Dioxygen reduction at a graphite electrode modified by mononuclear tetraneopentoxyphthalocyaninatocobalt(II) and related polynuclear species

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Potentiodynamic data were obtained under argon for the mononuclear species tetraneopentoxyphthalocyaninatocobalt(II) species adsorbed on glassy carbon (GC), ordinary pyrolytic graphite (OPG), and highly oriented pyrolytic graphite (HOPG). Comparative data show that the most convenient material to use is HOPG whereon a limiting monolayer is apparently achieved. Data were also presented for the mononuclear and polynuclear analogues on HOPG under both argon and dioxygen. Comparison is made of the potential data obtained in water and in organic solvent. A pH dependence study shows that the dioxygen reduction potential tracks the Co(II)TNPc/Co(I)TNPc redox couple with a slope of approximately −65 mV/pH for the mononuclear species, in the acid regime, but substantially less than −65 mV/pH for the polynuclear species. There is no pH dependence in the alkaline regime. Possible mechanisms are discussed.

Key words: phthalocyanine, electrochemistry, dioxygen reduction, pH dependence, graphite electrode, cobalt phthalocyanine.

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Opérant sous de l'argon, on a déterminé des données potentiodynamiques pour des espèces mononucléaires du tétranéopentoxyphtalocyaninatocobalt(II) adsorbées sur du charbon vitreux (CV), sur du graphite pyrolytique ordinaire (GPO) et sur du graphite pyrolytique hautement orienté (GHPO). Des données comparatives ont permis de démontrer que le matériau le plus commode à utiliser est le GPHO sur lequel il semble possible se déposer une monocouche. On présente aussi des données relatives aux analogues mononucléaires et polynucléaires, sur le GPHO, tant sous un atmosphère d'argon que d'oxygène moléculaire. On a établi une comparaison des potentiels obtenus dans l'eau et dans un solvant organique. Une étude effectuée dans le but de déterminer l'influence du pH a permis de démontrer que, en milieu, le potentiel de réduction des espèces mononucléaires par l'oxygène moléculaire coupe le couple redox Co(II)TNPc/Co(I)TNPc avec une pente d'environ −65 mV/pH, valeur beaucoup plus faible que la valeur de −65 mV/pH qui est observée avec les espèces polynucléaires. En milieu alcalin, il n'y a aucune variation en fonction du pH. On discute des divers mécanismes qui pourraient être impliqués.

Mots clés : phtalocyanine, électrochimie, réduction de l'oxygène moléculaire, relation avec le pH, électrode de graphite, phtalocyanine de cobalt.

Introduction

Macrocyclic complexes of iron and cobalt have proven useful in the development of a better dioxygen reduction catalyst for a fuel cell (1) cathode (2–45). In this regard phthalocyanine species are of particular interest (2–4, 7–9, 16, 17). Recently we have reported (30) data for a series of binuclear cobalt phthalocyanine complexes whose electrocatalytic activity exceeds that of the mononuclear control molecule [3,9,16,23-tetra(neopentoxy)phthalocyanato]cobalt(II),[2] **1** by an amount proportional to the degree of molecular electronic coupling within the binuclear system. During these studies, control data were collected for mononuclear complex **1** on various graphite substrates over a range of pH. The earlier work on the binuclear phthalocyanines was undertaken by depositing the phthalocyanine onto ordinary pyrolytic graphite (OPG) (30), but at that time no variable pH data were obtained. To obtain pH dependence data, this study was repeated on highly oriented pyrolytic graphite (HOPG) which is much more efficient to use since its surface can be prepared (renewed) much more readily than that of OPG. A tetranuclear species (46) was also studied. These data are now reported. Possible mechanisms for dioxygen reduction are discussed.

Experimental

Equipment

Potential scans (cyclic voltammetry) for dioxygen reduction were performed with a Pine Instruments RD3 potentiostat and the rotation studies with a Pine Instruments PIR rotator.

Materials

o-Dichlorobenzene (DCB) (Aldrich, Gold Label) was used as supplied. Tetrabutylammonium perchlorate (TBAP) (Kodak) was recrystallized from absolute ethanol and dried at 50°C under vacuum for 2 days. Water was purified by double distillation over $KMnO_4$, followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges. Fisher certified 1 *N* sodium hydroxide was used for pH 14 aqueous dioxygen reduction studies. Potassium hydrogen phosphate buffers were made up as required for other pH values and checked against a Beckman pH meter. Dilute H_2SO_4 was used for pH 0.7 and 1.0.

Argon gas (Linde) was purified by passage through preheated copper filings, anhydrous $CaSO_4$ (Drierite), molecular sieves (BDH type 3A), and glass wool. Oxygen gas (Linde) was purified by passage through anhydrous $CaSO_4$, NaOH pellets (AnalaR analytical grade), anhydrous $CaSO_4$, molecular sieves, and glass wool.

[3,9,16,23-tetra(neopentoxy)phthalocyanato]cobalt(II), **1** (47, 48), metal-free 3,9,16,23-tetra(neopentoxy)phthalocyanine, **2** (47, 48), and the polynuclear complexes were prepared by literature methods. The polynuclear complexes were 1,2-bis[2′-(9′,16′,23′-trineopentoxyphthalocyanino) cobalt(II)]ethane, C(2)[CoTrNPc]$_2$ (**3**) (49) two cobalt trineopentoxyphthalocyanine rings linked via —CH_2CH_2—; bis-[2′-(9′,16′,23′-trineopentoxyphthalocyanino) cobalt(II)] ether, O(1)[CoTrNPc]$_2$ (**4**) (50) two cobalt trineopentoxyphthalocyanine

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[2] For simplicity one isomer of species **1**, and of its analogues are labelled here; however, recognize that due to different neopentoxy group substitution patterns, there will be several isomers which are generally inseparable.

rings linked via a single dioxygen (ether) bridge; Ethylmethylbis-[2′-(9′,16′,23′-trineopentoxy phthalocyaninoxymethyl) cobalt(II)]-methane, EtMeO(5)[CoTrNPc]$_2$ (**5**) (47, 48) two cobalt trineopentoxyphthalocyanine rings linked via —OCH$_2$C(Me)(Et)CH$_2$O—; 1,2-bis-[2′-(9′,16′,23′-trineopentoxyphthalocyaninoxy) cobalt(II)]benzene, Cat(4)[CoTrNPc]$_2$ (**6**) (49) two cobalt trineopentoxyphthalocyanine rings linked via —O—C$_6$H$_4$—O— (*o*-catechol). These complexes are henceforth abbreviated by the label appearing before the square bracket immediately above, namely C(2), O(1), EtMeO(5), and Cat(4), the numeral representing the number of atoms in the bridge. The study also included the tetranuclear spiro species, 1,1,1,1-tetrakis[2′-(9′,16′,23′-trineopentoxyphthalocyaninoxymethyl) cobalt (II)] methane, [Co(II)TrNPc(−2)]$_4$ (**7**) (46), abbreviated Tet.

Electrodes

Ordinary pyrolytic graphite (OPG), and highly oriented pyrolytic graphite (HOPG), sometimes called stress annealed pyrolytic graphite (SAPG) were obtained from Union Carbide. The OPG was mounted in Teflon to expose a circular area of 0.493 cm^2. The glassy carbon (GC) electrode, of area 0.07 cm^2, was purchased from Tokai Carbon Ltd., Japan.

Electrodes fabricated from OPG, GC, and Pt were cleaned by polishing with 1.0, 0.3, and 0.05 μM alumina suspended in water. The cell for the adsorption experiments employed an SCE electrode, a graphite working electrode, and a platinum wire counter electrode.

The HOPG was similarly mounted in a Teflon holder to expose a circular area of 0.44 cm^2. The basal plane of the graphite was perpendicular to the axis of the electrode. This enables a fresh surface of electrode material to be exposed when a piece of Scotch brand "Magic Transparent" tape is momentarily pressed onto the surface and then gently lifted off. Usually at least two layers are removed between each adsorption study. The new surface thus revealed is used within a few minutes of exposure.

Catalyst coated electrodes were prepared by immersing and rotating (ca. 400 rpm) (on open circuit) the freshly prepared graphite surface in DCB solutions of a phthalocyanine of concentration approximately $5 \times 10^{-5} M$ (varied from $1 \times 10^{-7} M$ to $5 \times 10^{-5} M$ in the case of **1**). The coated electrode was washed with ethanol and distilled water and dried under reduced pressure.

The time required to achieve a steady state surface concentration of a designated phthalocyanine may be conveniently monitored by cyclic voltammetry (v = 100 mV/s). For these experiments, solutions containing the desired phthalocyanine were made 0.1 M in TBAP and the state of the adsorbed layer was monitored at 5 min intervals, until the peak current corresponding to a redox reaction of the adsorbed catalyst remained constant. Redox processes corresponding to the adsorbed and bulk species occur at different potentials and are thus easily distinguished. The adsorption equilibrium (as evidenced by constant first CV scan) was established in $10^{-7} M$ **1** in about 40 min and in about 10 min (or less) in the case of $5 \times 10^{-5} M$ solution. Unlike the situation with similarly active (11) tetrasulfonated phthalocyanines (TSPc) (12) well-defined voltammetric peaks were obtained without cycling of the electrode during the adsorption step. Indeed, continuous cycling during adsorption, in any potential range, significantly decreased the amount of **1** adsorbed at the surface.

Data in non-aqueous solution were referenced to SCE via incorporation of ferrocene as an internal calibrant (51).

Note that for good reproducibility of the dioxygen reduction data, the catalyst surface was renewed for every individual experiment, *i.e.*, for every scan. Successive scans, under dioxygen, using the same surface show variations (shift in potential, loss of current etc.) which may be due to loss of catalyst and/or some catalyst decomposition.

Results and discussion

(i) Adsorption of 1 on GC, OPG, and HOPG

Since it is feasible to study dioxygen reduction by laying down one or more layers of catalyst upon various types of graphitic surface, especially OPG, HOPG, and GC, the best conditions to prepare electrodes modified by **1** were first investigated.

Phthalocyanines applied to the electrode by simple evaporation of their solution in an organic solvent can form uneven multi-layer films which are often microcrystalline. In addition, only a fraction of the film may be electrochemically active, leading to problems of reproducibility. The slow diffusion of oxygen (and counter ions) from the solution into the film, and the potential drop caused by the resistance of the film and hence potential shift of the votammetric curve also provide complicating factors (52, 53). While vapour deposition provides a convenient method (54) for film preparation especially where insoluble, but volatile, phthalocyanines are concerned, adsorption is a simpler procedure for organic solvent soluble metallophthalocyanines. A monolayer of the catalyst formed at the electrode surface by adsorption yields much better electrochemical results under the conditions where adsorption is highly irreversible and the bare surface of the electrode shows minimal electrocatalytic activity toward dioxygen reduction. Such layers were laid down according to the procedures outlined in the experimental section.

No adsorption was found on a Pt electrode. In the case of OPG and especially HOPG strong adsorption was observed (Fig. 1). Essentially the same results were seen with **2**, thus adsorption does not seem to involve metal ion interaction with defects on the surface. Low coverage and weak adsorption were observed on amorphous GC (Fig. 1*D*) which does not have the oriented graphitic structure of other electrodes.

On the OPG surface, the phthalocyanine surface concentration calculated to be present varies with the cleaning procedure. An OPG electrode polished by alumina, and washed only by distilled water yields a lower coverage (Fig. 1*B*) than an electrode in which the surface after the alumina treatment is further cleaned using a clean wet polishing cloth or ultrasonic cleaner. In the former case a highly hydrophilic surface is formed, presumably covered by alumina particles which can block the adsorption of TNPc. The surface cleaned using the second method is hydrophobic, as judged qualitatively from the water contact angle, and the amount of adsorbed TNPc is higher (Fig. 1*A*). Thus the degree of coverage is variable and dependent upon the details of cleaning (55, 56). Moreover, there is a relatively large residual current from the OPG surface, hindering the observation of waves of low faradaic current. Thus this material provides an unsatisfactory surface for routine and reproducible study of the electroactivity of supported phthalocyanines. The HOPG surface was undoubtedly the preferred surface with a low residual current and high reproducibility. When the bare electrode is rotated in a *ca.* $10^{-5} M$ DCB solution of **1**, the cyclic voltammogram rapidly reaches an equilibrium current maximum. This maximum, adopting the macroscopic area of the electrode, and assuming a one-electron redox couple (see below), corresponded approximately to an average surface concentration of a 6×10^{-11} mol/cm^2. It is conceivable that the phthalocyanine molecules lie flat and form π–π bonds with the graphite lattice yielding an area of about 200 Å^2. Other aromatic molecules similarly show high affinity for graphite (54, 56). The coverage, Γ, then approaches a monolayer (Fig. 1*C*). Compounds **2**–**7** may be similarly adsorbed but no evidence was collected to determine their detailed surface behaviour.

The limit of one monolayer for **1** is instructive. If the molecules are lined up perpendicular to the surface with a smaller effective area (e.g. as suggested for tetrasulfonated cobalt phthalocyanine (13)), then the amount of charge, C_p, would correspond to an incompletely covered surface and further adsorption would have been anticipated.

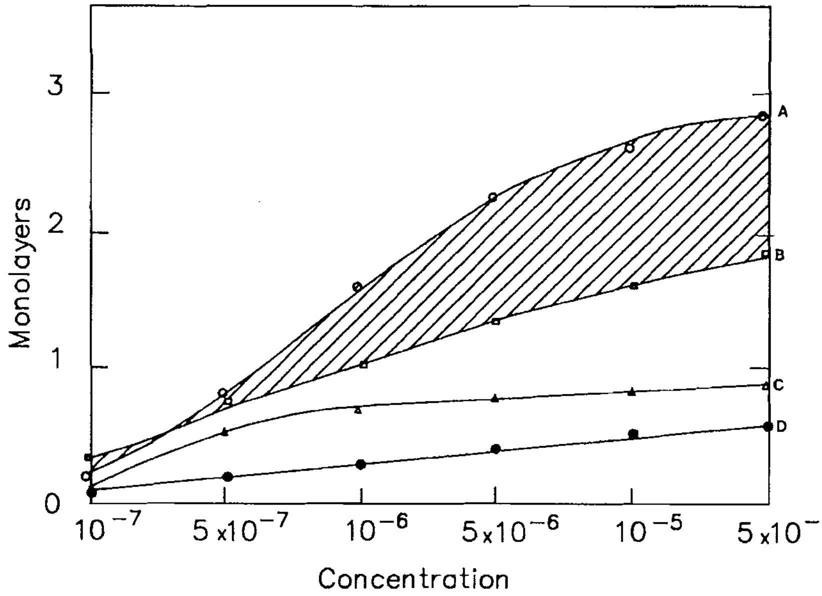

FIG. 1. Adsorption isotherms for Co(II)TNPc, **1**. Number of monolayers versus concentration of Co(II)TNPc in depositing solution (0.1 *M* TBAP/DCB) at 20°C. (*A*) OPG hydrophobic surface, (*B*) OPG hydrophilic surface, (*C*) HOPG, (*D*) GC. The shaded region shows a continual gradation between highly hydrophobic and highly hydrophilic surfaces.

TABLE 1. Charge under the Co(II)TNPc/Co(I)TNPc redox couple of complex **1** as a function of scan rate[a]

Scan rate (V/s)	Current (μA) i_p	Charge (μC) C	i_p/C
0.15	8.5	7.64	1.13
0.125	6.0	6.31	0.93
0.1	5.0	6.80	0.75
0.075	4.0	7.20	0.54
0.05	2.0	6.10	0.34

[a] Plot of i_p/C versus scan rate, including the origin point, yields a least-squares slope of 7.58 (for $nF/4RT$) corresponding to n = 0.78 and with a regression coefficient of 0.998.

The assumption that the redox couples observed under argon were one-electron in nature, was checked using eq. [1]. Thus:

$$i_p = n^2F^2\Gamma v/4RT$$

and since

$$C_p = nF\Gamma$$

then:

$$[1] \quad i_p/C_p = nFv/4R$$

where i_p and C_p are the current and charge densities, respectively. Thus a plot of the ratio of these quantities against scan rate v, provides a measure of n, the number of electrons (14). Experimentally, using the Co(II)TNPc(−2)/[Co(I)TNPc(−2)]$^-$ redox couple of **1**, a value of n = 0.78 is obtained (Table 1).

Alternatively, if a Langmuir isotherm is assumed to be valid to describe the adsorption of the catalyst on the surface (see refs. 30, 57 for detailed discussion), then the number of electrons, n, is related to the half-bandwidth of the cyclic voltammetric peak, $W_{1/2}$, by

$$[2] \quad n = 2RT[\ln(3 + 2\sqrt{2})/FW_{1/2}]$$

This yields a n value of 1.1–1.2 electrons for the several voltammetric peaks involved, using **1**. The deviation from unity probably reflects some deviation from true Langmuir isotherm behaviour, *i.e.* probably some interaction between adjacent molecules. Note, however, that the use of any isotherm requires a dynamic equilibrium between surface and solution, and the absence of any phthalocyanine catalyst in solution precludes such an equilibrium here.

In the HOPG case, the true surface area of the electrode and that measured macroscopically are not likely to be very disparate. A significantly higher coverage on OPG seems to be caused by a higher roughness factor of the OPG surface which is also confirmed by a higher residual current, *i.e.* the true microscopic surface area is larger than the macroscopically measured area.

Comparative CV data taken in DCB and in water show that the catalyst layer survives the transfer to the water medium.

(ii) *Electrochemical behaviour of an HOPG electrode covered by a monolayer of 1*

Under argon

The redox peaks of a monolayer of catalyst on the surface, under argon, can readily be observed in water solutions (Fig. 2*a*). A pair of voltammetric peaks in the region negative of 0 V vs. SCE, under argon, correspond to the [Co(II)TNPc(−2)]/[Co(I)TNPc(−2)]$^-$ couple, by analogy with a wealth of data collected in solvent media (58–67). They are adsorption peaks having a current proportional to the scan rate (not its square root) (68), and approach more reversible behaviour in acidic solution, the separation between the anodic and cathodic components decreasing with pH (Table 2). The half-wave potential for the [Co(II)TNPc(−2)]/[Co(I)TNPc(−2)]$^-$ couple in the alkaline range, near −700 mV vs. SCE, is essentially the same as that observed in the aprotic organic solvents such as DCB (67) (Table 3), but distinctly more negative than either CoPc or CoTsPc under the same adsorption conditions. A second reduction peak at more negative potentials arises from the [Co(I)-TNPc(−2)]$^-$/[Co(I)TNPc(−3)]$^{2-}$ redox process.

The catalyst oxidation peaks are seen near (+475) − (+720) mV, vs. SCE (Fig. 2*a*) and are composite, at some pH showing two clear cathodic components. Solution studies (67) reveal

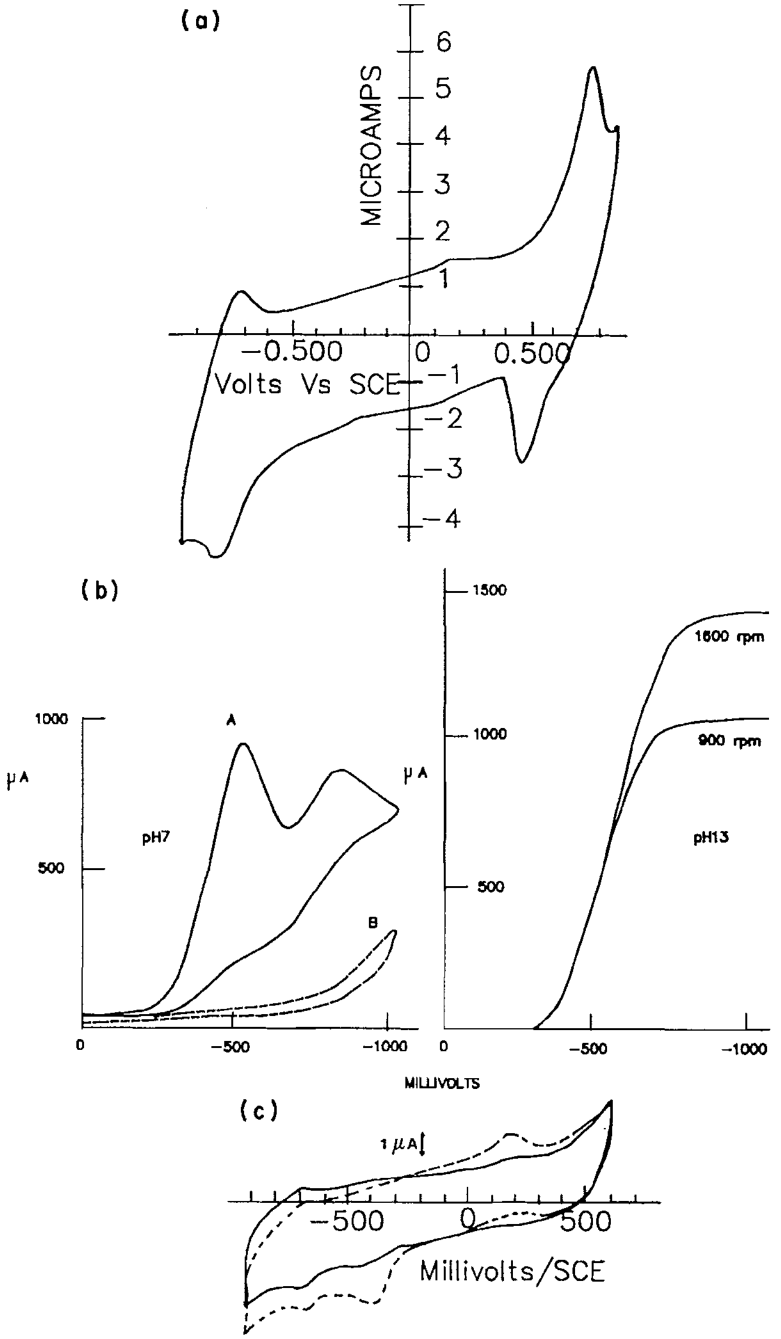

FIG. 2. (*a*) Cyclic voltammogram for Co(II)TNPc (**1**) layer deposited from a TBAP/DCB solution onto a HOPG electrode, and immersed in 0.1 *M* aq. phosphate buffer at pH 7, under argon. The left-hand couple is Co(II)TNPc(−2)/[Co(I)TNPc(−2)]$^-$, while the right-hand couple is probably an overlap of the Co(III)/Co(II) and Pc(−1)/Pc(−2) couples. (*b*) Left-hand plot: (A) Cyclic voltammogram for Co(II)TNPc (**1**) layer deposited from a TBAP/DCB solution onto a HOPG electrode, and immersed in 0.1 *M* aq. phosphate buffer at pH 7, saturated with dioxygen at 20°C. (B) as (A) but a bare unmodified HOPG surface. Right-hand plot: rotating disc electrode study of a Co(II)TNPc (**1**) layer deposited from a TBAP/DCB solution onto a HOPG electrode, and immersed in 0.1 *M* aq. NaOH at pH 13, saturated with dioxygen at 20°C. The lower scan is observed at 900 rpm and the upper at 1600 rpm. (*c*) Cyclic voltammogram for Co(II)TNPc (**1**) layer deposited from a TBAP/DCB solution onto a HOPG electrode, and immersed in 0.1 *M* NaOH at pH 13, under argon. Solid line — as described; hatched line with addition of 0.5 mL of 1×10^{-3} *M* O_2 dissolved in 0.1 *M* NaOH. The new peak at −420 mV in the second spectrum corresponds to dioxygen reduction while the new peak at +170 mV corresponds to hydrogen peroxide oxidation.

that the [Co(II)TNPc(−1)]$^+$/Co(II)TNPc(−2) and [Co(III)-TNPc(−2)]$^+$/Co(II)TNPc(−2) oxidation couples are likely to be close together and critically dependent upon potentially ligating groups in solution (or on the surface). In the absence of clearly defined behaviour for these couples their discussion will be postponed for later study.

Under dioxygen

It is very convenient that the bare HOPG surface also has a low catalytic activity towards dioxygen reduction in water solutions, allowing one to measure the electrocatalytic activity of the catalyst without interference of the bare surface (Fig. 2*b*).

An HOPG electrode surface modified with a layer of the

TABLE 2. Voltammetric data (mV) for CoTNPc under dioxygen and argon, as a function of pH

pH	Argon/CV[a]	Dioxygen/CV[b] Wave 1	Dioxygen/CV[b] Wave 2	Dioxygen/RDE[c]
1	−420(60)	−300		−280
2	−460(40)	−340	−855	−330
3	−510(40)	−425	−1000	−390
4	−570(40)	−480	−865	−390
5	−630(60)	−520	−905	−400
6	−685(90)	−520	−830	−470
7	−720(70)	−500	−830	−440
8	−720(85)	−500	−840	−460
9	−700(100)	−485		−435
10		−475		−425
11	−700(80)	−480		−435
12	−695(80)	−470		−430
13	−720(40)	−465		−420

[a] Cyclic voltammogram under argon — average of anodic and cathodic waves; peak-to-peak separation in parentheses.

[b] Cyclic voltammogram under dioxygen, peak observed at a scan rate of 0.10 V/s; wave 1 is dioxygen to hydrogen peroxide and wave 2 is hydrogen peroxide to water.

[c] Half-wave potential of rotating disc electrode peak, under dioxygen.

metal free **2** does not show any electrocatalytic activity. However, the cobalt complex **1** is active. In Fig. 2*c* are shown the cyclic voltammograms for the **1** modified HOPG electrode in water solution at pH 13, under argon, to which has been added 0.5 mL of solution containing $10^{-3}\,M$ dioxygen. The appearance of a signal due to dioxygen reduction can clearly be observed at a potential positive of the catalyst reduction peak (Table 2). The hydrogen peroxide re-oxidation wave can also be observed at +170 mV (Fig. 2*c*).

As shown in Fig. 2*b*, with excess dioxygen, the anodic peak (observed under argon) corresponding to the re-oxidation of $[\mathrm{Co(I)TNPc}(-2)]^-$ completely disappears since the $[\mathrm{Co(I)TNPc}(-2)]^-$ has already been oxidized by dioxygen to Co(II)TNPc(−2).

(a) Cyclic voltammetry

The current exhibited by the dioxygen reduction wave is proportional to the square root of the scan rate and is therefore a diffusion wave (68). The dioxygen reduction wave occurs positive of the catalyst Co(II)/Co(I) redox couple, by about 250 mV in the alkaline regime decreasing to about 100 mV in the acid regime (Table 2, Fig. 2*b*).

The pH dependence of the dioxygen reduction potential for **1** parallels that of the $\mathrm{Co(II)TNPc}(-2)/[\mathrm{Co(I)TNPc}(-2)]^-$ couple with a slope, in the acid region, of −66 mV/pH. We return to this issue below.

At a more negative potential, a second reduction wave is observed (Table 2), which corresponds to the successive reduction of hydrogen peroxide to water. Scanning positively again after the first reduction peak yields a hydrogen peroxide re-oxidation wave at about 0.2 V (Fig. 2*c*). Further proof was obtained by adding microlitre quantities of dioxygen-free hydrogen peroxide to the electrochemical cell and observing an increase in the height of this second wave, relative to the first. The pH dependence of the second reduction wave is not very clearly defined since it is observed very close to the solvent limit and is therefore subject to some error. This behaviour is very similar to that observed with a crown phthalocyanine cobalt species (69–71) where a well-defined pH dependence was observed (71). Previous studies of the two-electron reduction of dioxygen to hydrogen peroxide, have noted the existence of a second reduction process ascribed to hydrogen peroxide reduction (4, 23, 31, 72). In acid solution, under argon, the second reduction process, namely $[\mathrm{Co(I)TNPc}(-2)]^-/[\mathrm{Co(I)TNPc}(-3)]^{2-}$ occurring very close to the $\mathrm{Co(II)TNPc}(-2)/[\mathrm{Co(I)TNPc}(-2)]^-$ couple (12), may catalyse the hydrogen peroxide reduction to water. In alkaline solution, this couple moves dramatically more negative (12), explaining why the hydrogen peroxide to water reduction process is not observable in alkaline solution.

(b) Rotating disc and ring disc electrode (RDE and RRDE) studies

The magnitude of the limiting current, i_L, in the RDE dioxygen reduction wave depends linearly on the square root of the rotation rate in the range of 400–2500 rpm and is in agreement with the two-electron reduction of dioxygen to peroxide throughout the pH range studied. The halfwave potential $E_{1/2}$ of the dioxygen reduction wave tracks the $\mathrm{Co(II)TNPc}(-2)/[\mathrm{Co(I)TNPc}(-2)]^-$ pH dependence (Fig. 3*a*).

The standard expression for the limiting current of a diffu-

TABLE 3. Variation of redox potentials (V) of cobalt phthalocyanine reduction processes as a function of environment[a]

Cobalt species[b]	Conditions[c]	$[\mathrm{Co(I)TNPc}(-2)]^-/[\mathrm{Co(I)TNPc}(-3)]^{2-}$	$[\mathrm{Co(II)TNPc}(-2)]/[\mathrm{Co(I)TNPc}(-2)]^-$	Reference
CoTsPc/ads	Aq. pH 13	−1.37	−0.51	12
CoTsPc/ads	Aq. pH 2	−0.60	−0.31	12
CoTNPc/ads	Aq. pH 8		−0.71	This work
CoTNPc/ads	Aq. pH 4		−0.57	This work
CoTNPc	DCB soln.	−1.76	−0.60	67
CoTNPc	DMF soln.	−1.76	−0.54	67
CoCRPc/ads	Aq. pH 11		−0.60	69, 71
CoCRPc/ads	Aq. pH 2	−0.48	−0.34	69, 71
CoPc	Py		−0.61	92
CoPc/ads[d]	pH 14		−0.57	93
CoPc/ads[d]	pH 2		−0.29	93

[a] Versus SCE.

[b] TsPc = tetrasulphonated phthalocyanine; TNPc = tetraneopentoxyphthalocyanine, CRPc = tetracrown-phthalocyanine, ads = adsorbed on HOPG.

[c] DCB = *o*-dichlorobenzene, DMF = dimethylformamide, Py = pyridine.

[d] Adsorbed on ordinary pyrolytic graphite.

sion limited RDE plateau is given by (68)

$$[3] \quad i_L = 0.620nFAD_0^{2/3}\Omega^{1/2}v^{-1/6}C_{ox}$$

where $\Omega = 2\pi f/60$ (f in rpm). The terms $D_0^{2/3}v^{-1/6}C_{ox} = 1.77 \times 10^{-9}\,\mathrm{mol\,cm^{-2}\,s^{-1/2}}$ calibrated with a platinum electrode assumed to be well behaved (73) and to provide a four-electron limiting wave, and the kinematic viscosity, v, = 9.97 × $10^{-3}\,\mathrm{cm^2/s}$. The expression yields a limiting two-electron current of 1066 μA at 900 rpm compared with an experimental value of 1075 μA (complex **1**) (Fig. 2*b*).

Logarithmic analysis of the current, *i*, *i.e.*, a plot of potential versus log $[i/(i_L - i)]$ yields a value falling between −110 and −130 mV/pH unit (Tafel slope) through the pH range from ca. 1.0 to 13, with a regression coefficient generally of 0.999. This corresponds to a charge transfer coefficient, α = 0.5 and a one-electron rate-determining step, a common observation with cobalt macrocycle catalysts which reduce dioxygen to hydrogen peroxide (14, 74). Similar results are obtained for the binuclear and polynuclear species described immediately below.

Finally, a rotating ring disc experiment (RRDE, OPG, gold ring), with the ring polarised to oxidise any hydrogen peroxide which may be formed, provides additional proof of the generation of hydrogen peroxide in this experiment (at pH 9.2, Fig. 4).

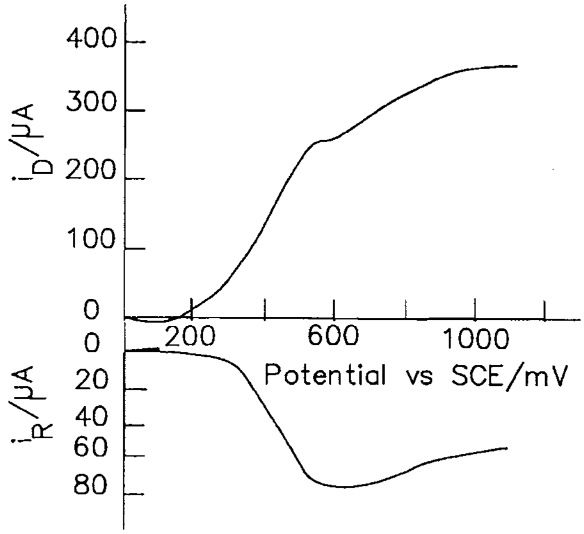

FIG. 4. A rotating ring disk experiment with Co(II)TNPc (**1**). Gold ring — OPG disk (0.18 cm² area) response for adsorbed **1** immersed in 0.1 *M* phosphate buffer at pH 9.2, saturated with dioxygen at 20°C. The upper curve shows reduction of dioxygen at the disk, and the lower response, re-oxidation of hydrogen peroxide at the ring (polarised at +1.0 V). Rotation rate is 400 rpm, and scan rate is 10 mV/s.

(iii) Binuclear and tetranuclear species, 3–7, adsorbed on to HOPG

Figure 3*b*–*f* illustrates the pH dependence of the Co(II)/Co(I) couple under argon, and the dioxygen reduction peak potentials, as a function of pH, for complexes **3–7**. In all cases, and similar to the monomeric species **1** the Co(II)/Co(I) couple has a ca. −(60–70) mV/pH unit dependence in the acid regime, between pH 1 and ca. 5.0, and then becomes pH independent.[3]

The dioxygen reduction wave appears at some 200–250 mV more positive a potential than the Co(II)/Co(I) wave, in the alkaline range, dropping to about 50 mV more positive in the acid range. However, there is characteristic difference between the polynuclear species and the control species **1**. In the latter, the slope of the dioxygen reduction wave is ca. −65 mV/pH in the acid range, but for the polynuclear species it is invariably significantly smaller (Table 4). Indeed, the dioxygen reduction wave and Co(II)/Co(I) wave in these polynuclear species will occur at essentially the same potential near pH 0 (see intercept in Table 4).

TABLE 4. Line equations in the acidic range[a]

Complex	Couple	Slope (mV/pH)	Intercept[b] (mV)	Correlation coefficient
Monomer	Co[c]	−53	−359	0.99
	O_2[d]	−58	−239	0.98
Binuclears				
O(1)	Co	−83.4	−224	0.98
	O_2	−41	−252	0.98
C(2)	Co	−73.6	−247	0.975
	O_2	−48.1	−253	0.985
Cat(4)	Co	−63.4	−299	0.97
	O_2	−32.5	−288	0.95
EtMeO(5)	Co	−65.1	−290	0.98
	O_2	−45.7	−247	0.99
Tet	Co	−69.2	−263	0.99
	O_2	−49.3	−239	0.97

[a] Data for least-square lines from approximately pH 2 to 5. Data are presented in millivolts.
[b] Intercept with respect to SCE.
[c] Refers to the Co(II)TnPc(−2)/[Co(I)TnPc(−2)]⁻ couple.
[d] Refers to the dioxygen reduction couple.

(iv) Mechanism and pH dependence

The −65 mV/pH unit dependence of the Co(II)TNPc(−2)/[Co(I)TNPc(−2)]⁻ couple, seen with all the species investigated here, implies that the reduced and negatively charged [Co(I)TNPc(−2)]⁻ species binds a proton, probably to a peripheral nitrogen atom (12). This pH dependence is very similar to that observed with the TsPcM(II)/[TsPcM(I)]⁻ redox couples (M = Co, Fe) (12) and differs from that generated by the TsPcM(III)/TsPcM(II) redox couple (M = Co, Fe) where the pH dependent region lies above 7 rather than below 7.

There have been a number of studies of the role of pH on the dioxygen reduction potential of macrocyclic catalysts (3, 14, 18, 20, 23, 25, 27, 29, 37, 38, 76, 77) including a similar study of the pH dependence of the unsubstituted cobalt phthalocyanine in its Co(II)/Co(I) redox couple (3, 77).

Ni and Anson have (28) discussed the relative potentials for reduction of the adsorbed species, for various cobalt macrocyclic catalysts under argon and under dioxygen. They note that where the Co(III)/Co(II) couple of an adsorbed catalyst is involved, reduction of dioxygen often occurs at a potential *considerably more negative* than the Co(III)/Co(II) couple. The mechanism is perceived to be a "CE catalytic" mechanism where Co(II) is formed and subsequently reacts with dioxygen

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[3] The data for the mononuclear species **1** were obtained at York, while the data for the polynuclear species were obtained by the same procedure in Prague, but using a different electrode and different equipment. These latter data are more scattered than the York data, with a probable error of at least ±20 mV. The reason for this scatter is not known, but it does not invalidate the general conclusions.

$$\begin{tikzcd}
\mathrm{Co(II)TNPc} + e^- \arrow[rr, leftrightarrow, "{[4]}"] \arrow[d, leftrightarrow, "{O_2\ [4'L]}"] & & \mathrm{Co(I)TNPc}^- \arrow[d, leftrightarrow, "{O_2\ [4'R]}"] \\
\mathrm{CoTNPc(O_2)} + e^- \arrow[rr, leftrightarrow, "{[5]}"] \arrow[d, "{H^+\ [5'L]}"] & & \mathrm{CoTNPc(O_2)}^- \arrow[d, "{H^+\ [5'R]}"] \\
\text{Intermediates} \arrow[r, "{[6]}"] & H_2O_2 & \text{Intermediates} \arrow[l, "{[6]}"']
\end{tikzcd}$$

Scheme 1

(the C step) prior to eventual electron transfer with reduction of dioxygen (the E step) (28, 78). This is construed to differ from other systems where the reduction of the catalyst drives the dioxygen reduction immediately in an "EC catalytic" mechanism. This occurs both in homogenous solution (4, 25, 29, 39, 42, 43, 79) and for some adsorbed catalysts (25, 27, 29, 39, 41, 42, 76, 77), where the dioxygen reduction occurs at, or slightly negative of, the catalyst redox couple.

However, dioxygen reduction may occur at a potential positive of the catalyst redox process. This may be a consequence of an EC mechanism where the chemical and E step are so fast (80, 81) that dioxygen reduction can occur to a significant extent at a potential positive of the half-wave potential of the catalyst redox process, where a nernstian-determined small concentration of the active reduced form of the catalyst will occur.

However, if this process occurs some 250 mV or more positive of the catalyst redox wave, the quantity of reduced catalyst (e.g. Co(I)Pc here) is so small that the rate constant for dioxygen reduction needs to be excessively if not impossibly high (25, 29, 78, 80–86). Thus this likelihood is discounted, i.e., even though the dioxygen reduction tracks the Co(II)/Co(I) couple, it is not Co(I)Pc which is the primary active species. This conclusion is further supported by the observation of dioxygen reduction some 800 mV positive of the Co(II)Pc/Co(I)Pc wave at pH 14 using a newly investigated system (87).

A general set of relevant equations may be written as in Scheme 1. It is generally assumed that Co(III)TNPc species are not involved in dioxygen reduction.

Dioxygen reduction catalysis is not a consequence of activation by Co(I)TNPc, at least at the higher potentials (positive of the Co(II)/Co(I) wave). Thus the right-hand channel ([4], [4′R], [5′R]) is not important until very close to or beyond the Co(II)-TNPc/[Co(I)TNPc]$^-$ redox potential. Thus reaction must occur with Co(II)TNPc species.

Then the reaction mechanism may be written following [4′L], [5′L]. Equilibrium [4′L] lies well to the top since, at room temperature, there is little tendency to form a dioxygen adduct with Co(II)Pc. Such species are, however, observed at reduced temperatures (88). A significant overpotential is required to drive the reaction towards hydrogen peroxide. The Co(III)Pc/Co(II)Pc couple is pH independent in the acid regime (89) emphasizing that the pH dependence seen for dioxygen reduction in the acid regime must involve the irreversible binding of a proton to the coordinated di-oxygen as a first step towards hydrogen peroxide formation (85, 90); the fact that it appears to track the Co(II)/Co(I) wave is then fortuitous.

It is significant that the slope of the dioxygen reduction potential versus pH plot is less than −65 mV/pH for all the polynuclear species (Table 4), but is close to −65 mV/pH for dioxygen reduction at the mononuclear species, and for the Co(II)TNPc/Co(I)TNPc couple for the mononuclear and polynuclear species. That the dependence is about −65 mV/pH for this latter couple in the polynuclear species shows that the reduction of each Co(II) is unconcerted, *i.e.*, the reduction of one Co(II) moiety has no detectable electrochemical consequence for the other even though the electronic spectra of the polynuclear Co(II)TrNPc species shows evidence of some electronic coupling (46, 91).

A slope of less than −65 mV/pH can arise through the inclusion partially or wholly of a concerted two-electron dioxygen reduction process in the polynuclear species. That this is observed with the polynuclear species and not the mononuclear is quite credible. Consider, for example, the concerted process [7], [8]

$$[7]\quad \mathrm{Bridge[Co(II)TrNPc]_2} + O_2 \rightleftharpoons \mathrm{Bridge[TrNPcCo(III)(O_2^{2-})Co(III)TrNPc]}$$

$$[8]\quad \mathrm{Bridge[TrNPcCo(III)(O_2^{2-})Co(III)TrNPc]} + H^+ + 2e^- \dashrightarrow O_2H^- + \mathrm{Bridge[Co(II)TrNPc]_2}$$

It is not at all unreasonable that the formation of a most likely bridged peroxo derivative in at least those polynuclear CoTrNPc species capable of cofacial configurations in one or more of their conformations could lead to some concerted character in the dioxygen reduction and re-formation of the starting polynuclear Co(II) species. We see no direct evidence in these complexes for such a binuclear peroxo species which need, however, only be present to a small equilibrium degree to give rise to the observed electrochemical behaviour. In the cofacial crown phthalocyanine cobalt species, however, there is much more direct evidence for the formation of such a dioxygen adduct (69, 75).

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