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Synthesis of Hydroxy-Substituted Macrocyclic Ligand Complexes of Cobalt and Isolation of a Macrocycle Precursor

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A series of macrocyclic ligand complexes of cobalt(II) having bromides in the axial position and containing one or two hydroxyl groups have been synthesized from either biacetyl or benzil and 1,3-propanediamine and 1,3-diamino-2-hydroxypropane. By adding one diamine and the diketone followed by Co(II) and the second diamine yields of the unsymmetrical macrocyclic ligands containing one hydroxyl were obtained rather than a statistical distribution of ligands containing the two diamines. A macrocycle precursor from condensation of two benzils with one 1,3-propanediamine was prepared and isolated. This precursor would only react further with a second diamine if Co(II) is present, demonstrating the template nature of the reaction.

Introduction

The synthesis of unsymmetrical tetraaza macrocycles is generally achieved by template synthesis using β-keto imines[1-6] although a novel nontemplate synthesis using the 1,2-dithiolium cation has been reported.[7,8] Few synthetic macrocycles are available containing substituents other than alkyl or arene.[9]

It is the purpose of this work to prepare a series of macrocycles based on the TIM framework[11-13] (Figure 1(a)) containing one or two hydroxyl groups. The hydroxyl group was chosen because it does not interfere with macrocycle formation and this functional group could have practical utility as a means of attaching pendant coordinating groups which could occupy one or both the axial coordination positions. This ability to attach pendant groups could be useful in preparing model structures for biological systems or catalytically active macrocycles.[14-17] Some success has been achieved in attaching pendant groups but no generally useful procedure is available.[18]

During the course of this work a novel macrocycle precursor, 1,2,8,9-tetraphenyl-3,7-diazaduohepta-2,7-diene-1,9-dione (KIM: Figure 1(g)) was isolated.

Experimental Section

Reagent grade solvents and starting materials were purchased and used without further purification. 1,3-Diamino-2-hydroxypropane (tn-2-OH) (95%) and benzil were obtained from Aldrich Chemical Co., Inc. Air-sensitive reactions were performed in Schlenk type glassware under N_2. Analyses were performed at the University of Guelph and by Chemalytics, Inc., Tempe, Ariz.

Proton magnetic resonance data are summarized in Table I and structures and proton designations are shown in Figure 1. Spectra were recorded on a Varian A-60A spectrometer. Infrared spectra were recorded on a Beckman IR5. The molecular weight determination was performed by M-H-W Laboratories, Garden City, Mich.

[Co{6,13-(OH)$_2$-2,3,9,10-Me$_4$[14]1,3,8,10-tetraeneN$_4$}Br$_2$]Br ([Co(TIM-6,13-(OH)$_2$)Br$_2$]Br). The diamine (4.5 g, 50 mmol) was added to methanol (150 mL), followed by an equimolar amount of HBr (8.15 g of 48% of aqueous HBr). The solution was stirred and degassed with N_2 for 5 min. A nitrogen atmosphere was maintained for the remainder of the reaction. Biacetyl (4.3 g, 50 mmol) was added and the reactants were stirred for 30 min. Then $Co(OAc)_2·4H_2O$ (6.23 g, 125 mmol) was added, with stirring. While stirring was continued for 3 h at room temperature, a purple Co(II) complex precipitated. After 48% HBr (19 mL) was added, air was bubbled through the solution for 30 min. The precipitated green Co(III) product was collected, washed with 5% methanolic HBr (5 mL) and ether, and air-dried. The product was recrystallized from 5% aqueous HBr and washed as before; yield 1.5 g = 10%. Anal. Calcd for $CoC_{14}H_{24}N_4O_2Br_3$: C, 29.04; H, 4.18; N, 9.68. Found: C, 28.94; H, 4.29; N, 9.79.

[Co{6,13-(OH)$_2$-2,3,9,10-Me$_4$[14]1,3,8,10-tetraeneN$_4$}Br$_2$]BF$_4$ ([Co(TIM-6,13-(OH)$_2$)Br$_2$]BF$_4$). The corresponding bromide salt (0.5 g) was dissolved in nearly boiling 5% aqueous HBr (15 mL). Addition of $NaBF_4$ (10 g) in H_2O (10 mL) precipitated the fluoroborate salt virtually quantitatively on cooling. The hexafluorophosphate salt is prepared analogously using NH_4PF_6. Anal. Calcd for $CoC_{14}H_{24}N_4O_2Br_2BF_4$: C, 28.70; H, 4.13; N, 9.56; Br, 27.28. Found: C, 28.44; H, 3.97; N, 9.54; Br, 28.33.

[Co(6-OH-2,3,9,10-Me$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br ([Co(TIM-6-OH)Br$_2$]Br). 1,3-Propanediamine (tn) (2.1 mL, 25 mmol) was added to methanol (50 mL), followed by an equimolar amount of HBr (4.2 g of 48% HBr, 25 mmol). The solution was stirred and degassed with N_2 for 5 min after which a nitrogen atmosphere was maintained. Biacetyl (4.3 g, 50 mmol) was added and the reactants were stirred for 30 min. At this time a degassed solution of tn-2-OH (2.25 g, 25 mmol) and 48% HBr (4.2 g, 25 mmol) in methanol (25 mL) was added and the reaction was again stirred for 30 min. Then $Co(OAc)_2·4H_2O$ (6.23 g, 25 mmol) was added and the reaction was stirred for 24 h under N_2, during which time a Co(II) salt precipitated. Then 48% HBr (20 mL) was added and air was bubbled through the solution for 30 min. The green Co(III) product was collected, washed three times with 5% methanolic HBr (5 mL) followed by ether, and air-dried. Recrystallization can be carried out from 5% methanolic HBr if necessary; yield 1.9 g = 13.5%. Anal. Calcd for $CoC_{14}H_{24}N_4OBr_3$: C, 29.86; H, 4.30; N, 9.95. Found: C, 29.72; H, 4.31; N, 9.88.

[Co(2,3,9,10-Ph$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br·CH$_3$OH ([Co-(Ph-TIM)Br$_2$]Br·CH$_3$OH). To 50 mL of methanol was added tn (2.59 mL, 30 mmol), followed by an equimolar amount of HBr (5.0 g of 48% HBr). The solution was stirred and degassed with N_2 for 5 min after which a nitrogen atmosphere was maintained. After heating of the solution to 60–65 °C, benzil (6.5 g, 30 mmol) was added and the reactants were stirred for 20 min after complete dissolution of the benzil. Then $Co(OAc)_2·4H_2O$ (3.85 g, 130 mmol) was added and stirring at 60–65 °C was continued for 3 days while a blue Co(II) complex precipitated. At this time 48% HBr (15 mL) was added and air was bubbled through for 30 min. The green Co(II) precipitate was collected by filtration, washed three times with 5% methanolic HBr (5 mL) and two times with ether, and air-dried; yield 3.5 g, 28%. This crude product was recrystallized (0.7 g/50 mL) twice from boiling 5% methanolic HBr and washed as before. The complex apparently precipitates with a methanol of crystallization which can be removed by evacuation at 10^{-3} Torr for 1 h or by moderate heating. Anal. Calcd for $CoC_{34}H_{32}N_4Br_3·CH_3OH$: C, 50.8; H, 4.38; N, 6.76. Found: C, 50.14; H, 4.59; N, 6.63. (Molecular weight in $CHCl_3$ was determined by osmometry to be 778 (formula weight 795).)

[Co(6,13-(OH)$_2$-2,3,9,10-Ph$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br ([Co(Ph-TIM-6,13-(OH)$_2$)Br$_2$]Br). This compound is prepared analogously to [Co(Ph-TIM)Br$_2$]Br using tn-2-OH (2.78 g) instead of tn. The blue Co(II) complex with precipitates is air stable and was collected by filtration (yield 6.1 g = 53%). Then the Co(II) complex was placed in 5% methanolic HBr (40 mL) and stirred while 30% H_2O_2 (2 mL) was added. The slurry was stirred and aerated for 10 min. The green Co(II) product was collected, washed two times with 5% methanolic HBr (5 mL) and three times with ether, and finally air-dried; yield 5.3 g = 42% based on benzil. The crude product can be recrystallized (0.5 g/400 mL) from boiling 5% methanolic HBr if necessary. Anal. Calcd for $CoC_{34}H_{32}N_4O_2Br_3$: C, 49.35; H, 3.91; N, 6.77. Found: C, 49.18; H, 4.03; N, 6.67.

[Co(6-OH-2,3,9,10-Ph$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br ([Co(Ph-TIM-6-OH)Br$_2$]Br). tn (1.3 mL) was added to methanol (50 mL), followed by an equimolar amount of HBr (2.5 g of 48% HBr). The solution was stirred and degassed with N_2 for 5 min after which a nitrogen atmosphere was maintained. After heating of the solution to 60–65 °C, benzil (6.5 g) was added and the reactants were stirred

Table I. Proton Magnetic Resonance Spectral Data[a, b]

Compd	CH_3	α	α^*	β	β^*	Ph
$[Co(TIM)Br_2]Br$	2.81 (12)	4.27 (8)		2.70 (4)		
$[Co(TIM\text{-}6\text{-}OH)Br_2]Br$	2.84 (8)	4.24 (4)	4.53 (4)	2.58 (1)	5.20 (1)	
$[Co\{TIM\text{-}6,13\text{-}(OH)_2\}Br_2]Br$	2.88 (8)		4.55 (8)		5.20 (2)	
$[Co(Ph\text{-}TIM)Br_2]Br$		4.27 (8)		2.70 (4)		7.25, 7.55 (20)
$[Co(Ph\text{-}TIM\text{-}6\text{-}OH)Br_2]Br$		4.32 (4)	4.59 (4)	2.70 (1)	5.00 (1)	7.20, 7.55 (20)
$[Co\{Ph\text{-}TIM\text{-}6,13\text{-}(OH)_2\}Br_2]Br$			4.58 (8)		5.08 (2)	7.20, 7.55 (20)
KIM[c]		3.63 (4)		2.11 (2)		7-8 (20)

[a] Spectra taken in CF_3CO_2H solutions unless otherwise stated. [b] Assignments refer to Figure 1. Chemical shifts are in ppm relative to internal Me_4Si. Relative number of protons is given in parentheses. [c] Spectrum recorded using $CDCl_3$ as solvent.

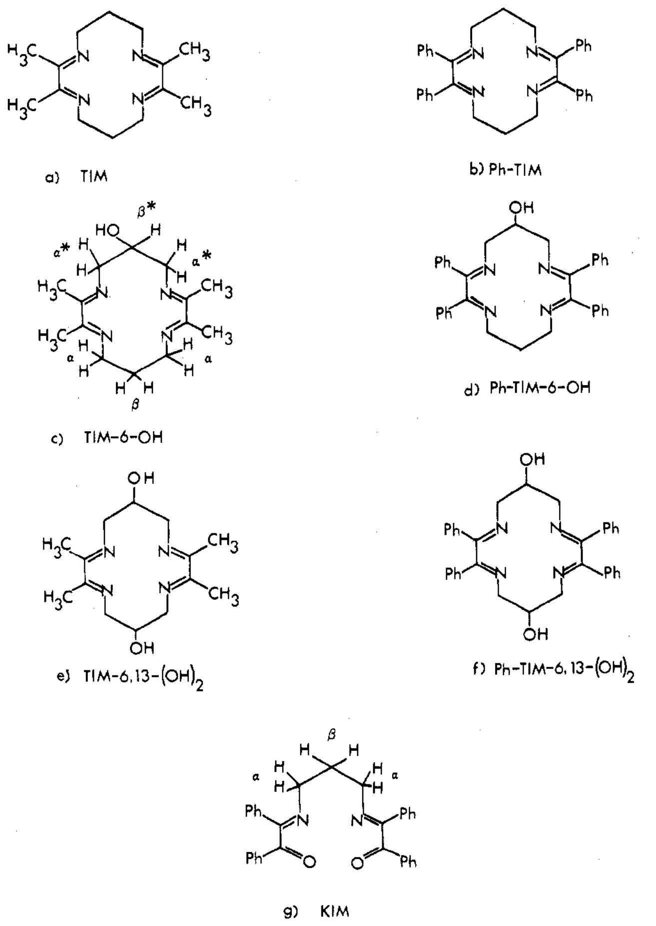

Figure 1. Structures of the macrocycles.

for 20 min after complete dissolution of the benzil. A degassed methanol (25 mL) solution of tn-2-OH (1.39 g) and 48% HBr (2.5 g) was added at this time, followed immediately by $Co(OAc)_2\cdot 4H_2O$ (3.85 g). The reaction was stirred and heated for 3 days. A blue Co(II) complex precipitated. Anal. Calcd for $CoC_{34}H_{32}N_4OBr_2$: C, 55.83; H, 4.42; N, 7.66. Found: C, 54.43; H, 4.45; N, 7.44. The Co(II) complex was collected and washed with 5% methanolic HBr. The Co(II) compound was then oxidized to the Co(III) compound using the procedure described for the Ph-TIM-6,13-$(OH)_2$ compound but the wash procedure was altered. After being washed three times with 5% methanolic HBr, the product was washed with acetone until the wash acetone was no longer green and finally with ether and air-dried; yield 2.6 g = 20.6%. Anal. Calcd for $CoC_{34}H_{32}N_4OBr_3$: C, 50.33; H, 3.98; N, 6.91. Found: C, 50.02; H, 4.08; N, 6.71.

1,2,8,9-Tetraphenyl-3,7-diazaduohepta-2,7-diene-1,9-dione (KIM). Benzil (17.0 g, 80 mmol) was dissolved in boiling methanol (100 mL) and a slight excess of tn (3.6 mL, 42 mmol) in methanol (100 mL) was added dropwise to the hot solution. The volume was then reduced by boiling to about 100 mL, then cooled, stirred occasionally, and allowed to stand overnight. The resulting white crystalline product (15 g, 39%) was collected, washed with cold methanol, and dried in vacuo for 2 h; mp 100–112 °C. Anal. Calcd for $C_{31}H_{26}N_2O_2$: C, 81.19; H, 5.73; N, 6.11. Found: C, 80.70; H, 6.09; N, 5.96.

Results

The TIM and Ph-TIM series, Figure 1, of Co(III) complexes are synthesized by methods adapted from the preparation of $[Co(TIM)Br_2]Br$ by Busch and co-workers.[13] Each of the new compounds is a readily collected deep blue or purple Co(II) complex which precipitates during the reaction.

While the chemical properties of the TIM series of complexes are rather similar to members of the Ph–TIM series, they differ considerably in ease of oxidation of Co(II) to Co(III). Analogously to the TIM compounds, a suspension in methanol of the Co(II) complex, $Co(Ph\text{-}TIM)Br_2$, reacts with oxygen in 30 min to yield the corresponding Co(III) salt. Under identical conditions $Co(Ph\text{-}TIM\text{-}6\text{-}OH)Br_2$ showed signs of reaction only after a few days and $Co(Ph\text{-}TIM\text{-}6,13\text{-}(OH)_2)Br_2$ did not react with oxygen after 1 week's aeration. Along with spectral and analytical evidence this difference of reactivity establishes the integrity of the Ph-TIM-6-OH macrocycle and infers that a statistical distribution of each macrocycle is not the preparative result. Both hydroxy-substituted Ph-TIM complexes are more conveniently oxidized by H_2O_2.

As expected the Ph-TIM series of complexes is far less soluble in aqueous or methanolic solutions than the TIM compounds. Oddly, $[Co(Ph\text{-}TIM)Br_2]Br$ is extremely soluble in CH_2Cl_2 or $CHCl_3$ unlike any other Co(III) compound in either series. Molecular weight measurements indicate it dissolves as an ion pair.

Spectra of the Complexes. Infrared spectra of the TIM series recorded as Nujol mulls closely resemble the spectrum of $[Co(TIM)Br_2]Br$ with the characteristic sharp peak near 1220 cm^{-1} and the weak C=N stretch near 1660 cm^{-1}.[14] Hydroxy-substituted species show a broad strong peak around 3300 cm^{-1}. Spectra of the Ph-TIM compounds are complicated in the fingerprint region by phenyl absorptions but notably the 1220-cm^{-1} peak characteristic of the TIM macrocycle is absent. Phenyl absorptions at 1580 and 1600 cm^{-1} similar to those for benzil appear and the OH stretch becomes far sharper near 3300 cm^{-1} in the hydroxy-substituted complexes.

Electronic spectra of the complexes are not significantly different from that of the previously reported $[Co(TIM)Br_2]Br$.[13]

The ^1H NMR spectra of the Co(III) complexes reported in Table I provide the most useful evidence for confirming the tetraaza macrocyclic structures. Basically the presence of a hydroxyl group in the six-membered ring is characterized by a shift of the β^* proton multiplet of $\sim$2.5 ppm downfield relative to the β protons of an unsubstituted ring. Integration of the α:α^*:β:β^* peaks yields a 4:4:2:1 ratio respectively for both $Co(Ph\text{-}TIM\text{-}6\text{-}OH)Br_2$ (Figure 2) and $[Co(TIM\text{-}6\text{-}OH)Br_2]Br$. Further indication of the hydroxyl is the downfield shift of $\sim$0.3 ppm for the α^* signals relative to those for the α protons. The broad triplet of the α protons due to splitting by two β protons simplifies concomitantly with replacement of a β proton with a hydroxyl. As indicated in Table I, the spectra of complexes of the 6,13-dihydroxy ligands

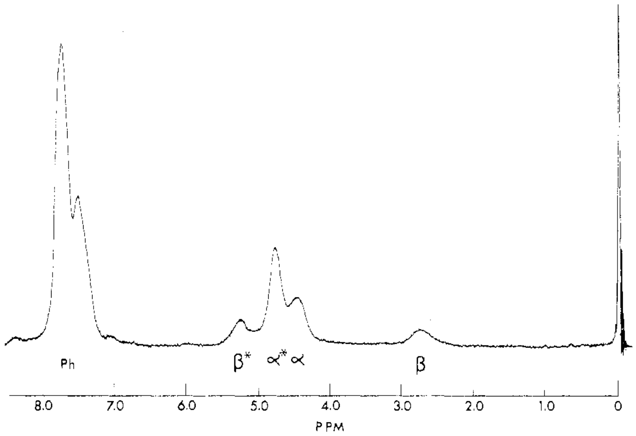

Figure 2. ^{1}H NMR spectrum of [Co(Ph-TIM-6-OH)Br_2]Br in CF_3COOH. Assignments are shown in Figure 1.

contain signals assignable only to α^* and β^* type protons. Although isomers should exist for the dihydroxy-substituted complexes, their NMR spectra do not distinguish two distinct forms if indeed they are present.

[Co(Ph-TIM)Br_2]Br precipitates with a methanol of crystallization when isolated as in the preparative procedure. Two peaks whose positions are highly solvent and concentration dependent are observed in the ^{1}H NMR spectrum. Spectra of chloroform-*d* solutions show peaks at 3.4 and ~2.7 ppm integrating at 3:1, while trifluoroacetic acid solutions have peaks at 4.2 and ~3.8 ppm integrating at 3:1, respectively. The integration futher reveals a ratio of 1 mol of methanol/mol of the complex. The methanol can be readily removed in vacuo as indicated in the Experimental Section.

Reactivity of the Hydroxyl Groups. Preliminary experiments indicate the hydroxyl functions on complexed TIM macrocycles are unreactive toward a variety of common reagents including phenyl isocyanate, acetyl chloride, benzenesulfonyl chloride, and benzenesulfonyl isocyanate. Reactions were attempted in acetonitrile using fluoborate salts of the TIM complexes in each case with no success.

The Macrocycle Precursor KIM. The reaction of 2 mol of benzil and slightly more than 1 mol of tn produces in high yield the diketone KIM, mp 110–112 °C (Figure 1(g)). The infrared spectrum of KIM as a Nujol mull clearly shows bands assigned to the C=O stretch (1675 cm^{-1}), C=N stretch 1632 cm^{-1}), and benzil-like phenyl absorptions (1600 and 1584 cm^{-1}). In the ^{1}H NMR spectrum (Figure 3) a quintet and a triplet corresponding to the β (2.11 ppm) and α (3.63 ppm) protons, respectively, are observed in addition to the phenyl proton multiplets. Further a 2,4-dinitrophenylhydrazone derivative forms in seconds with 2,4-dinitrophenylhydrazine reagent.

In the actual reaction scheme for Co[(Ph-TIM)Br_2]Br, the precursor KIM can be isolated by cooling the reaction mixture prior to the addition of $Co(OAc)_2{\cdot}4H_2O$. Equimolar amounts of benzil, tn, and HBr are present initially in this scheme and apparently after reaction of 1 mol of diamine with two benzils the remaining diprotonated diamine does not react until addition of the metal acetate. Mixing the precursor KIM and $Co(OAc)_2{\cdot}4H_2O$ followed by addition of diprotonated diamine (tn or tn-2-OH) results in macrocyclic ligand complexes in yields comparable to those of the in situ procedure.

Substitution of tn-2-OH in the KIM reaction sequence for tn does not produce an isolable analogue of KIM.

Discussion

The synthesis of the substituted series of TIM and Ph-TIM macrocyclic complexes extends the range and variability of macrocyclic complexes available. Macrocyclic ligands with reactive functional groups provide potential routes to complexes with pendant groups capable of coordinating in the fifth and sixth positions. The nonreactivity of the hydroxyls in the complexes described in this study could probably be overcome by isolating the free ligands although preliminary attempts to do so were unsuccessful. While the template effect limits the reactions to an extent, the problem of statistical distribution of product ligands in unsymmetrical complexes (TIM-6-OH or Ph-TIM-6-OH) encountered by Holm[8] in a nontemplate route is not observed.

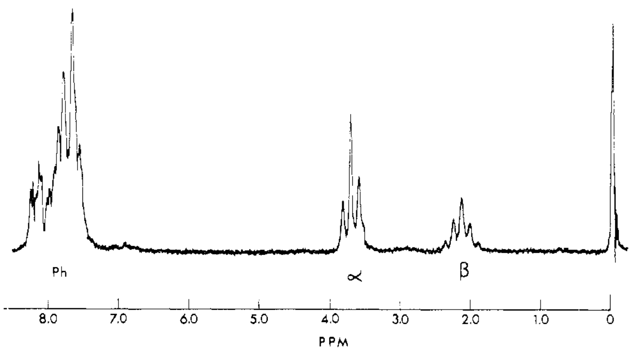

Figure 3. ^{1}H NMR spectrum of KIM in $CDCl_3$. Assignments are shown in Figure 1.

The nonreactivity of the hydroxyl groups was surprising but there is precedent in the literature. Thus Bailar and co-workers found the hydroxyl groups in Co(III), Pd(II), and Pt(II) complexes of *N*-2-hydroxyethylethylenediamine to be inert.[20] In at least some complexes this inertness results from complexing of the hydroxyl groups to the metal.[21] Bronsted did succeed in reacting a neutral complex of Co(III) and $HO(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ with thionyl chloride to give the corresponding chloride.[22] Also a cationic complex of the same ligand and Pt(II) underwent the same reaction. However, it is not known if the hydroxy group in these compounds is less reactive than the free ligand toward other electrophilic reagents. Krause and Goldby found that the hydroxyl groups of bis(2-hydroxyethyliminodiacetato)chromium(III) ion react very slowly with ketone and almost not at all with acetylating reagents.[23]

Direct synthesis of the α-keto imine KIM provides the first example of such compounds to be used in macrocycle synthesis although β-keto amines have been extensively studied.[1–5] The 2:1 benzil:diamine stoichiometry in the condensation product is an interesting contrast to related reactions of other α-diketones in which both carbonyls react and the stoichiometry is reversed.[24,25] Addition of Co(II) salts to KIM solutions does not result in isolable complexes but addition of diamines in the presence of Co(II) effects ring closure under appropriate conditions. The cyclization reactions in all cases apparently proceeds via a metal ion template effect.

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Registry No. [Co(TIM)Br_2]Br, 39177-15-6; [Co(TIM-6-OH)-Br_2]Br, 63765-49-1; [Co{TIM-6,13-$(OH)_2$}Br_2]Br, 63765-48-0; [Co(Ph-TIM)Br_2]Br, 63765-47-9; [Co(Ph-TIM-6-OH)Br_2]Br, 63765-46-8; [Co{Ph-TIM-6,13-$(OH)_2$}Br_2]Br, 63765-45-7; [Co-(TIM-6,13-$(OH)_2$)Br_2]BF_4, 63765-44-6; KIM, 23954-21-4; tn-2-OH, 616-29-5; tn, 109-76-2; biacetyl, 431-03-8; benzil, 134-81-6.

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Kinetics and Mechanism of the Demetalation of Iron(III) Porphyrins Catalyzed by Iron(II)[1]

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The demetalation of iron(III) porphyrins by HCl in acetic acid is catalyzed by iron(II). Rate determinations for three compounds support a mechanism consisting of two steps: reduction to the iron(II) porphyrin and decomposition of the latter by HCl. The first step follows the rate law $k_1[\mathrm{ClFe^{III}P}][\mathrm{Fe(II)}][\mathrm{HCl}]$ and the second $k_2[\mathrm{Fe^{II}P}][\mathrm{HCl}]^n$, with n = 2 or 3 depending upon the porphyrin. Depending on concentration variables, either of the steps may be rate determining. The role of the iron(II) porphyrin as an intermediate is supported by measurements of its competitive reactions with HCl and with iron(III).

Introduction

Demetalation of iron(III) porphyrins in acetic acid is shown in eq 1, where P represents the porphyrin and H_4P^{2+} its

$$\mathrm{ClFe^{III}P + 5HCl = HFeCl_4 + H_4P^{2+} + 2Cl^-} \qquad (1)$$

completely protonated dication. Demetalation does not proceed spontaneously,[2] however, requiring addition of a reducing agent to act as catalyst, such as an iron(II) salt,[2a] tin(II) chloride,[3] metallic mercury,[4] and diazomethane.[5]

In contrast to this slow demetalation, iron(II) porphyrins are readily demetalated by HCl. On the basis of such qualitative observations, Fischer et al.[6] proposed that the sequence of reactions 2 and 3 constitutes the mechanism by

$$\mathrm{ClFe^{III}P + Fe(II) \rightleftarrows Fe^{II}P + Fe(III)} \qquad (2)$$

$$\mathrm{Fe^{II}P + 4HCl \rightarrow Fe(II) + H_4P^{2+}} \qquad (3)$$

which iron(II) catalyzes reaction 1, as well as the reason for the requirement that salts of iron(II), not iron(III), be used in the synthesis of iron(III) porphyrins.[6]

The proposed sequence has not been verified, although Morell and Stewart[7] carried out some semiquantitative measurements to establish conditions under which iron(III) porphyrins might be demetalated rapidly and quantitatively at room temperature. They found that the extent of demetalation in a given time period increased with the concentrations of Fe(II) and of HCl (above 0.550 M HCl the rate then decreases, although $[H_2O]$ was not constant during that variation). They also noted that chlorohemin *a* was always demetalated to a greater extent than the less strongly oxidizing chloroiron(III) protoporphyrin IX, consistent with the electron-transfer process of reaction 2 being the first step in the sequence.

We have carried out kinetic studies to determine the effects of the pertinent concentration variables–$\mathrm{ClFe^{III}(P)}$, Fe(II), Fe(III), HCl, and (to some extent) H_2O. In addition experiments were conducted on the fate of independently prepared $\mathrm{Fe^{II}P}$ in the presence of varying concentrations of Fe(III) and/or HCl, since $\mathrm{Fe^{II}P}$ occurs as an intermediate in the proposed mechanism. The studies were carried out with the iron porphyrins shown in Figure 1; the deuteroporphyrin IX dimethyl ester complex (**1a**, ClFeDPE) and its 2,4-dibromo derivative (**1b**, ClFeDBDPE) were used, with a less extensive study of the Fe(III) complex of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (**2**, ClFeTPP). The measurements were made at 24.8 °C in acetic acid containing 5% water by volume ($[H_2O]$ = 2.80 M).

Results

General Observations. Both HCl and Fe(II) are required to effect demetalation of the $\mathrm{ClFe^{III}P}$ complexes shown in Figure 1. Demetalation in acetic acid containing 5% water proceeds with half-times of 10–1600 s for the ranges of $\mathrm{Fe^{II}}$ (typically 10^{-4} to 10^{-2} M) and HCl (0.05–1.3 M) employed.

The spectral changes accompanying the reaction are marked by the disappearance of bands characteristic of the $\mathrm{Fe^{III}(P)Cl}$ species and the growth of bands characteristic of the H_4P^{2+} dication. Appropriate isosbestic points were maintained throughout,[8] substantiating the presence of only two porphyrin species at appreciable concentration throughout the course of the reaction. Typical spectral scans at various time intervals are given in Figure 2 for Fe(DPE)Cl and in Figure 3 for Fe(DBDPE)Cl and Fe(TPP)Cl.

Only very slight dissociation of HCl occurs in glacial acetic acid.[9] The state of ionization of HCl upon addition of 5% H_2O (=2.80 M H_2O) is not known although, by assuming HCl acts as a weak electrolyte, an internally consistent formulation was realized.

The predominant species of nonporphyrin iron(III) in this medium is $HFeCl_4$. Solutions of $Fe(OAc)_3$ in acetic acid containing 0.42 M HCl and 2.80 M H_2O obey Beer's law over a concentration range 1.2×10^{-4} to 1.2×10^{-2} M. The same spectrum results from either LiCl or HCl, remains independent of added excess chloride, and matches closely that of $HFeCl_4$