

Interaction of nitric oxide with cobalt(II) phthalocyanine: kinetics, equilibria and electrocatalytic studies

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Abstract—The coordination of nitric oxide (NO) to cobalt(II) phthalocyanine (CoPc) in dimethyl sulphoxide (DMSO) has been studied. CoPc coordinates with NO in a 1:1 ratio, forming a CoPc(NO) species. The IR band observed at 1680 cm^{-1} is assigned to the coordinated NO. In the presence of excess NO, pseudo first order kinetics were followed. The observed rate constant, k_r , was determined to be $15.0 \pm 0.3\text{ dm}^{-3}\text{ mol}^{-1}\text{ s}^{-1}$ and the equilibrium constant was $K = 5.4 \pm 0.4 \times 10^4\text{ dm}^3\text{ mol}^{-1}$. Solution or adsorbed CoPc catalyses the reduction of NO. The products of reduction include NH_3 and NH_2OH . © 1998 Elsevier Science Ltd. All rights reserved

Keywords: cobalt; phthalocyanine; nitric oxide; catalysis; kinetics; equilibria.

INTRODUCTION

Nitric oxide (NO) has been found to be an essential component of many physiological processes. NO is believed to have a wide range of functions including regulation of blood pressure, neurotransmission and ability to kill intracellular parasites and tumorous cells [1–4]. NO readily forms complexes with transition metal ions, including those found in metalloproteins. Studies into the binding of NO by metalloporphyrins have aided in the understanding of how NO interacts with haem containing biomolecules such as haemoglobin and myoglobin. NO has been shown to have a high affinity for ferrous haem [3]. Both iron(II) and iron(III) porphyrins have been shown to coordinate NO, forming $\text{Fe}^{\text{II}}\text{P}(\text{NO})$ and $\text{Fe}^{\text{III}}\text{P}(\text{NO})$ complexes, respectively [5–7]. Autoreduction of the $\text{Fe}^{\text{III}}\text{P}(\text{NO})$ complex to the $\text{Fe}^{\text{II}}\text{P}(\text{NO}^+)$ species has been reported [4, 6]. NO adducts of cobalt substituted myoglobin and haemoglobin have been reported [8], hence the substitution of iron by cobalt in synthetic porphyrins has gained considerable attention. Studies into the coordination of NO to cobalt porphyrin (CoP) complexes are of interest. $\text{Co}^{\text{II}}\text{P}$ readily binds NO forming

the $(\text{NO})\text{Co}^{\text{II}}\text{P}$ species. Cobalt(III) tetrakis(*N*-methyl-2-pyridyl)porphine ($[\text{Co}^{\text{III}}(2\text{-TMPyP})]^{5+}$) is known to bind with NO through reductive nitrosylation with the formation of the $[(\text{NO})\text{Co}^{\text{II}}(2\text{-TMPyP})]^{4+}$ species [9]. Exposure of the $[(\text{NO})\text{Co}^{\text{II}}(2\text{-TMPyP})]^{4+}$ species to air rapidly converts it to $[(\text{NO}_2)\text{Co}^{\text{III}}(2\text{-TMPyP})]^{4+}$. Metallophthalocyanine (MPc) complexes have a similar structure to the metalloporphyrins and have been used to mimic the properties of the naturally occurring metalloporphyrin complexes. MPc have an added advantage in that they are more stable to degradation than metalloporphyrin complexes. $\text{Fe}^{\text{II}}\text{Pc}$ has been shown to reversibly bind NO in dimethylsulphoxide (DMSO) according to eq. (1) [10, 11]



Axial coordination of NO to solid MnPc, CoPc and ZnPc has also been reported [12, 13]. Results from X-ray photoelectron spectroscopy showed that coordination of NO to MnPc, FePc and CoPc was accompanied by some electron transfer between the central metal and the NO molecule [13]. We report in this work on the kinetics and equilibria of the coordination of NO to CoPc in solution. It has recently been demonstrated that NO bonds to nickel(II) tetrasulphophthalocyanine ($[\text{Ni}^{\text{II}}\text{TSPc}]^{4-}$) in aqueous solu-

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tion. It was suggested that autooxidation of the $[\text{Ni}^{\text{III}}\text{TSPc}]^{4-}$ occurred following coordination of NO with the formation of a $[\text{Ni}^{\text{III}}\text{TSPc}(\text{NO}^-)]^{4-}$ species [14]. Interestingly, in all the studies on the coordination of NO to metalloporphyrin or MPc complexes, only one mole of NO coordinates to one mole of the metalloporphyrin or MPc complex. However, it has been shown that axial ligand substitutions in MPc complexes occur in a stepwise manner, with the consecutive coordination of the two ligands [15].

Even though there are reports on the binding of NO to CoPc complexes, kinetic or equilibria information on this binding has not been reported. Binding of NO or NO_2^- to CoPc is of importance for analysis of these species, since ring substituted cobalt phthalocyanine complexes have demonstrated an excellent selectivity toward the electroreduction of nitrite ion [16].

There are a number of reports on the use of metalloporphyrin complexes [7, 17–24] and haemoglobin [25] for the electrochemical detection of NO and as electrocatalysts for the reduction of NO to ammonia and other products [9, 26]. Reports on the use of MPc complexes for the detection of NO are limited [27]. Selective reduction of NO to NH_3 has been reported [27] for CoPc adsorbed on a glassy carbon electrode. However, very low yields of NH_3 were observed at $\text{pH} > 4$ [27]. It is important to understand the role played by the MPc complexes during the electrocatalytic reactions. It has been suggested that electron transfer reactions mediate electrochemical detection of NO, using metalloporphyrin complexes [7]. Metal and ring-based reduction and oxidation processes can occur in CoPc complexes. In this work, we study the electrocatalytic ability of CoPc (in solution or adsorbed onto the electrode) for the reduction of NO.

EXPERIMENTAL

Materials

Cobalt(II) and iron(II) phthalocyanine (CoPc and FePc, respectively) were purchased from Aldrich and used without further purification. The solid complex between NO and CoPc was prepared by stirring CoPc in dimethylformamide (DMF) in an NO atmosphere for 4 h, then evaporating the solvent to dryness. NO was prepared by adding saturated sodium nitrite dropwise to a $0.2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution under nitrogen atmosphere. The NO produced was bubbled into nitrogen saturated deionized water or passed through a drying agent into nitrogen saturated, dimethylsulphoxide (DMSO). NO solutions in water or DMSO were prepared freshly before use and kept in a glass flask fitted with a rubber septum. The concentration of NO in DMSO was determined by the method proposed by Ascenzi *et al.* [11], using the reaction of NO with FePc in DMSO. The con-

centration of NO in DMSO could also be calculated using its solubility of $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ [11]. NO concentration in water was calculated using the reported solubility of $2.2 \times 10^{-3} \text{ mol dm}^{-3}$ [11].

Electrochemical methods

Electrochemical data were collected with the Bio-analytical Systems (BAS) model CV-50 W voltammetric analyser. For cyclic voltammetry, a glassy carbon electrode (3.0 mm diameter) was used as a working electrode and a platinum wire as an auxiliary electrode. For nonaqueous studies, the reference electrode was the BAS nonaqueous reference electrode containing a silver wire immersed in a $0.01 \text{ mol dm}^{-3} \text{ AgNO}_3$ and containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) in DMSO. The electrolyte was TEAP for all electrochemical experiments in nonaqueous solutions. For cyclic voltammetry in aqueous solutions, the reference electrode was the Ag/AgCl ($3 \text{ mol dm}^{-3} \text{ KCl}$). Concentrations of CoPc in DMSO for cyclic voltammetry were in the 10^{-4} – $10^{-3} \text{ mol dm}^{-3}$ range.

For electrocatalytic reactions, a glassy carbon electrode modified with CoPc (CoPc-GCE) was employed as a working electrode. The GCE was modified by the drop dry method, in which a drop of a saturated ($\sim 1 \times 10^{-3} \text{ mol dm}^{-3}$) solution of CoPc in pyridine was placed on the GCE and dried in air. Prior to coating with the CoPc complex, the GCE was polished with alumina on a Buehler felt pad, followed by soaking in dilute nitric acid and rinsing in water, acetone and the solvent of interest. For bulk electrolysis, a two compartment cell was employed, with a platinum plate of area 2.2 cm^2 as counter electrode and a Ag/AgCl ($3 \text{ mol dm}^{-3} \text{ KCl}$) reference electrode. The working electrodes consisted of a carbon rod (area = 0.2 cm^2) coated with CoPc using the drop dry method. Electrical contact with the working electrode was established via a copper wire. Phthalate buffer, pH 4, was used for studies of NO in aqueous solutions. A nitrogen atmosphere was maintained for all electrochemistry experiments. Yields of ammonia were determined by the Nessler method [28] and by monitoring the absorbance at 400 nm. Hydroxylamine was determined spectroscopically using the specific test described in the literature [9].

Kinetics and equilibria

Kinetic and equilibrium studies were run at 20°C and monitored with the Cary 1E UV-VIS spectrophotometer. We monitored the appearance of the spectra due to the product formed following the addition of NO to solutions of the CoPc in DMSO. Typically, a known volume of the DMSO solution of CoPc was added to a 1 cm path length cell and deaerated using nitrogen. Then a known volume of a deaerated solution of NO in DMSO was added to the cell

and the spectra monitored with time. Bubbling of nitrogen into the cell was continued while adding the NO solution. NO is readily oxidized by oxygen, hence the cell was fitted with a stopper to avoid oxygen affecting the reaction. Concentrations of the CoPc were kept constant at $4.5 \times 10^{-6} \text{ mol dm}^{-3}$, while NO concentrations were varied from 6.2×10^{-5} to $1.2 \times 10^{-4} \text{ mol dm}^{-3}$. Since the concentration of the NO was larger than that of CoPc by a factor of at least 10, pseudo-first order conditions were assumed for kinetic studies.

Infra red spectra were recorded with the Perkin Elmer Spectrum 2000 IR spectrophotometer, using CaF_2 windows and dichloromethane as the solvent.

RESULTS AND DISCUSSION

Spectral characterization

In DMSO solutions, CoPc is known to be a six coordinate complex [29], hence the starting complex for our studies is expected to be the $(\text{DMSO})_2\text{CoPc}$ species. The *Q* band of the $(\text{DMSO})_2\text{CoPc}$ species is centred at 660 nm. Figure 1 shows the absorption spectral changes observed when DMSO solutions of NO ($1.1 \times 10^{-4} \text{ mol dm}^{-3}$) were added to solutions of $(\text{DMSO})_2\text{CoPc}$. On addition of NO, the *Q* band of the $(\text{DMSO})_2\text{CoPc}$ species shifts isospectically from 660 to 666 nm. An isosbestic point was observed at 657 nm. The presence of an isosbestic point is a clear indication that only two species are absorbing in the

Q band region of the spectra. X-ray photoelectron spectroscopy studies [13] have shown that electron transfer from the metal to NO occurs following coordination of NO to CoPc. On the other hand, reductive nitrosylation has been reported for the coordination of NO to Co^{II} porphyrin complexes [9]. We investigated the possibility of the oxidation of $\text{Co}^{\text{II}}\text{Pc}$ to the $\text{Co}^{\text{III}}\text{Pc}$ species, following addition of NO to $(\text{DMSO})_2\text{CoPc}$ in solution. When NO was added to solutions of chemically generated $\text{Co}^{\text{III}}\text{Pc}$ species in DMSO, the *Q* band of the resulting complex was observed at 665 nm, a wavelength very close to that obtained in Fig. 1(b) following addition of NO to $\text{Co}^{\text{II}}\text{Pc}$. It is thus likely that the $\text{Co}^{\text{III}}\text{Pc}$ species is formed in Fig. 1. Based on the absorption spectral data and on the X-ray photoelectron spectroscopic data, we represent the complex formed following coordination of NO to $\text{Co}^{\text{II}}\text{Pc}$ as the $\text{Co}^{\text{III}}\text{Pc}(\text{NO})$ species. We used IR spectroscopy to study the interaction between NO and $\text{Co}^{\text{II}}\text{Pc}$. For IR studies, dichloromethane and not DMSO was employed as a solvent due to the strong IR vibrations of the latter in the region of NO vibrations. The IR spectra of $\text{Co}^{\text{II}}\text{Pc}$ in CH_2Cl_2 showed a new IR band at 1680 cm^{-1} in the presence of NO. The IR spectra of free NO was observed at 1847 cm^{-1} . The IR spectra of cobalt(II) porphyrins in CH_2Cl_2 and in the presence of NO, show the ν_{NO} in the $1681\text{--}1695 \text{ cm}^{-1}$ region [30]. Thus, the IR band observed at 1680 cm^{-1} is assigned to bound NO. Vibrational frequencies of NO greater than 1700 cm^{-1} have been associated [14] with the electron

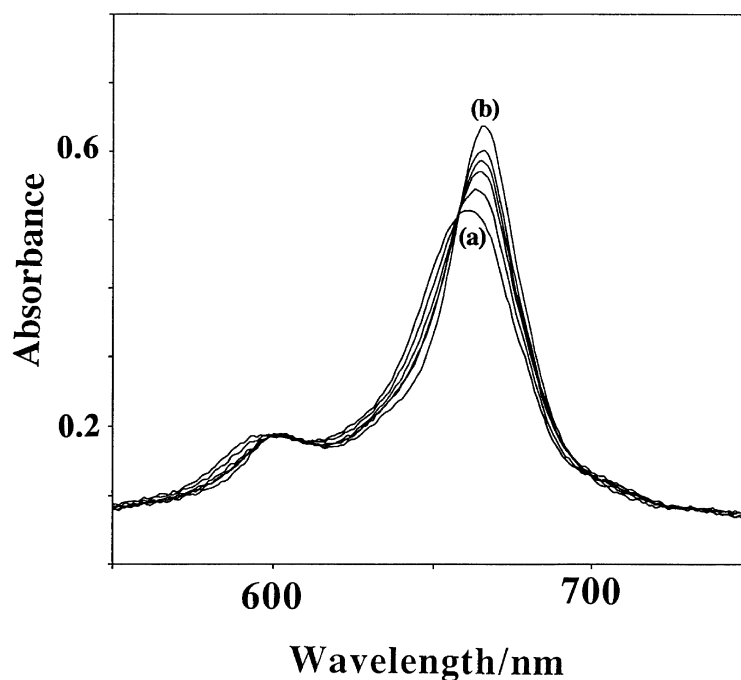


Fig. 1. Absorption spectral changes observed on addition of NO ($1.1 \times 10^{-4} \text{ mol dm}^{-3}$) to $(\text{DMSO})_2\text{CoPc}$ in DMSO. (a) spectra before addition of NO (b) spectra 18 min after addition of NO.

transfer from NO to the central metal and NO vibrational frequencies less than 1700 cm^{-1} , to the metal to NO electron transfer [14]. Thus, the observation of an NO frequency lower than 1700 cm^{-1} for the complex formed when NO is added to $\text{Co}^{\text{II}}\text{Pc}$, supports the formation of the $(\text{NO})\text{Co}^{\text{III}}\text{Pc}$ species as a result of electron transfer from the central metal to NO. Attempts to synthesize solid $(\text{NO})\text{CoPc}$ species by bubbling NO to solutions of CoPc in dimethylformamide, then evaporating off the solvent resulted in the formation of a complex that was more soluble in organic solvents than the original species. Absorption spectral studies of the $(\text{NO})\text{CoPc}$ complex showed the presence of a $\text{Co}^{\text{III}}\text{Pc}$ species.

Kinetic and equilibrium studies

Kinetic and equilibria data for the coordination of NO to CoPc were determined by monitoring the formation of the $(\text{NO})\text{CoPc}$ species. The increase in the Q band of this species at 666 nm was monitored for kinetic and equilibrium measurements. Equilibrium data were determined by standard spectroscopic techniques using eq. (2)

$$\log [(A_{\text{eq}} - A_0)/(A_{\infty} - A_{\text{eq}})] = \log K + n \log [\text{NO}]. \quad (2)$$

In eq. (2), A_{eq} is the equilibrium absorbance at 666 nm , A_0 is the absorbance before addition of NO and A_{∞} , the absorbance after complete formation of the $(\text{NO})\text{CoPc}$ complex, was determined from the final absorbance at 666 nm . Figure 2 shows a plot of

$\log [(A_{\text{eq}} - A_0)/(A_{\infty} - A_{\text{eq}})]$ vs $\log[\text{NO}]$. A linear plot with a slope near unity ($n = 0.9 \pm 0.1$) was obtained, showing that only one mole of NO is coordinated to the CoPc species. The linearity of the plot confirms the coordination of NO to the CoPc complex. Least square analysis gave an equilibrium constant of, $K = 5.4 \pm 0.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$.

Plots of the observed rate constant, k_{obs} , vs the concentration of NO were linear, Fig. 3, showing that the coordination is first order in NO. Axial ligand substitution reactions in metallophthalocyanines are dissociative with the formation of a highly reactive five-coordinate intermediate [15, 31]. The axial ligand substitution in $(\text{DMSO})_2\text{CoPc}$ may thus be represented by the reactions of eqs. (3) and (4)



The rate law for axial ligand exchange reactions in MPc complexes shown by the reactions of eqs. (3) and (4) is generally given by eq. (5)

$$k_{\text{obs}} = k_{\text{f}}[\text{NO}] + k_{\text{r}}, \quad (5)$$

where k_{f} , the rate constant for the forward reaction, is given by $k_1 k_2 / k_{-1} [\text{DMSO}]$ and k_{r} is the rate constant for the reverse reaction. Least square analysis of the data presented in Fig. 3 gave $k_{\text{f}} = 15.0 \pm 0.3 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ from the slope and from the intercept, $k_{\text{r}} = 3.1 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$ was obtained. Using these values of rate constants, the value of the equi-

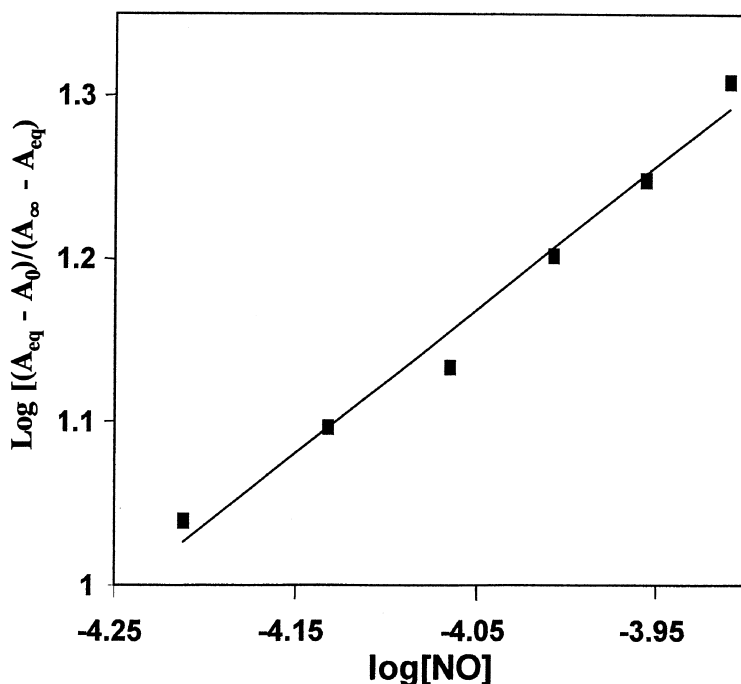


Fig. 2. Plot of $\log [(A_{\text{eq}} - A_0)/(A_{\infty} - A_{\text{eq}})]$ vs $\log[\text{NO}]$ for the formation of the $(\text{NO})\text{CoPc}$ species.

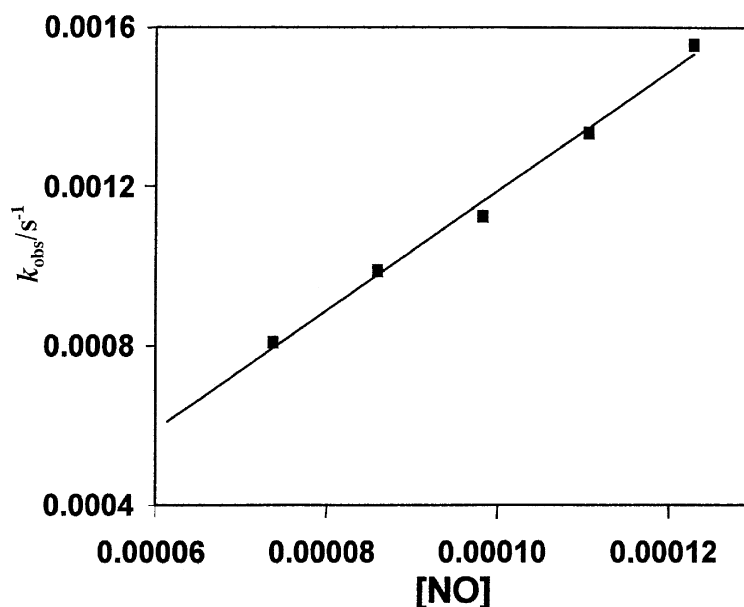


Fig. 3. Plot of the observed rate constant, k_{obs} , vs the concentration of NO for the formation of the (NO)CoPc species.

librium constant for NO coordination to CoPc was estimated to be $K_1 = 4.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ from the relationship, $K_1 = k_f/k_r$, in excellent agreement with the value determined above from the equilibrium data.

For the coordination of NO to $(\text{DMSO})_2\text{FePc}$, Ascenzi *et al.* [10] obtained an equilibrium constant of $1.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$ and $k_f = 2.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These values are much larger than the values obtained in this work for the coordination of NO to $(\text{DMSO})_2\text{CoPc}$. The coordination of pyridine in $(\text{DMSO})_2\text{FePc}$ also occurred [32] with much larger equilibrium and rate constants than the coordination of pyridine in $(\text{DMSO})_2\text{CoPc}$. This implies that the five coordinate $(\text{DMSO})\text{FePc}$ species are more reactive than the corresponding $(\text{DMSO})\text{CoPc}$. The equilibrium constants observed for coordination of NO to CoPc are of the same order of magnitude as the equilibrium constants reported for the coordination of NO to cytochrome C and metmyoglobin [6]. The rate constant for the coordination of NO to CoPc is similar to the rate constants reported for the coordination of NO to Mn porphyrin complexes [26].

Electrocatalytic reduction of NO

Cyclic voltammetry of CoPc in donor solvents such as DMSO is well documented [33]. Figure 4(a) shows the cyclic voltammogram of CoPc in DMSO in the absence of NO. The first reduction in CoPc is known [33] to occur at the central Co^{II} metal to form the $\text{Co}^{\text{I}}\text{Pc}$ species. Subsequent reductions occur at the phthalocyanine ring. Thus, the reduction labelled I in Fig. 4(a) is assigned to $\text{Co}^{\text{II}}\text{Pc}(-2)/\text{Co}^{\text{I}}\text{Pc}(-2)$. The metal reduction in $\text{Co}^{\text{II}}\text{Pc}$ in dimethylacetamide was

observed at -0.2 V vs saturated calomel electrode [33]. The rest of the reductions in Fig. 4(a) are then due to ring-based processes. The half-wave potentials for couples I, II, III and IV were respectively found to be -0.08 , -0.36 , -0.66 and -0.93 V vs Ag/AgCl.

On addition of NO to solutions of CoPc in DMSO, the cyclic voltammogram shown in Fig. 4(b) was obtained. Following the discussion above, the cyclic voltammogram in Fig. 4(b) should be due to the $(\text{NO})\text{Co}^{\text{III}}\text{Pc}$ species in DMSO. Three quasi-reversible reduction couples were obtained in Fig. 4(b). The reduction couples were enhanced relative to the reduction couples for CoPc in the absence of NO. Also the reduction couples in Fig. 4(b) are observed at slightly different potentials than the potentials for the reduction of $(\text{DMSO})_2\text{Co}^{\text{II}}\text{Pc}$. A considerable enhancement in the cathodic currents was observed for the fourth reduction, labelled IV in Fig. 4(b) on addition of NO to $(\text{DMSO})_2\text{CoPc}$. There was no corresponding return peak for IV following addition of NO. The large increase in cathodic current relative to the anodic currents is typical behaviour for catalytic reduction. The catalytic peak was observed at -0.93 V vs Ag/AgCl. The potential for the catalytic peak shifted to more negative potentials, with increase in NO concentration. The catalytic currents for the reduction of NO increased with increase in concentration as shown in Fig. 5, clearly showing that the peak (IV) is due to the reduction of NO. The catalytic peak currents also increased linearly with increase in the square root of scan rate, for scan rates ranging from 50 to 500 mV/s^{-1} , confirming a diffusion controlled process for the reduction of NO.

It is expected that the reduction of $\text{Co}^{\text{II}}\text{Pc}$ species

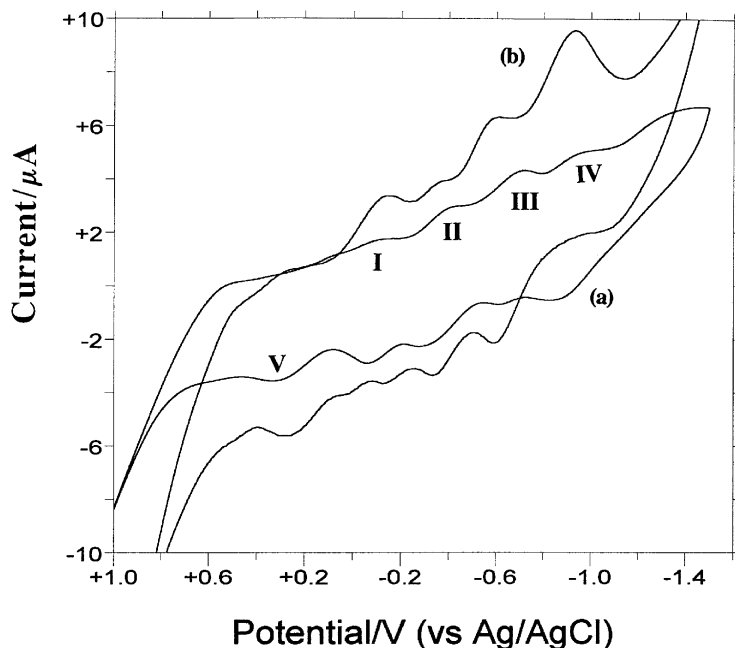


Fig. 4. Cyclic voltammogram of CoPc in DMSO (a) before and (b) after addition of NO ($1.1 \times 10^{-4} \text{ mol dm}^{-3}$) to the same concentration of CoPc as in (a). Electrolyte is 0.1 mol dm^{-3} TEAP and the scan rate 100 mV/s .

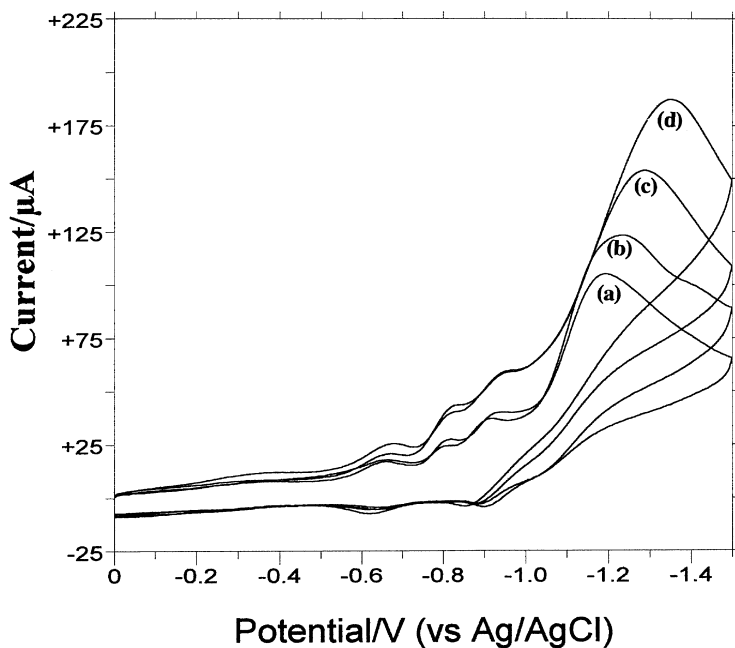


Fig. 5. Cyclic voltammograms of CoPc in DMSO, in the presence of increasing concentrations of NO: (a) 4.6×10^{-4} ; (b) 5.7×10^{-4} ; (c) 6.7×10^{-4} and (d) $8.3 \times 10^{-4} \text{ mol dm}^{-3}$. Electrolyte is 0.1 mol dm^{-3} TEAP and the scan rate 100 mV/s .

would occur by consecutive one-electron reductions. The reduction occurs first at the central metal to give a $\text{Co}^{\text{I}}\text{Pc}$ species. Subsequent reductions are expected to occur at the phthalocyanine ring. The reduction labelled IV is at the potentials reported [33] for ring reductions of the CoPc species. The fact that we

observe an enhancement in the cathodic currents of the peaks associated with phthalocyanine ring-based reductions on addition of NO to CoPc, suggests that it is these reductions that are involved in catalysing the reduction of NO. In many reductions involving CoPc as a catalyst, metal-based reduction processes

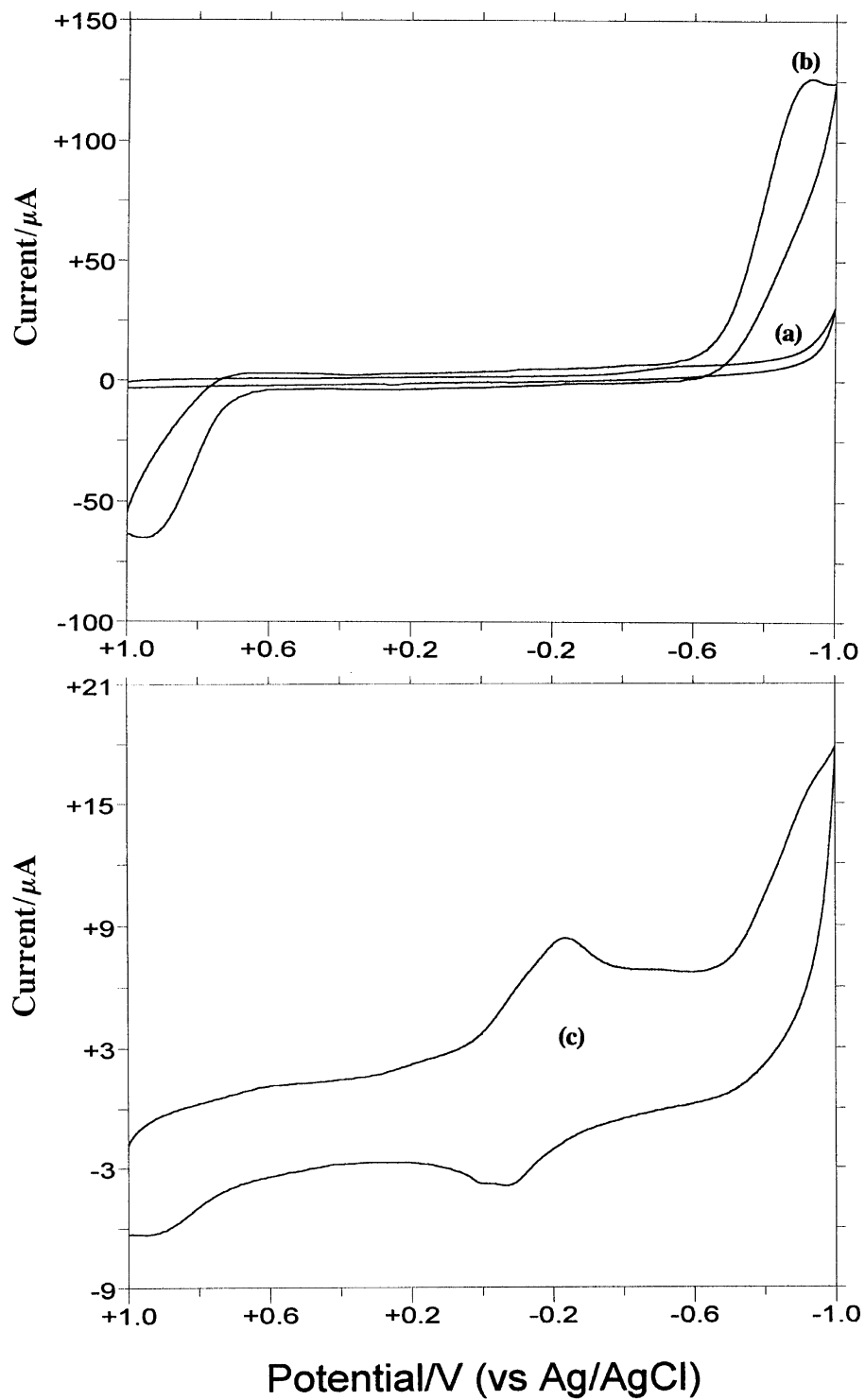
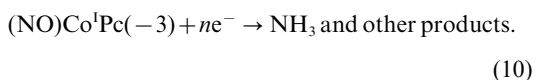
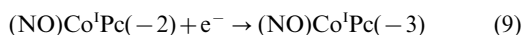
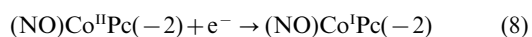
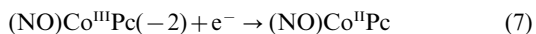


Fig. 6. Cyclic voltammograms of NO ($7.0 \times 10^{-4} \text{ mol dm}^{-3}$) on (a) unmodified glassy carbon electrode and (b) CoPc modified glassy carbon electrode. (c) cyclic voltammogram of CoPc-GCE in buffer alone. Electrolyte pH 4 buffer. The scan rate is 100 mV/s.

have been suggested as playing a major role [12]. This work, however shows that ring-based processes may be involved in the catalytic reduction of NO using CoPc. The following mechanism is thus proposed for the reduction of NO using CoPc in solution:



The DMSO solvent and the overall charge have been left out of the above equations for clarity. Following the formation of the reduction products it is expected that the Co^{II}Pc species would be regenerated.

Figure 6 shows the cyclic voltammograms of NO reduction on unmodified glassy carbon electrode and on a glassy carbon electrode modified with CoPc. In the absence of NO the reduction peaks due to adsorbed CoPc are observed near -0.15 V vs Ag/AgCl, Fig. 6(c). Reduction peaks observed for adsorbed CoPc have been assigned to Co^{III}/Co^{II} and Co^{II}/Co^I [12]. In the presence of NO, a catalytic reduction current rose sharply from about -0.6 V and showed a reduction peak at -0.93 V . The catalytic currents did not decrease significantly with subsequent scan on the same CoPc-GCE, indicating that the electrode was not deactivated by the adsorption of the reduction products. The catalytic currents observed

in Fig. 6(b) for NO on CoPc-GCE, were much higher than the reduction currents observed for NO on an unmodified glassy carbon electrode, Fig. 6(a). Catalytic currents were also observed for the oxidation of NO on CoPc-GCE, with a peak at 0.94 V vs Ag/AgCl. The reduction currents at -0.93 V increased linearly with increase in the concentration of NO, Fig. 7. The reduction peak for the reduction of NO on a glassy carbon electrode modified with CoPc was observed before at -0.8 V in a citric acid-hydrochloric acid solution [27].

Bulk electrolysis of a solution containing NO in a pH 4 buffer at potentials of the catalytic reduction currents (-0.95 V), gave $n=5$, where n =number of moles of electrons involved in the reaction. Since reduction of NO to ammonia requires five electrons, the value of $n=5$ confirms that NH_3 is one of the reduction products of NO, as has been observed before. Analysis of the solution following bulk electrolysis gave a 35% yield of ammonia (with respect to NO) after 2 h of electrolysis of 10 cm^3 solution containing $2.1 \times 10^{-3}\text{ mol dm}^{-3}$ NO. Hydroxylamine was also detected as one of the reduction products.

In conclusion, we have shown in this work that NO coordinates to CoPc in DMSO solutions, forming a (NO)CoPc species. The equilibrium and rate constants for this interaction are lower than reported for the interaction of NO with FePc. There was evidence for electron transfer from the central Co ion to NO, with the formation of the (NO)Co^{III}Pc species. Axial ligand exchange reactions in metallophthalocyanine and complexes normally involve the exchange of both ligands in (L)₂Mpc complexes. The coordination of

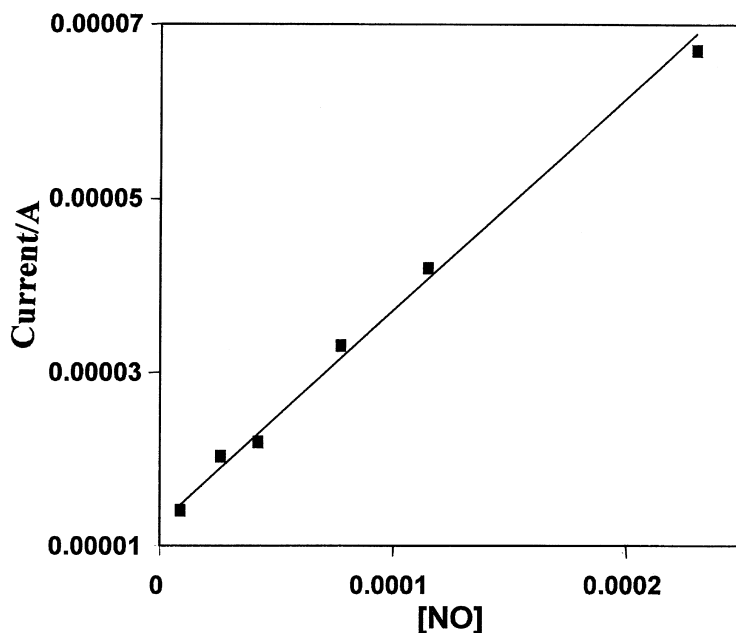


Fig. 7. Plot of [NO] vs catalytic reduction currents for the reduction of NO on CoPc-GCE. Electrolyte is pH 4 buffer and the scan rate 100 mV/s .

the second NO ligand to CoPc was not observed. Cyclic voltammetry studies showed that phthalocyanine ring-based reductions of the CoPc species catalyse the reduction of NO.

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