Reactions of a Water Soluble Cobalt Porphyrin with Thiocyanate

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Rate and equilibrium constants have been determined for the reactions of Cobalt(III)Tetra(N-methyltetrapyridyl)Porphine with thiocyanate as a function of pH. The porphyrin ligand increases the substitution rates at the Co(III) center by several orders of magnitude relative to many other Co(III) complexes. The rates of formation and dissociation of the thiocyanate complexes are also dependent on the nature of the axial ligand trans to the water molecule being removed.

Metalloporphyrin complexes occupy an important position in biology because of the diversity of their essential functions. Frequently, this function depends on the addition or substitution of a ligand in an axial position on the metal ion. We are interested in the manner in which the immediate environment of the metal ion influences these ligation reactions. As part of our studies, we are now reporting on the reactions of cobalt(III)tetra(N-methyltetrapyridyl)-porphine* with SCN^- over an extensive pH range.

Materials and Methods

The CoTMPyP was prepared by a method described elsewhere.[1] The Evans method[2-4] was used to show that the cobalt ion is in its +3 oxidation state. All other chemicals were purchased from the Baker Chemical Co. and used without further purification. Visible spectra were determined on a Cary 14 spectrophotometer. Porphyrin solutions were freshly prepared and protected from direct sunlight and fluorescent light.

Relaxation experiments were carried out on a T-jump apparatus described elsewhere.[5] The stopped flow apparatus used is a portion of a combined SF-TJ apparatus.[6,7] All kinetic and equilibrium experiments were carried out at an ionic strength of 0.5 M, made up with $NaNO_3$.

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*We use the symbol CoTMPyP as a general one for this porphyrin when it is inconvenient or unnecessary to designate the axial ligands. Otherwise, the symbol $CoP(H_2O)_2$ is used as, for example, the diaquo complex.

Results and Discussion

CoTMPyP was shown to obey Beer's law over a wide concentration range and to show no relaxation effects within the time range of our apparatus. We have shown previously[8,9] that porphyrins which tend to aggregate in solution exhibit relaxation effects in the microsecond to millisecond time range and we therefore conclude that this porphyrin is monomeric in aqueous solution.

We have found that the scheme which accounts for our spectral and kinetic data is:

SCHEME

$$\begin{tikzcd}
\arrow[r, shift left, "-H^+"] & \arrow[l, shift left, "+H^+"] \\
\arrow[d, shift right, "+SCN^-"'] & \\
\arrow[u, shift right, "-SCN^-"'] &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{CoP(H_2O)_2} \arrow[r, shift left, "K_{a1}"] \arrow[d, shift right, "k_1"'] & \mathrm{CoP(OH)(H_2O)} \arrow[l, shift left] \arrow[r, shift left, "K_{a2}"] \arrow[d, shift right, "k_1'"'] & \mathrm{CoP(OH)_2} \arrow[l, shift left] \\
\mathrm{CoP(H_2O)(SCN)} \arrow[u, shift right, "k_{-1}"'] \arrow[r, shift left, "K_{a1}'"] \arrow[d, shift right, "k_2"'] & \mathrm{CoP(OH)(SCN)} \arrow[l, shift left] \arrow[u, shift right, "k_{-1}'"'] & \\
\mathrm{CoP(SCN)_2} \arrow[u, shift right, "k_{-2}"'] & &
\end{tikzcd}$$

Spectrophotometric titrations of the porphyrin with sodium hydroxide lead to $pK_{a1} = 6.0$ and $pK_{a2} = 10.0$. Experiments with SCN^- were conducted at pH 2, 8 and 11.5. A summary of the spectra and conditions is given in Table I. At pH 2, spectra were obtained in the Soret region as a function of SCN^- concentration where $1 \times 10^{-4} < [SCN^-] < 0.4$ M. From these spectral data we obtain

$$K_1 = \frac{[\mathrm{CoP(H_2O)(SCN)}]}{[\mathrm{CoP(H_2O)_2}][\mathrm{SCN}]} = 6.4 \times 10^3\ M^{-1}$$

$$\text{and} \quad K_2 = \frac{[\mathrm{CoP(SCN)_2}]}{[\mathrm{CoP(H_2O)(SCN)}][\mathrm{SCN}]} = 10\ M^{-1}$$

where charges have been omitted for convenience.

The kinetics of SCN^- addition at pH 2 in the concentration range $1 \times 10^{-4} < [SCN^-] < 5 \times 10^{-3}$ M were studied and the reaction proved to be first order in porphyrin and first order in SCN^- with rate constants $k_1 = 2.1\ M^{-1}sec^{-1}$ and $k_{-1} = 3.1 \times 10^{-4}\ sec^{-1}$ (Figure 1). A value of K_1 obtained from these kinetic measurements ($K_1 = k_1/k_{-1}$) is $6.8 \times 10^3\ M^{-1}$, in excellent agreement with the value obtained from spectral measurements. Stopped-flow experiments in which

Table I

Spectra of CoTMPyP and Its Thiocyanate Complexes as a Function of pH

Conditions	Species	λ_{max}(mμ)	ϵ_{max}($M^{-1}cm^{-1}$)
pH 2	$CoP(H_2O)_2$	434	2.14×10^5
pH 8	$CoP(OH)(H_2O)$	437	1.7×10^5
pH 11.5	$CoP(OH)_2$	445	1.4×10^5
pH 2 [SCN] = 10^{-3} M	$CoP(H_2O)(SCN)$	438	1.9×10^5
pH 8 [SCN] = 1×10^{-2}	$CoP(H_2O)(SCN)$ or $CoP(OH)(SCN)$	438	$\sim 1.8 \times 10^5$
pH 2 [SCN] = 0.5 M	$CoP(SCN)_2$	455	1.2×10^5

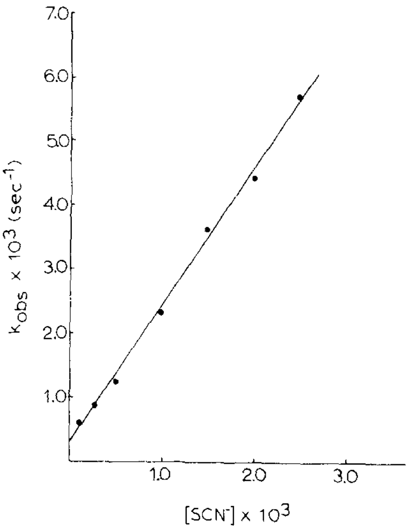

Fig. 1.

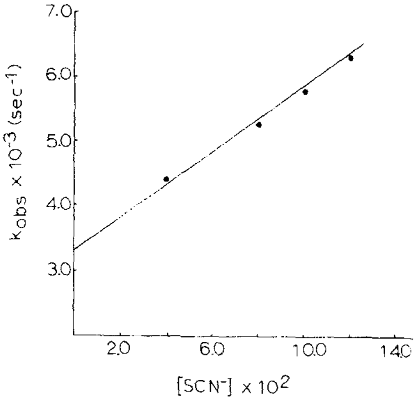

Fig. 2.

Figure 1: A plot of k_{obs} vs thiocyanate concentration at pH 2 in the low concentration range.

Figure 2: A plot of k_{obs} vs thiocyanate concentration at pH 2 in the high concentration range. These data are obtained from temperature-jump experiments.

$CoP(H_2O)_2$ was mixed with SCN^- at much higher concentration of SCN^- led to observed rate constants consistent with those obtained at lower SCN^- concentration although in the latter studies some $CoP(SCN)_2$ is also formed. This preliminary evidence implies that the addition of SCN^- to $CoP(H_2O)(SCN)$ is more rapid than the addition of SCN^- to $CoP(H_2O)_2$. This premise was confirmed using the temperature-jump technique in the concentration range $4 \times 10^{-2} < [SCN^-] < 0.12$ M. A plot of $1/\tau$ vs $[SCN^-]$ leads to a value of $k_2 = 2.8 \times 10^4$ $M^{-1}sec^{-1}$ and $k_{-2} = 3.0 \times 10^3$ sec^{-1} (Figure 2). The kinetically obtained $K_2 = 9.3$ again in very good agreement with the value obtained spectrally.

At a pH of 8 (.001 M borate buffer), spectral evidence was obtained that the final mixed-ligand product is $CoP(H_2O)(SCN)$ rather than $CoP(OH)(SCN)$. Very little shift is observed when SCN^- is added to $CoP(OH)(H_2O)$ at pH 8 as shown in Table I, suggesting that the product may have a similar charge to the reactant porphyrin specie. Further evidence that $CoP(H_2O)(SCN)$ is the product formed at pH 8 is that the addition of a second SCN^- is a very rapid process. If SCN^- were replacing OH^- in the second ligand substitution step, we would expect that this reaction would be quite slow to be consistent with our results at pH 11.5. The reaction of $CoP(OH)(H_2O)$ with SCN^- is quite rapid, requiring the stopped-flow technique in the concentration range $1.0 \times 10^{-2} < [SCN^-] < 5 \times 10^{-2}$ M. Yet at pH 11.5, SCN^- replacement of OH^- is very slow. Therefore, we conclude that at pH 8 SCN^- replaces a water molecule at an axial position leading to an intermediate, $CoP(OH)(SCN)$ which, in a very rapid step, protonates to form the final product. The value of pK_{ai}' is probably not very different from pK_{a2} and at a pH of 8, the hydroxy-thiocyanato complex is therefore not likely to exceed 1% of the total mixed ligand complex concentration. The equilibrium constant obtained at pH 8 is

$$K_3 = \frac{[CoP(H_2O)(SCN)]}{[CoP(OH)(H_2O)][SCN]a_H} = \frac{K_i'}{K_{ai}'}$$

where $K_i' = \dfrac{[CoP(OH)(SCN)]}{[CoP(OH)(H_2O)][SCN]}$ and $K_{ai}' = \dfrac{[CoP(OH)(SCN)]a_H}{[CoP(H_2O)(SCN)]}$.

It may be noted that because there is a cyclic portion to the Scheme, K_3 =

K_1/K_{a1}. Therefore, we can calculate a value of $K_3 = 64$ at a pH of 8. Our stopped-flow data at pH 8 leads to $k_f = k_1' = 1.1 \times 10^2\ M^{-1} sec^{-1}$ and $k_r = K_{a1}'k_{-1}' = 2.3\ M\ sec^{-1}$. The kinetically obtained K_3 is thus 48 at pH 8.

The substitution reactions of CoTMPyP are, therefore, very much more rapid than those of most cobalt(III) complexes. A similar result was obtained by Fleischer and co-workers in their study of cobalt(III)hematoporphyrin.[10] There is general agreement that these reactions proceed via an S_N1 mechanism and it may, therefore, be concluded that the porphyrin moiety greatly labilizes the remaining water molecules on the cobalt ion. Fleischer concludes that the oxidation state formalism might be misleading for these porphyrin cases. It is interesting to note that our study indicates that the identity of the axial ligand also has a profound influence on the remaining water molecule; in comparing the relative labilizing influence of H_2O, OH^- and SCN^- we obtain $SCN^-:OH^-:H_2O$ as $3 \times 10^4:10^2:1$. This effect may reflect the relative stabilities of the five-coordinate intermediates presumably formed via an S_N1 pathway, with stabilities decreasing in the order $SCN^- > OH^- > H_2O$.

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