J. Chem. Soc., Faraday Trans. 1, 1984, 80, 1139-1149

# Electrocatalytic Reduction of Dioxygen by Cobalt Tetra(4-NN'N"-trimethylanilinium)porphyrin

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Received 22nd July, 1983

Cobalt tetra(4-NN'N"-trimethylanilinium)porphyrin (CoTMAP) has been studied in aqueous solutions using cyclic voltammetry, differential pulse voltammetry as well as by RRDE and spectroelectrochemical methods. The Co<sup>III</sup>/Co<sup>II</sup>TMAP couple dissolved in 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> has a redox potential of +0.14 V. The  $\lambda_{max}$  of the Soret band are 427 and 412 nm for Co<sup>III</sup> and Co<sup>III</sup>TMAP, respectively. The rate constant for the reaction between Co<sup>II</sup>TMAP and dioxygen in 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> was estimated to be  $3 \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The Co<sup>III</sup>TMP has been found to absorb at monolayer levels on glassy carbon surfaces and to have a catalytic effect on dioxygen electroreduction in aqueous solutions. This catalytic effect is strongly dependent on electrolyte pH. The overvoltage of O<sub>2</sub> reduction is reduced by 480 mV and insignificant amounts of H<sub>2</sub>O<sub>2</sub> are produced at pH 1, while an overvoltage decrease of 300 mV and an H<sub>2</sub>O<sub>2</sub> yield of 70% are observed at pH 8.

Macrocyclic metal complexes are known to play an important biological role as activators of molecular oxygen and as electron mediators.<sup>1</sup> Water-insoluble metal phthalocyanines, metal porphyrins and haemins adsorbed on electrode surfaces have been used as catalysts for oxygen reduction for possible use in fuel cells<sup>2-5</sup> or in electrochemical solar-energy-conversion devices.<sup>6</sup> Recently, the electrocatalytic reduction of dioxygen was studied using water-soluble iron and cobalt tetrakis(*N*-methyl-4-pyridyl)porphyrins (FeTMPyP, CoTMPyP).<sup>7-12</sup>

In this paper we report some electrochemical and spectroscopic properties of cobalt tetra(4-NN'N''-trimethylanilinium)porphyrin (CoTMAP). The catalytic effect on oxygen reduction is also described and compared with those of FeTMAP<sup>13</sup> and MnTMAP<sup>14</sup> reported previously.

#### **EXPERIMENTAL**

The iodide salt of tetra(4-NN'N''-trimethylanilinium)porphyrin (TMAP) and the chloride salt of Co<sup>III</sup>TMAP were obtained from Man-Win chemicals. Unlike TMAP, which is soluble in aqueous solutions in the entire pH range, the cobalt(III) complex shows solubility only at pH < 2.

Glassy carbon (GC) electrodes (EA 276/2), obtained from Metrohm, were polished to a bright surface using alumina powder. The electrodes were then washed with 0.05 mol dm<sup>-3</sup>  $H_2SO_4$  and distilled water to remove any alumina. Adsorption of Co<sup>III</sup>TMAP was accomplished by dipping the electrode in an ethanolic solution of the porphyrin with sufficient time (*ca*. 5 min) allowed for adsorption equilibrium. The electrode was then washed with 0.05 mol dm<sup>-3</sup>  $H_2SO_4$  and distilled water. The geometric area of the electrode exposed to the solution in the electrochemical cell was 0.15 cm<sup>2</sup>.

A GC/GC rotating ring-disc electrode (RRDE, Pine Instrument Company) was used. The area of the disc was 0.37 cm<sup>2</sup>. The collection coefficient, determined using the ferrocyanide-ferricyanide couple, was 0.365. The RRDE was pretreated mechanically and electrochemically. The electrode was polished with alumina powder, washed with an 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

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solution and distilled water and introduced in 0.1 mol dm<sup>-3</sup> KCl argon-saturated solution. The potentials of the disc and ring electrodes were then cycled in the range from +0.3 to -0.8 V until a minimum residual current density was obtained (ca. 1  $\mu$ A cm<sup>-2</sup>). In order to avoid absorption of CoTMAP on the ring electrode on dipping the RRDE in porphyrin solution, a drop of an ethanolic solution of CoTMAP was allowed to dry on the disc.

Spectroelectrochemistry was conducted using an optically transparent thin-layer cell constructed with a gold minigrid working electrode sandwiched between two quartz plates which were separated by Teflon tape spaces along the edges. The pathlength of the thin cell (ca. 0.1 mm)was determined by measuring the adsorbance of a solution of K<sub>3</sub>Fe(CN)<sub>6</sub> whose concentration had been predetermined in a calibrated 1 cm cell. A Cary 17 spectrophotometer, with a cell compartment modified to permit introduction of electrical leads, was used for the spectropotentiostatic experiments.

Cyclic voltammetry and spectroelectrochemistry were performed using a PAR 174 potentiostat coupled with a PAR 175 sweep generator. The RRDE experiments were performed using a double potentiostat (RRDE 3, Pine Instrument Company) and differential pulse voltammetry using a PAR 173 polarograph.

All reported potentials are with respect to a saturated calomel electrode (SCE) and the experiments were conducted at room temperature ( $20 \pm 1$  °C).

## **RESULTS AND DISCUSSION**

Fig. 1 shows a typical differential pulse voltammogram for a solution of TMAP in 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> [curve (a)]. Three reduction peaks appear at -0.42, -0.65and -0.75 V. The differential pulse voltammogram of the Co<sup>III</sup>TMAP complex [curve (b)] is characterized by reduction processes at +0.34, +0.08, -0.20, -0.36and -0.59 V. The peaks at +0.34 and +0.08 V are assigned to reduction of the central metal ion while the other waves were found to correspond to irreversible processes (no cyclic voltammetric oxidation wave) and have been suggested to result from reduction of the porphyrin ring.<sup>13</sup> The strong covalency of the metal-to-ligand bond in the complex is suggested to be responsible for the positive shift in the reduction potentials of the porphyrin ring in CoTMAP compared with the reduction of TMAP.<sup>15</sup> The presence of two reduction waves for the metal ion in the porphyrin was also reported for CoTPyP,9 FeTMAP13 and FeIII protoporphyrin IX16 adsorbed on glassy carbon. In all cases, these waves were also separated by ca. 200 mV. Moreover, only one of the waves was found to catalyse O<sub>2</sub> reduction effectively, as can be seen from curves (c)-(i) for CoTMAP: the peak current at +0.08 V increases as the oxygen concentration in the solution is increased. The presence of the prewave (+0.34 V) could be the result of strong adsorption,<sup>17</sup> strong interaction of various oxygen functionalities on the glassy carbon surface with the axial position of the metal ion in the porphyrin<sup>9</sup> or various forms (monomeric, dimeric) of the adsorbed porphyrin.16

Further characterization of the dissolved CoTMAP in 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> was studied by thin-layer spectroelectrochemistry using a gold minigrid electrode. The cyclic voltammograms exhibited well defined reduction and oxidation waves for the  $Co^{III}/Co^{II}$  couple, and an  $E^{\Theta'}$  value of +0.14 V vs SCE was calculated by averaging the cathodic and anodic peak potentials:

$$Co^{III}TMAP + e \rightleftharpoons Co^{II}TMAP \quad E^{\Theta'} = +0.14 \text{ V}. \tag{I}$$

Consecutive cycles gave identical voltammograms, indicating that the oxidation state of the cobalt can be reversibly cycled between (III) and (II) in the thin-layer cell. Coulometric experiments conducted at potentials 250 mV more negative or positive than the  $E^{\ominus'}$  value confirmed a one-electron reduction/oxidation of the cobalt ion.





Fig. 1. Differential pulse voltammograms (2 mV s<sup>-1</sup>, 25 mV modulation) of a deaerated 0.05 mol dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> solution containing (a)  $3.6 \times 10^{-4}$  mol dm<sup>-3</sup> TMAP and (b)  $4.9 \times 10^{-4}$  mol dm<sup>-3</sup> Co<sup>111</sup>TMAP. Curves (c)–(i) are obtained for the same condition as (b) with a gradual increase in dioxygen concentration in the solution.

The successive spectra of the cobalt porphyrin as observed during incremental reduction are exhibited in fig. 2: the 427 nm peak of Co<sup>III</sup> diminishes and a peak at 412 nm characteristic of the Co<sup>II</sup> species appears. Both the oxidized and reduced forms of CoTMAP were stable, as shown by the reproducibility of the respective spectra. No demetallation was observed as reported for Mn<sup>II</sup>TMAP at pH < 3.6.<sup>14</sup> Table 1 lists the main absorption maxima and extinction coefficients of TMAP, Co<sup>III</sup>TMAP and Co<sup>III</sup>TMAP. The spectral data are in agreement with studies on cobalt tetraphenylphorphyrins. <sup>18</sup>Pasternack concluded from the similar spectral properties of CoTMPyP that Co<sup>III</sup>P(H<sub>2</sub>O)<sub>2</sub> is the only chromophore present in appreciable amounts in aqueous solutions at pH  $\leq 2.^{19, 20}$ 

To investigate the effect of the presence of CoTMAP on oxygen reduction, cyclic voltammetry was performed in air-saturated 0.05 mol dm<sup>-3</sup>H<sub>2</sub>SO<sub>4</sub> solutions containing various concentrations of Co<sup>III</sup>TMAP. At porphyrin: O<sub>2</sub> concentration ratios > 1, oxygen reduction occurred at a peak potential of  $\pm 0.06$  V, which is close to the redox potential of Co<sup>III</sup>/Co<sup>II</sup>TMAP (fig. 3). The catalytic peak current ( $i_{p, cat}$ ) was linearly proportional to the square root of the scan rate, as expected from diffusion-controlled transfer reactions (inset of fig. 3). Assuming the validity of the Randles–Sevcik equation,<sup>21</sup> an *n* value of  $3.7 \pm 0.4$  was evaluated, thus indicating catalytic reduction of oxygen to water rather than to hydrogen peroxide:

$$2Co^{11}TMAP + O_2 + 4H^+ \rightarrow 2Co^{111}TMAP + 2H_2O.$$
 (II)



Fig. 2. Spectra obtained during incremental reduction at -0.4 V of a deaerated 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution containing  $6.3 \times 10^{-4}$  mol dm<sup>-3</sup> Co<sup>111</sup>TMAP. The arrows indicate the direction of the OD change during reduction.

Table 1. Spectral data in the Soret region of TMAP, Co^{111}TMAP and Co^{11}TMAP in 0.05 mol dm<sup>-3</sup>  $H_2SO_4$ 

compound	absorption maxima/nm	extinction coefficient /10 <sup>4</sup> dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>
ТМАР	412	6.5
	432	27.8
Co <sup>111</sup> TMAP	427	8.0
Co <sup>11</sup> TMAP	412	6.5

The apparent rate constant of reaction (II) was calculated for cobalt porphyrin concentrations much lower than that of oxygen (concentration ratio < 10) using

$$i_{\rm p,\,cat} = n F A C_{\rm p} D_{\rm p} K^{\frac{1}{2}} C_{\rm O_2}^{\frac{1}{2}} \tag{1}$$

where  $i_{p, cat}$  is the catalytic current (A), F is the Faraday constant, A is the electrode area (cm<sup>2</sup>),  $C_p$  and  $C_{O_2}$  are the porphyrin and oxygen concentrations, respectively (mol



Fig. 3. Cyclic voltammograms of dioxygen reduction for an aerated 0.05 mol dm<sup>-3</sup>  $H_2SO_4$  solution containing  $4.9 \times 10^{-4}$  mol dm<sup>-3</sup> Co<sup>111</sup>TMAP. Scan rates are 10, 20, 50 and 100 mV s<sup>-1</sup> for curves (a)–(d), respectively. Inset: plot of peak current as function of the square root of scan rate.



Fig. 4. Cyclic voltammograms at a scan rate of 100 mV s<sup>-1</sup> in a solution of 0.05 mol dm<sup>-3</sup>
 H<sub>2</sub>SO<sub>4</sub>: (a) deaerated solution, (b) air-saturated solution, (c) same as (a) with CoTMAP adsorbed on the GC electrode and (d) same as (b) with adsorbed CoTMAP.



**Fig. 5.** RRDE voltammograms  $(E_{\rm R} = +1.0 \text{ V}, \text{ scan rate of disc potential } 2 \text{ V min}^{-1})$  of an air-saturated solution of  $10^{-1} \text{ mol dm}^{-3}$  NaCl and  $10^{-2} \text{ mol dm}^{-3}$  phosphate buffer (pH 8.1). Curves (a)-(d) are for adsorbed CoTMAP on the GC disc while curves (e)-(h) are obtained when the catalyst is absent.

cm<sup>-3</sup>),  $D_p$  is the diffusion coefficient of the porphyrin (cm<sup>2</sup> s<sup>-1</sup>) and K is the apparent rate constant (mol<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>), and assuming a pseudo-first-order *ec* catalytic mechanism [reactions (I) and (II)], with reaction (II) being irreversible.<sup>22</sup> The rate constant of reaction (II) was calculated to be  $(3 \pm 0.4) \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

Co<sup>III</sup>TMAP was found to adsorb irreversibly on glassy carbon. Typical cyclic voltammogram curves for adsorbed CoTMAP in deaerated as well as air-saturated solutions are shown in fig. 4. The  $E_{p,a}$  and  $E_{p,c}$  of the adsorbed species in a deaerated 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution (devoid of porphyrin) were close ( $\pm 20$  mV) to those found for the dissolved porphyrin. The large peak potential separation ( $E_{p,a} - E_{p,c} \approx 100$  mV) instead of the expected value of zero can be explained by the existence of the porphyrin species at different environmental sites on the electrode surface.<sup>23, 24</sup> The surface concentration of the porphyrin was estimated by electrochemical methods cited in the literature<sup>23</sup> to be ( $3\pm 0.6$ ) × 10<sup>-10</sup> mol cm<sup>-2</sup>. Assuming an area of 200 Å<sup>2</sup> for the CoTMAP molecule and also that the complex lies flat on the





Fig. 6. Half-wave potential obtained with the RRDE as function of pH for adsorbed CoTMAP in air-saturatured solution (conditions as in fig. 5).

electrode surface,<sup>25</sup> this corresponds to monolayer coverage. Assuming that the surface redox couple obeys the Nernst equation, the peak current for the cyclic voltammograms is given by<sup>23</sup>

$$i_{\rm p} = \frac{n^2 F^2 \Gamma v}{4RT} \tag{2}$$

where *n* is the number of electrons per molecule,  $\Gamma$  is the surface concentration (mol cm<sup>-3</sup>) and *v* is the potential scan rate. Experimental values of the peak current and surface concentration give  $n = 0.9 \pm 0.2$ , indicating one-electron reduction. As for the results obtained for dissolved CoTMAP in 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, the redox process with  $E^{\Theta'} = +0.14$  V is likely to involve the metal centre:

$$(Co^{III}TMAP)_{ads} + e \rightleftharpoons (Co^{II}TMAP)_{ads}.$$
 (III)

Also shown in fig. 4 are the i-E curves for oxygen reduction. The overpotential for oxygen reduction in the presence of adsorbed porphyrin is about the same (480 mV) as found for dissolved Co<sup>III</sup>TMAP. This result suggests that the dioxygen reduction is essentially determined by a surface *ec* catalytic mechanism.

Oxygen electroreduction was also studied using the rotating ring-disc electrode (RRDE), which allows the amount of  $H_2O_2$  formed during the reaction to be determined quantitatively. Typical RRDE voltammograms are shown in fig. 5 for an air-saturated electrolyte solution with and without adsorbed Co<sup>II</sup>TMAP on the GC disc electrode (no dissolved porphyrin in the solution). The presence of adsorbed porphyrin on the disc causes a positive shift in the half-wave potential ( $E_2$ ) of oxygen reduction by 300 mV at pH 8.2. The  $E_2$  of oxygen reduction correlated well with that of the adsorbed porphyrin in deaerated solutions at all pH values. From fig. 6 it can be seen that  $E_3$  is pH dependent in the pH range from 1 to 6. An approximate decrease



Fig. 7. (A) Levich plots of RRDE curves for adsorbed CoTMAP in the same solution as in fig. 5. (B) Kouteck-Levich plots prepared from the data of (A).

of 60 mV per pH unit was observed in the pH range from 2 to 5, indicating a reduction which involves one electron per proton. At pH < 2, the  $E_{\frac{1}{2}}$  value is shifted to much higher potentials than expected from the slope at higher pH values. A similar effect was reported for CoTPyP.<sup>9</sup> The potential shift could be the result of a change in the axial position of the metal ion as reported for similar cobalt porphyrins:<sup>19</sup>

$$\begin{array}{ccc} H_2O & HO \\ | & | \\ Co^{III}TMAP \rightleftharpoons Co^{III}TMAP + H^+. \\ | & | \\ H_2O & H_2O \end{array}$$
(IV)

However, further study of this effect is required.

Levich plots<sup>26</sup> of the disc limiting currents  $(i_{D, L})$  against the square root of the rotation speed  $(\omega^{\frac{1}{2}})$  were linear [fig. 7(A)] with correlation factors > 0.995. Fig. 7(B) shows the corresponding Kuteck-Levich plots<sup>27</sup> of  $i_{D,L}^{-1}$  against  $\omega^{-\frac{1}{2}}$ . The intercepts of these plots provide values of the kinetic currents  $(i_k)$  which are linearly related to the bimolecular rate contant governing the reaction between oxygen and adsorbed porphyrin.<sup>28</sup> Since the cross-sectional concentration of the porphyrin could not be calculated precisely in solutions at high pH, the rate constant of oxygen reduction was not evaluated. However, a plot of  $i_k$  against pH [fig. 8, curve (a)] shows an increase in oxygen reduction rate with increasing pH in the ranges from 2 to 6 and from 10 to 12. Since the redox potential shifts to higher values when the pH decreases from 6 to 2 (fig. 6), it should be easier for oxygen to oxidize Co<sup>II</sup> in solutions at high pH.<sup>29</sup>

The ring electrode potential was set at +1.0 V to monitor the  $H_2O_2$  formed at the

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Fig. 8. Kinetic currents obtained from Kouteck-Levich plots and hydrogen peroxide yield as function of pH.



Fig. 9. Ratio of the disc and ring currents as a function of  $\omega^{-\frac{1}{2}}$ , for adsorbed CoTMAP in air-saturated solutions of 0.1 mol dm<sup>-3</sup> NaCl and 10<sup>-2</sup> mol dm<sup>-3</sup> phosphate buffer at pH (a) 4.0, (b) 6.3, (c) 8.2 and (d) 12.0.

disc. The  $H_2O_2$  yield was calculated<sup>30</sup> by plotting the ratio  $i_D/i_R$  ( $i_D$  and  $i_R$  are the disc and ring currents, respectively) against  $\omega^{-\frac{1}{2}}$  (fig. 9). The low slope and invariance of the current ratio with rotation speed indicate that  $H_2O_2$  is formed only as a parallel product and not as an intermediate in dioxygen reduction. Once  $H_2O_2$  is formed, no further reduction to  $H_2O$  takes place at the disc.<sup>31</sup> As shown in fig. 8, the  $H_2O_2$ 

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yield is strongly dependent on electrolyte pH: while insignificant amounts of  $H_{a}O_{a}$ are produced at pH < 6, the major reduction product at pH > 8 is hydrogen peroxide.

# CONCLUSIONS

The reduction potentials of Co<sup>III</sup>TMAP and dioxygen coincide over the pH range from 1 to 12. This correspondence indicates that the potential governing reduction  $O_2$  is the redox potential of the Co<sup>III</sup>/Co<sup>III</sup>TMAP couple. This is consistent with an ec mechanism, which has also been proposed for other water-soluble porphyrins.<sup>12</sup> The more positive potential at which CoTMAP catalyses the reduction of O<sub>2</sub>, compared with FeTMAP<sup>13</sup> and MnTMAP<sup>14</sup> (ca. +0.1, -0.1 and -0.3 V for Co, Fe and MnTMAP, respectively) is in accord with the relative positions of the redox potentials of these complexes. The catalysed process is strongly dependent on electrolyte pH. Unlike FeTMAP,<sup>13</sup> CoTMAP tends to produce H<sub>2</sub>O<sub>2</sub> as the end product at pH > 6. A similar difference was reported for FeTMPyP and CoTMPyP. This difference between iron and cobalt porphyrins in the extent of dioxygen reduction was suggested to be related to the ability of the lower valent form of the metal to bind axially with the peroxide ions.12

CoTMAP adsorbed on GC electrodes shows much higher catalytic activity in acidic than in basic solutions. This is deduced by the following observations: (a) the overpotential of dioxygen electroreduction is reduced by ca. 480 mV at pH 1 compared with ca. 300 mV at pH 8 and (b) dioxygen reduction proceeds mostly through a four-electron reduction in acidic solutions in the presence of adsorbed (or dissolved) CoTMAP. This finding is in agreement with the report in which a dicobalt cofacial porphyrin appears to be able to reduce O<sub>2</sub> to H<sub>2</sub>O in acidic solutions and hydrogen peroxide becomes a major product when the proton supply to the electrode is depleted.5

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