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Kinetic Study of the Reaction of Meso-Tetra(4-N-methylpyridyl)porphinediaquocobalt(III) with Cyano Complexes of Cobalt(III), Iron(III), Molybdenum(V) and Tungsten(V) in Aqueous Solution

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The reaction of meso-tetra(4-N-methylpyridyl)porphinediaquocobalt(III), $CoP(H_2O)_2^{5+}$, *with* $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$ *and* $W(CN)_8^{3-}$ *has been studied at 15, 25 and 35 °C in 0.1* M H^+ *with* μ = *1.00* M *(*$NaClO_4$*). The stability constants for* $CoP(H_2O)(anion)^{2+}$ *were determined as 446, 1320, 3100, and 1380* M^{-1} *for anion = cyano complexes of Co, Fe, Mo and W respectively. Only one water molecule is displaced during the reactions which are first-order with respect to the complex cyanide's concentration. The value for the second-order rate constants for the addition of the anions to* $CoP(H_2O)_2^{5+}$ *at 25 °C are 0.345, 0.544, 2.54 and 3.73* M^{-1} s^{-1} *for the complex cyanides of Co, Fe, Mo and W respectively. The values of the rate constants and stability constants for the anation reactions of* $CoP(H_2O)_2^{5+}$ *with various ligands were compared. The tentative conclusion is made that a dissociative activation is occurring in these reactions.*

Introduction

Kinetic studies of the substitution of the axial water ligands of meso-tetra(4-N-methylpyridyl)porphinediaquocobalt(III), $[CoP(H_2O)_3]^{5+}$, by NCS^-, I^-, Br^-, Cl^- [1, 2] and pyridine [3] have been reported. Both water molecules can be substituted by other ligands. It is well known that cyano complexes such as $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ ban be bound to other metal ions to form compounds with the general formula $M_a^A[M^B(CN)_6]_b$ [4] where M^A and M^B are ions like Fe(III), Co(III) *etc.* M^A is bonded to the cyano complex through the nitrogen atom of the cyano ligand in these compounds. It seems thus reasonable to expect that a cyano complex might be a good incoming ligand. This study was undertaken in an attempt to extend the knowledge of the aqueous reaction patterns, the bonding properties and the reaction mechanism of cobalt(III) porphines as well as the labilizing effect of the porphyrin ligand. The labilization of the axial water ligands in cobalt(III), rhodium(III) and chromium(III) porphines has been documented [1, 5–7]. The extent of labilization is dependent upon the comparison reaction. If the rate constants for the anation reactions of the complexes $[M(NH_3)_5H_2O]^{3+}$ and $[MTPPS_4(H_2O)_2]^{3-}$ ($TPPS_4$ = meso-tetrakis(*p*-sulfonatophenyl)porphine) are compared the labilization due to porphine for cobalt(III) is about 10^9 [5, 8], for rhodium(III) about 10^3 [6, 9] and for chromium about 10^2 [7, 10].

Experimental

The chemicals used were of analytical grade unless otherwise specified. Redistilled water was used in all the experiments. Meso-tetra(4-N-methylpyridyl)porphine tetraiodide, (practical grade) was obtained form Strem Chemicals. $K_3Co(CN)_6$ (BDH-Chemicals) was converted to $Na_3Co(CN)_6 \cdot 2H_2O$ to make it possible to work in a perchlorate medium. $K_3Co(CN)_6$ was reacted with $AgNO_3$. The insoluble $Ag_3Co(CN)_6$ was washed several times with distilled water. NaBr was added to a suspension of $Ag_3Co(CN)_6$ ($Ag_3Co(CN)_6$ in an excess) in water and stirred for about one hour at room temperature. The AgBr formed and the unreacted $Ag_3Co(CN)_6$ was filtered off and the $Na_3Co(CN)_6 \cdot 2H_2O$ allowed to crystallize. $Cs_3Mo(CN)_8 \cdot 2H_2O$ and $Cs_3W(CN)_8 \cdot 2H_2O$ were prepared as described previously [11–13]. Anation reactions with these two compounds and with $K_3Fe(CN)_6$ were conducted at low cyano complex concentrations to prevent precipitation of $KClO_4$ and $CsClO_4$. $[CoP(H_2O)_2](ClO_4)_5$ was synthesized by heating a solution of 150 mg mesotetra(4-N-methylpyridyl)porphine tetraiodide and a 10-fold excess of $CoCl_2 \cdot 6H_2O$ in 50 cm^3 water on a waterbath for two hours. Oxygen was bubbled through the solution during the reaction. Concentrated $HClO_4$ was added dropwise to the solution until the precipitation of $[CoP(H_2O)_2](ClO_4)_5$ was near completion.

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TABLE I. Absorption Maxima and Molar Absorptivities of the Cobalt(III) Porphines.

Compound	λ, nm	ε, $10^5 M^{-1} cm^{-1}$
$CoP(H_2O)_2^{5+}$	436	1.8
$CoP(H_2O)(Co(CN)_6)^{2+}$	450	1.3
$CoP(H_2O)(Fe(CN)_6)^{2+}$	453	1.4
$CoP(H_2O)(Mo(CN)_8)^{2+}$	452	1.4
$CoP(H_2O)(W(CN)_8)^{2+}$	442	1.4

The precipitate was removed by filtration, washed with ethyl alcohol and dried at 90 °C for two hours. The visible spectrum proved this compound to be identical with the one prepared by Ashley [1] by a different method.

A Pye Unicam SP 1700 spectrophotometer equipped with a constant temperature block was used for all spectrophotometric measurements. The stability constant of $[CoP(H_2O)(Co(CN)_6)]^{2+}$ was determined spectrophotometrically at $[H^+] = 0.1$ *M* and $\mu = 1.0$ *M* ($NaClO_4$). The kinetics of the anation reaction were studied under pseudo-first-order conditions at the desired temperatures. The pseudo-first-order rate constants were obtained from plots of log $(A - A_\infty)$ *vs.* t where A is the absorbance at time t and A_∞ is the absorbance after about 10 half-lives. The plots of $\log(A - A_\infty)$ *vs.* t were linear for at least three half-lives.

Results

The position of the soret band, λ_{max}, and the molar absorptivities of the various cobalt(III) porphines are listed in Table I.

In the spectrophotometric determination of the stability constant, K_1, of $CoP(H_2O)(Co(CN)_6)^{2+}$ the concentration of $Co(CN)_6^{3-}$ was varied from 5×10^{-6} *M* to 0.15 *M*. A plot of absorbance *versus* $[Co(CN)_6^{3-}]$ (see Fig. 1) revealed that only one axial water ligand was replaced by the incoming $Co(CN)_6^{3-}$ ligand. The reaction may thus be represented by

$$CoP(H_2O)_2^{5+} + Co(CN)_6^{3-} \underset{}{\overset{K_1}{\rightleftharpoons}} CoP(H_2O)(Co(CN)_6)^{2+} + H_2O \qquad (1)$$

From Beer's Law, the mass balance and the definition of K_1, equation 2 can be derived.

$$A = \frac{Ar + ApK_1[Co(CN)_6^{3-}]}{1 + K_1[Co(CN)_6^{3-}]} \qquad (2)$$

Ar is the absorbance of the reactant, Ap the absorbance of the product and A the absorbance of the solution at the particular concentration of the incoming ligand. The absorbance *versus* $[Co(CN)_6^{3-}]$ data were fitted to equation 2 by using a nonlinear least-squares program [14]. The calculated value of K_1 is 446 ± 50 M^{-1}. Note in Table II that the kinetical derived value of K_1 is in good agreement. K_1 for the other cyano complexes was calculated only kinetically (see Table II) because of the high absorbances of the cyano complexes at the wavelengths used.

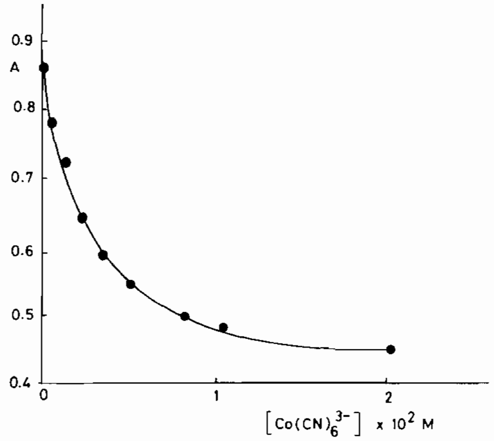

Fig. 1. Plot of absorbance *versus* $[Co(CN)_6^{3-}]$ at 25 °C, $\mu = 1.00$ *M* ($NaClO_4$) and $[H^+] = 0.100$ *M* ($HClO_4$).

Since Ka_1 (reaction 3) is 3.45×10^{-6} *M* at 25 °C and $\mu = 1.00$ *M* [1] the anticipation that the reaction would be $[H^+]$ independent at low pH values was proved by runs at $[H^+] = 0.01$ *M* and $[H^+] = 0.1$ *M* with $Co(CN)_6^{3-}$ as incoming ligand which yielded identical values for the rate constants.

$$CoP(H_2O)_2^{5+} \overset{Ka_1}{\rightleftharpoons} CoP(H_2O)(OH)^{4+} + H^+ \qquad (3)$$

The anation of $CoP(H_2O)_2^{5+}$ by $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ was studied at 15, 25, and 35 °C in 0.1 *M* $[H^+]$ and $\mu = 1.00$ *M* ($NaClO_4$). The rate law is

$$-\frac{d[CoP(H_2O)_2^{5+}]}{dt} = (k_1[L] + k_{-1})[CoP(H_2O)_2^{5+}] \qquad (4)$$

The pseudo-first-order rate constant, k_{obs}, is given by

$$k_{obs} = k_1[L] + k_{-1} \qquad (5)$$

This rate law is indicative of an equilibrium reaction (6):

$$CoP(H_2O)_2^{5+} + L^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoP(H_2O)L^{2+} + H_2O \qquad (6)$$

where L = the particular cyano complex ion. Table II contains a summary of the kinetic data derived by a

TABLE II. The Values of the Rate Constants, Equilibrium Constants and Activation Parameters for the Anation Reactions of $CoP(H_2O)_2^{5+}$.

	Cl^- [1]	Br^- [1]	I^- [1]	$Co(CN)_6^{3-}$ (a)	$Fe(CN)_6^{3-}$ (a)	$Mo(CN)_8^{3-}$ (a)	$W(CN)_8^{3-}$ (a)	NCS^- [1, 2]	Pyridine [3]
k_1 (M^{-1} s^{-1})	9.2×10^{-2}	2.5×10^{-1}	1.6	3.45×10^{-1}	5.44×10^{-1}	2.54	3.73	2.1	7×10^{-1}
k_{-1} (s^{-1})	1.18	1.81	1.5×10^{-2}	7.4×10^{-4}	4.1×10^{-4}	8.2×10^{-4}	2.7×10^{-3}	3.1×10^{-4}	6×10^{-7}
K_1 (M^{-1})	8×10^{-2}	1.4×10^{-1}	3.4×10^{1}	4.66×10^{2}	1.32×10^{3}	3.10×10^{3}	1.38×10^{2}	6.40×10^{3}	1.16×10^{6}
ΔH* (k_1 (KJ/mol)	–	–	84.9	73.2	66	72	65	79.5	–
ΔS* (k_1) (J/(K mol))	–	–	43.5	−8.3	−28	5	−16	30.5	–

[a] This work.

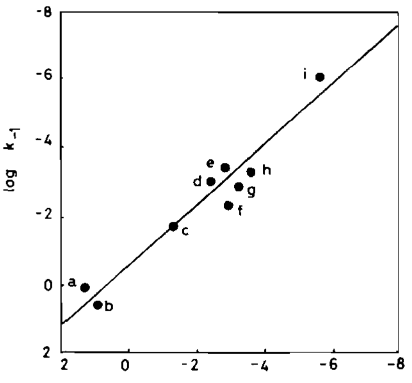

Fig. 2. A plot of $-\log K_1$ *versus* $\log k_{-1}$. a = Cl^-, b = Br^-, c = I^-, d = $Co(CN)_6^{3-}$, e = $Fe(CN)_6^{3-}$, f = $W(CN)_8^{3-}$, g = $Mo(CN)_8^{3-}$, h = NCS^-, i = pyridine.

least-squares fit of the k_{obs} versus [L] data to equation 5. The activation parameters were calculated by a nonlinear least squares fit of the data to the Eyring–Polanyi equation and are also given in Table II.

Discussion

λ_{max} for the soret band and the molar absorptivities, E_{max}, for $CoP(H_2O)_2^{5+}$ agree very well with those reported by Ashley [1]. Another similarity with the latter work is the shifting of the band maxima to longer wavelengths when the negative ligands replace one of the neutral aquo ligands. This phenomena is a qualitative indication that the negative charge of the incoming ligand lowers the energy of the $\pi \rightarrow \pi^*$ transitions in the porphine macrocycle [1].

The values of the stability constants for the different ligands are presented in Table II. These values are in the order pyridine > NCS^- > $Mo(CN)_8^{3-}$ > $W(CN)_8^{3-}$ > $Fe(CN)_6^{3-}$ > $Co(CN)_6^{3-}$ > I^- > Br^- > Cl^-. The order for the cyano complexes is what would be expected since the M–C bond strength order should be the reverse.

Since the reactions of the cyano complexes with $CoP(H_2O)_2^{5+}$ show no deviation from second-order kinetics, there is no kinetic evidence for an intermediate. The reactions thus probably occur by an I_d stoichiometric mechanism. A comparison of the stability constants (Table II) give an indication of the mode of activation. The stability constants vary by a factor of about 10^7 while the rate constants (k_1) vary by only a factor of 40. This is clearly indicative of a dissociative activation since the reaction rate is not sensitive to the incoming ligand, but very sensitive to the leaving group. If a dissociative mode of activation is operative any difference in K_1 (for the anation reactions of $CoP(H_2O)_2^{5+}$ as a factor 10^7) should be due to differences in k_{-1} since k_1 is not sensitive to the incoming group (for a dissociative activation) and can be considered as relatively constant. From the relationship $K_1 = k_1/k_{-1}$ it follows therefore that $\log k_{-1} = -\log K_1 + \log k_1$ for a dissociative activation so that a plot of $\log k_{-1}$ *versus* $-\log K_1$ for the anation reactions with various ligands should be linear with a slope of 1. This linear relationship (shown in Fig. 2) is thus indicative of an I_d mechanism.

When the rate constants for the anation reactions of $Co(NH_3)_5(H_2O)^{3+}$ and $CoP(H_2O)_2^{5+}$ are compared, it is clear that the porphine exhibits a large *cis*-labilizing effect upon the cobalt(III). This labilization effect of the porphine may be due to the ability of the electron rich porphine to donate electron density to the cobalt(III) ion making it more like cobalt(II) and stabilizes a five-coordinate intermediate during the course of the substitution reactions.

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