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The study of the interactions of cobalt(II) tetrasulfophthalocyanine with cysteine and histidine

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Abstract—Kinetics for the interaction of cobalt(II) tetrasulfophthalocyanine ($[Co^{II}TSPc]^{4-}$, Pc(−2) = phthalocyanine dianion) with the amino acids, histidine and cysteine, in pH 7.2 phosphate buffer were studied. The rates were found to be first order in both the $[Co^{II}TSPc]^{4-}$ and the amino acid. The formation of the $[Co^{III}TSPc]^{3-}$ species in the presence of histidine occurred with a rate constant of 0.16 $dm^3\ mol^-\ s^{-1}$, whereas the formation of the $[Co^{I}TSPc]^{5-}$ species in the presence of cysteine gave a rate constant of 2.2 $dm^3\ mol^-\ s^{-1}$.

Keywords: cysteine; histidine; cobalt; tetrasulfophthalocyanine; cystine; amino acids.

Metallophthalocyanine (MPc, Pc(−2) = phthalocyanine) are important industrially for their use in dyestuffs. Research into the application of MPc complexes as electrocatalysts and photocatalysts is continuing to receive considerable attention. Many of the applications of MPc complexes involve exchange of electrons and coordination of the reactants or products to the MPc species. The catalytic activity of MPc complexes is strongly dependent on the nature of the central metal ion [1]. MPc complexes whose central metal ion can reversibly bind both the reactants and products are expected to show good catalytic activity. Cobalt phthalocyanine ($Co^{II}Pc$) complexes are known to be good catalysts for many reactions including oxidation of cysteine [1–4].

It is well known [4,5] that the interaction between the water soluble cobalt(II) tetrasulfophthalocyanine ($[Co^{II}TSPc]^{4-}$) species and cysteine results in the formation of the reduced $[Co^{I}TSPc]^{5-}$ species and the oxidation of cysteine to cystine. The autoreduction of the $[Co^{II}TSPc]^{4-}$ species in the presence of cysteine occurs only at pH's greater than 4. Below this pH, the electrocatalytic oxidation of cysteine by $Co^{III}Pc$ species has been reported [2,3]. The electrocatalysed oxidation of cysteine on $Co^{II}Pc$ modified electrodes is believed to be a two-step process initiated by the electrochemical oxidation of $Co^{II}Pc$ to $[Co^{III}Pc]^+$ species, followed by the electron transfer from cysteine to the $[Co^{III}Pc]^+$ species as shown by eqs 1 to 3.

$$Co^{II}Pc \rightarrow [Co^{III}Pc]^+ + e^- \quad (1)$$

$$[Co^{III}Pc]^+ + RSH \rightarrow Co^{II}Pc + RS^{\cdot} + H^+ \quad (2)$$

$$2RS^{\cdot} \rightarrow RSSR \quad (3)$$

There have been reports of the catalytic oxidation of cysteine by other MPc complexes such as oxomolybdenum phthalocyanine (OMoPc) [6] and by porphyrin complexes [7]. Coordination of cysteine to $OMo^{V}Pc$ or porphyrin species was suggested to occur prior to the electron transfer reactions.

Interactions between histidine and $[Co^{II}TSPc]^{4-}$ have been reported [8]. It was observed that histidine and other substituted imidazoles promote the oxidation of $[Co^{II}TSPc]^{4-}$ species to $[Co^{III}TSPc]^{3-}$ in the presence of air. In this work we report on the kinetics of the interaction of the $[Co^{II}TSPc]^{4-}$ species with histidine and cysteine and on the axial ligation of these amino acids to the cobalt(II) tetrasulfophthalocyanine prior to electron transfer reactions.

EXPERIMENTAL

Tetrasodium salt of cobalt(II) tetrasulfophthalocyanine ($Na_4[Co^{II}TSPc]$) was synthesized and purified according to established procedures [9,10]. Kinetic studies were run at room temperature and monitored with the Cary IE spectrophotometer. Phosphate

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buffer (pHs 6–10) was employed for all experiments. Typically a known volume of the $[Co^{II}TSPc]^{4-}$ solution was added to a spectrophotometric cell of 1 cm pathlength, then a known volume of a solution of *l*-histidine or *l*-cysteine in the appropriate buffer was added to the cell. The cell was then stoppered and the spectral changes monitored with time. The concentration of the $[Co^{II}TSPc]^{4-}$ solution was kept constant for all reactions, while the histidine and cysteine concentrations were varied from 0.001 to 0.30 mol dm^{-3}. $[Co^{II}TSPc]^{4-}$ species form aggregates in aqueous solutions hence the exact concentration may be difficult to determine. We estimated the concentration of the dimeric cobalt(II) tetrasulfophthalocyanine species, with an absorption maxima at 624 nm to be 8×10^{-6} mol dm^{-3} using a published extinction coefficient of 5.8×10^4 dm^3 mol^{-1} cm^{-1} [11]. Since the concentration of the phthalocyanine species was much less than that of the cysteine or histidine species, pseudo-first order condition was maintained for kinetic studies. Infra-red spectra (KBr discs) were collected with a Perkin–Elmer Model 180 IR spectrometer.

RESULTS AND DISCUSSION

Interactions of $[Co^{II}TSPc]^{4-}$ *with histidine*

It is now well established that metal tetrasulfophthalocyanine species exist in aggregated form in aqueous solutions [11,12]. The electronic spectra of $[M^{II}TSPc]^{4-}$ in water has been explained in terms of equilibria between the dimeric and monomeric species [11,12]. In general for $[M^{II}TSPc]^{4-}$ species, the high energy peak near 620 nm is associated with the dimeric species and the peak near 670 nm with the monomer. Figure 1 shows the spectral changes observed when histidine was added to solutions of $[Co^{II}TSPc]^{4-}$ in phosphate buffer (pH 7.2). On addition of histidine, the peak due to dimeric species at 624 nm decreases in intensity with time, while the peak due to monomeric species at 666 nm increases in intensity and shifts to 672 nm. The spectral changes occur with isosbestic points at 717, 645 and 405 nm. The presence of isosbestic points implies that only two species exist in solution. The increase in the peak in the section of the spectra associated with the monomeric species shows that addition of histidine favours the formation of the monomeric $[Co^{II}TSPc]^{4-}$ species.

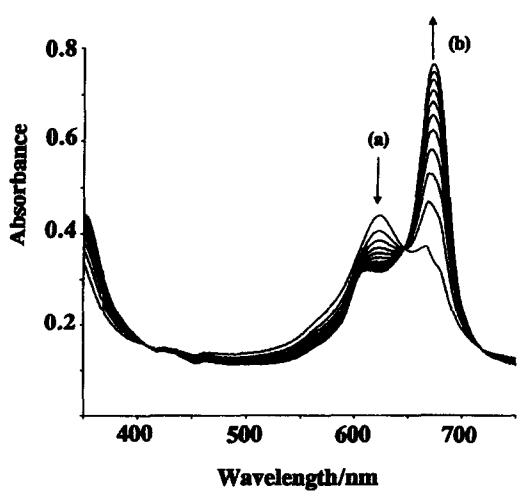

Fig. 1. Spectral changes observed when histidine (0.085 mol dm^{-3}) was added to solutions containing 8×10^{-6} mol dm^{-3} of $[Co^{II}TSPc]^{4-}$ dissolved in pH = 7.2 phosphate buffer. Spectra (a) immediately after addition of histidine and (b) 10 h after addition of histidine.

The final spectra with the peak at 672 nm in Fig. 1, is similar to the spectra obtained on oxidation of $[Co^{II}TSPc]^{4-}$ to the $[Co^{III}TSPc]^{3-}$ species [4]. We obtained similar spectra when we added bromine to solutions of $[Co^{II}TSPc]^{4-}$. Thus, the final spectra obtained on addition of histidine to $[Co^{II}TSPc]^{4-}$, Fig. 1(b), is attributed to the oxidation of the central metal ion with the formation of $[Co^{III}TSPc]^{3-}$. The spectral changes shown in Fig. 1 are indeed typical of metal oxidation in MPc complexes [13]. When reducing agents, e.g. $NaBH_4$, were added to solutions containing $[Co^{III}TSPc]^{3-}$, at the end of the reaction between histidine and the $[Co^{II}TSPc]^{4-}$ species, the original spectra due to $[Co^{II}TSPc]^{4-}$ was regenerated. This goes further to confirm that the spectral changes shown in Fig. 1 are due to the formation of an oxidized species.

The spectral changes shown in Fig. 1 were not observed when oxygen was deliberately excluded from the solution by bubbling nitrogen. This confirms earlier reports [8] which suggested that histidine and other substituted imidazole ligands facilitated the oxidation of $[Co^{II}TSPc]^{4-}$ to $[Co^{III}TSPc]^{3-}$ by atmospheric oxygen. The actual role of histidine in the oxidation processes has however not been determined. There have been suggestions that electron transfer in related complexes such as the Fe^{II} cytochrome species is mediated by oxygen oxidation of both histidine and Fe^{II} cytochrome, with a subsequent phosphorylation of the oxidized histidine molecule [14].

An increase in the absorption due to the monomeric species followed by a further shift to lower energy has been observed [11] when oxygen was bubbled through an alkaline solution of $[Co^{II}TSPc]^{4-}$. The final spectrum in this reaction was attributed to the formation of an adduct between oxygen and $[Co^{II}TSPc]^{4-}$ [11]. In neutral media however, these spectral changes were not observed unless the solution was heated. We used a stoppered cell in order to avoid variations in the oxygen dissolved in the phosphate buffer after mixing histidine with $[Co^{II}TSPc]^{4-}$. We observed no changes in the spectra with time for the solutions of $[Co^{II}TSPc]^{4-}$ in pH = 7.2 phosphate buffer in the absence of histidine, showing that the oxygen available in the phosphate buffer is not enough to oxidize the $[Co^{II}TSPc]^{4-}$ species without the facilitatory role of histidine. This observation confirms that histidine plays an important role in the oxidation process. It is also

important to note that the spectral changes shown in Fig. 1 were not observed when phosphate buffer at pH = 6 was employed. These spectral changes were observed only in basic conditions, for phosphate buffer pH's varying from 7.2 to 10. The rate of autooxidation of $[Co^{II}TSPc]^{4-}$ to the $[Co^{III}TSPc]^{3-}$ species is known to depend strongly on the axial ligands [15], with the oxidation being favoured by strong δ donor ligands [16]. Thus, the differences in the ability of histidine to influence the oxidation of $[Co^{II}TSPc]^{4-}$ at different pH values could be attributed to the differences in the electron donor ability of histidine at various pHs.

Addition of histidine or other imidazole ligands to solutions of $[Co^{II}TSPc]^{4-}$ is known to result in the axial ligation of the former to the later [8,15], with the resulting complex then undergoing oxidation to the $[Co^{III}TSPc]^{3-}$ species. Since $[Co^{II}TSPc]^{4-}$ is known to be coordinated to two water molecules in aqueous solutions [12], we suggest that histidine replaces at least one of the water molecules from $[(H_2O)_2Co^{II}TSPc]^{4-}$ with the formation of the $[(His)(H_2O)Co^{II}TSPc]^{4-}$ complex (where His represents histidine). The $[(His)(H_2O)Co^{II}TSPc]^{4-}$ complex thus formed then undergoes oxidation as shown in eqs 4 and 5.

$$[(H_2O)_2Co^{II}Pc]^{4-} + His \rightarrow [(His)(H_2O)Co^{II}Pc]^{4-} + H_2O \quad (4)$$

$$[(His)(H_2O)Co^{II}Pc]^{4-} \xrightarrow{O_2} [(His)(H_2O)Co^{III}Pc]^{3-} \quad (5)$$

Axial ligand substitution reactions in MPc complexes are known to be stepwise with the coordination of the first ligand occurring much faster than that of the second ligand [17–19]. The substitution of each ligand often occurs with distinct spectroscopic changes. We associate the initial increase in the peak at 666 nm with the monomeric $[(His)(H_2O)Co^{II}TSPc]^{4-}$ species formed by the axial ligation of histidine to the $[(H_2O)_2Co^{II}TSPc]^{4-}$ species prior to the electron transfer reactions shown in eq. 5. The final spectra due to the oxidized $[Co^{III}TSPc]^{3-}$ species, represents a shift of 6 nm from the spectra of the monomeric $[Co^{II}TSPc]^{4-}$ species. In an attempt to confirm the coordination of histidine to the $[Co^{II}TSPc]^{4-}$ species, we studied the IR spectra of a solid remaining after evaporation of the solvent from the solution containing the oxidized $[Co^{III}TSPc]^{3-}$ species and histidine and compared it with the IR spectra of histidine, phosphate and $[Co^{II}TSPc]^{4-}$. We observed a broadening of the bands around 735 cm^{-1}. Bands in the 900–600 nm range are normally associated with ring absorptions in imidazoles [20]. Disruptions of the histidine IR spectra in this region may suggest the presence of coordinated histidine.

The fact that the original spectra due to the $[Co^{II}TSPc]^{4-}$ species is regenerated, without any shift in the absorption band maxima, following the reduction of the final $[(His)(H_2O)Co^{III}TSPc]^{3-}$ species with chemical reductants implies that the histidine molecules are reversibly bound to the Co^{II} tetrasulfophthalocyanine species and that histidine ligands are lost on reduction of the oxidized Co^{III} tetrasulfophthalocyanine. A small shift in spectra of the original $[(H_2O)_2Co^{II}TSPc]^{4-}$ would be observed if a lasting change in axial ligation had occurred.

We followed the formation of the $[Co^{III}TSPc]^{3-}$ species at 672 nm kinetically. Since the excess of histidine was used, pseudo-first order conditions were assumed in the determination of the rate constant for the oxidation of $[Co^{II}TSPc]^{4-}$ in the presence of histidine. Plots of the logarithm of absorbance against time were linear for the formation of the $[Co^{III}TSPc]^{3-}$ species. The linearity of the plots, confirm that the reaction is first order with respect to the $[Co^{III}TSPc]^{3-}$ species. The slopes of the plots of logarithm of absorbance versus time, gave the observed rate constant, k_{obs} and plots of k_{obs} against the concentration of histidine were also linear, Fig. 2, showing first order dependence of the reaction on histidine. The slope of the plot of k_{obs} versus concentration of histidine gave a rate constant, $k' = 0.16 \pm 0.01$ mol^{-1} dm^3 s^{-1}. The increase of the observed rate constant with increase in concentration suggests that the rate law followed by the oxidation of $[Co^{II}TSPc]^{4-}$ in the presence of histidine is given by eq. 6.

$$\frac{d[Co^{III}TSPc]^{3-}}{dt} = k_{obs}[Co^{III}TSPc]^{3-} \quad (6)$$

where $k_{obs} = k'[His]$ and His = histidine.

The rate constant of 0.16 mol^{-1} dm^3 s^{-1} is low when compared, for example, with the rate constant for the autoreduction of Fe^{III} porphyrin species in the presence of cyanide ($k' = 240$ mol^{-1} dm^3 s^{-1}) [21]. Since ligand exchange of histidine for at least one water molecule is assumed to occur prior to the oxidation of the resulting complex, as discussed above, the coordination of histidine to the $[Co^{II}TSPc]^{4-}$ species is expected to show a larger rate constant than the oxidation process.

Histidine itself is not known to be an oxidising agent. The fact that the oxidized $[Co^{III}TSPc]^{3-}$ species is not formed in the presence of histidine, in oxygen-free solutions, shows that histidine is not an oxidizing agent for the $[Co^{II}TSPc]^{4-}$ species. The observed linear dependence of the observed rate constant on the concentration of histidine needs to be closely examined. Other researchers have shown that histidine is oxidized during the oxidation of Cu^{I} histidine complexes by molecular oxygen [14]. It has also been proposed that electron transport in cytochromes is mediated by the oxygen oxidation of the imidazole ring of histidine, leading to the suggestion that both Fe^{II} cytochrome and histidine act as one-electron donor to O_2 [14]. The observed linear dependence of the rate of formation of $[Co^{III}TSPc]^{3-}$ on the concentration of histidine may be explained by proposing

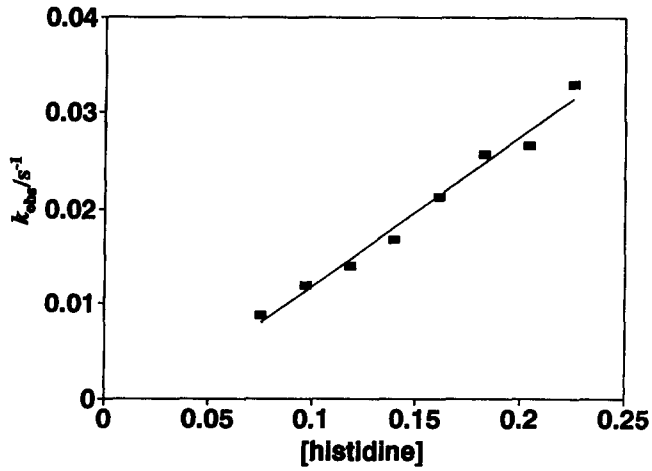

Fig. 2. The plot of the observed rate constant, k_{obs} (s^{-1}) versus the concentration of histidine.

that both histidine and $[Co^{II}TSPc]^{4-}$ transfer one electron to oxygen as was suggested for the electron transfer reactions in cytochromes. This proposal would explain the increase in the rate with increase in histidine concentration, and hence may represent an important step in the understanding of the role of histidine and other ligands in the oxidation of the $[Co^{II}TSPc]^{4-}$ species. Spectral changes shown in Fig. 1 were not observed when histidine was added to solutions of $[Ni^{II}TSPc]^{4-}$ and $[Pd^{II}TSPc]^{4-}$ in pH = 7.2 phosphate buffer. Oxidation in these complexes is known to occur at the ring and not at the central metal[13] unlike in $[Co^{II}TSPc]^{4-}$ where oxidation occurs at the metal.

Interactions of $[Co^{II}TSPc]^{4-}$ *with cysteine*

The interaction of cysteine with the $[Co^{II}TSPc]^{4-}$ species is known to result in the oxidation of the former to cystine and the reduction of $[Co^{II}TSPc]^{4-}$ to $[Co^{I}TSPc]^{5-}$ [4,5]. The coordination of cysteine to MPc or metalloporphyrin complexes prior to electron transfer reactions has been suggested [6,7]. Addition of cysteine to solutions of $[Co^{II}TSPc]^{4-}$ in pH 7.2 phosphate buffer resulted initially in the spectral changes shown in Fig. 3. These spectral changes show an increase in the absorption at 660 nm, in the part of the spectrum associated with the monomeric $[Co^{II}TSPc]^{4-}$ species, Fig. 3(b). We associate the spectral changes shown in Fig. 3 with coordination of cysteine to the $[Co^{II}TSPc]^{4-}$ species. And again assuming that water molecules occupy the axial positions in this complexes we suggest that the coordination of cysteine occurs by eq. 7.

$$[(H_2O)_2Co^{II}Pc]^{4-} + RSH \rightarrow [(RSH)(H_2O)Co^{II}Pc]^{4-} + H_2O \quad (7)$$

where RSH = cysteine.

The fact that the peak due to the monomeric $[Co^{II}TSPc]^{4-}$ species is observed at 666 nm in the presence of histidine and at 660 nm in the presence of cysteine, is a good indication that these amino acids form slightly different species with $[Co^{II}TSPc]^{4-}$. This observation is in agreement with the proposed occurrence of axial ligand exchanges on addition of histidine or cysteine to solutions of $[Co^{II}TSPc]^{4-}$. Small differences in the spectra are expected on changing ligands in axial positions in MPc complexes. The monomeric $[(RSH)(H_2O)Co^{II}Pc]^{4-}$ species is expected to show a slightly different Q band maxima than the $[(His)(H_2O)Co^{II}Pc]^{4-}$ species.

The peak associated with the axial ligand exchange, Fig. 3(b) rapidly decreased in intensity with time, as did the peak at 624 nm associated with the dimeric species. As these two peaks decreased in intensity, peaks associated with the $[Co^{I}TSPc]^{5-}$ species were

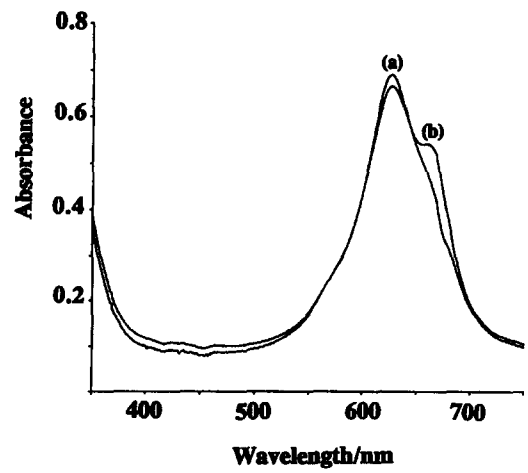

Fig. 3. Spectral changes observed when cysteine (0.0069 mol dm^{-3}) was added to solutions containing 8×10^{-6} mol dm^{-3} of $[Co^{II}TSPc]^{4-}$ dissolved in pH = 7.2 phosphate buffer. Spectra (a) before and (b) 1 min after addition of cysteine.

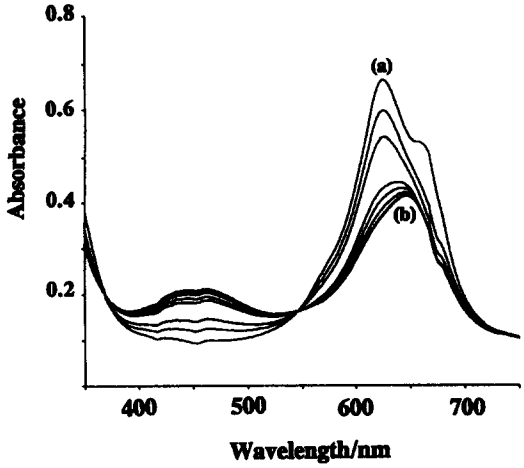

Fig. 4. Spectral changes observed when cysteine (0.0069 mol dm^{-3}) was added to solutions containing 8×10^{-6} mol dm^{-3} of $[Co^{II}TSPc]^{4-}$ dissolved in pH = 7.2 phosphate buffer. Spectra (a) 1 min after addition of cysteine and (b) 16 min after addition of cysteine.

formed (Fig. 4). The later was formed with isosbestic points at 546 and 369 nm and shows two broad peaks at 646 nm and near 450 nm. The final spectra in Fig. 4(b) is typical of the spectra of the $[Co(I)TSPc]^{5-}$ species [4].

We followed the disappearance of the spectra due to the $[Co^{II}TSPc]^{4-}$ species at 624 nm with time and obtained linear plots of the logarithm of absorbance versus time, thus confirming a first order dependence of the reaction of the $[Co^{II}TSPc]^{4-}$ species as was observed above for the interaction of this species with histidine. The plots of k_{obs} versus the concentration of cysteine was linear (Fig. 5) and the slope of the plot in Fig. 5 gave a rate constant of $k' = 2.2 \pm 0.2$ mol^{-1} dm^3 s^{-1}. Since the concentration of cysteine was much larger than the concentration of the $[Co^{II}TSPc]^{4-}$ species, pseudo first order conditions were assumed. The observed linear dependence of k_{obs} on the concentration of cysteine suggests that the rate law followed by the reaction is as given by eq. 8:

$$\frac{-d[Co^{II}TSPc]^{4-}}{dt} = k_{obs}[Co^{II}TSPc]^{4-} \quad (8)$$

where $k_{obs} = k'[RSH]$.

This rate law is similar to that shown in eq. 6 for the oxidation of $[Co^{II}TSPc]^{4-}$ in the presence of histidine, except that in equation 6, the formation of the oxidized $[Co^{III}TSPc]^{3-}$ species was followed. In the case of the reduction of $[Co^{II}TSPc]^{4-}$ in the presence of cysteine, the disappearance of the peak due to the dimeric species was followed. We propose that in the presence of cysteine, the equilibrium between the monomeric and dimeric $[Co^{II}TSPc]^{4-}$ species is shifted towards the monomeric species. Spectral changes shown in Fig. 3 do give evidence of the formation of the monomeric species on addition of cysteine to solutions containing the $[Co^{II}TSPc]^{4-}$ species. Equations 9 and 10 show the likely mechanism for electron transfer reactions involving the $[(RSH)(H_2O)Co^{II}Pc]^{4-}$ species formed by eq. 7:

$$[(RSH)(H_2O)Co^{II}TSPc]^{4-} \rightarrow [(RS^{\cdot})(H_2O)Co^{I}TSPc]^{5-} + H^{+} \quad (9)$$

$$2[(RS^{\cdot})(H_2O)Co^{I}TSPc]^{5-} \rightarrow 2[(H_2O)Co^{I}TSPc]^{5-} + RSSR \quad (10)$$

The transfer of an electron from cysteine to the central Co^{II} metal in $[(RSH)(H_2O)Co^{II}TSPc]^{4-}$ results in the formation of the $[Co^{I}TSPc]^{5-}$ species and cystine, following the loss of the oxidized $RS^{\cdot}$ species from the axial position. Solutions of $[Co^{I}TSPc]^{5-}$ could be oxidized back to the starting $Co^{II}TSPc$ species without any changes in the original spectra of the latter, thus showing that cysteine is reversbility bound to the axial position in $[(RSH)(H_2O)Co^{II}TSPc]^{4-}$. The mechanism proposed above is consistent with the linear

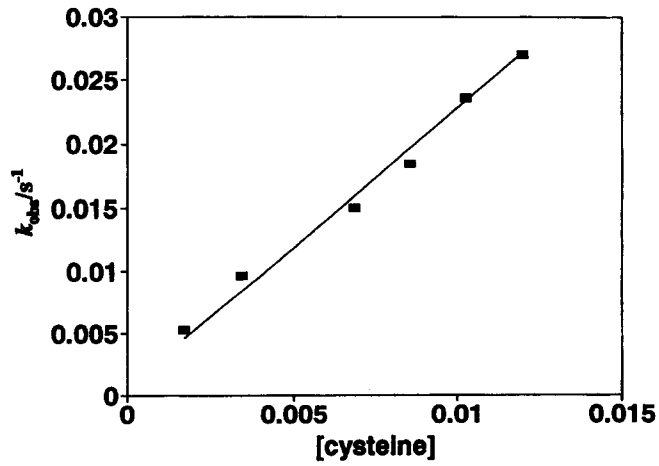

Fig. 5. The plot of the observed rate constant, k_{obs} (s^{-1}) versus the concentration of cysteine.

dependence of the k_{obs} on the concentration of cysteine.

CONCLUSIONS

The interaction of $[Co^{II}TSPc]^{4-}$ with histidine facilitates the air oxidation of the later to the $[Co^{III}TSPc]^{3-}$ species. Whereas the interaction between $[Co^{II}TSPc]^{4-}$ and cysteine results in the electron transfer from the later to the former and the formation of the $[Co^{I}TSPc]^{5-}$ and cystine, respectively. The observed differences in the products obtained on the interaction of the two amino acids with $[Co^{II}TSPc]^{4-}$ may be explained by the fact that oxidation of cysteine is favoured relative to the oxidation of histidine due to the presence of the sulfhydryl group in the former. We have confirmed that there is no electron transfer between $[Co^{II}TSPc]^{4-}$ and histidine. The observed rate constants for the interaction of either histidine or cysteine with the $[Co^{II}TSPc]^{4-}$ species show a linear dependence on the concentration of the amino acids. Studies of the mechanisms for the interaction of amino acids with porphyrins or porphyrin-type molecules such as phthalocyanines are of biological importance, since these compounds are important models for biological systems. The study of the interaction of $[Co^{II}TSPc]^{4-}$ with histidine or cysteine, is an important step towards the understanding of the mechanism of the interaction between phthalocyanines and biological systems.

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