A Kinetic Study of the Reaction of *N,N'*-Ethylenebis(salicylideneiminato)cobalt(II) with Bis(hexafluoroacetylacetonato)copper(II)

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Abstract: The reaction of Co(salen) and $Cu(hfac)_2$ in dichloromethane yields Cu(salen)·$Co(hfac)_2$, the product of a coordination sphere interchange reaction. The kinetics of this reaction were studied over a range of Co(salen) concentrations from 6.45×10^{-4} to 1.65×10^{-3} M, and $Cu(hfac)_2$ concentrations from 5.19×10^{-3} to 5.42×10^{-2} M. The kinetics are complex, and indicate the initial formation of an intermediate postulated to be Co(salen)·$Cu(hfac)_2$, followed by its decay to the product via two pathways, one first order in intermediate, and the other first order in intermediate and first order in $Cu(hfac)_2$. Computer simulation of the kinetic data yielded values for the rate constants for the various steps in this reaction mechanism, as well as the extinction coefficient of the intermediate. The reaction is catalyzed by water, and is independent of the concentration of added Et_4Nhfac. The reaction of Co(salen) with $Cu(tfac)_2$ in dichloromethane exhibits kinetic behavior similar to that of the $Cu(hfac)_2$ system, but at an overall lower rate level.

Recently we reported on a series of binuclear metal complexes of the type M(salen)·$M'(hfac)_2$.[2,3] In particular the complex Cu(salen)·$Co(hfac)_2$, *N,N'*-ethylenebis(salicylideneiminato)copper(II) bis(hexafluoroacetylacetonato)cobalt(II) was characterized by x-ray crystal structure determination, mass spectroscopy, and magnetic susceptibility measurements. At that time we noted that this binuclear complex could be generated via the direct reaction of Cu(salen) with $Co(hfac)_2 \cdot 2H_2O$, as well as by a ligand interchange process using Co(salen) and $Cu(hfac)_2$ (eq 1). The latter reaction was very rapid at room temperature in dilute dichloromethane solution.[2,3]

$$\mathrm{Co(salen)} + \mathrm{Cu(hfac)_2} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{Cu(salen)} \cdot \mathrm{Co(hfac)_2} \quad (1)$$

This result was intriguing and unexpected in this solvent, in which ligand displacement and the generation of coordinatively unsaturated ionic species are regarded as highly unlikely. Furthermore, facile metal interchange between multidentate systems with variations in metal site preference has potential implications for metal interchange experiments in metalloprotein systems. We therefore conducted a kinetic investigation of the reaction of Co(salen) with $Cu(hfac)_2$ in dichloromethane in order to determine the mechanism of this unique metal ion-coordination sphere exchange process.

Experimental Section

N,N'-Ethylenebis(salicylideneiminato)cobalt(II) [Co(salen)],[4] *N,N'*-ethylenebis(salicylideneiminato)copper(II) [Cu(salen)],[3] diaquobis(hexafluoroacetylacetonato)copper(II) [$Cu(hfac)_2 \cdot 2H_2O$],[5,6] diaquobis(hexafluoroacetylacetonato)cobalt(II) [$Co(hfac)_2 \cdot 2H_2O$],[7] bis(1,1,1-trifluoroacetylacetonato)copper(II) [$Cu(tfac)_2$],[5] and the adducts Cu(salen)·$Co(hfac)_2$[3] and Cu(salen)·$Co(tfac)_2$ were prepared as previously described.[3] Dichloromethane was refluxed over CaH_2 for at least 48 h and distilled under dry N_2. Anhydrous $Cu(hfac)_2$ was prepared by sublimation at 80 °C and 1 Torr, followed by storage over P_2O_5 in vacuo. This procedure was repeated until only the anhydrous complex, a dark blue crystalline solid, was obtained. Co(salen) was purified by recrystallization from CH_2Cl_2 in an inert atmosphere box to prevent contamination from oxidized species. Anal. Calcd for $CoC_{16}H_{14}N_2O_2$: C, 59.09; H, 4.34; N, 8.61; Co, 18.12. Found: C, 59.12; H, 4.26; N, 8.68; Co, 18.09. These complexes were stored in an inert atmosphere box.

The solutions of the compounds used in the stopped-flow kinetic experiments and in the visible spectroscopic studies utilizing a Cary 14 spectrophotometer were prepared in an inert atmosphere box. Standard volumetric techniques were employed in preparing solutions containing additional components. Stock solutions of one reagent were diluted with aliquots of the second reagent to yield the desired solutions. All transfers to the stopped-flow apparatus were made in serum-stoppered bottles under an argon purge to exclude moisture.

Accurate extinction coefficients for the reactants and products were determined at 470 nm from the least-squares slope of an absorbance vs. concentration plot from a minimum of five independently prepared solutions. Verification of Beer's law behavior at 470 nm and several other wavelengths for the complexes Co(salen), $Cu(hfac)_2$, $Cu(tfac)_2$, Cu(salen)·$Co(hfac)_2$, and Cu(salen)·$Co(tfac)_2$ in dichloromethane was made over a 100-fold concentration range using 1-mm, 1-cm, and 10-cm quartz cells, and their extinction coefficients at 470 nm are 2.93×10^3, 4.2, 8, 165, and 162 $M^{-1}\ cm^{-1}$, respectively. Molecular weight determinations were carried out in dichloromethane by vapor phase osmometry. Magnetic susceptibilities were determined in CH_2Cl_2 by the Evans method.[8]

All kinetic experiments were performed using a stopped-flow spectrophotometer which has been previously described.[9] The reaction was monitored at 470 nm, which corresponds initially to the disappearance of Co(salen). The bath temperature was maintained at 25.0 ± 0.1 °C. Data were collected on a 32-channel analogue input buffer, collecting points at intervals of 5–1000 ms. These data were then transferred to disk storage on the PLATO IV computer-based teaching system CDC Cyber 73 computer.[10] Transmittance of 100% was equated to T_{inf}, and experimental curves of % T vs. time were generated by connecting the data points with straight line segments.

The product Cu(salen)·$Co(hfac)_2$ was isolated from the effluent of the stopped-flow apparatus by evaporating the solvent and subliming away the excess $Cu(hfac)_2$. Its visible spectrum was identical with the visible spectrum of a sample prepared as previously described.[2] Anal. Calcd for $CoCuC_{26}H_{16}N_2O_6F_{12}$: mol wt, 802.8; Co, 7.34; Cu, 7.91; C, 38.90; H, 2.01; N, 3.49. Found: mol wt, 812; Co, 7.41; Cu, 7.90; C, 39.17; H, 2.02; N, 3.45.

Preparation of Cu(salen)·$Cu(hfac)_2$. $Cu(hfac)_2$ (2.40 g, 5 mmol) was dissolved in 50 ml of freshly distilled dichloromethane, and Cu(salen) (1.66 g, 5 mmol) was added to the dark blue-green solution, which turned deep reddish brown on dissolution of the Cu(salen). The reaction was continued for 30 min with gentle warming, followed by evaporation of 25 ml of solvent. A deep reddish brown crystalline solid began to form, and the solution was allowed to cool to room temperature. The product was collected on a frit, recrystallized from dichloromethane, and dried in vacuo. Yield, 3.1 g (76%). Anal. Calcd for $Cu_2C_{26}H_{16}N_2O_6F_{12}$: mol wt, 807.5; Cu, 15.74; C, 38.67; H, 2.00; N, 3.47. Found: mol wt, 801, Cu, 15.86; C, 38.53; H, 2.02; N, 3.60. $\mu_{\mathrm{eff}} = 2.59\ \mu_B$.

Preparation of Co(salen)·$Co(hfac)_2$. $Co(hfac)_2 \cdot 2H_2O$ (1.0 g, 2 mmol) and Co(salen) (0.65 g, 2 mmol) were slurried in 25 ml of purified CH_2Cl_2 and heated to boiling for 1 h in an inert atmosphere box. The evaporated solvent was periodically replaced. After cooling to room temperature, a fine red crystalline solid was isolated, recrystallized from CH_2Cl_2, and dried in vacuo. This compound was found to be air-sensitive when in solution, but was stable as a solid. Yield, 0.9 g

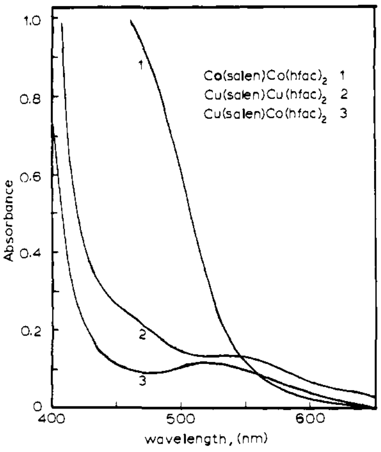


Figure 1. Visible spectra of the binuclear complexes (5×10^{-3} M in CH_2Cl_2, 1.0 mm).

(56%). Anal. Calcd for $Co_2C_{26}H_{16}N_2O_6F_{12}$: mol wt, 798.3; Co, 14.76; C, 39.12; H, 2.02; N, 3.51. Found: mol wt, 799; Co. 14.73; C, 39.31; H, 2.08; N, 3.72. $\mu_{eff} = 5.11\ \mu_B$.

Preparation of Tetraethylammonium Hexafluoroacetylacetonate (Et$_4$Nhfac). Hexafluoroacetylacetone (5.3 ml, 38 mmol), a 10% molar excess, was added via syringe to 50 ml of 10% Et_4NOH (34 mmol) in H_2O. The resulting yellow solution was stirred for 30 min, after which the water was removed on a rotary evaporator, yielding a yellow-white solid. This was placed in vacuo over P_2O_5 for 24 h. The crude product was dissolved in 50 ml of hot anhydrous acetone and allowed to cool to room temperature. Ether, 50 ml, was added, and the resulting solution was placed on dry ice for 2 h. The white crystalline solid that precipitated was collected on a Schlenk frit at −78 °C, warmed to room temperature under vacuum, washed with ether, and dried under vacuum for 24 h. The product is extremely hygroscopic and was stored in an inert atmosphere box. Anal. Calcd for $C_{13}H_{21}NO_2F_6$: C, 46.56; H, 6.38; N, 4.15. Found: C, 46.96; H, 6.46; M, 4.38. NMR ($CDCl_3$) τ 4.49 (s, 1 H), 6.72 (q, 8 H), 8.73 (t of t, 12 H).

Data Analysis. Data analysis for the rather complex kinetic behavior exhibited for reaction 1 was facilitated by the use of computer methods. The differential equations corresponding to a proposed mechanism were numerically integrated for a specified set of initial conditions on the PLATO IV computer system using an improved Euler method, which was shown to give the same results as a fourth-order Runge–Kutta method. After several iterations, the integrated concentrations of all species and their corresponding extinction coefficients were used to calculate the percent transmittance (% *T*) at that time. The theoretical % *T* vs. time curves were constructed by connecting the points calculated in this fashion with straight line segments.

The drastically differing rates for the initial reaction generating the intermediate and its subsequent decay to products permitted a pseudo-first-order kinetic treatment of the disappearance of intermediate. Standard first-order plots for this portion of the reaction were linear over several half-lives, and rate constants were taken from unweighted linear least-squares analysis.

Results

Product Analysis. The product of the reaction of Co(salen) with Cu(hfac)$_2$ in dichloromethane was identified as Cu(salen)·Co(hfac)$_2$ by examination of the visible spectrum of the reaction mixture, and by isolation and identification of the product. As the kinetic studies were conducted with Cu(hfac)$_2$ in large excess, it was necessary to confirm that the presence of excess Cu(hfac)$_2$ did not alter the products. This was done by comparing the visible spectrum of an authentic sample of Cu(salen)·Co(hfac)$_2$ with that of the reaction mixture containing a ca. 50-fold excess of Cu(hfac)$_2$, with an equivalent concentration of Cu(hfac)$_2$ in the reference beam. In contrast to an earlier report,[2] the experimentally determined molecular weight of 812 found for Cu(salen)·Co(hfac)$_2$ is in excellent agreement with the calculated value of 803, indicating that Cu(salen)·Co(hfac)$_2$ is not significantly dissociated in dichloromethane at ca. 10^{-3} M concentration.

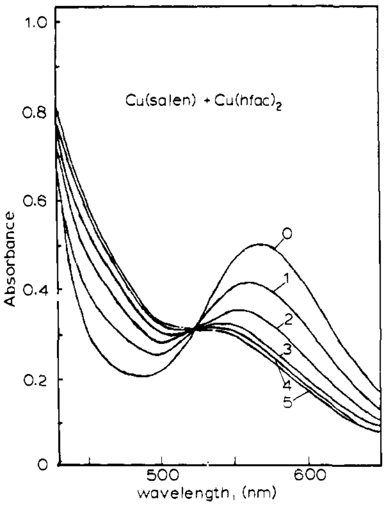


Figure 2. Visible spectrum of Cu(salen) (1.17×10^{-3} M) in CH_2Cl_2 (1.0 mm) in the presence of increasing concentrations of Cu(hfac)$_2$: [Cu(hfac)$_2$], 0, 0; 1, 4.14×10^{-4} M; 2, 8.28×10^{-4} M; 3, 1.24×10^{-3} M; 4, 1.66×10^{-3} M; 5, 2.07×10^{-3} M.

The existence of the possible by-products Cu(salen)·Cu(hfac)$_2$ and Co(salen)·Co(hfac)$_2$ was confirmed by their direct synthesis. A comparison of their visible spectra with that of the product (Figure 1) rules out the possibility of their presence in any significant proportion in the product. Additional spectroscopic studies enabled us to determine the equilibrium constant for adduct formation in the reaction of Cu(salen) with Cu(hfac)$_2$. An isosbestic point is observed in the successive addition of Cu(hfac)$_2$ to a 1.17×10^{-3} M solution of Cu(salen) (Figure 2). At concentrations of Cu(hfac)$_2$ greater than 2.5×10^{-3} M, the isosbestic point is lost. The equilibrium constant determined using a slightly modified Rose–Drago treatment[11] of the absorbance changes at 570 nm was $(2.7 \pm 0.3) \times 10^4$ M^{-1}. These two new complexes, Cu(salen)·Cu(hfac)$_2$ and Co(salen)·Co(hfac)$_2$, react with each other quite rapidly in CH_2Cl_2 to yield Cu(salen)·Co(hfac)$_2$. The physical properties and reactivity of these complexes will be the subject of a subsequent report.

Kinetics. The kinetics of the reaction between Co(salen) and Cu(hfac)$_2$ in dichloromethane at 25.0 °C were studied by stopped-flow visible spectrophotometry with Cu(hfac)$_2$ present in 3- to 80-fold excess. The reaction was monitored at 470 nm, which corresponds to a flat region in the visible spectrum of Co(salen) ($\epsilon_{470}{}^{Co(salen)}$ 2.93×10^3 M^{-1} cm^{-1}) and a minimum in the Cu(hfac)$_2$ spectrum ($\epsilon_{470}{}^{Cu(hfac)_2}$ 4.2 M^{-1} cm^{-1}).

Typical curves of percent transmittance (% *T*) vs. time for the reaction of Co(salen) with Cu(hfac)$_2$ are shown in Figure 3. Even under conditions of ca. 80-fold excess of Cu(hfac)$_2$ the overall reaction does not exhibit pseudo-first-order kinetic behavior. The kinetic curves indicate the very rapid formation of an intermediate, which proceeds to product at a much slower rate. Figure 4 shows the rate profiles for the reaction of a more dilute Co(salen) solution at a faster time base with a series of Cu(hfac)$_2$ solutions. The rate of disappearance of Co(salen) increases as the Cu(hfac)$_2$ concentration is increased. The initial reaction is so rapid at high [Cu(hfac)$_2$] to [Co(salen)] ratios that it appears to be nearly complete during the flow sequence (Figure 4, run 3). These facts suggest that the formation of the intermediate is a second-order process, first order in each reactant.

The further reaction of the intermediate appears to be catalyzed by Cu(hfac)$_2$, as can be seen by comparing the rate

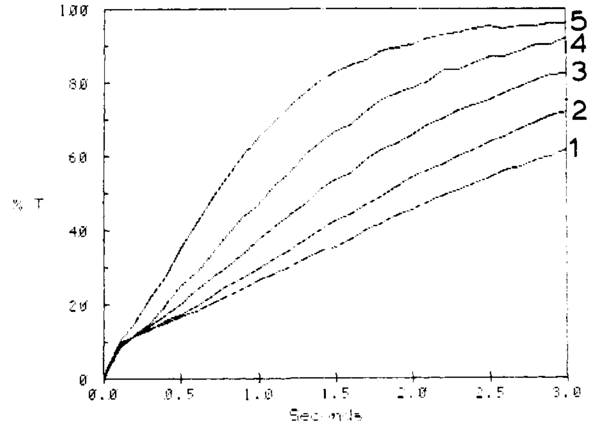


Figure 3. Rate profiles of the reaction of a 1.65 × 10^{-3} M Co(salen) solution with $Cu(hfac)_2$ in increasing concentrations: [Cu(hfac)] 1, 5.19 × 10^{-3} M; 2, 8.87 × 10^{-3} M; 3, 1.22 × 10^{-2} M; 4, 2.71 × 10^{-2} M; 5, 5.42 × 10^{-2} M.

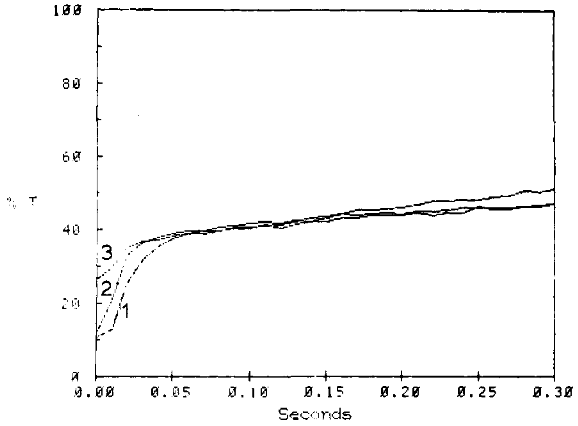


Figure 4. Rate profiles of the reaction of a 6.45 × 10^{-4} Co(salen) solution with $Cu(hfac)_2$ in increasing concentrations: $[Cu(hfac)_2]$ 1, 5.19 × 10^{-3} M; 2, 8.87 × 10^{-3} M; 3, 2.71 × 10^{-2} M.

profiles as the $Cu(hfac)_2$ concentration is increased at constant Co(salen) concentration (Figure 3). The rate of disappearance of the intermediate was subjected to a pseudo-first-order kinetic treatment. A plot of k_{obsd} for the decay of the intermediate vs. $[Cu(hfac)_2]$ yields a straight line with slope = 23.3 M^{-1} s^{-1} and intercept = 0.53 s^{-1} (Figure 5); therefore, $k_{obsd} = k + k'[Cu(hfac)_2]$. This implies that there are competing pathways for rearrangement of the intermediate to product, one of which involves a second molecule of $Cu(hfac)_2$.

A study of the related reaction of $Cu(tfac)_2$ with Co(salen) revealed kinetic behavior very similar to that observed with $Cu(hfac)_2$. However, the break in % T vs. time curves only appeared in the $Cu(tfac)_2$ system at ratios of $[Cu(tfac)_2]\cdot$[Co(salen)] greater than 40, suggesting that formation of the intermediate is an equilibrium process. Since a break was always observed in the $Cu(hfac)_2$ reaction, the equilibrium constant for formation of the intermediate in the $Cu(hfac)_2$ system must be substantially larger than that in the $Cu(tfac)_2$ system. Catalysis of the ligand interchange by $Cu(tfac)_2$ was also observed, although the rate of the overall reaction was considerably slower than that of the reaction of $Cu(hfac)_2$ with Co(salen). A pseudo-first-order treatment was applied to the disappearance of intermediate in solutions containing greater than a 40-fold excess of $Cu(tfac)_2$. Good first-order kinetics were observed, and a plot of k_{obsd} vs. $[Cu(tfac)_2]$ was linear with slope = 16.2 M^{-1} s^{-1} and intercept = 0.22 s^{-1} (Figure 5).

The appearance of a sharp break in the % T vs. time curves

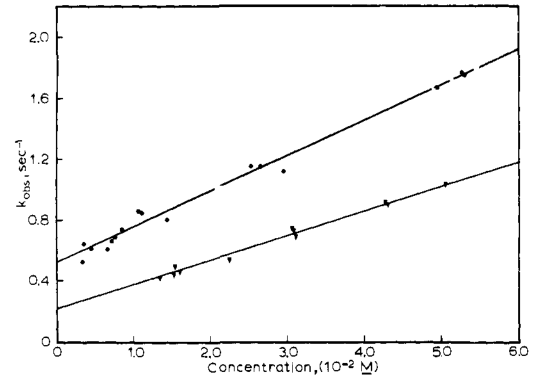


Figure 5. A plot of the pseudo-first order rate constants for the decay of the intermediate vs. $Cu(hfac)_2$ (●) and $Cu(tfac)_2$ (▼) concentrations.

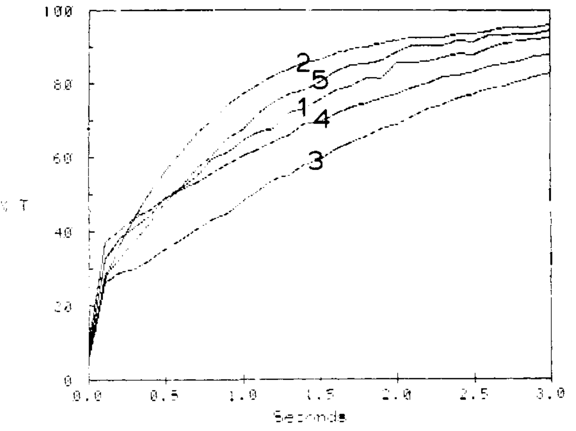


Figure 6. Rate profiles for the reaction of Co(salen) (7.5 × 10^{-4} M) with $Cu(hfac)_2$ (1.13 × 10^{-3} M) in the presence of additives at 5 × 10^{-4} M: 1, no additives; 2, trifluoroacetic acid; 3, pyridine; 4, hexafluoroacetylacetone; 5, water.

in the reaction of $Cu(hfac)_2$ with Co(salen) permits an approximation of the extinction coefficient and of the equilibrium constant for formation of the intermediate. This treatment is feasible because the rate of formation of the intermediate is so much greater than that of its subsequent decay that negligible reaction of the intermediate has taken place by the time the break occurs. The percent transmittance at the point of the break can be converted into an absorbance using eq 2 and 3.

$$\% T = 100 \times 10^{-(\Sigma \epsilon_i C_i - A_{inf})} \quad (2)$$

$$A_{inf} = \epsilon_{product}[Co(salen)]_0 - \epsilon_{Cu(hfac)_2}\{[Cu(hfac)_2]_0[Co(salen)]_0\} \quad (3)$$

The changes in absorbance (the differences between the initial absorbance and that at the break) in a series of reactions employing different Co(salen) and $Cu(hfac)_2$ concentrations are used in the calculation of the equilibrium constant and $\Delta\epsilon$ using a modified Rose–Drago treatment.[11] An approximate K_{eq} of 1 × 10^5 M^{-1} and a $\Delta\epsilon$ of 2.13 × 10^3 M^{-1} cm^{-1} resulted from this treatment. The extinction coefficient of the intermediate is therefore 8.0 × 10^2 M^{-1} cm^{-1}.

Kinetic Effects of Added Reagents. In Figure 6 are plotted the % T vs. time curves for the reaction of 7.5 × 10^{-4} M Co(salen) with 1.13 × 10^{-2} M $Cu(hfac)_2$ solutions containing various additives at 5 × 10^{-4} M. Curve 1 was obtained in the absence of additives. Curve 2 was obtained when trifluoroacetic acid was added, and it indicates that the overall reaction has apparently taken a different course altogether. The depressed rate seen in curve 3 was observed with added pyridine. Curve 4 indicates that the presence of hexafluoroacetylacetone

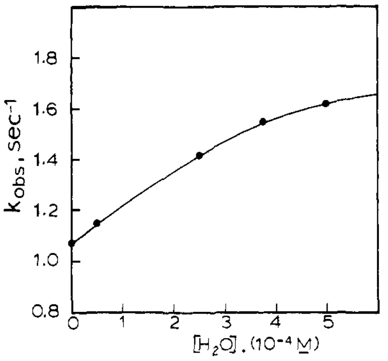


Figure 7. A plot of the pseudo-first-order rate constant for the decay of the intermediate vs. added water concentration.

slightly decreases the rate of disappearance of the intermediate. Curve 5 shows that the presence of additional water at a concentration of 5×10^{-4} M increases the overall rate of the reaction, while maintaining the same general shape as seen in curve 1.

A quantitative study of the kinetic effect of *added* water upon the reaction of Co(salen) with $Cu(hfac)_2$ was undertaken. The rate of disappearance of the intermediate was found to increase approximately linearly with increasing water concentration (Figure 7). Inhibition of the overall reaction was observed only at higher water concentrations.

Kinetics in the Presence of Added Et_4Nhfac. Kinetic experiments were conducted with varying concentrations of free ligand in the form of Et_4Nhfac added to the $Cu(hfac)_2$ solutions. However, spectroscopic studies indicated that the hfac$^-$ did not remain as a free ligand in solution, but was fully complexed to the $Cu(hfac)_2$, as evidenced by Figure 8 in which an isosbestic point was observed for reaction 4. An equilibrium constant of 5×10^5 M^{-1} was calculated for eq 4.

$$Cu(hfac)_2 + hfac^- \rightleftarrows Cu(hfac)_3^- \qquad (4)$$

Further complications were revealed by visible spectroscopic studies which indicated that the products of the reaction of Co(salen) and $Cu(hfac)_2$ are altered in the presence of Et_4Nhfac. The visible spectrum of a reaction solution originally containing Co(salen) (1.1×10^{-3} M), $Cu(hfac)_2$ (1.17×10^{-2} M), and Et_4Nhfac (1.3×10^{-3} M) was *not* the sum of the spectra of Cu(salen)·$Co(hfac)_2$ (1.1×10^{-3} M), $Cu(hfac)_2$ (9.3×10^{-3} M), and $Et_4NCu(hfac)_3$ (1.3×10^{-3} M). However, it very closely approximated the visible spectrum expected for a solution containing Cu(salen)·$Cu(hfac)_2$ (1.1×10^{-3} M), $Cu(hfac)_2$ (9.3×10^{-3} M), $Et_4NCo(hfac)_3$ (1.1×10^{-3} M), and $Et_4NCu(hfac)_3$ (2×10^{-4} M), suggesting that the net reaction was eq 5.

$$\begin{aligned} &Co(salen) + Cu(hfac)_2 + Et_4NCu(hfac)_3 \\ &\quad \rightarrow Cu(salen){\cdot}Cu(hfac)_2 + Cu(hfac)_2 \\ &\qquad + Et_4NCo(hfac)_3 + Et_4NCu(hfac)_3 \qquad (5) \end{aligned}$$

The kinetics of the reaction of 1.09×10^{-2} M $Cu(hfac)_2$ with 1.01×10^{-3} M Co(salen) in the presence of (1.04-2.07) $\times 10^{-3}$ M added Et_4Nhfac indicated that the reaction pathway again consisted of the rapid formation of an intermediate, followed by its disappearance. The pseudo-first-order rate constants calculated for the disappearance of the intermediate were independent of the concentration of Et_4Nhfac.

Discussion

Mechanism of Reaction of Co(salen) with $Cu(hfac)_2$. The kinetic data presented above are qualitatively consistent with a number of chemically reasonable mechanisms. In order to test the validity of specific mechanisms, the PLATO IV computer-based education system was used to calculate theoretical curves of % T vs. time via numerical integration of the differential equations corresponding to a proposed mechanism. The unknown rate constants and extinction coefficients were varied to obtain the optimum fit of the model to the experimental data. Plots of experimental data were superimposed upon the calculated curves in order to visually estimate the accuracy of the fit.

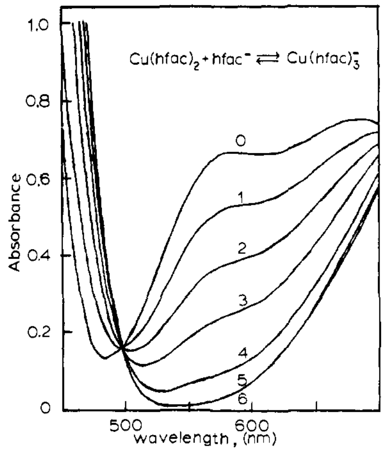


Figure 8. The visible spectrum of $Cu(hfac)_2$ (2.51×10^{-2} M, 1.0 cm) in the presence of increasing concentrations of Et_4Nhfac: [Et_4Nhfac] 0, 0; 1, 5.11×10^{-3} M; 2, 1.02×10^{-2} M; 3, 1.53×10^{-2} M; 4, 2.04×10^{-2} M; 5, 2.56×10^{-2} M; 6, 3.07×10^{-2} M.

The simplest mechanism which is consistent with the results presented above is shown in Scheme I.

Scheme I

$$Co(salen) + Cu(hfac)_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} Co(salen) \cdot Cu(hfac)_2 \ \text{(adduct)} \qquad (6)$$

$$Co(salen) \cdot Cu(hfac)_2 \xrightarrow{k_3} Cu(salen) \cdot Co(hfac)_2 \ \text{(product)} \qquad (7)$$

$$Co(salen) \cdot Cu(hfac)_2 + Cu(hfac)_2 \xrightarrow{k_4} Cu(salen) \cdot Co(hfac)_2 + Cu(hfac)_2 \qquad (8)$$

The differential equations associated with this mechanism are

$$\frac{d[Cu(hfac)_2]}{dt} = \frac{d[Co(salen)]}{dt} = -k_1[Co(salen)][Cu(hfac)_2] + k_2[\text{adduct}]$$

$$\frac{d[\text{adduct}]}{dt} = k_1[Co(salen)][Cu(hfac)_2] - (k_2 + k_3)[\text{adduct}] - k_4[\text{adduct}][Cu(hfac)_2]$$

$$\frac{d[\text{product}]}{dt} = k_3[\text{adduct}] + k_4[\text{adduct}][Cu(hfac)_2]$$

Numerical integration of these equations allows the calculation of a theoretical curve of % T vs. time according to eq 2 and 3 in which 100% T has been equated to T_{inf}. The only parameters in the calculations which may be varied are the four rate constants and the extinction coefficient of the adduct.

We have been successful in fitting the kinetic curves for Co(salen) concentrations of 6.45×10^{-4} to 1.65×10^{-3} M, and $Cu(hfac)_2$ concentrations of 5.19×10^{-3} to 5.42×10^{-2} M

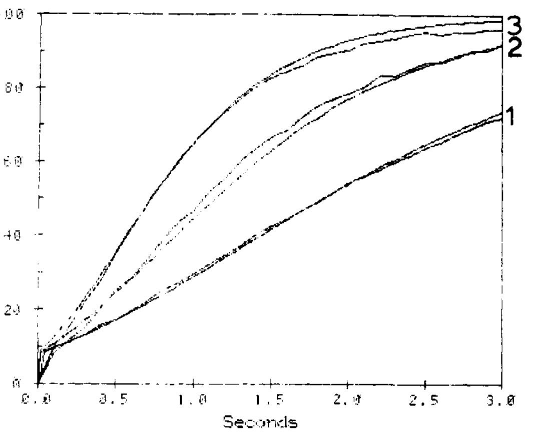


Figure 9. Superposition of the computer simulated kinetic curves and the actual experimental curves: Co(salen), 1.65×10^{-3} M; and Cu(hfac)$_2$ 1, 8.87×10^{-3} M; 2, 2.71×10^{-2} M; 3, 5.42×10^{-2} M.

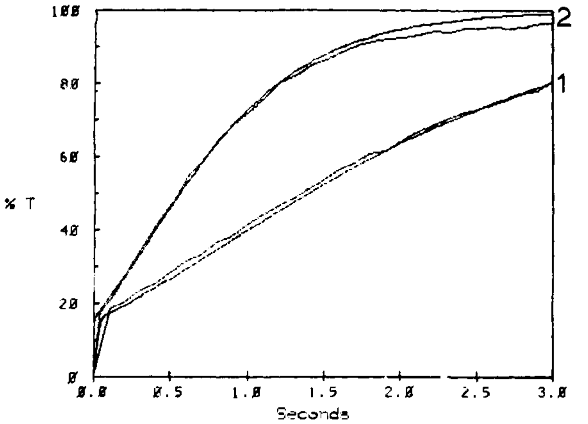


Figure 10. Superposition of the computer simulated kinetic curves and the actual experimental curves: Co(salen), 1.24×10^{-3} M; and Cu(hfac)$_2$ 1, 8.87×10^{-3} M; 2, 5.42×10^{-2} M.

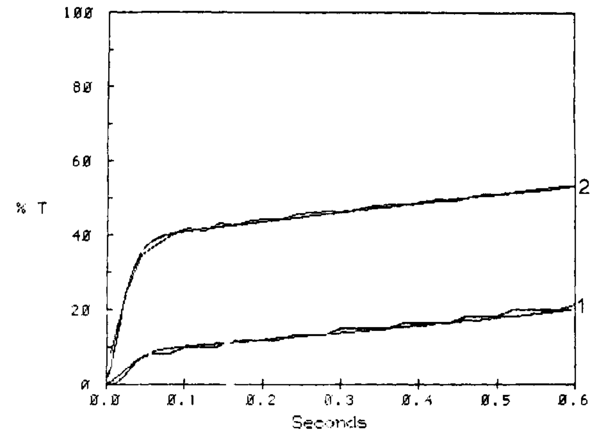


Figure 11. Superposition of computer simulated kinetic curves and actual experimental curves: 1, Co(salen), 1.65×10^{-3} M, and Cu(hfac)$_2$, 8.87×10^{-3} M; 2, Co(salen), 6.45×10^{-4} M, and Cu(hfac)$_2$, 5.19×10^{-3} M.

Table I. Rate Parameters Obtained by Computer Fitting of Kinetic Data from the Reactions of Co(salen) with Cu(hfac)$_2$ at 470 nm

	System	
Parameter	Cu(hfac)$_2$ + Co(salen)	Cu(tfac)$_2$ + Co(salen)
k_1	1.5×10^4 M^{-1} s^{-1} [a]	3×10^2 M^{-1} s^{-1} [a]
k_2	0.1 s^{-1} [a]	1 s^{-1} [a]
k_3 [c]	0.528 s^{-1}; [b] 0.53 s^{-1} [a]	0.22 s^{-1} [b]
k_4 [c]	23.3 M^{-1} s^{-1}; [b] 24 M^{-1} s^{-1} [a]	16.1 M^{-1} s^{-1} [b]
ϵ_{adduct}	820 M^{-1} cm^{-1} [a]	825 M^{-1} cm^{-1} [a]

[a] Parameters are the average of those obtained by computer fitting. [b] Parameters were obtained via the pseudo-first-order treatment of the disappearance of the intermediate. [c] Estimated uncertainties in rate constants are ±5%, based on the range of values necessary to optimally fit all the kinetic curves.

using the mechanism outlined in Scheme I. An average set of parameters obtained by fitting the curves over the entire concentration range studied is listed in Table I. Examples of the quality of the fits, using the values for the five parameters listed in Table I, are seen in Figures 9-11.

The values for k_1 and k_2 were determined by fitting the data obtained from kinetic runs at low absolute concentrations (Figure 11). Their relative magnitudes indicate that the intermediate is formed essentially quantitatively very early in the reaction. The ratio k_1/k_2 indicates that the equilibrium constant for the formation of the intermediate is ca. 1.5×10^5 M^{-1}, in close agreement with the value of 1×10^5 M^{-1} obtained from the decrease in absorbance by the time of the break (vide supra).

The average values obtained for k_3 and k_4 by the data-fitting procedure are in very close agreement with those obtained from a pseudo-first-order treatment of the disappearance of the intermediate, plotting k_{obsd} vs. Cu(hfac)$_2$. The rate law for the decay of the intermediate is thus eq 9

$$-\mathrm{d}(\text{adduct})/\mathrm{d}t = \{k_3 + k_4[\text{Cu(hfac)}_2]\}[\text{adduct}] \quad (9)$$

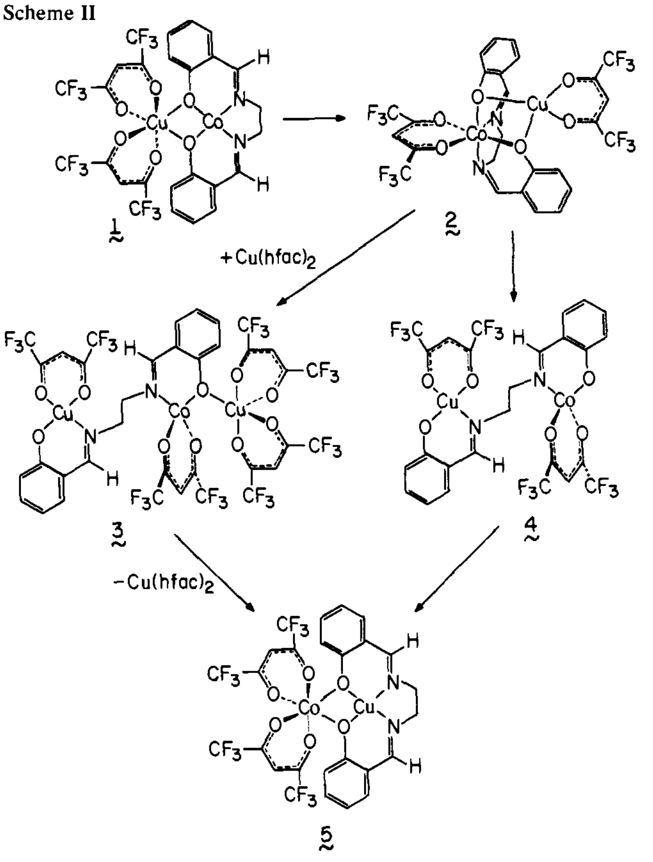
It is significant that the parameters in Table I give excellent fits to the data over the entire concentration range studied: from low Cu(hfac)$_2$ concentrations where the reaction is dominated by first-order decay of the intermediate, to high Cu(hfac)$_2$ concentrations where the second-order pathway predominates.

Detailed Mechanisms. The mechanism represented by reactions 6-8 is consistent with our experimental observations. The first step may be visualized as an acid-base reaction in which the phenolic oxygens of the Co(salen) act as bases toward the strongly acidic Cu(hfac)$_2$. This step was therefore treated as an equilibrium process; the equilibrium constant, k_1/k_2, has a value of 1.5×10^5 M^{-1}, the same order of magnitude as the equilibrium constant determined for the formation of Cu(salen)·Cu(hfac)$_2$ from Cu(salen) and Cu(hfac)$_2$.

The adduct is assumed to have a structure similar to that of the final product, except that the metal ions have not yet exchanged coordination spheres. This intermediate is generated very rapidly, then reacts via two pathways to yield the final product. Reaction 7 may represent an intramolecular rearrangement to yield Cu(salen)·Co(hfac)$_2$, although a stepwise process is not kinetically distinguishable from a concerted rearrangement. Indeed, the latter is difficult to visualize. Equation 8 represents a pathway in which the exchange of coordination spheres is catalyzed by Cu(hfac)$_2$. Our kinetic data do not preclude the formation of a second discrete intermediate composed of two Cu(hfac)$_2$ moieties and a Co(salen). Alternatively, a second Cu(hfac)$_2$ molecule may simply be present in the transition state.

A number of structural arrangements have been found for the salen ligand complexed to metal ions.[12,13] The most common conformation found for first-row transition metal complexes is square planar.[12] However, several metal complexes have been characterized structurally in which the salen ligand is in a strained, nonplanar conformation.[14] This type of structure is a plausible transition state for the conversion of the initial adduct **1** in Scheme II into a possible subsequent in-

Scheme II



termediate **2**. The strained nonplanar environment would permit the migration of a hexafluoroacetylacetonate ligand from the copper ion to the cobalt ion. Rotation of the salen ligand about the ethylene bridge could lead to structure **4**, in which the salen ligand is acting as a bidentate ligand to each of two metal centers, which are thus bridged by the ethylene chain. Similar structural arrangements for the salen ligand have been encountered in some lanthanide complexes,[15] as well as in cobalt(III) complexes.[16] Further rotation of salen about the ethylene bridge leads to the final product **5**.

The catalysis of the ligand rearrangement process by $Cu(hfac)_2$ can be accounted for by an alternate reaction pathway in which $Cu(hfac)_2$ assists the unwinding of the salen ligand from around the cobalt ion. Structure **3** in Scheme II represents a possible intermediate generated by this reaction sequence. Rotation of the salen ligand and expulsion of one $Cu(hfac)_2$ moiety again leads to the final product **5**. All of the reactions shown in Scheme II are postulated to occur without dissociation of an $hfac^-$ ligand.

Ionic Mechanism. Several mechanisms can be envisioned in addition to the one described above. An ionic mechanism involving the loss of a $hfac^-$ ligand from the intermediate as the slow step, followed by the exchange of coordination spheres and recapture of the $hfac^-$ ligand, is perhaps the most likely alternative. The catalysis by $Cu(hfac)_2$ might be accounted for by a step in which the $hfac^-$ is transferred from the intermediate to $Cu(hfac)_2$. In such a mechanism the presence of $hfac^-$ (or $Cu(hfac)_3^-$) should lead to inhibition of the coordination sphere exchange process. Since no inhibition was observed as the concentration of added Et_4Nhfac was increased, our results more strongly support a mechanism involving a series of intramolecular rearrangements without dissociation of a ligand as the pathway for coordination sphere exchange.

Mechanism of Reaction of Co(salen) with $Cu(tfac)_2$. The similarity of the kinetic data for the reaction of Co(salen) with $Cu(tfac)_2$ to the data for the reaction of Co(salen) with $Cu(hfac)_2$ indicates that the mechanisms for coordination sphere interchange in the two systems are closely related. The equilibrium constant for formation of the initial adduct and its extinction coefficient were determined in the $Cu(tfac)_2$ system by computer fitting of the kinetic data. Consistent fits to the experimental data are obtained at ratios of $[Cu(tfac)_2]$ to [Co(salen)] of 20 or greater, and yield the rate constants seen in Table I.

A comparison of the rate parameters for the $Cu(hfac)_2$ reaction with those of the $Cu(tfac)_2$ reaction (Table I) indicates that the greatly reduced rate for the latter process is due primarily to the much smaller equilibrium constant for intermediate adduct formation. The rate constants for the exchange steps are of similar magnitude in both reactions, but the equilibrium constants differ by a factor of 500. The increased equilibrium constant in the $Cu(hfac)_2$ system parallels the increased acidity found for the Cu(II) acetylacetonates upon substitution of the methyl groups by trifluoromethyl groups: $Cu(hfac)_2 > Cu(tfac)_2 > Cu(acac)$.[17,18]

The kinetic results suggest that initial adduct formation is required before the coordination sphere exchange process can proceed, consistent with the observations that the coordination sphere exchange does not proceed in more basic or more acidic solvents, such as acetone or $CHCl_3$.[3] In the basic solvents (e.g., acetone), the $Cu(hfac)_2$[17,18] is rendered unreactive because it is complexed by solvent molecules; in acidic solvents ($CHCl_3$) the phenolic oxygens are prevented from bridging to the $Cu(hfac)_2$ by hydrogen bonding interactions with solvent.[19]

The exchange reaction does not proceed in the reaction of Co(salen) with $Cu(acac)_2$,[2] in contrast to the fact that the expected product, Cu(salen)·$Co(acac)_2$, can easily be prepared by the reaction of anhydrous $Co(acac)_2$ with Cu(salen).[3] The reduced acidity of the unfluorinated β-diketonate Cu(II) complex and the resulting instability of the initial adduct, coupled with an increase in Cu–O bond strength for the unfluorinated species,[7,17] account for this behavior.

Effect of Water upon the Rate of Reaction. The catalysis of the coordination sphere exchange process by $Cu(hfac)_2$ and $Cu(tfac)_2$ is similar to that found in metal ion-assisted and proton-assisted dechelation reactions.[20] Binuclear intermediates are postulated in the metal ion-assisted reactions, in which the second metal ion coordinates to the end of a chelating arm of the multidentate ligand and helps it to unwind from the first metal ion (Scheme II, **2** → **3**).[21,22] The catalysis by H_2O in the reaction of $Cu(hfac)_2$ with Co(salen) can be accounted for by a process similar to that of the proton-assisted dechelation reaction.[20-22] The water molecule could protonate and sequester a phenolic oxygen on the salen ligand, while the hydroxide coordinates to the Co ion (or bridges Co and Cu ions) and maintains the neutrality of the complex. A series of subsequent rearrangements could then proceed with the final displacement of water to yield the product.

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The Outer-Sphere Reductions of Pyridinepentaamminecobalt(III) and Pyridinepentaammineruthenium(III) by Hexacyanoferrate(II)[1a,b]

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Abstract: The rate law for the $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ reaction is $k_{et}^{Co}Q_p^{Co}[Fe(CN)_6^{4-}][Co(NH_3)_5py^{3+}]/(1 + Q_p^{Co}\cdot[Fe(CN)_6^{4-}])$. At 25 °C and ionic strength 0.10 M, $k_{et}^{Co} = (1.5 \pm 0.5) \times 10^{-2}\ s^{-1}$ and $Q_p^{Co} = (2.4 \pm 0.4) \times 10^3\ M^{-1}$. Q_p^{Co} is the equilibrium quotient for the formation of the outer-sphere complex $Co(NH_3)_5py^{3+}\cdot Fe(CN)_6^{4-}$ and k_{et}^{Co} is the rate constant for electron transfer within the ion pair. The equilibrium and rate constants (25 °C, ionic strength 0.10 M) for the $Ru(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ reaction are $(1.0 \pm 0.1) \times 10^{-2}$ and $(4.3 \pm 1.0) \times 10^6\ M^{-1}\ s^{-1}$, respectively. The rate constant at 25 °C and ionic strength 0.10 M for the $Ru(NH_3)_5py^{3+}$–$Ru(NH_3)_6^{2+}$ reaction is $(7.2 \pm 0.4) \times 10^5\ M^{-1}\ s^{-1}$. The mechanisms of these reactions are discussed in the context of Marcus' equation, electrostatic effects, and orbital symmetry considerations.

Electron transfer reactions between transition metal coordination compounds can proceed via inner-sphere or outer-sphere mechanisms. It is generally accepted that a sequence of three elementary steps brings about the overall reaction.[2] For outer-sphere reactions, the steps are formation of a reactant ion pair or outer-sphere precursor complex (eq 1), electron transfer (eq 2), and dissociation of the product ion pair or outer-sphere successor complex (eq 3).

$$\text{ox} + \text{red} \rightleftarrows \text{ox}\|\text{red} \qquad Q_p \qquad (1)$$

$$\text{ox}\|\text{red} \rightleftarrows \text{ox}^-\|\text{red}^+ \qquad k_{et} \qquad (2)$$

$$\text{ox}^-\|\text{red}^+ \rightleftarrows \text{ox}^- + \text{red}^+ \qquad 1/Q_s \qquad (3)$$

The first and third steps are diffusion-controlled reactions, and reaction 2 is often rate determining. If one of the reactants is in excess (say red) and the reaction proceeds to completion, this mechanism leads to the rate law given by eq 4.

$$\text{rate} = \frac{Q_p k_{et}[\text{red}][\text{ox}]}{1 + Q_p[\text{red}]} \qquad (4)$$

For most systems, $Q_p[\text{red}] \ll 1$ because the reactants have the same charge (and therefore Q_p is very small) and/or because the reactions are very fast (and therefore to obtain measurable rates, [red] is very small). Under these circumstances, measured second-order rate constants are equal to $Q_p k_{et}$.

It is important to obtain quantitative information about the individual elementary steps, and we previously[3] reported the results of our studies of the $Co(NH_3)_5OH_2^{3+}$–$Fe(CN)_6^{4-}$ reaction. The presence of a precursor outer-sphere complex was detected kinetically, and the first-order rate constant for intramolecular electron transfer within the ion pair was calculated. The success in obtaining values of Q_p and k_{et} for this system is associated, in part, with the choice of reactants of high and opposite charge. This results in the formation of substantial amounts of the precursor complex even at relatively low reactant concentrations.

On the basis of these results, a systematic study of outer-sphere electron transfer reactions between ions of high and opposite charge was undertaken. In the present paper we report our results on the reduction of the low-spin d^5 and d^6 ions $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$ by $Fe(CN)_6^{4-}$. For comparative purposes, we have also studied the reduction of $Ru(NH_3)_5py^{3+}$ by $Ru(NH_3)_6^{2+}$.

Experimental Section

Materials. House distilled water was passed through a Barnstead ion exchange demineralizer, and then distilled in a modified Corning AG-1b distilling apparatus. Sodium perchlorate, obtained by neutralization of sodium carbonate with perchloric acid, was recrystallized three times. Analytical grade sodium hexacyanoferrate(II) decahydrate was recrystallized twice. Argon was purified by passing it through BTS catalyst. All other chemicals were reagent grade and used as received.

Preparation of Complexes. Pyridinepentaamminecobalt(III) perchlorate prepared by the method of Nordmeyer and Taube[4] was found to be contaminated with hexaamminecobalt(III) perchlorate. Therefore, a concentrated aqueous solution of the impure product was treated with half its volume of alcohol, and the precipitate was discarded. Perchloric acid was added to the filtrate and the precipitate of $[Co(NH_3)_5py](ClO_4)_3$ that formed was collected, washed with alcohol and ether, and then dried in air.