refluxing hexane was reported, but low yields[9] were obtained for large-scale reactions.[4] However, we have found the yields to be vastly improved by using **1** instead of the MeCN analogue. A large-scale reaction between **1** and cycloheptatriene in refluxing heptane for 64 h, followed by isolation essentially according to the published procedure, gave a 49% yield of $W(CO)_3(cht)$. An even more remarkable improvement was found for the analogous preparation[4] of $W(CO)_2(chd)_2$. Whereas we obtained only barely detectable amounts of this complex using $W(CO)_3(NCMe)_3$, a 51% yield resulted from **1**. The higher solubility of **1** undoubtedly is a key factor in these reactions, although EtCN may also be more readily displaced than MeCN. The reaction of $W(CO)_3(NCPr)_3$ with cycloheptatriene was more rapid than that of the NCEt analogue and also gave favorable yields, although its lower melting point was disadvantageous (see Experimental Section). As a final example of the propitious features of **1**, an 81% yield of *mer,trans*-$W(CO)_3(PCy_3)_2(SO_2)$[6] was obtained from **1** upon sequential addition of PCy_3 and SO_2 in acetone at room temperature, as opposed to 50% from $W(CO)_3(NCMe)_3$.

In conclusion, surprisingly few complexes containing alkyl cyanides other than MeCN have been reported. The results reported herein indicate that the use of the higher homologues of MeCN as ligands in transition-metal chemistry should be encouraged and may lead to complexes with properties significantly different from and more advantageous than those of MeCN complexes.

Registry No. 1, 83732-33-6; *fac*-$W(CO)_3(NCPr)_3$, 83732-34-7; $W(CO)_6$, 14040-11-0; $W(CO)_3(cht)$, 12128-81-3; $W(CO)_2(chd)_2$, 12131-26-9; *mer,trans*-$W(CO)_3(PCy_3)_2(SO_2)$, 73682-35-6.

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[9] Although the reported yield for a 60-mmol scale reaction was 33%, we and others[10] obtained less than half this amount, even when heptane was used as solvent or when long reaction times were used.

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Contribution from the Department of Chemistry,
Howard University, Washington, DC 20059

Full pH Study of the Incorporation of Zinc(II) into Uroporphyrin I

Abdullah Shamim and Peter Hambright*

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The mechanisms of metal ion incorporation into porphyrin molecules have been studied by many workers.[1-3] While it seems apparent that different forms of the same metal exhibit differing reactivities,[4] such conclusions arise from work on various porphyrins where kinetics taken over a limited pH range have been used to assign relative rates. For example, literature data[5-8] might indicate that, for zinc, the incorporation order is $Zn(OH)^+ > Zn^{2+} > Zn(OH)_2(sol) > Zn(OH)_3^- > Zn(OH)_4^{2-}$. A careful stability constant study by Sekine,[9] however, showed the total absence of $Zn(OH)^+$ and the low concentration of $Zn(OH)_2(sol)$ at any pH in zinc(II) solutions. The reactivity sequence of zinc(II) forms is of some interest as the heavy metal lead acts as a poison in the body and blocks the insertion of Fe^{2+} into protoporphyrin IX, whereupon Zn^{II}(Proto-IX) is formed. By fluorometric analysis, the amount of Zn^{II}(Proto) in the blood is proportional to the amount of lead present.[10] Similarly, the explanation of the nature of the porphyrin N–H/N–D isotope effect on the rate of porphyrin metalation by zinc(II) in DMF was based on postulated $Zn(DMF)_5(OH)^+/Zn(DMF)_5(OD)^+$ reactants.[11]

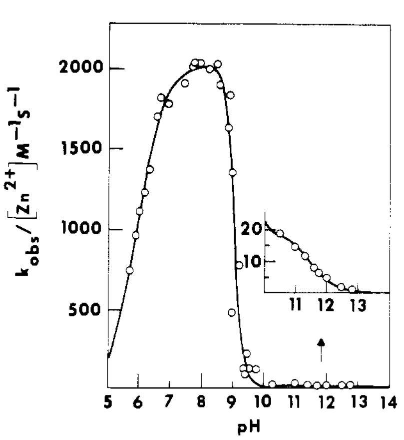

Figure 1. pH profile of the specific rates of zinc(II) perchlorate reactions with uroporphyrin I at 25 °C and $I = 0.1$ ($NaClO_4/NaOH$). Circles are the experimental points, and the solid line was calculated from eq 5.

We report the kinetics of Zn(II) incorporation into uroporphyrin I from pH 5.5 to 13 and the ionic strength dependence of the Zn^{2+}/porphyrin reactions using porphyrins of different peripheral charges. The results indicate that Zn^{2+} and $Zn(OH)_3^-$ are the major substrates for the free-base form of the porphyrin over the entire pH range.

Experimental Section

The kinetics of zinc perchlorate incorporation into uroporphyrin I were followed spectrophotometrically in the Soret region with use of total porphyrin concentrations of ca. 5×10^{-8} M at $I = 0.1$ ($NaOH/NaClO_4$) and 25 °C. The solutions were buffered with[12] 10^{-3} M Hepes, Pipes, Mes, and Tris from pH 5 to 9.5. Zn^{II}(uro) has bands at 574, 538, and 408 nm, with extinction coefficients of 1.4×10^4, 1.8×10^4, and 3.4×10^5 M^{-1} cm^{-1}, based on $\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1} (552 nm, 1 M HCl) for uroporphyrin I.[13] Under pseudo-first-order conditions, the reactions were first order in porphyrin over 3 half-lives and first order in zinc from 2×10^{-4} to 2×10^{-5} M at pH 12 and from 1×10^{-5} to 2×10^{-6} M at pH 7.6. At constant pH, the observed rate constant, k_{obsd}, was independent of buffer identity and concentration between 10^{-3} and 10^{-4} M, and duplicate kinetic runs agreed to within 8%.

Results

Figure 1 shows the pH profile of zinc incorporation into uroporphyrin I. As one goes from pH 5.5 to 8, the specific rates $k_{obsd}/[Zn]$ increase and reach a plateau. In this region, the reactions considered[14] were

$$H_3\text{-}P^+ = H_2\text{-}P + H^+ \quad K_e \qquad (1)$$

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$$Zn^{2+} + H_2\text{-}P \rightarrow Zn\text{-}P + 2H^+ \quad k_{Zn} \qquad (2)$$

The porphyrin monocation $H_3\text{-}P^+$ is in equilibrium with the free base $H_2\text{-}P$, and only $H_2\text{-}P$ reacts with Zn^{2+}. The observed rate law is $k_{obsd}/[Zn] = k_{Zn}K_e/[(H^+) + K_e]$. A plot of $([Zn]/k_{obsd})$ vs. $[H^+]$ was linear, giving $pK_e = 6.0 \pm 0.1$ and $k_{Zn} = (2.0 \pm 0.2) \times 10^3$ M^{-1} s^{-1}. The equilibrium constant K_e was determined independently by a spectrophotometric titration in the absence on zinc, and the pK_e was also found equal to 6.0 ± 0.1.

The insert in Figure 1 shows that $k_{obsd}/[Zn]$ decreases from ca. 15 M^{-1} s^{-1} at pH 11 to ca. 0 at pH 13. By analogy with previous work,[6,8] the reactions considered in this pH range are

$$Zn(OH)_3^- + OH^- = Zn(OH)_4^{2-} \quad K_3 \qquad (3)$$

$$H_2\text{-}P + Zn(OH)_3^- \rightarrow Zn\text{-}P + OH^- + 2H_2O \quad k_{Zn(OH)_3^-} \qquad (4)$$

Hence, $k_{obsd}/[Zn] = k_{Zn(OH)_3^-}/(1 + K_3[OH^-])$. A graph of $([Zn]/k_{obsd})$ vs. $[OH^-]$ was linear, with $k_{Zn(OH)_3^-} = 20 \pm 2$ M^{-1} s^{-1} and $K_3 = (3.6 \pm 0.4) \times 10^2$ M^{-1}.

From the data of Sekine[9] at $I = 0.1$, $\beta_4 = [Zn(OH)_4^{2-}][H^+]^4/[Zn^{2+}] = 2.5 \times 10^{-39}$. The ratio $\beta_4/(\beta_3K_W) = K_3$, and with our K_3, $\beta_3 = 7.0 \times 10^{-28}$. $Zn(OH)_2$(sol) was found not to exceed 5% of the total zinc concentration at any pH,[9] and thus we neglect β_2. At low zinc levels, Sekine's hydrolysis study gave no indication of the existence of $Zn(OH)^+$, and we also assume $\beta_1 = 0$. With Zn^{2+} and $Zn(OH)_3^-$, the major reactants toward $H_2\text{-}P$, the full incorporation rate law is thus

$$k_{obsd}/[Zn] = K_e/(K_e + [H^+]) \times [k_{Zn} + k_{Zn(OH)_3^-}\beta_3[H^+]^{-3}]/(1 + \beta_3[H^+]^{-3} + \beta_4[H^+]^{-4}) \qquad (5)$$

Figure 1 shows excellent agreement between the observed specific rates (circles), and those calculated from eq 5 (solid line) over the entire pH range studied.

The ionic strength dependence of Zn^{2+} incorporation into the octanegatively charged uroporphyrin I, the tetranegative coproporphyrin III, and the dinegative deuteroporphyrin IX were studied at pH 7.5 at ca. 10^{-7} M porphyrin levels. The specific rates increased with a decrease in ionic strength (I), and Figure 2 shows the linear relationship between log $(k_{obsd}/[Zn])$ vs. $I^{1/2}/(1 + I_{1/2})$ of the form

$$\log (k_{obsd}/[Zn]) = \log (k_{obsd}/[Zn])_{I=0} + A(I^{1/2}/(1 + I^{1/2})) \qquad (6)$$

For Uro-I, $(k_{obsd}/[Zn])_{I=0} = 36\,000$ M^{-1} s^{-1} and $A = -5.4$, for Copro-III, the respective values are 1600 M^{-1} s^{-1} and −3.4, and for Deutero-IX, the respective values are 60 M^{-1} s^{-1} and −0.8.

Discussion

Uroporphyrin I was chosen for this study because it is a β-pyrrole-substituted naturally occurring porphyrin (as opposed to meso-substituted synthetic porphyrins) that is monomeric[15] at $I = 0.1$. It exhibits favorably high specific rates for zinc incorporation, a convenient feature since zinc at ca. 10^{-6} M levels must be used to avoid $Zn(OH)_2$ precipitation in the weakly basic region. Uro-I is insoluble between pH 5 and 2 due to protonation of the carboxylic acid groups and redissolves below pH 1 as the unreactive dication form $H_4\text{-}P^{2+}$.

As found for nine other water-soluble porphyrins,[14,16] the monocation, $H_3\text{-}P^+$, protonated at the central nitrogen sites is unreactive, and only the free base $H_2\text{-}P$ Uro-I reacts with zinc. Irrespective of how they arise, the activated complex for metal incorporation into porphyrins contains a metal species and the free-base porphyrin, as found in this study. One would predict that, at low zinc levels, $Zn(OH)_4^{2-}$, $Zn(OH)_3^-$, $Zn(OH)_2$(sol), $Zn(OH)^+$, and Zn^{2+} would form as the pH decreases from 14. Above pH 11, several groups[2,6,8] have found that $Zn(OH)_3^-$ is more reactive than $Zn(OH)_4^{2-}$. While the incorporation rate into Uro-I approaches zero above pH 13, where $[Zn] \approx [Zn(OH)_4^{2-}]$, we can never prove that the latter does not react with Uro-I. Our data suggest that $Zn(OH)_4^{2-}$ is at least 30-fold less reactive than $Zn(OH)_3^-$ (20 M^{-1} s^{-1}), making $k_{Zn(OH)_4^{2-}} \ll 1$ M^{-1} s^{-1}. Zn^{2+} incorporates 100 times faster ($k_{Zn} = 2000$ M^{-1} s^{-1}) than $Zn(OH)_3^-$ into Uro-I. $Zn(OH)_2$(sol) never reaches more than 5% of the total zinc concentration,[9] and our rate data can be adequately explained without including a $Zn(OH)_2$ term.

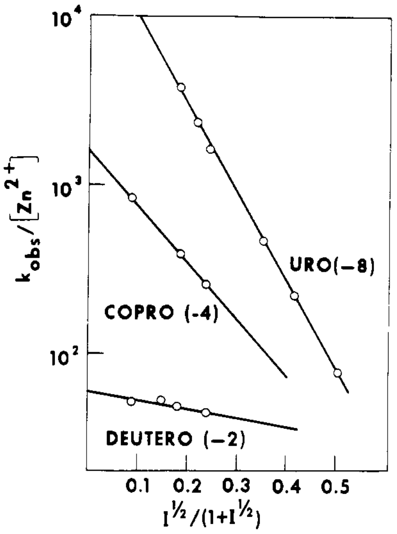

Figure 2. Ionic strength dependence of the incorporation of Zn^{2+} into uroporphyrin I, coproporphyrin III, and deuteroporphyrin IX at 25 °C and pH 7.5.

pK_a values of ca. 9 for the $[Zn(OH)^+][H^+]/[Zn^{2+}]$ equilibria derived from potentiometric and solubility data have been reported.[18,19] Sekine[9] studied the distribution of radioactive ^{65}Zn between water and benzene containing a long chain amine, where the benzene phase was assumed to extract only uncharged $Zn(OH)_2$. The distribution coefficient as a function of pH and Zn was used to calculate hydrolysis constants. Within experimental accuracy, Sekine found the "remarkable" result that $Zn(OH)^+$ is present in water in negligible amounts. One critical compilation of stability constants accepts his conclusions,[17] while another[18] simply references his work but accepts the existence of $Zn(OH)^+$ on the basis of more "straightforward" solubility measurements. Our rather complicated pH dependence of the observed rates can be explained without invoking the $Zn(OH)^+$ species. A value of $\beta_4 = 10^{-38.6}$ from Sekine[9], ($10^{-38.3}$ from Gubelli and Ste-Marie[19]) was thus the only literature equilibrium constant used in eq 5.

Previous metalation work[5,7] under different conditions has indicated that $Zn(OH)^+$ is about 50 times more reactive than Zn^{2+}. The relatively small rate variations with pH noted in such studies, at pH values and ranges well removed from the assumed pK_a can probably be attributed to causes other than a high $Zn(OH)^+$ reactivity. One such factor might be the marked ionic strength dependence of the incorporation rate. As expected for the positive Zn^{2+}, a decrease in ionic strength

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leads to more rapid metalation reactions with porphyrins having negatively charged substituent groups, with the largest rate enhancements found for the most highly charged substrate. Thus, Uro-I has k_{Zn} = 75 M^{-1} s^{-1} at I = 1.0, 2000 M^{-1} s^{-1} at I = 0.1, and 36 000 M^{-1}/s^{-1} at I = 0. The formally dinegative Deutero-IX varies only from 60 M^{-1} s^{-1} at I = 0 to 25 M^{-1} s^{-1} at I = 1.0. At high ionic strengths, the observed Zn^{2+} rates approach one another, and such ionic leveling effects must be taken into account before porphyrin structure reactivity data can be developed. Such effects perhaps account for the observation that six porphyrins of varying basicity[20,21] exhibit similar incorporation rates toward $Zn(OH)_3^-$ at high ionic strengths.[8]

At I = 0, the formally octa-, tetra-, and dinegative porphyrins react with Zn^{2+} in the order 36 000:1600:60, in the ratio 600:25:1, and a similar order (380:27:1) was found for the same porphyrin charge types by Kassner and Wang[22] for Fe(II) incorporation in a buffered water/pyridine mixture. They demonstrated that the activation energy was constant, and the activation entropy term was responsible for the variation of rate with porphyrin charge, at constant ionic strength. If "A" in eq 6 can be considered equal to Z_aZ_b, the formally 8− porphyrin acts an an effective 2.7− charged ion, the 4− porphyrin as 1.7−, and the 2− derivative as a 0.4− species. Similar lowered effective charge behavior is also found for positively charged porphyrins.[7]

In summary, we report the first full pH and ionic strength profile of a metal–porphyrin incorporation reaction in aqueous solution. Such a rate profile can be explained in terms of the free-base form of the porphyrin reacting with zinc in the order $Zn^{2+} > Zn(OH)_3^- >> Zn(OH)_4^{2-}$. This order may in part reflect electrostatic stabilization of metal–negatively charged porphyrin outer-sphere and activated complexes. In contrast to the case for negative porphyrins, positive porphyrins show incorporation rate increases with increases in ionic strength.[5] However, possible specific-anion catalysis associated with the porphyrin[4] or metal[1] or both complicate interpretations. With uncharged porphyrins in DMF, the metalation rates are fairly independent of ionic strength[1] and show isokinetic behavior,[2] and the overall porphyrin structure becomes influential. For Cu^{2+} in DMF, $k_{Cu} \approx 3 \times 10^2$ M^{-1} s^{-1} for *N*-methylporphyrins, ca. 10^{-2} M^{-1} s^{-1} for tetraphenylporphyrin,[1] ca. 10^{-4} M^{-1} s^{-1} for the "picket fence" porphyrin,[23] and ca. 10^{-5} M^{-1} s^{-1} for the "capped" porphyrin, a factor of over 10^7 at 25 °C. The rate-determining step in such reactions has been postulated to involve a deformed porphyrin with simultaneous loss of the central proton from the porphyrin and solvent from the metal ion.[14]

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Registry No. Zn, 7440-66-6; URO, 607-14-7; COPRO, 14643-66-4; DEUTERO, 448-65-7.

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Communications

Unusual Photobehavior of *trans*-Dicyano(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate[1]

Sir:

We report here the results of a photostudy of the Cr(III) complex *trans*-$[Cr(cyclam)(CN)_2]ClO_4$, where cyclam is the macrocyclic tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane. The photobehavior observed in room-temperature solution is in marked contrast to that normally displayed by Cr(III) complexes. The compound shows no discernible photochemical reactivity and exhibits an intense, long-lived (335-μs) $^2E_g \rightarrow {}^4B_{1g}$ phosphorescence. Furthermore, deuteration of the cyclam N–H protons results in a marked increase in the intensity and lifetime of the emission. This *solution* behavior is reminescent of that observed for most Cr(III) complexes at liquid-N_2 temperature[2,3] and for several *solid-state* Cr(III) systems at room temperature.[4] The details and possible significance of these observations are discussed below.

In a recent report Zinato and co-workers[5] described the photochemical behavior of *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$. This complex differs from most Cr(III) amine systems in that the axial cyanide ligands have stronger ligand field (LF) strengths than the in-plane NH_3 ligands. As a result, for the first spin-allowed quartet excited state the $^4B_{2g}$ component lies substantially lower in energy (~2500 cm^{-1}) than the ^4E_g component.[5,6] An important consequence of this energy ordering is the expectation[5,7] that photolabilization should be essentially restricted to the in-plane NH_3 positions—a prediction experimentally confirmed by Zinato and co-workers[5] (for example, on 440-nm excitation, $\phi_{NH_3} = 0.24$ and $\phi_{CN^-} < 0.005$). A more limited photochemical investigation by Kirk and Porter[8] of the analogous ethylenediamine system, *trans*-$[Cr(en)_2(CN)_2]ClO_4$, provides further experimental confirmation of this theoretical prediction for species with the $^4B_{2g}$ excited-state component lying lowest in energy. Thus, for such complexes, if amine ligand loss could also be prevented without significant alteration of the overall electronic properties, then photoreactivity might be effectively eliminated altogether.

With this latter objective in mind, we have synthesized and characterized the complex *trans*-$[Cr(cyclam)(CN)_2]ClO_4$.[9] We were hopeful that the presence of the macrocyclic ring would seriously restrict cleavage of an individual Cr–amine bond and render complete cyclam ligand loss highly improbable. LF photolysis (436 nm) was carried out on 0.001 M

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[1] Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982.

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