

medium such as Nujol and is essentially complete after 8 h at 85 °C or 30 min at 115 °C.

Although the structure of the starting complex **1-6** is not known, it is presumed to have the essential features of the other 1/1 quinhydrones and to consist of hydrogen-bonded chains of alternating quinone and hydroquinone molecules stacked to form charge-transfer complexes in a second direction. The structure of the product **2-5** is more complicated.<sup>5c</sup> Clearly, extensive repacking accompanies reaction. The details are not known, but the change is complicated since it involved loss both of an electron pair and of two protons, one from each end of a hydroquinone molecule, presumably to two different quinone neighbors.

Although the potential of <sup>13</sup>C NMR as a tool for the study of reactions in the solid state is very great, it is apparent that its application is not nearly as straightforward as might have been anticipated from NMR studies in solution.

**Acknowledgment.** We are indebted to the National Science Foundation (USA) (Grant CHE 82-09393) for partial support of this work.

**Registry No.** **1**, 106-51-4; **2**, 137-18-8; **3**, 527-17-3; **4**, 130-15-4; **5**, 123-31-9; **6**, 615-90-7; **7**, 527-18-4; **8**, 571-60-8; **1-5** (1:1), 106-34-3; **1-6** (1:1), 87970-32-9; **1-8** (1:1), 87970-33-0; **2-5** (1:2), 87970-37-4; **3-7** (1:1), 96914-21-5; **4-5** (1:1), 60706-28-7.

## Spectral, Electrochemical and Base-Binding Studies of Heterodinuclear Ruthenium-Cobalt Complexes of *meso*- $\alpha,\alpha,\alpha,\alpha$ -Tetra(nicotinamidophenyl)porphine

C. Michael Elliott,\* J. Kenneth Arnette, and R. R. Krebs

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received December 26, 1984

**Abstract:** The spectral, electrochemical, and ligand addition properties of metal complexes of the modified porphyrin (nic)<sub>4</sub>H<sub>2</sub>TPP have been examined. The porphyrin has the feature that two metal ions may be coordinated and held in close proximity to each other, one ion in the porphyrin ring and the other coordinated to the pyridine-like nitrogens of the nicotinamide pickets. The results for the RuCl<sub>2</sub>(nic)<sub>4</sub>CoTPP complex studied indicate that the "neutral" fixed axial ligand Ru<sup>II</sup>Cl<sub>2</sub> has very little effect on the electrochemistry and spectroscopy of the cobalt porphyrin when compared with simple CoTPP. However, oxidation of Ru(II) to Ru(III) greatly increases the Lewis acid strength of Co(II) relative to the strength of that center in CoTPP. The binding constant for the Ru(III)-Co(II) species with pyridine is found to be three orders of magnitude larger than that for Ru(II)-Co(II); the binding constant for Ru(III)-Co(III) with pyridine is seven orders of magnitude greater than that for Ru(III)-Co(II). In the presence of high concentrations of *N*-methylimidazole, the Ru(III)-Co(III) appears to form a bis-adduct, presumably by allowing partial entry of a 1-MeIm molecule into the porphyrin pocket.

The preparation and study of metal complexes containing multiple metal centers in well-defined geometric arrangements are of considerable interest. This fact is especially true when the metals are arranged so that they can exert a significant influence on one another with respect to such properties as redox potential, magnetic ground states, and propensity for ligand binding. Aside from the purely fundamental aspects of metal-metal interactions, multiple metal centers are known to be important in many unique catalytic processes carried out by some enzymes.<sup>1</sup> They have been implicated without proof in an even larger number of biological reactions.<sup>1</sup> Synthetic multimetal systems, therefore, are often useful in helping to better understand complex biological systems. Also, they sometimes possess properties of both fundamental and practical interest which are absent in the separate monomeric units.<sup>2-4</sup>

For a number of years we have been interested in heterodinuclear complexes of the ligand *meso*- $\alpha,\alpha,\alpha,\alpha$ -tetra(*o*-nicotinamidophenyl)porphyrin. We have reported, in preliminary form, studies on a variety of complexes of the form RuCl<sub>2</sub>(nic)<sub>4</sub>TPPM where M is a metal species coordinated in the porphyrin pocket.<sup>5</sup> Herein we report a detailed study of the cobalt complex from this

series, primarily from the standpoint of its redox and ligand binding properties. A major factor that makes these complexes unique is the ability to convert the ruthenium center from an overall neutral Ru(II) species (which exerts only a very modest effect on the porphyrin bound cobalt center) into a cationic Ru(III) species. As will be presented subsequently, this simple change in ruthenium oxidation state, and thus charge, induces dramatic but indirect effects in the chemistry of the cobalt, e.g., drastically increasing the binding constant for certain nitrogenous bases at the cobalt(II) center.

### Experimental Section

**Synthesis.** The structure of the ligand  $\alpha,\alpha,\alpha,\alpha$ -(nic)<sub>4</sub>H<sub>2</sub>TPP is given in Figure 1.

$\alpha,\alpha,\alpha,\alpha$ -(nic)<sub>4</sub>H<sub>2</sub>TPP (**1**). *meso*-Tetra(*o*-aminophenyl)porphyrin (H<sub>2</sub>TAPP) was prepared by the method of Collman.<sup>6</sup> The  $\alpha,\alpha,\alpha,\alpha$ -atropisomer was separated by the methods of Collman,<sup>6</sup> Elliott,<sup>7</sup> or Lindsey.<sup>8</sup> Nicotinoyl chloride hydrochloride (nic)Cl·HCl was prepared by dissolving 10 g of nicotinic acid in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> containing 15 mL of thionyl chloride (SOCl<sub>2</sub>, Fisher, reagent) and a few drops of *N,N*-dimethylformamide (DMF). The solution was stirred and refluxed for 0.5 h. Upon cooling, fine, slightly yellow crystals formed which were isolated by filtration, washed with CHCl<sub>3</sub>, and dried, all under an N<sub>2</sub> atmosphere.

The ligand  $\alpha,\alpha,\alpha,\alpha$ -(nic)<sub>4</sub>H<sub>2</sub>TPP was synthesized by dissolving  $\alpha,\alpha,\alpha,\alpha$ -H<sub>2</sub>TAPP (1.00 g) in 100 mL of dry CH<sub>2</sub>Cl<sub>2</sub>. To this solution, 6

(1) For example, see: Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223.

(2) Collman, J. P.; Marrocco, M.; Elliott, C. M.; L'Her, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 113-131.

(3) Collman, J. P.; Marrocco, M.; Denisevich, P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 117.

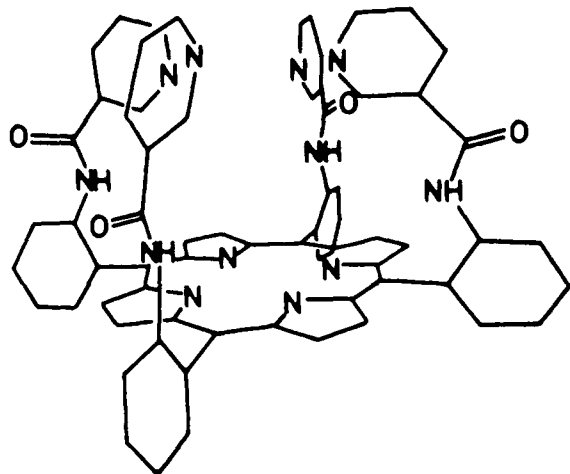
(4) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Anson, F. C.; Koval, C. *J. Am. Chem. Soc.* **1980**, *102*, 6027.

(5) Elliott, C. M.; and Krebs, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 4301.

(6) Collman, J. P.; Gagné, C. A.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.

(7) Elliott, C. M. *Anal. Chem.* **1980**, *52*, 666.

(8) Lindsay, J. J. *Org. Chem.* **1980**, *45*, 5215.



(1)

**Figure 1.** Schematic representation of the structure of **1**. Multiple bonds have been omitted for clarity.

equiv of (nic)Cl·HCl and 100 mL of dry pyridine were added. The solution was stirred and refluxed for 10 min. The reaction mixture was extracted with water twice, with 5% aqueous NaHCO<sub>3</sub> twice, and once more with water. The CH<sub>2</sub>Cl<sub>2</sub> was removed by rotary evaporation at room temperature, leaving the reaction product in pyridine solution. The (nic)<sub>4</sub>H<sub>2</sub>TPP was crystallized from the pyridine solution by the addition of pentane, then recrystallized from CH<sub>2</sub>Cl<sub>2</sub> by the addition of pentane.

**RuCl<sub>2</sub>(nic)<sub>4</sub>H<sub>2</sub>TPP (2).** (nic)<sub>4</sub>H<sub>2</sub>TPP (0.556 g) and Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub><sup>o</sup> (0.437 g) were dissolved in 200 mL of 1-propanol (Fisher, reagent) and 200 mL of absolute ethanol. The solution was refluxed with stirring under N<sub>2</sub> for 75 min, then rotary evaporated to dryness. The residue was chromatographed on silica gel and eluted with 25% acetone/75% benzene and recrystallized from methanol (yield: 61%). Anal. Calcd for C<sub>68</sub>H<sub>46</sub>N<sub>12</sub>O<sub>4</sub>Cl<sub>2</sub>Ru·CH<sub>3</sub>OH: C, 63.30; H, 3.88; N, 12.94. Found: C, 63.76; H, 3.52; N, 12.89.

**RuCl<sub>2</sub>(nic)<sub>4</sub>CoTPP (3).** RuCl<sub>2</sub>(nic)<sub>4</sub>H<sub>2</sub>TPP (0.103 g), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.193 g, Fisher, reagent), and 0.5 mL of 2,6-lutidine were added to 25 mL of DMF (Fisher, reagent) in a 50-mL round-bottom flask. The solution was refluxed with stirring for 30 min under N<sub>2</sub>, then cooled and rotary evaporated to dryness. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, chromatographed on silica gel, eluted with 25% acetone/75% benzene, and then recrystallized from methanol (yield: 55%). Anal. Calcd for C<sub>68</sub>H<sub>44</sub>N<sub>12</sub>O<sub>4</sub>Cl<sub>2</sub>RuCo: C, 61.68; H, 3.33; N, 12.70; Cl, 5.37. Found: C, 61.61; H, 3.42; N, 12.42; Cl, 5.48.

**Spectroscopic and Electrochemical Experiments. Chemicals.** All experiments were performed in CH<sub>2</sub>Cl<sub>2</sub>, which had been dried and purified by passing it through an activated alumina column. Pyridine (Aldrich, Gold label) was used as obtained. 1-Methylimidazole (Aldrich) was refluxed over KOH pellets for 3 h, then distilled at reduced pressure. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate, was prepared as described earlier,<sup>10</sup> and used at a concentration of 0.1 M.

**Equipment.** The electrochemical equipment and spectroelectrochemical cell have been described previously.<sup>10</sup> Electrochemical titrations were performed in a cell with isolated reference and auxiliary electrodes, using a platinum bead working electrode. Aliquots of base solution were delivered with use of a Gilmont micrometer buret previously calibrated with CH<sub>2</sub>Cl<sub>2</sub>. All potentials are vs. a saturated calomel reference electrode.

Optical measurements were performed with a Perkin-Elmer 552A spectrophotometer in either its normal configuration or with the sample compartment modified to accommodate the optically transparent thin-layer electrode cell (OTTLE).

Conductivity measurements were made with a Yellow Springs Instruments Model 31 conductivity bridge and cells 3403 (cell constant = 1.0 cm<sup>-1</sup>) or 3402 (cell constant = 0.1 cm<sup>-1</sup>).

Spectrophotometric titrations were accomplished with an all-glass and quartz cell consisting of a 2-mm quartz optical cell connected to a reservoir (ca. 40 mL volume) with stopcock. Aliquots of base solution were added by gas-tight syringe.

**Electrochemical Titrations.** Cyclic voltammetric *E*<sub>1/2</sub> potentials were obtained for the Ru(II/III), Co(II/III), and Co(II/I) redox couples as

a function of base concentration. The titration data were analyzed according to the method of Kolthoff and Lingane,<sup>11,12</sup> using the equation

$$(E_{1/2})_c = (E_{1/2})_s - \frac{0.059}{n} \log \left[ \frac{K_{ox}}{K_{red}} \right] - \frac{0.059}{n} (p - q) \log [L] \quad (1)$$

(*E*<sub>1/2</sub>)<sub>c</sub> and (*E*<sub>1/2</sub>)<sub>s</sub> are the half-wave potentials of the complexed and uncomplexed species, respectively. *K*<sub>ox</sub> and *K*<sub>red</sub> are the formation constants for the complexes of the oxidized and reduced species; *p* and *q* are the numbers of ligands bound to the oxidized and reduced species, respectively; [L] is the concentration of the complexing Lewis base; and *n* is the number of electrons transferred in the redox reaction.

**Spectrophotometric Titrations.** A sample solution of 25 mL of **3** (0.0248 mM) was placed in the titration cell. UV-vis spectra were recorded without base and after the addition of aliquots of base solution. All absorbances were corrected for dilution. After each aliquot, the cell was shaken for about 1 min to allow complete mixing and equilibration. No spectral changes were observed after a few seconds following base addition (up to 5 min). Also, unlike simple porphyrins such as CoTPP, no reaction with O<sub>2</sub> occurred even after several days of exposure to base and O<sub>2</sub> at room temperature. Thus, no attempt was made to exclude oxygen from the spectroscopic cell. Data analyzed at wavelengths in both the visible and Soret regions produced identical results within experimental error.

The spectral data were analyzed by using the following equations:<sup>13,14</sup>

$$[A - A_0]^{-1} = K_1^{-1}[A_\infty - A_0]^{-1}[L]^{-1} + [A_\infty - A_0]^{-1} \quad (2)$$

$$\log [(A - A_0)/(A_\infty - A)] = n \log [L] + \log K_n \quad (3)$$

where *A* is the absorbance measured at a given wavelength and *A*<sub>0</sub> is the absorbance of the uncomplexed species. *A*<sub>∞</sub> is the absorbance of the fully complexed species, *K*<sub>1</sub> is the formation constant for the mono-ligated species, *n* is the number of ligands bound in a complex with any number of ligands, and *K*<sub>*n*</sub> is the formation constant defined as

$$K_n = [ML_n]/[M][L]^n$$

where M denotes the metalloporphyrin. Use of eq 2 has an advantage over the use of eq 3, in that the equilibrium constant *K*<sub>1</sub> is found by dividing the intercept by the slope, thus eliminating the need to choose a value for *A*<sub>∞</sub>. However, eq 2 applies only to single-ligand addition reactions and so lacks the flexibility for application to more complex processes. For these reasons, spectral titration data were treated according to both equations to check for consistency, where possible.

**Spectroelectrochemistry.** UV-vis spectra were first obtained for all accessible oxidation states of **3** in pure solvent. Subsequently, small aliquots of pure base were added to the solution and the procedure repeated. By using increasing base concentrations, spectra of a given oxidation state as a function of base concentration were obtained. However, due to the volatility of CH<sub>2</sub>Cl<sub>2</sub> and the length of time needed to record spectra, the concentration of **3** changed somewhat over the course of the experiment, despite the fact that the N<sub>2</sub> stream was passed through a CH<sub>2</sub>Cl<sub>2</sub> tower before entering the cell. As a result some spectra which should have been exactly superimposable were slightly offset. Also, at positive potentials of around 1.0 V, the gold OTTLE oxidizes in the presence of large amounts of py or 1-MeIm. Thus Ru(III)-Co(III) spectra at large base concentrations were unobtainable.

## Results

**Conductivity Measurements.** These experiments were designed to determine the inertness of the Ru(II) center in **3** toward chloride displacement by py and 1-MeIm. The conductivity of the 1-MeIm solution without porphyrin was measured as 0.765 μmho cm<sup>-1</sup>. Addition of **3** to the solution caused no changes in the conductivity up to 1 h after the addition. Subsequent addition of an equimolar amount of FeTPPCl caused an immediate, sharp increase in the conductivity due to the displacement of the axial chloride by 1-MeIm. It is clear from the experiments that the two chlorides remain bound to the Ru(II) in **3** over any reasonable length of time. This conclusion is confirmed by electrochemical results with

(9) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

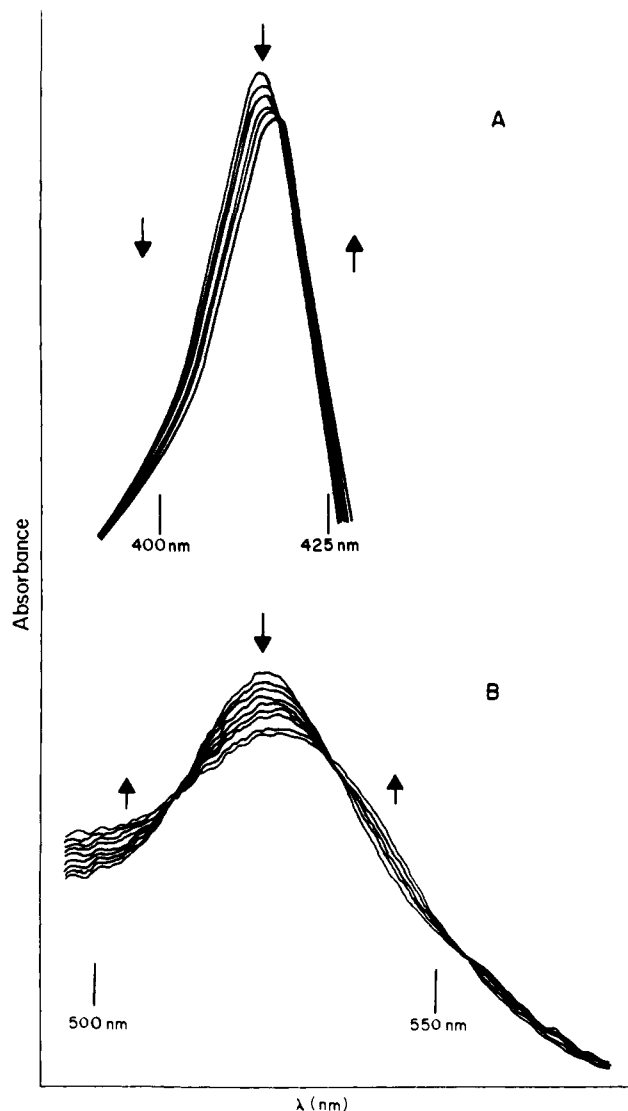
(10) Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558.

(11) Kolthoff, I. M.; Lingane, J. J. "Polarography"; 2nd ed.; Interscience: New York, 1952; Vol. 1, p 66.

(12) Kadish, K. M.; Bottomley, L. A.; Beroiz, B. *Inorg. Chem.* **1978**, *17*, 1124.

(13) Scheidt, W. R.; Lee, Y. J.; Luangdilok, W.; Haller, K. J.; Anzai, K.; Hatano, K. *Inorg. Chem.* **1983**, *22*, 1516.

(14) Rillema, B. P.; Wicker, C. M.; Morgan, R. D.; Barringer, L. F.; Scism, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 1276.



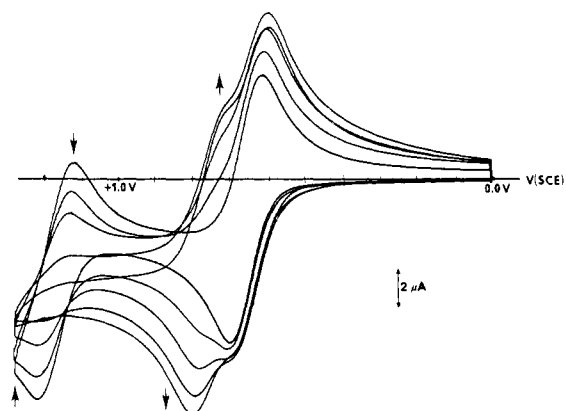
**Figure 2.** UV-vis spectra taken during titration of **3** with (A) 1-MeIm (Soret region) and (B) pyridine (visible region) in dichloromethane solution. The spectral changes observed for titrations with the two bases were qualitatively identical throughout the wavelength range examined.

$\text{RuCl}_2(\text{nic})_4\text{H}_2\text{TTP}$  (see below). Analogous conductivity experiments using py solution gave analogous results.

**Spectrophotometric Titrations.** In the oxidation state Ru(II)-Co(II),  $\text{RuCl}_2(\text{nic})_4\text{CoTPP}$  does not significantly bind py or 1-MeIm until relatively high base concentrations are reached. Absorbance changes due to binding of 1-MeIm were observable in the range  $1.5 \times 10^{-3} \text{ M} < [1\text{-MeIm}] < 1 \times 10^{-1} \text{ M}$ . For py, the observed concentrations range was  $4 \times 10^{-3} \text{ M} < [\text{py}] < 6 \times 10^{-2} \text{ M}$ .

During the 1-MeIm titration, isosbestic points were maintained at 417, 513, 535, and 554 nm throughout the concentration range given above (Figure 2A). The absorbances at 525 nm were corrected for dilution and fit to eq 3.  $A_\infty$  was taken from the first spectrum which fell below the isosbestic points. The slope of this plot (correlation coefficient = 0.996) is 0.98, indicating that one molecule of 1-MeIm is bound to Co(II). The intercept gives  $\log(K_{1m}^{2,2}) = 1.85$ . The superscript of  $K_{1m}^{2,2}$  indicates that the porphyrin is in the Ru(II)-Co(II) oxidation state (i.e., the first number refers to the formal oxidation state of the Ru and the second to the oxidation state of the Co). These results were confirmed by analysis both of absorbances at 414 nm (Soret region) by eq 2 and 3 and of absorbances at 525 nm by eq 2.

Isosbestic points for the py titration were 416, 511, 534, and 553 nm (Figure 2B). Again, the absorbances at 525 nm were corrected for dilution; however, the data were analyzed only by eq 2. No suitable  $A_\infty$  was reached due to the weaker binding of



**Figure 3.** Changes observed in the anodic cyclic voltammograms during the addition of substoichiometric amounts of pyridine to a solution of **3** in dichloromethane.

py. Equation 2 is well obeyed by the data (correlation coefficient = 0.994), and division of the intercept by the slope gives  $K_{py}^{2,2} = 35.0$  ( $\log K_{py}^{2,2} = 1.54$ ). It should be noted that neither base appears to form bis-adducts with the Ru(II)-Co(II) species.

**Electrochemistry of  $\text{RuCl}_2(\text{nic})_4\text{CoTPP}$ .** The cyclic voltammetry wave assignments for **3** (formal oxidation state assignments were made by analogy with cobalt tetraphenylporphyrin (CoTPP),  $\text{Ru}(\text{DENA})_4\text{Cl}_2$  (DENA = *N,N*-diethylnicotinamide),<sup>15</sup>  $\text{RuCl}_2(\text{nic})_4\text{H}_2\text{TTP}$ , and  $\text{RuCl}_2(\text{nic})_4\text{MTPP}$  (where  $\text{M} = \text{Zn}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Ag}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Mn}^{+3}$ , and  $\text{Fe}^{+3}$ )). On the cathodic scan, only one wave is observable due to the cathodic limit of  $\text{CH}_2\text{Cl}_2$ . This wave is assigned to the formal Co(II/I) couple and occurs at a half-wave potential ( $E_{1/2}$ ) of  $-0.976 \text{ V}$ , which is very nearly the same potential as observed for CoTPP.<sup>5</sup> The wave is a diffusion-controlled, one-electron process which is chemically nearly irreversible at slow scan rates. The chemical irreversibility is most likely due to the reaction of the Co(I) porphyrin with the solvent to give a Co alkyl compound (see below). By comparison, in DMF this couple is completely chemically reversible.

On the anodic scan (see Figure 3, line 1), three waves are observed. The first, corresponding to the Ru(II/III) couple, has an  $E_{1/2}$  of  $0.658 \text{ V}$  and is a one-electron, diffusion-controlled, quasi-reversible process. The second wave is formally assigned to the Co(II/III) couple and occurs at an  $E_{1/2}$  of  $1.18 \text{ V}$ . This too is a diffusion-controlled, quasi-reversible, one-electron process. As will be seen later from spectral results, in the absence of added axial base this oxidation is most likely best described as a ligand-based process. We will, however, use the Co(II/III) formalism, which is probably reasonable for the complex in the presence of axial base. The third wave (not shown in Figure 3) has an  $E_{1/2}$  of  $1.40 \text{ V}$  and is a two-electron process. This ligand oxidation is electrochemically quasi-reversible and not totally chemically reversible.

**Electrochemistry of  $\text{RuCl}_2(\text{nic})_4\text{CoTPP}$  with Pyridine.** The addition of py, in substoichiometric quantities, to a solution of **3** in  $\text{CH}_2\text{Cl}_2$  causes the disappearance of the wave at  $1.18 \text{ V}$  and the appearance of a new wave at  $0.746 \text{ V}$  (Figure 3) while leaving the other waves unaffected. The appearance of the new wave and the disappearance of the wave at  $1.18 \text{ V}$  are complete when roughly half an equivalent of py has been added to the solution. This apparent deviation from one-to-one stoichiometry is reasonable if it is assumed that the diffusion coefficient for py is about four times larger than that for **3**. In that case, the effective py concentration in the diffuse layer would be about twice the bulk py concentration.

At py concentrations above stoichiometric level, the Co(II/III) wave remains fixed while the Ru(II/III) wave shifts cathodically as  $[\text{py}]$  increases (Figure 4). This shift is clearly not due to coordination of py at the Ru center, as demonstrated by conductivity experiments. The inertness of Ru toward ligand exchange

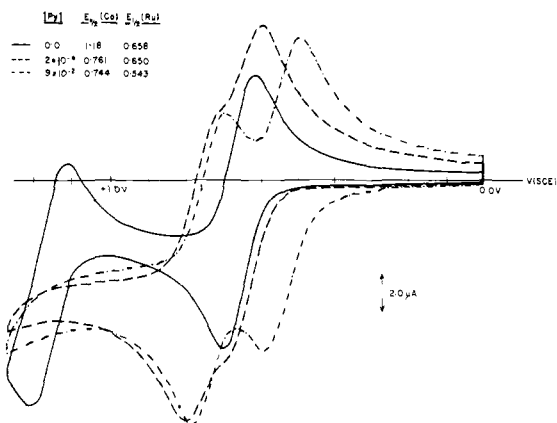


Figure 4. Cyclic voltammograms of **3** in  $\text{CH}_2\text{Cl}_2$  with no pyridine (—),  $2 \times 10^{-4}$  M pyridine (---), and  $9 \times 10^{-2}$  M pyridine (-.-).

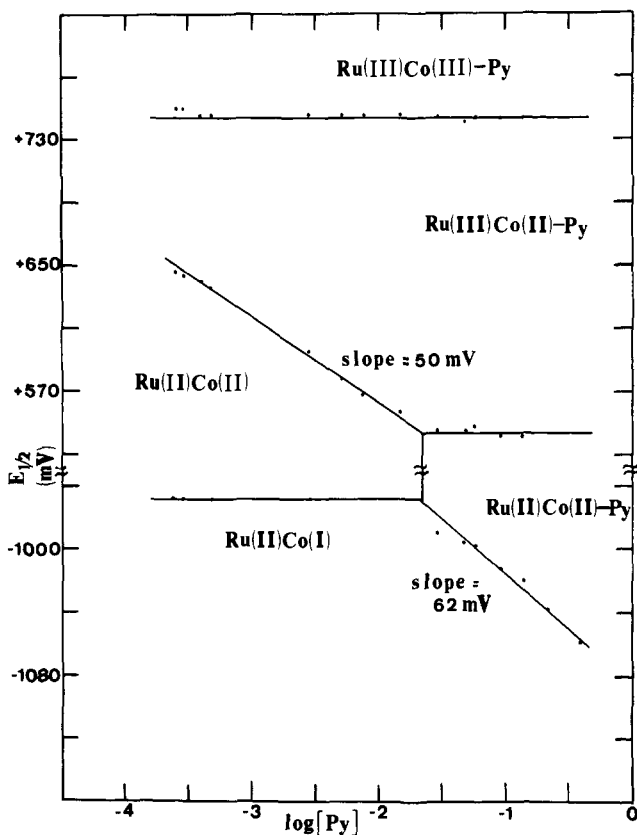


Figure 5.  $E_{1/2}$  vs.  $\log [\text{py}]$  for the three metal-centered redox couples of **3** during an electrochemical titration with pyridine.

was verified electrochemically by probing the dependence on  $[\text{py}]$  of the potential for the Ru(II/III) wave in  $\text{RuCl}_2(\text{nic})_4\text{H}_2\text{TPP}$ . The  $E_{1/2}$  of this wave was completely independent of  $[\text{py}]$  up to large py concentrations. The shift of the Ru wave of **3** must thus be in response to binding of py at the Co(II) center. At  $[\text{py}] \approx 3 \times 10^{-2}$  M the Ru wave stops shifting and the Co(II/I) wave, previously unaffected, begins to move cathodically (Figure 5). This shift persists throughout the remainder of the titration.

The key to interpreting the titration data, presented in Figure 5, is to realize that the four possible redox states represent different chemical species (Figure 6A). At 0.0 V, the solution species is Ru(II)-Co(II), which can be reduced to Ru(II)-Co(I) (bottom line, Figure 5) or oxidized to Ru(III)-Co(II) (middle line, Figure 5). Beyond the Ru(II/III) wave, the solution species is Ru(III)-Co(II), which can be oxidized further to Ru(III)-Co(III) (top line, Figure 5). Thus the conversion of the Co(II/III) couple is always carried out in the presence of Ru(III), whereas, for example, the conversion of Co(I/II) is always carried out in the presence of Ru(II).

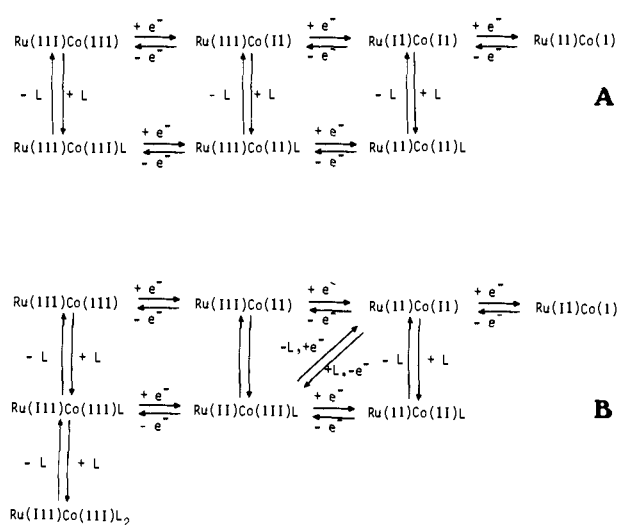
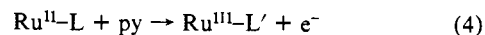


Figure 6. Redox and ligand exchange chemistry as functions of metal oxidation state and base concentration for **3** in the presence of (A) pyridine and (B) 1-MeIm.

With this point in mind, the analysis of the plot in Figure 5 is straightforward. The Ru(II)-Co(II/I) line (bottom) has zero slope until  $[\text{py}] \approx 3 \times 10^{-2}$  M. Since Co(I) porphyrins do not in general bind nitrogenous bases,<sup>12</sup> we conclude that  $p = q = 0$  in this region, i.e., that neither Ru(II)-Co(I) nor Ru(II)-Co(II) bind py when  $[\text{py}] < 3 \times 10^{-2}$  M. At higher concentrations the shift is linear with  $\log [\text{py}]$  and the slope of this line is  $-0.0620$  V or  $p - q = 1$ , indicating that Ru(II)-Co(II) binds one py molecule with formation constant  $K_{\text{py}}^{2,2}$ . The intercept of the Co(II/I) line, i.e., the point at which the log term in eq 1 equals zero, is  $-1.078$  V and  $(E_{1/2})_s$ , the Ru(II)-Co(II/I) potential in the absence of py, is  $-0.976$  V. Since Co(I) does not bind, we calculate  $\log K_{\text{py}}^{2,2} = 1.72$ , which compares favorably with the spectrophotometric result of 1.54.

The Ru(II/III)-Co(II) line (middle) is linear with slope  $-0.0503$  V or  $p - q = 1$ , until  $[\text{py}] \approx 3 \times 10^{-2}$  M, after which the slope is essentially zero. Conductivity experiments mentioned above unambiguously demonstrate that the pyridine is *not* binding to the ruthenium center but rather to the cobalt with formation constant  $K_{\text{py}}^{3,2}$  (i.e., Ru(III)-Co(II) oxidation state). It might at first seem contradictory that pyridine binding at the Co(II) should result in a Nernstian shift in the Ru(II/III) potential. One needs to keep in mind, however, that it is the change in the ruthenium oxidation state that triggers the pyridine binding at Co(II) and that the chloride-bridged cobalt porphyrin, itself, can be thought of as one of the ligands bound to Ru(II); then we can write



where  $\text{L} = -\text{Cl}-\text{Co}^{\text{II}}\text{P}$  and  $\text{L}' = -\text{Cl}-\text{Co}^{\text{II}}\text{P}-\text{py}$ . Viewed in this way, the data are perfectly consistent with what would be expected.

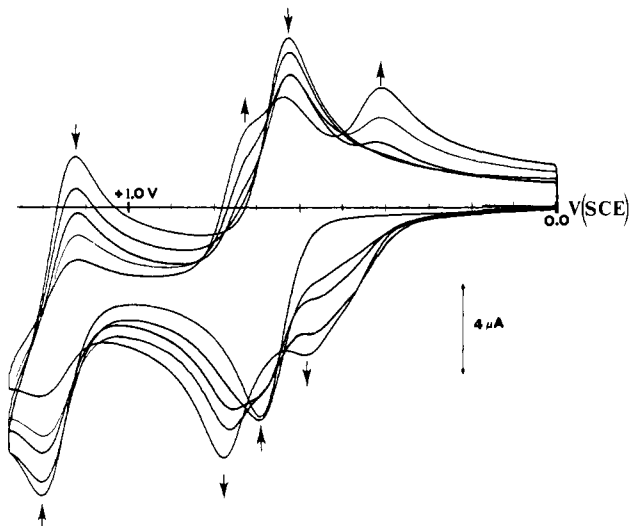
It now appears clear that the oxidation of Ru(II) to Ru(III) makes the Co(II) center a much stronger Lewis acid. This point will be discussed in more detail below. The zero slope of the Ru(II/III) line (Figure 5) above  $[\text{py}] = 3 \times 10^{-2}$  M reflects the fact that both Ru(II)-Co(II) and Ru(III)-Co(II) bind py above this concentration and so  $p = q = 1$ . The intercept of the Ru(II/III) line is 0.466 V and  $(E_{1/2})_s = 0.658$  V for the Ru(II/III)-Co(II) couple without py, giving  $\log(K_{\text{py}}^{3,2}/K_{\text{py}}^{2,2}) = 3.24$ . Using  $K_{\text{py}}^{2,2}$  from the Co(II/I) line, we find  $\log K_{\text{py}}^{3,2} = 4.96$ .

The Ru(III)-Co(II/III) line (top) has zero slope at all  $[\text{py}]$  above stoichiometric levels. Since shifts in this wave are the result of py binding to the Co center, we must conclude that  $p = q = 1$  and that both Ru(III)-Co(III) (with formation constant  $K_{\text{py}}^{3,3}$ ) and Ru(III)-Co(II) bind one py molecule when  $[\text{py}]$  is above stoichiometric levels. In this case, the intercept is equal to  $(E_{1/2})_c$  in eq 1 and is found to be 0.744 V.  $(E_{1/2})_s$  is 1.18 V and we calculate  $\log(K_{\text{py}}^{3,3}/K_{\text{py}}^{3,2}) = 7.43$ . Using  $K_{\text{py}}^{3,2}$  from the Ru(II/III) line, we find  $\log K_{\text{py}}^{3,3} = 12.4$ .

**Table I.** Absorption Maxima and Binding Constants of the Various Oxidation States of **3** and of Some Simple Co Porphyrins<sup>a</sup>

porphyrin <sup>c</sup>	$\lambda_{\max}$ nm	log <i>K</i>
Ru <sup>II</sup> -Co <sup>II</sup>	415, 525	
Ru <sup>III</sup> -Co <sup>II</sup>	412, 524, 554 (sh)	
Ru <sup>III</sup> -Co <sup>II</sup> P <sup>+</sup>	390 (sh), 414, 524, 546	
Ru <sup>II</sup> -Co <sup>II</sup> py	398 (sh), 416, 528	1.72
Ru <sup>III</sup> -Co <sup>II</sup> py	393 (sh), 415, 430 (sh), 531	4.96
Ru <sup>III</sup> -Co <sup>III</sup> py	400, 521 (sh), 550	12.4
Ru <sup>II</sup> -Co <sup>II</sup> -1-MeIm	400 (sh), 418, 524	1.85
Ru <sup>II</sup> -Co <sup>III</sup> -1-MeIm	389 (sh), 424, 532	<i>b</i>
Ru <sup>III</sup> -Co <sup>III</sup> -1-MeIm	401, 413 (sh), 525, 550	<i>b</i>
Co <sup>II</sup> TPP(py)		2.90 <sup>12</sup>
Co <sup>III</sup> TPP(py)		12.7 <sup>12</sup>
Co <sup>II</sup> ( <i>p</i> -OCH <sub>3</sub> )PP-1-MeIm		3.05 <sup>14</sup>

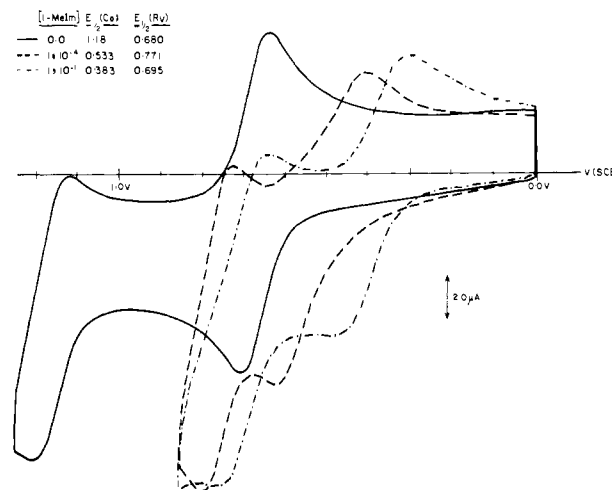
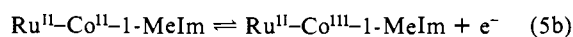
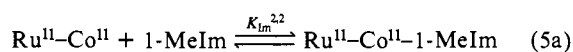
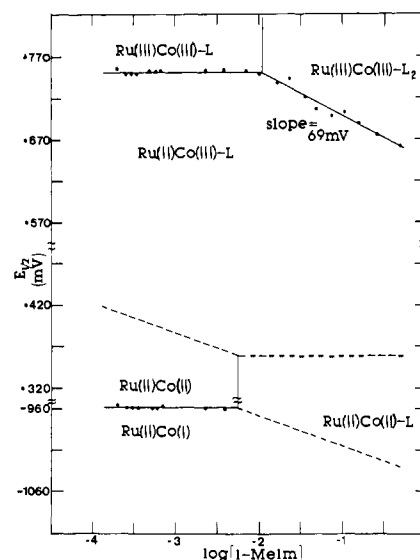
<sup>a</sup>All measurements performed in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>b</sup>Equilibrium binding constants are unavailable from the data obtainable in this study. <sup>c</sup>Ru<sup>II</sup>Co<sup>II</sup>, etc., refers to **3** in the respective oxidation state of each metal indicated by the Roman numerals.

**Figure 7.** Changes observed in the anodic cyclic voltammograms during the addition of substoichiometric amounts of 1-MeIm to a solution of **3** in dichloromethane.

The complete reaction scheme for **3** with pyridine is shown in Figure 6A. The equilibrium constants are summarized in Table I.

**Electrochemistry of RuCl<sub>2</sub>(nic)<sub>4</sub>CoTPP with 1-MeIm.** Figure 7 shows the cyclic voltammograms resulting from the titration of **3** with substoichiometric amounts of 1-MeIm. As in the case of py, the Co(II/I) wave remains unchanged while the original Co(II/III) wave disappears simultaneously with the appearance of a new wave at a more cathodic potential. However, the new Co(II/III) wave is shifted so far in the negative direction (650 mV) that it now precedes the Ru(II/III) wave. During this transition the original Ru(II/III) wave disappears and a new wave appears, shifted anodically by 95 mV. The shift of the Ru wave may be rationalized on the following basis: with 1-MeIm present, the Ru(II/III) couple is effected in the presence of Co(III) rather than Co(II); the Co(III) would be expected to draw electron density away from the Ru(II) through the bridging chloride, thus making the oxidation of Ru(II) more difficult. As with py, the new waves are completely formed when about half an equivalent of 1-MeIm has been added to the solution. Since py and 1-MeIm should have similar diffusion coefficients, our reasoning for the py case should hold for 1-MeIm as well.

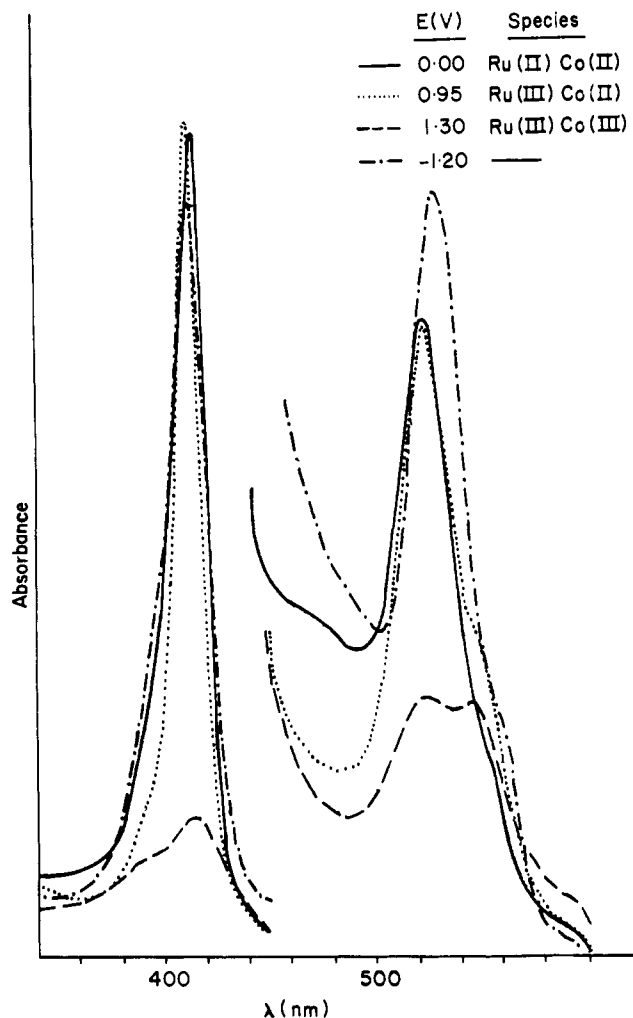
The appearance of the new Co(II/III) wave is an indication that the Ru(II)-Co(III) species is binding a 1-MeIm molecule at the Co site, probably through a CE mechanism:

**Figure 8.** Cyclic voltammograms of **3** in CH<sub>2</sub>Cl<sub>2</sub> with no 1-MeIm (—), 1 × 10<sup>-4</sup> M 1-MeIm (---), and 1 × 10<sup>-1</sup> M (— · —).**Figure 9.**  $E_{1/2}$  vs. log [1-MeIm] for the three metal-centered redox couples of **3** during an electrochemical titration. Dashed lines represent predicted electrochemical results if all couples were reversible. L is 1-MeIm.

Above the stoichiometric level of 1-MeIm, the analysis of the Co(II/III) potential as a function of [1-MeIm] is complicated by the irreversibility of the couple. The peak separation  $\Delta E_p$  varies from 210 mV at the beginning of the titration to 95 mV at the end, and the  $E_p$  values shift by different amounts for the anodic and cathodic processes. In such a case, eq 1 is not applicable and the large shift in  $E_{1/2}$  observed (Figure 8) can only be taken as further evidence of 1-MeIm binding to the Co(II) center.

The Co(II/I) wave remains in its base-free position until [1-MeIm]  $\cong 6 \times 10^{-3}$  M. At this point it both begins to move cathodically and becomes completely chemically irreversible. The irreversibility makes the calculation of  $E_{1/2}$ , and thus analysis of the Co(II/I) titration data, impossible. We note, however, that the onset of the shift in the Co(II/I) wave roughly corresponds to the beginning of the isobestic region ([1-MeIm] =  $1.5 \times 10^{-3}$  M) in the spectrophotometric titration. It is therefore fair to attribute the electrochemical behavior to the binding of 1-MeIm by Ru(II)-Co(II).

Figure 9 shows the titration data for the Ru(II/III) couple. Also included is a dashed line representing the predicted results for the Co(II/III) couple, were that process fast and reversible in the presence of 1-MeIm. The location of the break in the Co(II/III) line is based on the concentration of 1-MeIm for which the spectrophotometric titration first shows 1-MeIm binding to

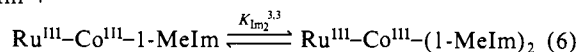


**Figure 10.** UV-vis spectra of **3** in its various oxidation states with no base in solution. The spectrum taken at  $-1.20$  V (— · —) is similar to those of  $\text{Ru}^{\text{II}}\text{-Co}^{\text{II}}$  and  $\text{Ru}^{\text{III}}\text{-Co}^{\text{II}}$ , suggesting that  $\text{Ru}^{\text{II}}\text{-Co}^{\text{I}}$  reacts with the solvent.

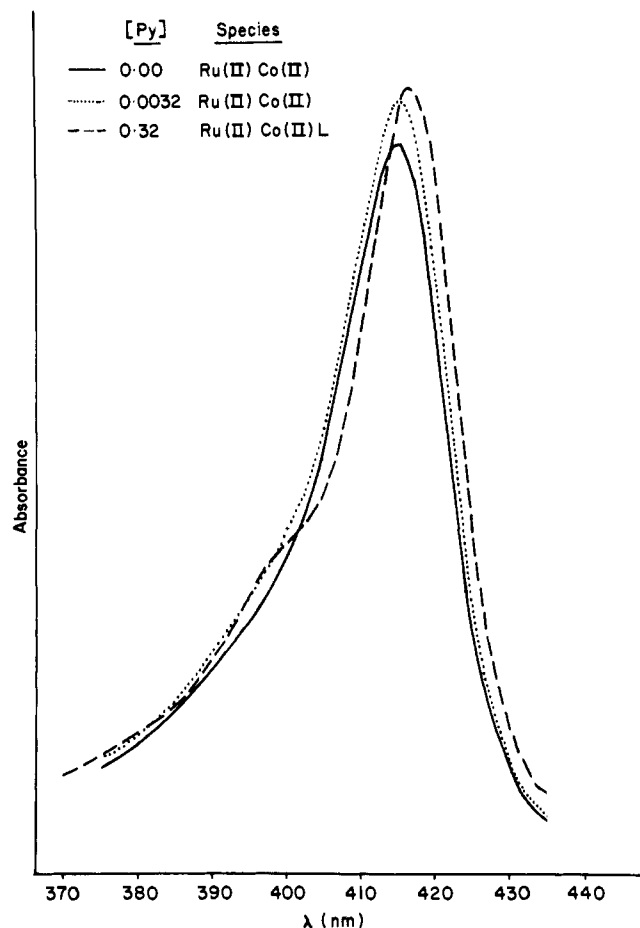
the Co(II) center, and on the concentration of 1-MeIm for which the Co(II/I) wave first begins to shift. The Co(II/I) line plotted shows the zero slope for the range in which this wave has some reversibility and a theoretical line with a predicted  $-59$  mV slope for the region in which Co<sup>II</sup>-1-MeIm binding is observed spectrophotometrically.

Of the three metal-centered couples, only the Ru(II/III) couple is amenable to analysis by eq 1 (see Figure 9). As pointed out above, this wave shows a slight anodic displacement up to the stoichiometric level of 1-MeIm. Beyond the stoichiometric level of 1-MeIm, the wave is fixed until  $[1\text{-MeIm}] = 1.3 \times 10^{-2}$  M where it begins to shift linearly with  $\log [1\text{-MeIm}]$ . The magnitude of the slope is  $-0.069$  V. Since the solution species in this concentration region is  $\text{Ru}^{\text{II}}\text{-Co}^{\text{III}}\text{-1-MeIm}$  (at the potential of the Ru(II/III) couple), the  $-69$  mV slope is indicative of the reaction

1-MeIm +



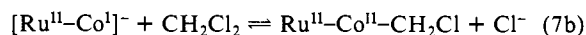
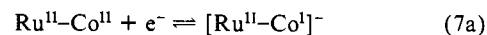
i.e., the complex is binding a second imidazole. We presume that the second 1-MeIm molecule enters the pocket between the two metals and binds at the Co(III) center rather than at Ru(III). This presumption is consistent with the typical substitution inertness of Ru(II) and (III) polypyridine compounds and the fact that the Ru(II/III) couple remains relatively electrochemically reversible in this range of 1-MeIm concentrations. Again, pyridine showed no evidence of binding a second time because of either its larger size or its weaker binding properties.



**Figure 11.** Soret band of **3** at 0 V for three [py], showing binding at Co(II) for high [py]. Note that the spectra for [py] = 0.0032 and 0.32 M are not exactly superimposable due to the evaporation of solvent.

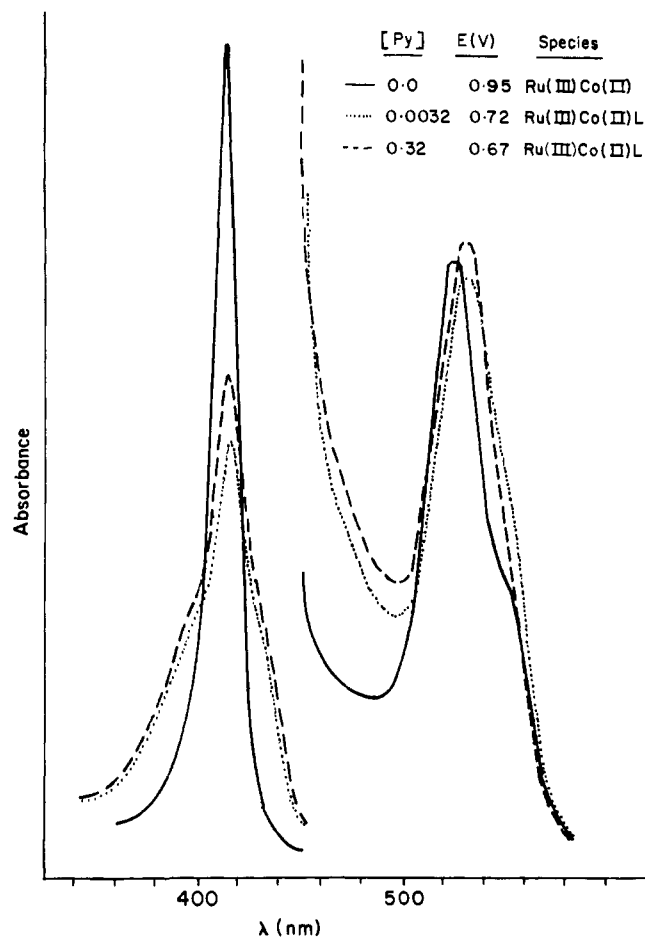
The complete reaction scheme for **3** with 1-MeIm is shown in Figure 6B.

**Spectroelectrochemistry of  $\text{RuCl}_2(\text{nic})_4\text{CoTPP}$ .** Figure 10 shows the UV-vis spectra at potentials corresponding to the four accessible oxidation states of **3** in the absence of base. The spectrum of Ru(III)-Co(II) (0.95 V) differs very little from that of Ru(II)-Co(II). Further oxidation to Ru(III)-Co(III) (1.3 V) dramatically changes both the Soret and visible absorptions. The visible peak is significantly reduced in intensity and is split into two peaks, while the Soret is reduced in intensity by at least a factor of eight and develops a shoulder. This large change in the Soret indicates that the second oxidation is probably ligand-based, and thus the fully oxidized species is better described as the cation radical,  $\text{Ru}^{\text{III}}\text{Co}^{\text{III}}\text{P}^+$ . The reduced species  $\text{Ru}^{\text{II}}\text{-Co}^{\text{I}}$  ( $-1.2$  V) has a spectrum very similar to that of Ru(II)-Co(II). This fact, together with the observation that the cyclic voltammetry shows decreasing chemical reversibility with decreasing scan rate, points to a chemical reaction subsequent to the electron transfer, most probably eq 7. Equations (7) are similar to those proposed by Lexa et al.<sup>16</sup> for the reaction between Co(I)TPP and alkyl bromides.



**Spectroelectrochemistry of  $\text{RuCl}_2(\text{nic})_4\text{CoTPP}$  with Pyridine.** The spectra as a function of py concentration for oxidation states Ru(II)-Co(II) (Figure 11) and Ru(III)-Co(II) (Figure 12) confirm our previous observations. The spectra of Ru(II)-Co(II)

(16) Lexa, D.; Saveant, J. M.; Soufflet, J. P. *J. Electroanal. Chem. Interfacial Electrochem.* 1979, 100, 159.



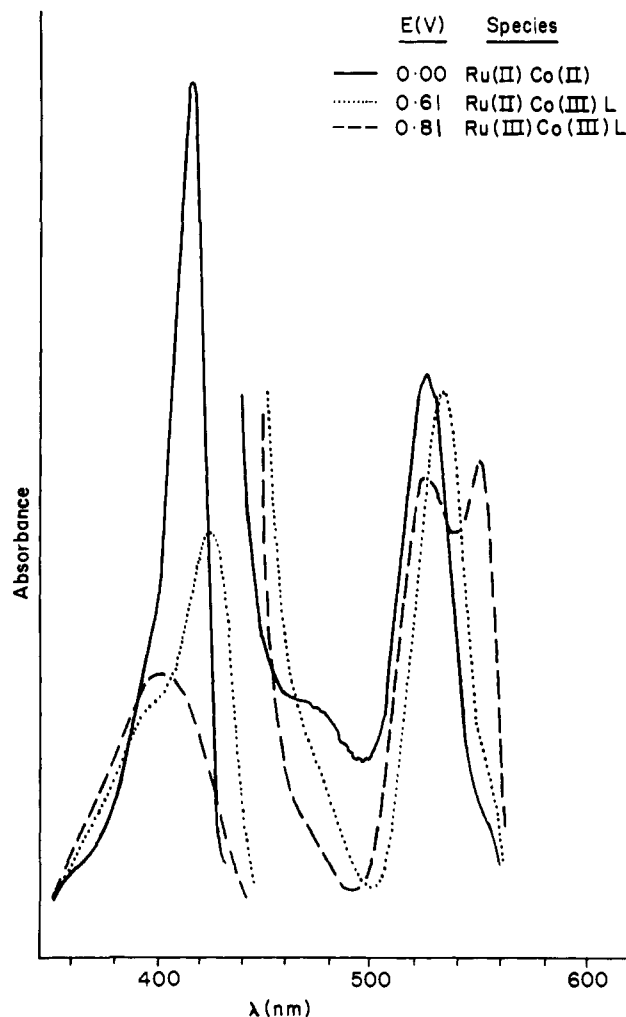
**Figure 12.** Spectra for Ru<sup>III</sup>-Co<sup>II</sup> as a function of [py]. Binding is indicated at low [py].

at [py] = 0.0 and  $3.2 \times 10^{-3}$  M are qualitatively the same, indicating no significant py binding at low [py]. The spectrum at [py] = 0.32 M shows a shoulder around 398 nm and a 1.5-nm red shift of the Soret, confirming py binding to Co(II) as observed in the spectrophotometric titration. When the complex is oxidized to Ru(III)-Co(II), the spectra for [py] = 0.0 and  $3.2 \times 10^{-3}$  M show considerable differences. The spectrum for [py] =  $3.2 \times 10^{-3}$  M has a shoulder at 390 nm, and the Soret is red shifted 1.5 nm from that of the [py] = 0.0 spectrum. This result is consistent with the proposal that oxidation of Ru(II) triggers py binding at Co(II). The spectrum of Ru(III)-Co(II) at [py] = 0.32 M is qualitatively the same as that at [py] =  $3.2 \times 10^{-3}$  M, showing that no further reaction occurs at higher [py].

We note that the Soret band for Ru<sup>III</sup>-Co<sup>III</sup>-py (not shown) is much sharper and is of greater intensity than that for Ru(III)-Co(III) (Figure 10). This suggests that when Co(II) is complexed by pyridine, the oxidation has more metal-centered character than when base is not present.

**Spectroelectrochemistry of RuCl<sub>2</sub>(nic)<sub>2</sub>CoTPP with 1-MeIm.** Figure 13 shows the spectra of the accessible oxidation states of **3** in the presence of  $1 \times 10^{-3}$  M 1-MeIm. The spectrum of Ru(II)-Co(II) shows no sign of complexation. The spectrum of Ru(II)-Co(III) (0.61 V) has a shoulder around 395 nm and the Soret band is red shifted about 12 nm; the visible band is also red shifted, by about 8 nm. These spectral changes demonstrate that the complex Ru<sup>II</sup>-Co<sup>III</sup>-1-MeIm is responsible for the wave at 0.53 V seen in cyclic voltammetry. As noted in the py case, the complexed Ru(III)-Co(III) spectrum shows a Soret band which is much sharper and more intense than that of the uncomplexed species.

Unfortunately, we could not obtain spectral evidence for the bis-adduct of 1-MeIm with **3** since this complex is formed only at high [1-MeIm], and under such conditions the gold OTTL grid is oxidized rather than the Ru-Co complex.



**Figure 13.** Spectra of **3** in the presence of  $1 \times 10^{-3}$  M 1-MeIm at 0 V (—), +0.61 V (···), and +0.81 V (---).

## Discussion

The results herein reported indicate that, except for sterically hindering one side of the porphyrin, the neutral Ru<sup>II</sup>Cl<sub>2</sub>(nic)<sub>4</sub> moiety exerts only very subtle effects on the Co(II) center. The visible spectrum is qualitatively very similar to that of Co<sup>II</sup>TPP.<sup>17</sup> The formation constant for the Ru<sup>II</sup>-Co<sup>II</sup>-py complex,  $\log K_{py}^{2,2} = 1.54$ , is reasonable for a hindered porphyrin given the  $\log K_{py}^{1,py} = 2.90$  measured for py-Co<sup>II</sup>TPP by Kadish et al.<sup>12</sup> Similarly, the formation constant  $\log K_{1m}^{2,2} = 1.85$  is reasonable compared to  $\log K_{1m}^{1,m} = 3.05$  for Co<sup>II</sup>T(*p*-OCH<sub>3</sub>)PP measured by Rillema et al.<sup>14</sup> The Co(II/I) redox potential is almost identical with that of CoTPP. The only significant deviation from typical Co(II) porphyrin behavior that we have observed is the inertness of **3** toward reaction with oxygen. In the presence or absence of Lewis bases, the solution electrochemistry and spectroscopy of **3** show no signs of oxygen binding to the Co(II) center. Even this is likely the result of the steric inaccessibility of one face of the porphyrin ring. Our previous preliminary studies with other porphyrin complexes suggest that the lack of perturbation of the metalloporphyrin by Ru(II) is not unique to the Co(II) case, but appears to be general for the eight Ru/M complexes which we have examined.<sup>5</sup>

The situation is clearly very different when the Ru(II) center is oxidized, giving the Ru<sup>III</sup>Cl<sub>2</sub>(nic)<sub>4</sub><sup>+</sup> form. This fixed cationic ligand greatly increases the Lewis acid strength of Co(II) relative to the strength of that center in CoTPP. For Ru(III)-Co(II) we measured  $\log K_{py}^{3,2} = 4.96$ , which is more than three orders of

(17) Edwards, L.; Dolphin, D. H.; Gouterman, M.; Adler, A. D. *J. Mol. Spectrosc.* **1981**, *38*, 16.

magnitude greater than  $K_{py}^{2,2}$ . For Ru(III)-Co(III), we found  $\log K_{py}^{3,3} = 12.4$ , which is about seven orders of magnitude greater than  $K_{py}^{3,2}$ . In the case of CoTPP in  $CH_2Cl_2$  solution,<sup>12</sup>  $\log K_1$  for pyridine binding increase from 2.90 for Co<sup>II</sup>TPP to 12.7 for Co<sup>III</sup>TPP. Thus for pyridine binding the oxidation of Ru(II) has a large effect on the Lewis acidity of Co(II) and has little effect on Co(III), at least when compared to Co<sup>III</sup>TPP. For 1-MeIm binding at Co(III), on the other hand, conversion of Ru(II) to Ru(III) allows the formation of the bis 1-MeIm adduct. We strongly suspect that the effects manifested by the Co(II) center upon oxidation of Ru(II) are electrostatic in origin, probably mediated by the bridging chloride. The Ru-Cl bond distance is not expected to shorten drastically upon oxidation ( $<0.1 \text{ \AA}$ ).<sup>18,19</sup> Also, if the  $Ru^{III}Cl_2(nic)_4^+$  moiety's effect were due to factors other than electrostatic, the Ru(II) should exert a greater influence on the Co(II) center than that observed, since the Co-Cl distance would be shorter in the Ru(II) form than in the Ru(III) form. However, unambiguous answers to questions about the origin and types of interactions between the Co and Ru ions must await further studies such as EPR, magnetic susceptibility, X-ray structural determination, and EXAFS, which are planned or in progress.

Irrespective of the origins of the interactive effects, this complex and the others in this series represent a unique class of porphyrin

compounds having (1) a fixed, cationic axial ligand (2) with a charge which can be turned on and off and (3) without any significant geometric rearrangement. On the basis of a recent X-ray crystal structure obtained for **3**, the Ru-Co distance has been established to be  $5.24 \text{ \AA}$ .<sup>20</sup> If there were any direct, non-electrostatic interactions such as spin coupling, these interactions would have to be mediated by the bridging chloride.

The large changes in both redox potential and binding properties of the cobalt center, triggered by changing the oxidation state and charge of the ruthenium, are both interesting and important observations because they suggest ways that one might tailor the properties of a particular porphyrin system in a desired way. For example, one could envision replacing the ruthenium with a less easily reduced metal, such as osmium or chromium, and produce similar changes in the M(II/III) couples for the more easily oxidized iron and manganese porphyrins (the oxidations of which occur at potentials negative of the Ru(II/III) couple). Similarly, replacing one or both of the ruthenium-bound chlorides with a suitable dianion would produce a fixed ligand with the opposite charge. We presently have such studies in progress.

**Acknowledgment.** Support of this work is gratefully acknowledged through US Department of Energy, Division of Chemical Sciences, Special Contract DE-AC02-81ER10968.

**Registry No.** 2, 97232-55-8; 3, 97170-40-6; pyridine, 110-86-1; *N*-methylimidazole, 616-47-7.

(18) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 925.

(19) Beattie, J. K.; Hush, N. S.; Taylor, P. R.; Raston, C. L.; White, A. H.; *J. Chem. Soc., Dalton Trans.* 1977, 1121.

(20) Anderson, O. P.; Schauer, C. K., unpublished results.

## The Characterization of a New Heteropolytungstoarsonate Anion, $[CH_3AsW_7O_{27}H]^{7-}$ . Topological Relationships among Ions Related to the Lindqvist Structure

Geoffrey B. Jameson,\*† Michael T. Pope,\*† and Sadiq H. Wasfi†

Contribution from the Chemistry Department, Georgetown University, Washington, D.C. 20057, and Chemistry Department, Delaware State College, Dover, Delaware 19901. Received January 29, 1985

**Abstract:** Guanidinium salts of the anions  $[RAsW_7O_{27}H]^{7-}$ , where  $R = CH_3, C_6H_5,$  and  $p-NH_2-C_6H_4$ , have been isolated in crystalline form from weakly basic solutions (pH 7-8.5) of  $RAsO_3^{2-}$  and  $WO_4^{2-}$ . Crystals of the methyl derivative as  $(CN_3H_6)_7[CH_3AsW_7O_{27}H] \cdot 3H_2O$  are orthorhombic, space group  $Pnma$ , with  $a = 17.605(3) \text{ \AA}$ ,  $b = 13.179(1) \text{ \AA}$ , and  $c = 19.869(3) \text{ \AA}$ ,  $Z = 4$ ,  $d_{calcd} = 3.29 \text{ g cm}^{-3}$ , and  $d_{obsd} = 3.32(2) \text{ g cm}^{-3}$ . Mirror symmetry is imposed upon the anion and upon several cation sites. Least-squares refinement (2184 data with  $I > 3\sigma(I)$  and  $(\sin \theta)/\lambda < 0.5958 \text{ \AA}^{-1}$ ) converged at values for  $R$  and  $R_w$  of 0.044 and 0.045. The  $CH_3AsO_3$  moiety sits above one or the other of two chemically distinct triangular  $O_3$  sites in a 75:25 ratio. The  $W_7O_{24}$  group comprises a horseshoe of four edge-shared  $WO_6$  octahedra linked at four vertices to a triangle of edge-shared octahedra. This group is topologically related to the Lindqvist  $M_7O_{24}^{6-}$  structure. Some selected metrical details for the major isomer are given with the esd of an individual bond and the esd of the average, respectively, in parentheses: 13(W=O) 1.73 (2, 3); 16(W-O<sub>bridging</sub>) 1.93 (1, 6); 2(W-O<sub>triplely bridging</sub>) 1.980 (13) and 2.213 (12); 3(W-O<sub>As</sub>) 2.201 (12)-2.47 (2)  $\text{ \AA}$ . The proton is almost certainly located for the major isomer on the doubly bridging oxygen atom to which the As is attached in the minor isomer (W-O = 2.215 (12)  $\text{ \AA}$ ) and very likely for the minor isomer on the triply bridging oxygen atom to which As is attached for the major isomer, although in this case the expected extension of the W-O separation is masked. In the solid state the <sup>13</sup>C CPMAS NMR spectrum shows the methyl resonance at 20.3 ppm with a shoulder at ca. 17 ppm attributed to the minor isomer. The heteropolyanion (<sup>1</sup>H NMR, 1.98 ppm, methyl) is rapidly converted into  $[(CH_3As)_2W_6O_{25}H]^{5-}$  (2.1, 2.4 ppm) and/or  $CH_3AsO_3^{2-}$  (1.8 ppm) in aqueous solution. Plausible mechanisms connecting  $W_7O_{24}^{6-}$  (paratungstate-A, Lindqvist structure) and  $RAsO_3^{2-}$  with both isomers of the title heteropolyanion are described.

Much of the current resurgence of interest in the chemistry of heteropolymolybdate and tungstate anions<sup>1</sup> may be attributed to the potential of these species for catalysis, especially since the structures of polyanions model metal oxide surfaces. For this and

other reasons the field of organic/organometallic derivatives of heteropolyanions has expanded greatly since 1975.<sup>2-12</sup> One

\* Georgetown University.

† Delaware State College.

(1) Pope, M. T. "Heteropoly and Isopoly Oxometalates"; Springer-Verlag: New York, 1983.

(2) (a) Kwak, W.; Pope, M. T.; Scully, T. F. *J. Am. Chem. Soc.* 1975, 97, 5735. (b) Stalick, J. K.; Quicksall, C. O. *Inorg. Chem.* 1976, 15, 1577.