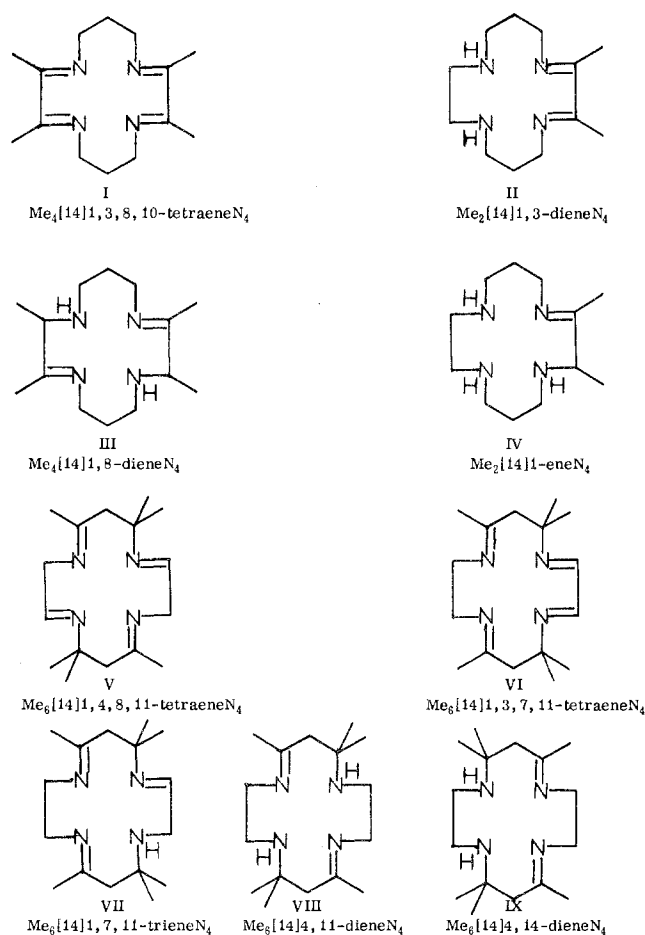Energy Research and Development Administration. We wish to thank K. Siegbahn for an opportunity to use the Uppsala spectrometer and G. M. Bancroft, J. W. Koepke, P. A. Malmqvist, W. B. Perry, and T. F. Schaaf for experimental assistance.

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Reactions of Coordinated Ligands. Selective Hydrogenation of α-Diimine Linkages in Complexes of Cobalt(III) with Macrocyclic Ligands

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The rapid expansion in the field of complexes of synthetic macrocyclic ligands can be traced to the application of novel chemical reactions to the synthesis of these materials. Thus, coordination template reactions,[1-3] metal ion promoted oxidative dehydrogenation reactions,[4-6] hydrogenation reactions of the free[7] and coordinated macrocycles,[1,3] and oxidation reactions of the chelate rings[8] have all led to new and important complexes; and for some macrocyclic ligands, these techniques

Figure 1. The macrocyclic ligands, showing the number of methyl substituents, the ring size in brackets, and the number and positions of unsaturation.[18,22]

remain as their only mode of preparation.

We report here a structure-specific reduction which has led to the synthesis and characterization of new 14-membered macrocyclic complexes of cobalt(III), in which the macrocyclic ligands contain either one or two coordinated azomethine functions in the five-membered chelate rings. Hypophosphorous acid has been used as the reducing agent and it has been found to be specific for hydrogenation of one of a pair of coordinated conjugated imine double bonds. Addition of the acid to the cobalt(III) complexes (Figure 1) of Me_4-$[14]1,3,8,10$-tetraeneN_4 (I) and $Me_2[14]1,3$-dieneN_4 (II) yields the cobalt(III) complexes of $Me_4[14]1,8$-dieneN_4 (III) and $Me_2[14]1$-eneN_4 (IV), respectively, as the only products. Unlike other common reducing agents, such as $NaBH_4$,[6,7,9,10] H_2/Pt,[11-13] or $NaOH/Ni-Al$,[11,14] which readily hydrogenate all of the imine functions present, hypophosphorous acid will not reduce isolated imine functions under our experimental conditions.

The results of electrochemical studies on broad series of complexes with macrocyclic ligands suggested that suitable reagents might lead to selective reductions of the kinds reported here.[15,16] In the case of nickel(II) complexes with macrocyclic ligands, one-electron reduction generally produces species that have been identified by ESR spectroscopy as nickel(I) derivatives.[16] In contrast, one-electron reduction of nickel(II) complexes of ligands that contain α-diimine linkages proceeds at relatively moderate potentials and the reduction products exhibit ESR spectra that signal the presence of free radicals. This has been explained as involving electron addition to the relatively low-energy π* orbital of the conjugated α-diimine moiety. It is reasonable to extend this reasoning to explain

an earlier report on the selective hydrogenation of certain nickel(II) complexes. Curtis found[6] that the complex [Ni(Me$_6$[14]1,4,8,11-tetraeneN$_4$)]$^{2+}$ (V) is not reduced by hypophosphorous acid whereas addition of that reducing agent to [Ni(Me$_6$[14]1,3,7,11-tetraeneN$_4$)]$^{2+}$ (VI), which contains two isolated imines and an α-diimine function, produces the nickel(II) complex of Me$_6$[14]1,7,11-trieneN$_4$ (VII) as the sole product. The product contains three isolated imine functions. We have established the nature and generality of this selective hydrogenation process by studies on complexes of cobalt(III).

Experimental Section

Preparation of Complexes. [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br and [Co(Me$_2$[14]1,3-dieneN$_4$)Br$_2$]ClO$_4$ were prepared according to published procedures.[17]

[Co(Me$_4$[14]1,8-dieneN$_4$)Br$_2$]ClO$_4$. A 5.46-g amount (0.01 mol) of [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br was slurried in 350 mL of methanol and 13.2 g (0.06 mol; 12 equiv) of 30% aqueous hypophosphorous acid was added with stirring. The solution rapidly changed color to a deep red-purple and all of the solids dissolved. The solution was stirred for 1 h during which time the color of the solution changed to red, red-brown, brown, and finally green. At this stage, 5 mL of 48% aqueous hydrobromic acid and 5 g of sodium perchlorate were added and the solution was aerated for 1 h. The green crystalline product was isolated by filtration and washed with 5% hydrobromic acid. This product was recrystallized from 50 mL of hot 5% hydrobromic acid containing a few milliliters of methanol. The deep green crystalline product was isolated from the cold solution, washed with ethanol, and dried in vacuo over P$_4$O$_{10}$; yield 3.0 g (52%). Anal. Calcd for CoC$_{14}$H$_{28}$N$_4$Br$_2$ClO$_4$: C, 29.46; H, 4.91; N, 9.82; Br, 28.03. Found: C, 29.58; H, 4.83; N, 9.56; Br, 28.00.

[Co(Me$_4$[14]1,8-dieneN$_4$)Cl$_2$]ClO$_4$. Two grams (0.0035 mol) of [Co(Me$_4$[14]1,8-dieneN$_4$)Br$_2$]ClO$_4$ was dissolved in 50 mL of very dilute hot ammonia solution and 10 mL of concentrated hydrochloric acid was added. This solution was refluxed for 0.5 h, cooled, and evaporated to near dryness. The isolated product was washed with a small amount of cold water and recrystallized from 100 mL of hot 5% hydrochloric acid containing 1 g of sodium perchlorate. Green needles of the product formed on cooling. These were isolated by filtration, washed with ethanol, and dried in vacuo over P$_4$O$_{10}$; yield 1.2 g (71%). Anal. Calcd for CoC$_{14}$H$_{28}$N$_4$Cl$_3$O$_4$: C, 34.90; H, 5.82; N, 11.63; Cl, 22.11. Found: C, 34.86; H, 5.64; N, 11.40; Cl, 21.98.

[Co(Me$_2$[14]1-eneN$_4$)Br$_2$]ClO$_4$. This complex was prepared in a manner similar to that given for the preparation of [Co(Me$_4$[14]-1,8-dieneN$_4$)Br$_2$]ClO$_4$ using 1.08 g (0.002 mol) of [Co(Me$_2$[14]-1,3-dieneN$_4$)Br$_2$]ClO$_4$ and 2.64 g (0.012 mol) of hypophosphorous acid in 40 mL of methanol at reflux temperature (there is not apparent reaction at room temperature). The lime green product was isolated after 30 min by addition of 4 mL of 48% hydrobromic acid and 1 g of sodium perchlorate followed by aeration. Recrystallization of this product from hot 5% aqueous hydrobromic acid yields, upon cooling, lime green crystals. These were washed with ethanol and dried in vacuo over P$_4$O$_{10}$; yield 0.5 g (46%). Anal. Calcd for CoC$_{12}$H$_{26}$N$_4$Br$_2$ClO$_4$: C, 26.46; H, 4.78; N, 10.30. Found: C, 26.26; H, 4.69; N, 10.29.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 457 recording spectrophotometer using Nujol mulls and polystyrene as a calibrant. The visible spectra were obtained with a Cary Model 14R recording spectrophotometer. The NMR spectra were recorded in dimethyl sulfoxide using tetramethylsilane as an internal standard on a JEOL 100-MHz spectrometer.

Discussion

The addition of excess hypophosphorous acid to the cobalt(III) complex of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (abbreviated Me$_4$[14]-1,3,8,10-tetraeneN$_4$) (I) or to the cobalt(III) complex of 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene (abbreviated Me$_2$[14]1,3-dieneN$_4$) (II) in methanol produces an immediate intense red-purple solution, the color of which rapidly fades to red, then brown, and finally to green. Addition of halo acids followed by aeration causes the cobalt(III) complexes of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene (abbreviated Me$_4$[14]1,8-dieneN$_4$) (III)

and of 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1-ene (abbreviated Me$_2$[14]1-eneN$_4$) (IV) to precipitate.

The infrared spectrum of [Co(Me$_4$[14]1,8-dieneN$_4$)Br$_2$]-ClO$_4$ shows a sharp N–H absorption at 3247 cm^{-1} and a strong sharp absorption at 1653 cm^{-1} characteristic of imine functions. This spectrum differs markedly from that of the starting material [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]ClO$_4$ which shows no absorption due to N–H, two weak absorptions in the 1570–1660-cm^{-1} region due to the α-diimine functions, and a strong sharp characteristic absorption at 1210 cm^{-1}.[17] This latter band disappears upon complete hydrogenation of the ligand, whereas the complexes of Me$_4$[14]1,8-dieneN$_4$ show a weak absorption near 1220 cm^{-1}. The infrared spectrum of [Co(Me$_2$[14]1-eneN$_4$)Br$_2$]ClO$_4$ also serves to distinguish it from the precursor Me$_2$[14]1,3-dieneN$_4$ complex in that it shows strong sharp absorptions at 3236 cm^{-1} (N–H) and at 1647 cm^{-1} (isolated imine band) and a weak absorption at 1234 cm^{-1}. By comparison the infrared spectrum of [Co(Me$_2$-[14]1,3-dieneN$_4$)Br$_2$]ClO$_4$ shows an N–H absorption at 3236 cm^{-1}, two weak absorptions in the 1575–1630-cm^{-1} region due to the α-diimine function, and a strong sharp characteristic band at 1234 cm^{-1}.[17] This band at 1234 cm^{-1} also disappears upon complete hydrogenation of the macrocyclic ligand.

The proton magnetic resonance spectra, recorded in dimethyl-d_6 sulfoxide, provide structure proofs for the reaction products. The complexes of both Me$_4$[14]1,3,8,10-tetraeneN$_4$ and Me$_2$[14]1,3-dieneN$_4$ show a sharp methyl resonance near 3.30 ppm, characteristic of methyl groups bound to carbon atoms of conjugated double bonds. Upon removal of this conjugation, by hydrogenation, the ^{1}H NMR spectra show a methyl singlet near 2.40 ppm and an equally intense methyl doublet centered near 1.60 ppm. By comparison, cobalt(III), nickel(II), and iron(II) complexes of Me$_6$[14]1,4,8,11-tetraeneN$_4$ (V) and Me$_6$[14]4,11-dieneN$_4$ (VII), containing a methyl group bound to an isolated imine function in a six-membered chelate ring, all show a methyl singlet in the 2.0–3.0-ppm region,[4,18–20] whereas cobalt(III), nickel(II), and iron(II) complexes of the fully saturated macrocyclic ligand, Me$_6$[14]aneN$_4$, containing lone methyl groups bound to saturated carbon atoms, show a methyl doublet in the 1.0–2.0-ppm region.[21–23]

The hydrogenation of the coordinated macrocyclic ligand Me$_4$[14]1,3,8,10-tetraeneN$_4$ could lead to complexes containing either three imine functions (Me$_4$[14]1,3,8-trieneN$_4$), two imine functions that are either isolated (Me$_4$[14]1,8-dieneN$_4$ or Me$_4$[14]1,10-dieneN$_4$)[24] or conjugated (Me$_4$-[14]1,3-dieneN$_4$), one imine function (Me$_4$[14]1-eneN$_4$), or no imine functions (Me$_4$[14]aneN$_4$). By stopping the reaction at various times or by refluxing the reaction mixture for extended periods of time we have attempted to isolate these other possible products. In all cases complexes of either the pure diene Me$_4$[14]1,8-dieneN$_4$ or mixtures of the diene and the starting material were obtained. The ^{1}H NMR spectra of such mixtures showed a sharp peak of variable intensity at 3.30 ppm, indicating the presence of Me$_4$[14]1,3,8,10-tetraeneN$_4$. None of these mixtures gave intensity ratios of 2:1:1 for the methyl resonances at 3.30, at 2.40, and near 1.60 ppm as is required for pure Me$_4$[14]1,3,8-trieneN$_4$, nor did the intensity ratios of the methyl resonances at 2.40 and near 1.60 ppm vary from 1:1 as required for the presence of either Me$_4$[14]1-eneN$_4$ or Me$_4$[14]aneN$_4$.

Similarly, the hydrogenation of complexes of Me$_2$[14]-1,3-dieneN$_4$ with hypophosphorous acid produces only the cobalt(III) complex of Me$_2$[14]1-eneN$_4$, with no evidence to suggest the presence of Me$_2$[14]aneN$_4$, the ^{1}H NMR spectrum of which should show only a methyl doublet near 1.60 ppm.

These observations support the expectation that hypophosphorous acid is specific for hydrogenation of one of a pair

of conjugated imine double bonds. Unlike sodium borohydride, it will not effect the hydrogenation of isolated imine functions. To further demonstrate this selectivity, hypophosphorous acid was added to solutions of the cobalt(III) complexes of $Me_4[14]1,8$-dieneN$_4$ (III), $Me_4[14]1$-eneN$_4$ (IV), $Me_6[14]$-1,4,8,11-tetraeneN$_4$ (V),[4,25] $Me_6[14]4,11$-dieneN$_4$ (VIII),[26] and $Me_6[14]4,14$-dieneN$_4$ (IX)[27] all of which contain only isolated imine functions. No reaction was observed at room temperature. Upon gently warming, these green solutions become pale brown and within 1 h, a pale pink product precipitates. Aeration and acidification of the filtrate produce, in each case, the starting material ($\leq$50% yield) as verified by the infrared and NMR spectra. The pink product has been identified as anhydrous $Co(H_2PO_2)_2$. The analytical figures 28.88% C, 2.26% H, and 32.76% P are in agreement with this formulation. The solid decomposes at 270 °C and dissolves in water to give $[Co(H_2O)_6]^{2+}$, as identified by the visible spectrum,[28] 19 600 (sh) and 21 600 cm^{-1}. The infrared spectrum of the pink solid shows three sharp bands in the 2390–2440-cm^{-1} region, four sharp bands in the 1060–1170-cm^{-1} region, two strong bands near 8.5 cm^{-1}, and a band at 510 cm^{-1}, all attributable to $H_2PO_2^{-}$.[29] Thus, hypophosphorous acid will reduce only conjugated imines or the central metal ion in the case of cobalt complexes.

The visible spectrum of $[Co(Me_4[14]1,8$-dieneN$_4)Cl_2]ClO_4$ shows two low-intensity bands ($\epsilon \sim 50$) at 16 300 and 22 200 cm^{-1} with an intense charge-transfer band at 37 700 cm^{-1} ($\epsilon \sim 10\,000$). Analysis of the spectrum after the method of Wentworth and Piper[30] leads to the values $Dt = 674$, $Dq^z = 1420$, and $Dq^{xy} = 2600$ cm^{-1}. The precursor complex $[Co(Me_4[14]1,3,8,10$-tetraeneN$_4)Cl_2]ClO_4$ has a ligand field strength Dq^{xy} of 2780 cm^{-1}.[17] The complexes $[Co(Me_4[14]1,8$-dieneN$_4)Br_2]ClO_4$ and $[Co(Me_2[14]1$-eneN$_4)Br_2]ClO_4$ both show a single d–d transition at 15 400 and 15 200 cm^{-1}, respectively. The ligand field strength of the macrocyclic ligand $Me_2[14]1$-eneN$_4$ has been estimated, assuming $Dq^z(Br) = 1277$ cm^{-1},[17] to have a value of 2520 cm^{-1}. By comparison, the ligand field strength of $Me_4[14]1,3$-dieneN$_4$, based on the dibromo complex, has been calculated to be 2630 cm^{-1}.[1]

Registry No. $[Co(Me_4[14]1,3,8,10$-tetraeneN$_4)Br_2]Br$, 39177-15-6; $[Co(Me_4[14]1,8$-dieneN$_4)Br_2]ClO_4$, 61491-31-4; $[Co(Me_4[14]1,8$-dieneN$_4)Cl_2]ClO_4$, 61491-33-6; $[Co(Me_2[14]1$-eneN$_4)Br_2]ClO_4$, 61491-35-8; $[Co(Me_2[14]1,3$-dieneN$_4)Br_2]ClO_4$, 39483-62-0.

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Kinetics of Copper Incorporation into Tetra(2-*N*-methylpyridyl)porphine. Effects of Basicity on Rate

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This note is concerned with the question of how the rate of metal ion incorporation into porphyrins to form metalloporphyrins is influenced by the basicity of the porphyrin molecule. In aqueous detergent solutions used to solubilize substituted deuterioporphyrin esters, the rates of copper incorporation paralleled porphyrin basicity.[1] However, in pyridine–water media,[2] other workers found that the rates of zinc porphyrin formation were independent of porphyrin basicity. Although plots of $\Delta G^{\ddagger}$ vs. Hammett σ values were presented[3,4] for copper metallation reactions in DMF, the reactions were run near the isokinetic temperature, and the observed rates were similar in magnitude. Related behavior was found for copper ligation of a series of natural porphyrin types studied in unbuffered ethanol solutions.[5]

We report a study of copper incorporation in aqueous solution into tetra(2-*N*-methylpyridyl)porphine, TMPyP(2). In contrast to other porphyrins,[6] this ortho isomer remains in the free base (H$_2$P) form in acidic solution. The rate law and activation parameters are compared with the more basic 3- and 4-*N*-methyl isomers,[7,8] TMPyP(3) and TMPyP(4).

Experimental Section

The tetramethylated porphyrin isomers were prepared by literature methods.[6] It is noted that microcrystalline metal derivatives of TMPyP(2) can be obtained by adding a concentrated solution of sodium perchlorate to a cooled solution of the metalloporphyrin nitrate, and refrigerating overnight. Since several of our perchlorate samples have exploded while drying, and other workers have noted similar behavior,[9] *the preparation of anhydrous perchlorates in the TMPyP series should be attempted with extreme caution.*

Cu-TMPyP(2) was made in solution by addition of an excess of copper nitrate to H$_2$-TMPyP(2) at pH 1. The absorption spectra as a function of time showed excellent isosbestic points at 675, 587, 525, and 478 nm, with major bands at 415 nm (ϵ 1.34 $\times$ 10^5), 543 nm (1.88 $\times$ 10^4) and 578 nm (1.17 $\times$ 10^4). The latter band appears as a shoulder in the 3- and 4- copper isomers. The copper adducts did not solvolyze after sitting for days at room temperature in 1.0