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NOTES

Exchange reactions of transition metal ions and labile cadmium porphyrins

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Electrophilic exchange reactions of one metal ion for another which is coordinated in a metalloporphyrin molecule eqn (1)

$$M_A + M_B\text{–}P \longrightarrow M_A\text{–}P + M_B \qquad (1)$$

have usually been done under conditions in which only a limited amount of kinetically derived information could be obtained[1–5]. The earliest product identification studies in pyridine media[6] established the types of coordinated metals that could be most readily replaced, and related kinetic work for the most part indicated rate laws first order in each reactant[1, 3]. The finding that many such exchange reactions in pyridine were faster than the related metal ion/free base porphyrin reactions ($M_A/H_2\text{–}P$) indicated that a dissociatively formed free base porphyrin was not a reaction intermediate, in agreement with spectral analysis during the course of the reaction[1, 3]. Studies of the Cu/Zn–P process in water where $H_2\text{–}P$ has a more plausible existence, were also interpreted in an S_E2 framework[2, 4]. Such Zn/Cd–P reactions studied at ambient temperatures in pyridine water media[3], where destruction of the macrocycle was not competitive with the exchange process[2] showed isokinetic behavior, where above the isokinetic temperature, the more basic the porphyrin, the faster the metal exchange. This was similar to the results of the related acid catalyzed metal ion solvolysis reactions (H^+/Zn–P), where bond making was more important than bond breaking[7]. The exchange reaction investigations of metal ions with metallo-*N*-methylporphyrins, where the central *N*-methyl group presumably blocks the distal side of the porphyrin to metal ion coordination, indicated that in normal metalloporphyrins, the entering and leaving metal ions could be on the same, or opposite sides of the porphyrin plane.

The majority of the exchange reactions have been done in nonaqueous media due to solubility limitations, and under such conditions the nature of the metal ion reactants is uncertain. Also the work with water soluble porphyrins has heretofore focused on the Cu/Zn–P reactions, using substitution inert zinc porphyrins. We report a kinetic study of the exchange reactions of Ni^{2+}, Co^{2+} and Zn^{2+} with cadmium tetrakis (*N*-methyl-4-pyridyl) porphyrin and cadmium tetrakis(4-sulfonatophenyl)porphyrin, (Cd–TMPyP(4) and Cd–$TPPS_4$ respectively), in aqueous solution. Such cadmium porphyrins are labile to cadmium exchange under the reaction conditions, and as such, allow a fuller development of the exchange rate law. Observations are also made on mercury porphyrin exchange reactions.

EXPERIMENTAL

The exchange reactions, followed spectrophotometrically, were run at 25°C, $I = 0.2$ ($NaNO_3$), in the presence of 2.5×10^{-2} M Pipes buffer. The metal ions were analyzed by EDTA titrations. The tosylate form to H_2–TMPyP(4) was converted into its nitrate salt by ion exchange methods, and the sodium salt of $TPPS_4$ was used for the kinetic studies. The porphyrins were obtained from Man-Win Chemicals, Washington, DC.

The equilibrium constants for the formation reactions (eqn 2):

$$Cd^{2+} + H_2\text{–}P = Cd\text{–}P + 2H^+ \quad K_{Cd} \qquad (2)$$

are known from mass law studies[9]. In the presence of Co^{2+}, the absorption bands of Cd–TMPyP(4) disappear, with the formation of those due to Co–TMPyP(4). Isosbestic points are found at 670,585 and 475 nm, indicating that Cd–P and Co–P are the major absorbing species. Two pathways were considered for the formation of the cobalt porphyrins:

$$Co^{2+} + H_2\text{–}P \longrightarrow Co\text{–}P + 2H^+ \quad k_1 \qquad (3)$$

$$Co^{2+} + Cd\text{–}P \longrightarrow Co\text{–}P + Cd^{2+} \quad k_2. \qquad (4)$$

The observed specific first order rate constant ($k_{obs}/(Co^{2+})$) should be of the form:

$$k_{obs}/(Co^{2+}) = [k_1(H^+)^2 + k_2K_{Cd}(Cd^{2+})]/[K_{Cd}(Cd^{2+}) + (H^+)^2]. \qquad (5)$$

Since it was demonstrated that the metal/free base porphyrin reaction (eqn 3) was substantially slower than the exchange pathway (eqn 4), the k_1 term was neglected, and eqn (5) can be rearranged into the following form:

$$[(Co^{2+})/k_{obs}] = (1/k_2K_{Cd})[(H^+)^2/(Cd^{2+})] + (k_2)^{-1}. \qquad (6)$$

Under pseudo-first order conditions, with an excess of metal ion to total porphyrin, the exchange reactions were found to be first order in porphyrin, with k_{obs} independent of total porphyrin concentration. In agreement with eqn (6), the reactions were first order in cobalt, and the specific rate was independent of cadmium concentration at cadmium ion levels where the porphyrin was almost exclusively in the Cd–P form. Figure 1 shows the linear relationship between $[(Co^{2+})/k_{obs}]$ and $[(H^+)^2/(Cd^{2+})]$ for TMPyP(4). It was found that $k_2 = 0.8\ M^{-1}\ s^{-1}$ and $K_{Cd} = 2.6 \times 10^{-8}$ M in unbuffered solution in satisfactory agreement with the K_{Cd} value of 2×10^{-8} M found from independent equilibrium studies[9] on Cd–TMPyP(4).

The majority of the exchange reactions were run at pH 6.5, under conditions such that the second term in eqn (2) was small in comparison to k_2^{-1} (saturation Cd–P conditions). The corresponding metal ion incorporation reactions into the free base porphyrins were run at the same pH, and the results are listed in Table 1.

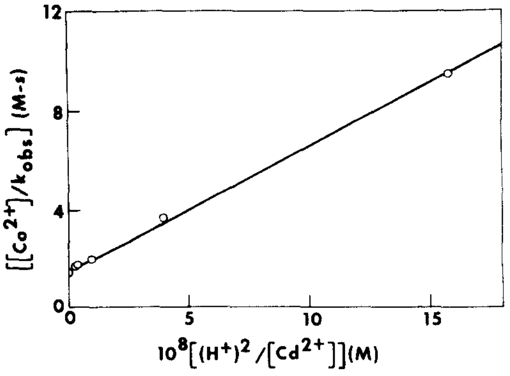

Fig. 1. Graph of $[(Co^{2+})/k_{obs}]$ vs $[(H^+)^2/(Cd^{2+})]$ for the reaction of Co^{2+} with Cd–TMPyP(4). See eqn (6). $I = 0.2$ ($NaNO_3$), 25°C, unbuffered solutions.

Table 1. Cadmium porphyrin—metal ion exchange rate data, 25°C, I = 0.2 ($NaNO_3$)

M^{2+}	M^{2+} / H_2-P k_1 ($M^{-1}s^{-1}$)[a]	M^{2+} / Cd-P k_2($M^{-1}s^{-1}$)	$\frac{k_2\ (M^{2+}\ /\ Cd\text{-}P)}{k_1\ (M^{2+}\ /\ H_2\text{-}P)}$	PORPHYRIN[b]
Zn^{2+}	2.7×10^{-1}	7.4×10^{1}	274	TMPyP(4)
Co^{2+}	6.0×10^{-3}	5.4×10^{-1}	90	TMPyP(4)
Zn^{2+}	1.0	2.3×10^{3}	2300	$TPPS_4$
Co^{2+}	5.2×10^{-2}	1.2×10^{1}	230	$TPPS_4$
Ni^{2+}	5.0×10^{-5}	1.8×10^{-2}	364	$TPPS_4$

a. pH = 6.5, 2.5×10^{-2} M Pipes buffer

b. TMPyP(4) is tetrakis(N-methyl-4-pyridyl)porphyrin, and $TPPS_4$ is tetrakis(4-sulfonatophenyl)porphyrin

DISCUSSION

The fully developed rate law for the reactions of the labile cadmium porphyrins with metal ions again[1-5] indicates that predissociation of the cadmium porphyrins into cadmium ions and porphyrin fragments does not occur; the activated complex contains both the entering and departing metal ions, and the porphyrin. The cadmium ion catalyzed metal ion incorporation reactions are from 90 to 2000 times faster than the reactions of the corresponding metals with the free base porphyrins. The exchange reaction rates parallel the water exchange rates of the entering metal ions, $Zn^{2+} > Co^{2+} > Ni^{2+}$, and such was shown before[10, 11] for the metalation of the free base porphyrins themselves. In addition, the exchange and incorporation reactions of the formally tetranegatively charged TPPS, are faster than those of the tetrapositively charged TMPyP(4) at the stated ionic strength.

The free base/metal ion incorporation reactions have been analyzed[10] in terms of three major steps: an initial outer sphere complex formation between the metal ion and the porphyrin, a porphyrin deformation step to position the central lone pair electrons in bonding positions, and a rate determining water loss from the metal ion and proton from the central porphyrin nitrogen atoms. The exchange reactions can be analyzed in a similar fashion. The M/Cd-$TPPS_4$ reactions might be faster than those of M/Cd-TMPyP(4) due partially to an electrostatically more favorable outer sphere equilibrium formation constant for the $TPPS_4$ reactants. However, $TPPS_4$ reactions are generally less sensitive to ionic strength effects than those of TMPyP(4), and valid comparisons[11] based simply on charge type cannot be readily made[12]. The green colors of the Cd-P complexes in solution, as has been postulated[13] for the green porphyrin di-cations (H_4-P^{2+}), could indicate a higher degree of porphyrin nucleus deformation in the cadmium porphyrins than found in the metal free, free base porphyrins. While the deformed porphyrin di-acids are non-reactive towards metal ions due to the lack of vacant lone pair coordination positions and electrostatic repulsion at the reaction site, such nucleus deformation would facilitate the Cd-P reactions. The necessity for desolvation of the reactant metal ions rationalizes the rate dependence on the replacing metal ion type. The rates of the exchange reactions also depend in many cases on the ion being replaced. Such exchange rates are faster than found for the free base porphyrins with cadmium (and mercury) porphyrins, but slower with more inert metal ions as found in the Cu/Zn-TMPyP(4) system[2].

The present study does not indicate whether both entering and leaving metals are on the same or opposite sides of the porphyrin plane. In an attempt to clarify this ambiguity, we attempted to study the exchange reactions of Zn^{2+} and Co^{2+} with mercury porphyrins, which presumably form, along with other species[14], trans coordinated Hg-P-Hg derivatives[15]. Unfortunately, the system M^{2+}/Hg/TMPyP(4) proved to be extremely complicated. No reasonable interpretations could be made of the results of several spectrophotometric titrations of H_2-TMPyP(4) with $Hg(NO_3)_2$, which in all cases lacked well defined isosbestic points. The low porphyrin levels studied (*ca.* 10^{-7} M) due to the high affinity of this porphyrin for mercury ions made trace metal contamination an extremely troublesome factor. In addition, precipitation was found with many buffer systems, and the kinetic results obtained were often not reproducible. Other workers have had similar problems with different porphyrin types[16]. However, certain conclusions did emerge. The green mercury porphyrins were more stable to acid solvolysis by several orders of magnitude than their Cd-P counterparts, and such mercury porphyrins could be transformed into cadmium porphyrins at high cadmium levels. The kinetics of the Zn^{2+} or Co^{2+} exchange reactions with the mercury porphyrins were always first order in porphyrin, and the replacing metal ion. In many cases, at constant pH, linear plots of $[(Zn^{2+})/k_{obs}]$ vs $(Hg^{2+})^{-2}$ were obtained, indicating a rate law of the form $[k_{obs}/(Zn^{2+})] = (Hg^{2+})^2/[a + b(Hg^{2+})^2]$, where k, a and b are constants. While rate saturation with hig concentrations of mercury was always found, the pH dependence of the reactions was never satisfactorily resolved. With saturation mercury levels (*ca.* 10^{-3} M), the saturation rates did not strongly depend on pH from pH 4 to 7. The saturation rates tended to decrease and then increase below pH 4, in the region of the pK_a of Hg(II).

The second order dependence of the rate on mercury concentration could indicate the existence of Hg_2-TMPyP(4), and Hg_2-$TPPS_4$ has been shown to form by mass law[15] analysis. The fact that the limiting metal ion-mercury porphyrin exchange rates showed no mercury inhibition could be evidence that one side of the porphyrin plane need not be vacant before attack of the entering metal ion. The limiting rate of the Co^{2+}/mercury/TMPyP(4) reaction was *ca.* 0.3 $M^{-1}\,s^{-1}$ at pH 4.2, and that of Zn^{2+} with the same mercury porphyrin was *ca.* 200 $M^{-1}\,s^{-1}$. Both rates are faster than the incorporation of the same metals into the free base porphyrins. More importantly, the limiting exchange rates of the mercury porphyrin are similar to the limiting exchange rates of the same metal ions with the more well defined cadmium porphyrin (Table 1). While the mercury porphyrins might be binuclear, and are definitely more stable to proton hydrolysis than their cadmium counterparts, the exchange rate similarity is classic evidence that factors that lead to bond formation between the entering metal ion and labile metalated porphyrins, are relatively more important than factors that facilitate bond breaking between the porphyrin and the departing cadmium or mercury ions. These reactions appear to be associatively activated S_E2 processes.

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Phenylmercury(II) compounds—III. Pyridine and quinoline carboxylic acid compounds

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We report herein a series of hitherto unknown phenylmercury(II) compounds with pyridine- and quinoline-carboxylic acids. In some of these compounds the bridging and chelating properties of the ligands are displayed.

EXPERIMENTAL

Syntheses of [$C_6H_5 \cdot Hg(Pic)$], [$C_6H_5 \cdot Hg(Nic)$], [$C_6H_5 \cdot Hg(Quin)$]. 0.002 moles of phenylmercuric acetate[1] were dissolved in hot ethanol (~25 ml) and filtered into an ethanolic solution (~10 ml) of 0.002 mole of the ligand (picolinic acid, PicH; nicolinic acid, NicH; quinaldinic acid, Quin H) concerned. The mixture was refluxed for half an hour and the complex obtained on concentrating the solution to ~15–20 ml. The products were recrystallised from ethanol.

The compounds [$C_6H_5 \cdot Hg(Pic)$] and [$C_6H_5 \cdot Hg(Quin)$] were also obtained from basic phenylmercuric nitrate [$C_6H_5 \cdot Hg \cdot OH \cdot Hg \cdot C_6H_5$]$NO_3$ by reacting with the ligands concerned in the appropriate molar ratio.

Synthesis of [$C_6H_5 \cdot Hg(Pic)(PicH)$]. This compound was obtained by reacting picolinic acid with phenylmercuric acetate or basic phenylmercuric nitrate in ethanol in appropriate ratios.

Synthesis of [$C_6H_5 \cdot Hg(Nic)Hg \cdot C_6H_5$]$NO_3$. 0.001 mole of basic phenylmercuric nitrate was dissolved in hot ethanol (~150 ml) and filtered into an ethanolic solution (~10 ml) of 0.001 mole of nicotinic acid. The mixture was refluxed for 0.5 hr and concentrated on a steam-bath to about 15–20 ml. On cooling the compound separeted as glistening crystals.

Synthesis of [$C_6H_5 \cdot Hg(Dipic)\ Hg \cdot C_6H_5$]. 0.001 mole of basic phenylmercuric nitrate was dissolved in 1 : 1 ethanol–water mixture (~120 ml) and to this solution 0.001 mole of dipicolinic acid dissolved in water (~10 ml) was added. After refluxing for an hour the solution was concentrated to ~60 ml and then cooled. The glistening crystals were filtered and digested with hot water for 0.5 hr to remove any unreacted dipicolinic acid. The crystals were collected and finally washed with ethanol.

This compound was also obtained by the reaction of phenylmercuric acetate with dipicolinic acid in 2 : 1 molar ratio.

Elemental analyses and physical measurements. Carbon and hydrogen analyses were performed by M/s. Alfred Bernhardt Micro-analytische Laboratorium, West Germany. Nitrogen was estimated by Duma's method and mercury was determined by following our own procedure[2] (Table 1). Conductance was measured with a Phillips PR 9500 Bridge. IR spectra were run in C.D.R.I. Lucknow.

RESULTS AND DISCUSSION

Structural conclusions had to be made on the basis of elemental analyses, IR spectra and conductance data. Low solubility of the samples in suitable solvents excluded PMR spectra and evaluation of molecular weight.

A. [$C_6H_5 \cdot Hg(Pic)$], [$C_6H_5 \cdot Hg(Quin)$] *and* [$C_6H_5 \cdot Hg(Nic)$]

All the three complexes show very low molar conductance values (3.5–4.6 ohm^{-1}cm^{2}mole^{-1}) in methanol indicating their non-electrolytic nature.

The asymmetric stretching mode of COO^- group of picolinic acid at 1720 cm^{-1} is shifted to 1600 cm^{-1} in the complex. A small shift of the pyridine C=C and C=N stretch at 1570 cm^{-1} in the free ligand to 1580 cm^{-1} in the complex is observed. Strong bands at ~450 and ~400 cm^{-1} are attributed to Hg–O and Hg–N stretches[3, 4]. The Hg–C stretching frequency is seen at ~730 cm^{-1}[5]. All these indicate either a three-coordinate monomeric [$C_6H_5 \cdot Hg(Pic)$] or a four-coordinate oxo-bridged dimeric [$C_6H_5 \cdot Hg(Pic)$]$_2$.

IR spectral bands of the quinaldinato phenylmercury(II) show features which are quite comparable to those of the picolinato complex. The structure of this complex is likely to be analogous to that of the picolinato complex.

The asymmetric mode of the COO group at 1700 cm^{-1} in nicotinic acid is shifted to 1590 cm^{-1} in the complex suggesting bonding of the COO^- anion to phynylmercury(II). The pyridine nitrogen is not involved in coordination since there is no upward shift of the pyridine (coupled) C=C and C=N stretch[5–8] in the complex. This argument is confirmed by the absence of the ν_{Hg-N}