)_4$, a low n value (1.3 and 1.6, respectively, in the presence of piperidine and pyridine) was observed. This strongly suggests the participation of a monopiperidine (and to a lesser extent, of a monopyridine) complex in the equilibria. The absence of a single set of isosbestic points confirms this hypothesis.

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