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## Reduction of Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) by Hexaammineruthenium(II)

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The reduction of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) ( $\text{Co}^{\text{III}}\text{TMpyP}$ ) by  $\text{Ru}(\text{NH}_3)_6^{2+}$  has been studied as a function of pH and added anions. In the range  $2 \times 10^{-5} \leq [\text{H}^+] \leq 0.50$  M, the reactions are pH independent and the catalytic effects of chloride and thiocyanate ions are quite modest; rate constants ( $\text{M}^{-1} \text{s}^{-1}$ , 25 °C) in sulfonate media containing chloride and thiocyanate are given by  $1.2 \times 10^5 + 3.3 \times 10^5[\text{Cl}^-] + 6.6 \times 10^5[\text{SCN}^-]$ . A more pronounced influence on rate occurs when thiocyanate or azide ions are bonded directly to the cobalt site. The rate constants for the  $\text{Ru}(\text{NH}_3)_6^{2+}$  reduction of  $\text{CoP}(\text{H}_2\text{O})(\text{SCN})^{4+}$  is 10 times larger and that for  $\text{CoP}(\text{H}_2\text{O})(\text{N}_3)^{4+}$  is 20 times smaller than that for  $\text{CoP}(\text{H}_2\text{O})_2^{5+}$  in a similar medium.

### Introduction

Proteins containing metalloporphyrin complexes as prosthetic groups are involved in a wide variety of biological functions. Among these is the essential role played by metalloporphyrins in the oxidative phosphorylation network in which they function as both reducing and oxidizing agents. To obtain a more complete understanding of the mechanisms of these reactions and the factors influencing their rate and extent, we are studying redox reactions of simpler synthetic porphyrin complexes. We have reported on the reactions of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) ( $\text{Co}^{\text{III}}\text{TMpyP}$ ) with chromium(II)<sup>2</sup> ion and with sodium dithionite,<sup>3</sup> two potent reducing agents. Both of these substances not only reduce the metal site in  $\text{Co}^{\text{III}}\text{TMpyP}$  but also react rapidly with the ring system itself. We are now reporting on the reactions of this metalloporphyrin and its thiocyanate and azide complexes with a rather mild reducing agent,  $\text{Ru}(\text{NH}_3)_6^{2+}$ . This reducing agent reacts with the porphyrin ring system quite slowly and proves to be a convenient reagent to use for preparing fairly stable solutions of  $\text{Co}^{\text{II}}\text{TMpyP}$ .

### Experimental Section

( $\text{Co}^{\text{II}}\text{TMpyP}$ )<sub>1</sub>s was prepared, purified, and converted to the chloride form by methods described elsewhere.<sup>4,5</sup> The Evans method<sup>6</sup> had been previously employed to demonstrate that the complex is diamagnetic and, therefore, that the cobalt ion is in its +3 oxidation state.<sup>5</sup> This metalloporphyrin shows no tendency to aggregate in aqueous solution over a wide pH range at the concentration levels used here. Aqueous metalloporphyrin solutions are photosensitive and the solutions used in this work were protected from visible and fluorescent light.

Trifluoromethylsulfonic acid was purchased from the 3M Co., Minneapolis, Minn., and was doubly distilled. Hexaammineruthenium(III) chloride ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ ) was purchased from Matthey Bishop, Inc., Malvern, Pa., and purified by literature methods.<sup>7</sup> Europium(III) chloride ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ), purchased from Ventron, Alfa Products, Beverly, Mass., and all other chemicals were reagent grade and were used without further purification.

Solutions of europium(II) were prepared by reducing europium(III) with amalgamated zinc under an argon atmosphere.<sup>7</sup> A carefully measured, deficient amount of the europium(II) solution was transferred to a solution of hexaammineruthenium(III) under anaerobic conditions. The resulting hexaammineruthenium(II) was used within 20 min to reduce  $\text{Co}^{\text{III}}\text{TMpyP}$  solutions. The reaction rates were measured with a Durrum Model D110 stopped-flow apparatus and the spectral measurements were made with a Cary 14 spectrophotometer. Unless otherwise indicated, experiments were conducted at 25 °C and at an ionic strength of 0.5 M.

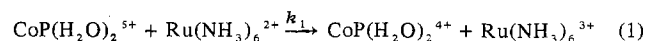
### Results

**Spectral Experiments.** Previous investigations of the reactions of  $\text{Co}^{\text{III}}\text{TMpyP}$  with  $\text{Cr}^{2+}$  and  $\text{S}_2\text{O}_4^{2-}$  were complicated by the fact that these substances not only reduce the metal site (from III  $\rightarrow$  II) but also attack the porphyrin ring system as well.<sup>2,3</sup> Hexaammineruthenium(II) is a relatively

mild reducing agent, and although it is effective at reducing  $\text{Co}^{\text{III}}\text{TMpyP}$  to  $\text{Co}^{\text{II}}\text{TMpyP}$ , it has little effect on the ring system for an extended period of time even when present in large excess. Figure 1 shows the Soret region of the spectrum of  $\text{Co}^{\text{III}}\text{TMpyP}$  and the reduced product at pH 2.0,  $\mu = 0.5$  M. The spectrum of the  $\text{Co}^{\text{II}}\text{TMpyP}$  remains unchanged for about 30 min in the presence of  $4 \times 10^{-4}$  M  $\text{Ru}(\text{NH}_3)_6^{2+}$  (about 100-fold excess of reducing agent). After 4 h, air oxidation of the product still converts about 40% of the material to  $\text{Co}^{\text{III}}\text{TMpyP}$ . The spectrum of  $\text{Co}^{\text{II}}\text{TMpyP}$  is thus more conveniently obtained with  $\text{Ru}(\text{NH}_3)_6^{2+}$  than with the reducing agents previously used and in this work we determined  $\lambda_{\text{max}} 429$  nm and  $\epsilon 1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . This is in excellent agreement with the result obtained with chromous ion; reaction of this reducing agent with  $\text{Co}^{\text{II}}\text{TMpyP}$  was accompanied by a marked decrease in absorbance at 434 nm and yielded a product having  $\lambda_{\text{max}} 428$  nm.<sup>2</sup> That the Soret band of  $\text{Co}^{\text{II}}\text{TMpyP}$  is at shorter wavelength than is the one for  $\text{Co}^{\text{III}}\text{TMpyP}$  parallels results obtained with cobalt cytochrome *c*:  $\text{Co}^{\text{III}}(\text{cyt } c)$  absorbs at 426 nm while  $\text{Co}^{\text{II}}(\text{cyt } c)$  absorbs at 416.5 nm.<sup>8</sup>

Spectral experiments in which  $8 \times 10^{-3}$  M thiocyanate ion was added to the  $\text{Co}^{\text{II}}\text{TMpyP}$  solution were also conducted. After sufficient time had elapsed<sup>4</sup> to allow the formation of  $\text{CoP}(\text{H}_2\text{O})(\text{SCN})^{4+}$ ,  $\text{Ru}(\text{NH}_3)_6^{2+}$  was added to the solution. The Soret peak shifted from 438 nm (characteristic of  $\text{CoP}(\text{H}_2\text{O})(\text{SCN})^{4+}$ ) to 434 nm. The predominant product of the reduction is thus not  $\text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})_2$  but is likely  $\text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})(\text{SCN})$ . Since the Soret peak for the reduced species remains unchanged for more than 15 min and since cobalt(II) complexes are highly labile,<sup>9</sup>  $\text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})(\text{SCN})$  has a stability relative to the diaquo complex which is at least comparable to that of  $\text{Co}^{\text{III}}\text{P}(\text{H}_2\text{O})(\text{SCN})$  relative to its diaquo complex. When  $\text{Ru}(\text{NH}_3)_6^{2+}$  was added to  $\text{Co}^{\text{III}}\text{TMpyP}$  which had been previously incubated with  $9 \times 10^{-3}$  M azide ion (pH 4.6), the Soret band shifted from 442 to 429 nm. The predominant reduced porphyrin form in this case is the diaquo complex.

**Kinetic Experiments.** The kinetic data for the  $\text{Ru}(\text{NH}_3)_6^{2+}$ - $\text{Co}^{\text{III}}\text{TMpyP}$  reaction in 0.5 M chloride medium of  $[\text{H}^+] = 0.010$  M are shown in Figure 2. More than 96% of the metalloporphyrin is in the diaquo form<sup>10</sup> under the conditions used. Experiments were conducted both in the presence and in the absence of added  $\text{Ru}(\text{NH}_3)_6^{3+}$  to determine whether this species has any effect on the reaction. The added  $\text{Ru}(\text{NH}_3)_6^{3+}$  was without effect; all of the data points can be described by a single straight line leading to the rate constant in 0.5 M chloride medium of  $k_1 = (3.0 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction



From experiments at 15.5 °C ( $k_1 = (2.4 \pm 0.3) \times 10^5 \text{ M}^{-1}$

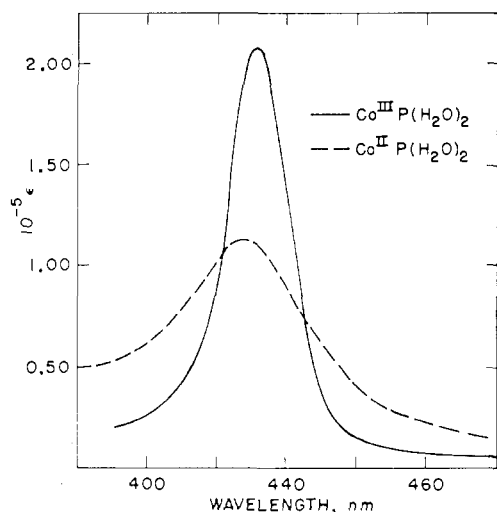


Figure 1. Spectra of  $\text{Co}^{\text{II}}\text{TmpyP}$  and  $\text{Co}^{\text{III}}\text{TmpyP}$  in the Soret region.

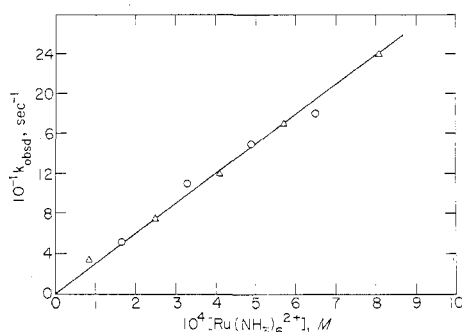


Figure 2. Plot of  $k_1$  vs.  $[\text{Ru}(\text{NH}_3)_6^{2+}]$  at pH 2 in 0.5 M chloride medium for the reaction  $\text{CoP}(\text{H}_2\text{O})_2^{5+} + \text{Ru}(\text{NH}_3)_6^{2+} \rightarrow \text{CoP}(\text{H}_2\text{O})_2^{4+} + \text{Ru}(\text{NH}_3)_6^{3+}$ . The circles represent solutions in which no additional  $\text{Ru}(\text{NH}_3)_6^{3+}$  was added to the reaction mixtures. All of the solutions represented by triangles were  $5 \times 10^{-3}$  M in  $\text{Ru}(\text{NH}_3)_6^{3+}$ .

$\text{s}^{-1}$ ) and  $35.4^\circ\text{C}$  ( $k_1 = (4.4 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) we obtain  $E_a = 5.4 \pm 0.8 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -17 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . The reduction of  $\text{CoP}(\text{H}_2\text{O})_2^{5+}$  by  $\text{Ru}(\text{NH}_3)_6^{2+}$  was studied at  $25^\circ\text{C}$  in 0.5 M chloride medium at pH 4.8 ( $1.5 \times 10^{-3}$  M acetate buffer). Under these conditions, we obtain  $k_1 = (2.6 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  leading us to conclude that the reaction rate is not proton dependent in the pH range 2–4.8.

Experiments were carried out in other media to determine the catalytic effect of added anions. Usually, in such studies, perchlorate ion is used as a standard to which other anions are compared. However,  $\text{Ru}(\text{NH}_3)_6^{2+}$  reacts with perchlorate<sup>7</sup> and, therefore, trifluoromethylsulfonate ( $\text{CF}_3\text{SO}_3^-$ ) was used as the standard. The results of these catalysis experiments are shown in Table I. In these experiments, the added anions ( $\text{Cl}^-$  and  $\text{SCN}^-$ ) were added to the  $\text{Ru}(\text{NH}_3)_6^{2+}$  solutions only. The relative rates of the oxidation–reduction and substitution reactions preclude the possibility that the added anions could enter the cobalt(III) inner coordination sphere prior to the electron-transfer event.<sup>3,4,10</sup> The kinetic data can be fitted to eq 2 and the calculated values of  $k_1$  shown in Table I were

$$k_1 (\text{M}^{-1} \text{ s}^{-1}) = 1.2 \times 10^5 + 3.3 \times 10^5 [\text{Cl}^-] + 6.6 \times 10^5 [\text{SCN}^-] \quad (2)$$

obtained from this expression. For  $[\text{Cl}^-] = 0.5 \text{ M}$  and  $[\text{SCN}^-] = 0$ , we calculate  $k_1 = 2.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in excellent agreement with the experimental value of  $(3.0 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  obtained in 0.5 M sodium chloride medium. The observed rate constants are thus independent of  $[\text{H}^+]$  in the hydrogen ion concentration range  $0.5 \geq [\text{H}^+] \geq 2 \times 10^{-5} \text{ M}$ .

Table I. Catalysis Studies on the Reduction of  $\text{Co}^{\text{III}}\text{TmpyP}$  by  $\text{Ru}(\text{NH}_3)_6^{2+}$  ( $25^\circ\text{C}$ ,  $\mu = 0.5 \text{ M}$ )

$10^4$ $[\text{Ru}(\text{NH}_3)_6^{2+}]$ , M	$[\text{H}^+]$ , M	$[\text{CF}_3\text{SO}_3^-]$ , M	$[\text{Cl}^-]$ , M	$[\text{SCN}^-]$ , M	$k_1, \text{M}^{-1} \text{ s}^{-1}$	
					Calcd	Obsd
0.608	0.50	0.50	0	0	7.3	8.0
1.82	0.50	0.50	0	0	22	22
3.01	0.50	0.50	0	0	36	37
4.20	0.50	0.50	0	0	50	52
5.95	0.50	0.50	0	0	71	72
0.608	0.50	0.257	0.243	0	12	9.5
1.21	0.50	0.257	0.243	0	24	22
1.82	0.50	0.257	0.243	0	36	34
0.621	0.010	0	0.50	0.033	19	17
0.621	0.010	0	0.50	0.057	20	20
0.621	0.010	0	0.50	0.10	22	23 <sup>a</sup>
0.621	0.010	0	0.50	0.11	22	24 <sup>a</sup>

<sup>a</sup>  $\mu = 0.6 \text{ M}$ .

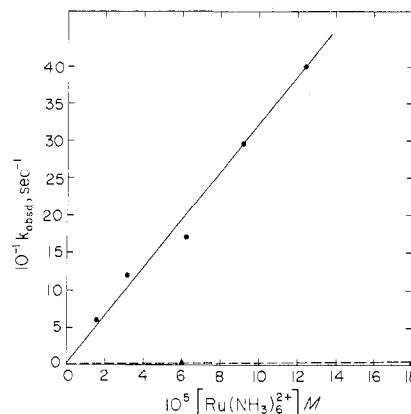
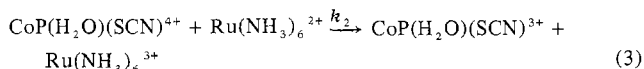


Figure 3. Plots of  $k_{\text{obsd}}$  vs.  $[\text{Ru}(\text{NH}_3)_6^{2+}]$  at pH 2 in 0.5 M chloride medium. The circles represent the data for  $\text{CoP}(\text{H}_2\text{O})(\text{SCN})^{4+}$  giving  $k_3 = 3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and the triangles are for  $\text{CoP}(\text{H}_2\text{O})(\text{N}_3)^{4+}$  for which  $k_3 = 1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

Kinetics experiments in which the porphyrin solutions were  $8 \times 10^{-3} \text{ M}$  in thiocyanate were also conducted in 0.5 M  $\text{Cl}^-$  medium at  $[\text{H}^+] = 0.010 \text{ M}$ . Since the association stability constants for thiocyanate<sup>4</sup> are  $6.4 \times 10^3 \text{ M}^{-1}$  and  $13 \text{ M}^{-1}$ , the predominant porphyrin form in solution at equilibrium under these conditions is  $\text{CoP}(\text{H}_2\text{O})(\text{SCN})^{4+}$ . The data for the reduction of this porphyrin species by  $\text{Ru}(\text{NH}_3)_6^{2+}$  are shown in Figure 3. For the reaction



we find that  $k_2 = 3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  in 0.5 M chloride medium at  $25^\circ\text{C}$ .

Similar experiments were conducted in which the porphyrin solutions were  $9 \times 10^{-3} \text{ M}$  in azide (pH 4.6,  $1.5 \times 10^{-3} \text{ M}$  acetate buffer,  $\mu = 0.5 \text{ M}$  (sodium chloride)). The predominant porphyrin species present under these conditions<sup>11</sup> is  $\text{CoP}(\text{H}_2\text{O})(\text{N}_3)^{4+}$ . The reaction of this metalloporphyrin complex with  $\text{Ru}(\text{NH}_3)_6^{2+}$  was studied over a tenfold concentration range of reducing agent ( $6 \times 10^{-5}$ – $6 \times 10^{-4} \text{ M}$ ) and we obtain a rate constant  $k_3 = 1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for the conversion of  $\text{Co}^{\text{III}}\text{TmpyP}$  to  $\text{Co}^{\text{II}}\text{TmpyP}$ . The rather dramatic difference between the two bound ligands can be seen in Figure 3.  $\text{Ru}(\text{NH}_3)_6^{2+}$  reduces  $\text{CoP}(\text{H}_2\text{O})(\text{SCN})^{4+}$  faster by at least 200 times than it reduces  $\text{CoP}(\text{H}_2\text{O})(\text{N}_3)^{4+}$ .

## Discussion

Hexaammineruthenium(II) is a well-characterized one-electron reducing agent which, because of its relative inertness with respect to ligand substitution, usually acts via an

Table II. Redox Reactions of Co(III) Complexes with Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>

Oxidizing agent	$k_{\text{Cr}^{2+}}$	$k_{\text{Ru(NH}_3)_6^{2+}}$	$k_{\text{Ru(NH}_3)_6^{2+}}/k_{\text{Cr}^{2+}}$	Mechanism for Cr <sup>2+</sup>
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	$8.0 \times 10^{-5}$ <sup>a</sup>	$1.1 \times 10^{-2}$ <sup>b</sup>	$1.4 \times 10^2$	Outer sphere
Co(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O) <sup>3+</sup>	$\leq 0.1$ <sup>c</sup>	$3.0$ <sup>b</sup>	$\geq 30$	Outer sphere or inner sphere involving a very poor bridging group
Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	$6 \times 10^5$ <sup>d</sup>	$2.6 \times 10^2$ <sup>b</sup>	$4 \times 10^{-4}$	Inner sphere
Co(phen) <sub>3</sub> <sup>3+</sup>	$30$ <sup>e</sup>	$\sim 1 \times 10^4$ <sup>f</sup>	$3 \times 10^2$	Outer sphere
CoP(H <sub>2</sub> O) <sub>2</sub> <sup>5+</sup>	$16$ <sup>g</sup>	$1.2 \times 10^5$ <sup>h</sup>	$8 \times 10^3$	Outer sphere or inner sphere involving a very poor bridging group

<sup>a</sup> A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). <sup>b</sup> J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964). <sup>c</sup> T. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971). <sup>d</sup> J. P. Candlin and J. Halpern, *ibid.*, **4**, 766 (1965). <sup>e</sup> Reference 13. <sup>f</sup> C. Creutz and N. Sutin, unpublished results. <sup>g</sup> Reference 2. <sup>h</sup> This work.

outer-sphere reduction pathway.<sup>7,12</sup> The kinetic and spectral results obtained for the reduction of Co<sup>III</sup>TMpyP by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> will therefore be discussed in terms of this type of mechanism. The situation for Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> may be contrasted with Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> which is very labile and which can act as either an outer-sphere or an inner-sphere reducing agent although the latter pathway is preferred where feasible.<sup>13</sup>

Table II compares rate constants for the reduction of a number of Co(III) complexes with Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. Large values for the ratio  $k_{\text{Ru(NH}_3)_6^{2+}}/k_{\text{Cr}^{2+}}$  suggest an outer-sphere pathway for chromium(II) or, possibly, bridging through a water molecule. The results obtained for CoP(H<sub>2</sub>O)<sub>2</sub> are therefore consistent with such an outer-sphere or poorly bridged pathway for Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> as was suggested earlier.<sup>2</sup> The details of the electron transfer from chromium(II) to Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Co(phen)<sub>3</sub><sup>3+</sup> are somewhat different for the two species. It has been suggested that the electron is transferred from one metal center to the other via the  $\pi$  system of the phenanthroline ligands in the latter complex.<sup>14</sup> No such pathway is available for the Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> complex. Since the rate constant ratio shown in Table II is very similar for Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Co(phen)<sub>3</sub><sup>3+</sup>, this ratio is not sensitive to this difference in electron-transfer pathway and thus we cannot determine on this basis whether or not electron transfer for the CoTMpyP involves the  $\pi$  system of the porphyrin.

Anions such as thiocyanate or chloride have been found to catalyze redox reactions.<sup>13</sup> For example, in the reduction of tetrakis(pyridyl)porphineiron(III) by chromium(II),<sup>15</sup> 1 M chloride ion enhances the rate by a factor of  $10^3$  and 1 M thiocyanate by  $3 \times 10^5$ . Smaller but still dramatic catalytic effects were reported for the reduction of tetrakis(4-N-methylpyridyl)porphinecobalt(III) for which the factors for chloride and thiocyanate are 30 and  $2 \times 10^3$ , respectively.<sup>2</sup> This difference in catalytic behavior is accounted for, at least in part, in terms of the difference in labilities of iron(III) and cobalt(III) porphyrins. The relative rates of substitution and reduction are such that the added ions can bridge the two metal centers for iron(III) porphyrins but not for cobalt(III) porphyrins. It appears necessary that the anion be bonded to the metal center of both the porphyrin and the reducing agent for large anion effects to be observed.<sup>2</sup>

In the present study we have conducted experiments in which thiocyanate and/or chloride ion has been added to the Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> solutions only. Once again the reduction reactions are sufficiently rapid that the anions cannot enter the inner coordination sphere of the cobalt(III) ion prior to electron transfer. Furthermore, because Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> is substitutionally inert, the added anions do not bond directly to ruthenium. As expected, the anions, now restricted to outer coordination spheres, provide only a modest catalytic effect, being about three for 1 M chloride and six for 1 M thiocyanate. A somewhat larger effect is found when thiocyanate or azide is bound directly to the cobalt site; the reduction of CoP(H<sub>2</sub>O)(SCN) is 10 times faster and that of CoP(H<sub>2</sub>O)(N<sub>3</sub>) is 20 times slower than the reduction of CoP(H<sub>2</sub>O)<sub>2</sub> by hexa-

ammineruthenium(II) in a mixed chloride-ligand medium.

The rates of outer-sphere redox reactions have been considered from a theoretical point of view by Marcus.<sup>16</sup> For reactions for which the value of  $\Delta G^\circ$  is not too negative, the rate constant for the redox process,  $k_{12}$ , is given by

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2}$$

where  $k_{11}$  and  $k_{22}$  are the self-exchange rate constants of the reactants and  $K_{12}$  is the equilibrium constant for the electron-transfer process. Assuming that the self-exchange rate for CoP(H<sub>2</sub>O)<sub>2</sub><sup>5+</sup>-CoP(H<sub>2</sub>O)<sub>2</sub><sup>4+</sup> is about the same as that for CoP(H<sub>2</sub>O)(SCN)<sup>4+</sup>-CoP(H<sub>2</sub>O)(SCN)<sup>3+</sup>, then  $k_2/k_1 = 3.6 \times 10^6/3.0 \times 10^5 = (K_2/K_1)^{1/2}$  where  $K_1$  and  $K_2$  are the equilibrium constants for reactions 1 and 3, respectively. Thus  $K_2/K_1 \approx 10^2$  or  $[\text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})(\text{SCN})]/[\text{Co}^{\text{III}}\text{P}(\text{H}_2\text{O})(\text{SCN})] \approx 100[\text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})_2]/[\text{Co}^{\text{III}}\text{P}(\text{H}_2\text{O})_2]$ . Put somewhat differently, CoP(H<sub>2</sub>O)(SCN)<sup>4+</sup> is more readily reduced to CoP(H<sub>2</sub>O)(SCN)<sup>3+</sup> than CoP(H<sub>2</sub>O)<sub>2</sub><sup>5+</sup> to CoP(H<sub>2</sub>O)<sub>2</sub><sup>4+</sup> by about 0.12 V.<sup>17</sup> How can this extra stability of CoP(H<sub>2</sub>O)(SCN)<sup>3+</sup> relative to CoP(H<sub>2</sub>O)(SCN)<sup>4+</sup> be rationalized? We have, on the basis of kinetic evidence for substitution processes, suggested that thiocyanate may well be bonded to the metal site in CoTMpyP through a sulfur atom.<sup>3</sup> Should this in fact be the preferred mode of bonding in this species, the redox results are readily understood. If the "soft" end<sup>18</sup> of the thiocyanate ligand is bonded to cobalt, further softening of the metal site, such as by lowering the oxidation state, would tend to stabilize this bond. The kinetic and spectral results obtained for the reduction of CoP(H<sub>2</sub>O)(N<sub>3</sub>)<sup>4+</sup> by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> are consistent with this model. The nitrogen-bound azide ion is expected to be complexed more strongly by Co<sup>III</sup>TMpyP than by Co<sup>II</sup>TMpyP thus making the free energy for the reduction of CoP(H<sub>2</sub>O)(N<sub>3</sub>)<sup>4+</sup> less favorable than that for CoP(H<sub>2</sub>O)<sub>2</sub><sup>5+</sup> or CoP(H<sub>2</sub>O)(SCN)<sup>4+</sup>. This effect manifests itself in a slower rate of reduction and a product which at equilibrium contains no azide.

Finally, it is worth taking special note of the experimental basis for this study. Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> is effective at reducing Co<sup>III</sup>TMpyP to Co<sup>II</sup>TMpyP. In solutions having  $\sim 10^{-6}$  M porphyrin, as little as  $10^{-4}$  M Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> in the presence of  $5 \times 10^{-3}$  M Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> completely reduces the metal site. Using the value of  $\epsilon^\circ = 0.1$  V<sup>7</sup> for the reaction  $\text{Ru}(\text{NH}_3)_6^{3+} + e^- \rightarrow \text{Ru}(\text{NH}_3)_6^{2+}$ , we can estimate that  $\epsilon^\circ \geq +0.3$  V for  $\text{Co}^{\text{III}}\text{P}(\text{H}_2\text{O})_2 + e^- \rightarrow \text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})_2$  from the lack of inhibition by added Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. However, the synthesis of Co<sup>III</sup>P(H<sub>2</sub>O)<sub>2</sub> begins with cobalt(II) chloride and air oxidation leads to the final product. One can then estimate that  $\epsilon^\circ \leq 0.8$  V for  $\text{Co}^{\text{III}}\text{P}(\text{H}_2\text{O})_2 + e^- \rightarrow \text{Co}^{\text{II}}\text{P}(\text{H}_2\text{O})_2$ .

This result can be compared with the experimentally determined half-cell potential for (tetraphenylporphinesulfonate)cobaltate(III), Co<sup>III</sup>TPPS<sub>4</sub>,  $\epsilon_{1/2} = -0.65$  V vs. SCE<sup>19</sup> or approximately -0.4 V vs. the standard hydrogen electrode. Clearly it is much more favorable energetically to reduce Co<sup>III</sup>TMpyP than Co<sup>III</sup>TPPS<sub>4</sub>. Part of this effect is Coulombic since the formal charge types are 5+ and 3-, respectively. However, the charged periphery is relatively distant

from the metal site and this interaction is unlikely to account for the rather substantial difference between the two metalloporphyrins. Rather, we believe that the charges at the periphery appreciably influence the size of the molecular orbitals containing the  $\pi$  electrons and hence the delocalization of the electron density off the metal center. We have in the past noted significant differences in the spectral, acid-base, aggregation, ligation, and substitution properties of water-soluble meso-substituted porphyrins which could be correlated with the charge type at the periphery of the molecule and the resultant influence on the  $\pi$  cloud of the porphyrin moiety.<sup>3-5,20-22</sup> We now see a dramatic effect of peripheral charge on the ease of reduction of the metal center; relative to the positively charged peripheries, the negative periphery leads to a concentration of electron density near the porphyrin core and makes the liganded metal ion more resistant to reduction.

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**Registry No.** Co<sup>III</sup>P(H<sub>2</sub>O)<sub>2</sub>, 51405-04-0; Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, 19052-44-9; CoP(H<sub>2</sub>O)(SCN)<sup>4+</sup>, 57808-60-3; CoP(H<sub>2</sub>O)(N<sub>3</sub>)<sup>4+</sup>, 57808-61-4; Cl<sup>-</sup>,

16887-00-6; SCN<sup>-</sup>, 302-04-5; Co<sup>II</sup>P(H<sub>2</sub>O)<sub>2</sub>, 58188-34-4.

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## Redistribution Reactions of Organometallic Complexes. Carbonyl, Halogen, and Organophosphine Exchange between Coordinately Unsaturated Rhodium(I) and Iridium(I) Complexes<sup>1</sup>

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Halide, carbon monoxide, and organophosphines undergo intermolecular exchange between four-coordinate species of the type MCOXL<sub>2</sub> [M = Rh, X = Cl, Br, L = PPh<sub>3</sub>, P(*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, PPh<sub>2</sub>Et, PPhEt<sub>2</sub>, PEt<sub>3</sub>, PPh<sub>2</sub>Me, AsPh<sub>3</sub>, Sb(*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, P(OPh)<sub>3</sub>; M = Ir, X = Cl, Br, L = PPh<sub>3</sub>, PPhEt<sub>2</sub>P(OPh)<sub>3</sub>]. Exchange of CO and X appears to be random. Exchange of organophosphines between rhodium complexes is random whereas phosphine-phosphite exchange between Rh and Ir strongly favors the mixed species MCOC[PR<sub>3</sub>][P(OR')<sub>3</sub>]. Exchange of CO and X is proposed to occur through four-center associative mechanisms whereas organophosphine exchange is proposed to occur via a dissociative process. No CO exchange was observed between Rh<sup>13</sup>COCl(PPh<sub>3</sub>)<sub>2</sub> and RhCOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>.

### Introduction

Transition metal organometallic redistribution reactions have received only a fraction of the extensive study given to redistributions between main group inorganic compounds.<sup>3</sup> Although the square-planar, coordinately unsaturated rhodium(I) and iridium(I) complexes MCOX(PR<sub>3</sub>)<sub>2</sub> have been extensively studied in oxidative addition reactions<sup>4-6</sup> and more specifically as hydrogenation and hydroformylation catalysts,<sup>7</sup> little is known about intermolecular interactions between these complexes in solution. We have, therefore, investigated intermolecular redistribution of ligands using infrared and phosphorus-31 NMR spectroscopy.

### Experimental Section

<sup>31</sup>P spectra were recorded in 5-mm o.d. tubes using the Fourier transform technique at 40.5 MHz on a Varian XL-100 spectrometer. All spectra were obtained under the conditions of white noise proton decoupling. Pulse delay times at 30° were typically 7.5 sec. Chemical shifts are given with respect to external 85% H<sub>3</sub>PO<sub>4</sub>, downfield shifts being negative. Line widths were typically 1 Hz.

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer,

values of  $\nu(\text{CO})$  being good to  $\pm 2 \text{ cm}^{-1}$ . All infrared and NMR samples were prepared under an atmosphere of argon. RhCOCl<sub>2</sub>, L = PPh<sub>n</sub>Et<sub>3-n</sub>, n = 3-0, PPh<sub>2</sub>Me, P(*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, and AsPh<sub>3</sub>, were prepared by addition of the appropriate ligand to hexane solutions of Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>. RhCOCl[Sb(*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sub>2</sub>,<sup>8</sup> RhCOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>9</sup> IrCOCl(PPh<sub>3</sub>)<sub>2</sub>,<sup>10</sup> and Rh<sub>2</sub>Cl<sub>2</sub>(COD)[P(OPh)<sub>3</sub>]<sub>2</sub><sup>11</sup> (COD = cyclooctadiene) were prepared by literature methods. Bromides were prepared by metathesis with LiBr in acetone.

**IrCOCl<sub>2</sub>, L = PPhEt<sub>2</sub>, P(OPh)<sub>3</sub>.** The insoluble blue powder which results from bubbling CO through a CHCl<sub>3</sub> solution of [IrCl(COT)]<sub>2</sub> (COT = cyclooctene) was suspended in benzene and a benzene solution of L was added dropwise until the blue suspension became a clear yellow solution. Excess L was removed by elution through an acid alumina column with chloroform. The resulting solution was reduced in volume and ethyl ether added to induce precipitation. The yellow crystalline solids thus obtained were washed with ethyl ether and dried under vacuum. The products exhibited satisfactory elemental analyses and infrared and <sup>31</sup>P spectra.

### Results and Discussion

**Carbon Monoxide Exchange.** Basolo et al. proposed that the instantaneous exchange of labeled CO with RhCOCl-