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Racemization, Reduction, and Substitution Reactions of Tris(chelating ligand)metal Complexes. 1. Thermolysis of (−)-Tris(2,2′-dipyridylamine)cobalt(III) Perchlorate in Water and DMF

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The complex ion $Co(HL)_3^{3+}$ is in equilibrium with its conjugate base $Co(HL)_2L^{2+}$ in solution. Aqueous solutions of these ions have been determined to undergo decomposition by a process that has first-order kinetics. At pH 3.04 (T = 70 °C, μ = 0.01) the former complex predominates, and the specific rate constant is $(3.08 \pm 0.23) \times 10^{-5}$ s^{-1}; at pH 8.03 (T = 70 °C, μ = 0.01) the latter complex predominates, and the specific rate constant is $(5.95 \pm 0.35) \times 10^{-5}$ s^{-1}. In aqueous solutions where the concentrations of the two ions are fixed by the equilibrium, only an average rate constant could be determined, its value being $(7.50 \pm 0.83) \times 10^{-6}$ and $(1.77 \pm 0.05) \times 10^{-5}$ s^{-1} at 60 and 70 °C, respectively. ($\Delta H^{\ddagger}$ = 93.3 ± 15% kJ mol^{-1}, $\Delta S^{\ddagger}$ = −63 ± 34% eu.) In DMF solution, the decomposition is more complicated. The CD spectra indicate the formation of a new optically active complex C, with maintenance of an isosbestic point during the first third of the experiments. Complex C then forms another new optically active complex D as the CD spectra decay away to the zero line. The mechanism appears to involve a slow reduction of $Co(HL)_3^{3+}$ ion to a cobalt(II) species. This cobalt(II) species then forms an inner-sphere complex stereospecifically with $Co(HL)_2L^{2+}$ ion through the bridging amide moiety. After electron transfer through the bridge, optically active C is formed with regeneration of the cobalt(II) complex. Fourth-order Runge–Kutta integration has been used to estimate specific rate constants for a simplified reaction scheme.

Introduction

The preparation and the resolution of cobalt(III) complexes of the bidentate ligand 2,2′-dipyridylamine (HL) have been reported.[1,2] The proton in the 3:1 complex has the ability to dissociate from the bridging amine moiety, and the complex thus behaves as an acid in solution, giving the series of complex ions $Co(HL)_3^{3+}$,[3] $Co(HL)_2L^{2+}$, $Co(HL)L_2^{+}$, and CoL_3. The first and the last two of these ions have been isolated and characterized.

Space-filling models indicate that the $Co(HL)_3^{3+}$ ion and CoL_3 are asymmetric because of the nonplanarity of HL,[4,5] and in fact the proton-decoupled ^{13}C NMR spectrum of CoL_3 shows resonances due to the 24 carbon atoms that have a nuclear Overhauser effect.[2]

The electronic absorption spectra of the 3:1 complexes show bands in the visible region that are far too intense to be ascribed to the d–d transitions usually associated with octahedral CoN_6 chromophores. The intensities are about 1 order of magnitude greater than those observed for the $Co(phen)_3^{3+}$ ion, for example. The enhancement of the intensity probably arises from steric interactions of the HL ligands in these complexes, with two possible results: either ligand transitions have been red shifted and are able to mix with the metal d–d transitions or ligand-to-metal charge-transfer excitation occurs in the visible region of the spectrum.

It is clear from the space-filling models of these complexes that, should a Co–N bond be broken, there is little likelihood that it would re-form, and the complexes should then undergo substitution or decomposition. The models also indicate that interconversion of enantiomers of these complexes by any twist mechanism is very unlikely.

The thermolytic study reported here was undertaken to determine if there is a racemization pathway for the enantiomers of these complexes or if loss of optical activity is accompanied by decomposition or substitution.

Experimental Section

Materials. Chemicals were purchased or prepared as follows: HL and Amberlite IRA-HOLS exchange resin was purchased from Aldrich Chemical Co.; *o*-phenanthroline monohydrate, 30% aqueous hydrogen peroxide, sodium perchlorate monohydrate, and reagent grade solvents were purchased from Fischer Scientific Co.; cobalt(II) perchlorate hexahydrate was purchased from G. Frederick Smith Co.; $[Co(HL)_3](ClO_4)_2$ was prepared according to the method of Goodgame;[6] $[Co(HL)_3](ClO_4)_3$ was prepared and resolved according to the method of Johnson and Geldard;[2] the resolving agent (+)-$K_3[Co(L\text{-}CYSU)_3]$ was prepared according to the method of Dollimore and Gillard.[7]

Instrumentation. Electronic spectra were recorded on a Bausch and Lomb Spectronic 2000 spectrophotometer. CD spectra were obtained by using a JASCO ORD/UV-5/CD-1 spectropolarimeter. Computation was done by using a IBM system 370, Model 3033. Measurements of pH were made with a Beckman Model 4500 pH meter.

Thermolysis Studies in Water and DMF. The optically active complex $[Co(HL)_3](ClO_4)_3$ was added to the respective solvent, which had been equilibrated at the reaction temperature (50, 60, and 70 °C), to give green solutions with a concentration range between 10^{-4} and 10^{-5} M. The temperature was maintained by a Forma-Temp Jr. Model 2095 recirculator to within ±0.5 °C. Aliquots were drawn at appropriate times and cooled instantly to 0 °C to quench the thermolysis, and the electronic and CD spectra were measured. The time delay in these measurements introduced negligible error because second measurements of the spectra were identical with the first.

Electron-Exchange Studies. A solution of (−)-$[Co(HL)_3](ClO_4)_3$ in DMF was divided into five portions. To the first portion was added a solution of cobalt(II) chloride; the original pale green solution changed to an intense blue color, but no change was observed in the CD spectrum over a period of 5.5 h. To the second was added a solution of HL. The color of the mixture was pale yellow, but no change in the CD spectrum was observed over a period of 2 days. Because the first portion exhibited no change in optical activity, the ligand phen was added to it. The CD spectrum changed instantly to one that resembled that of the first intermediate, designated the C complex, formed in the thermolysis experiments, but with diminished optical purity. To the third portion was added an equimolar amount of $[Co(phen)_3](ClO_4)_2$. The CD spectrum was unchanged over a period of several days. To the fourth portion was added an equimolar amount of solid $[Co(HL)_3](ClO_4)_2$. The CD spectrum changed instantly to that of the C complex; over the next 200 min, it continued to change just as in the thermolysis experiments. To the last portion was added aqueous ferrous sulfate solution. There was an instantaneous precipitate of reddish brown $Fe(OH)_3$, and the CD spectrum had collapsed to the zero line.

Reduction of $[Co(HL)_3](ClO_4)_3$ in DMF Saturated with HCl. The optically active complex (9.3×10^{-4} g) was dissolved in DMF (1.0 mL), which had been previously saturated with dry HCl gas. The temperature was maintained at 22 °C, and the loss of optical activity monitored for 500 min. The final product was identified as $CoCl_4^{2-}$ ion by its spectrum.

Results and Discussion

Thermolysis in Water. The two complex ions $Co(HL)_3^{3+}$ and $Co(HL)_2L^{2+}$ are in equilibrium with each other in aqueous so-

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(1) Johnson, W. L., III; Geldard, J. F. *Inorg. Chem.* **1978**, *17*, 1675.
(2) Johnson, W. L., III; Geldard, J. F. *Inorg. Chem.* **1979**, *18*, 664.
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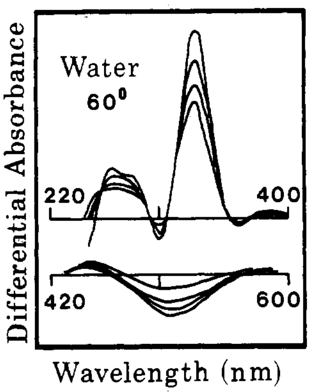


Figure 1. Decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in water at 60 °C: 0 (0.70), 310 (0.59), 918 (0.49), 1030 (0.44).[28]

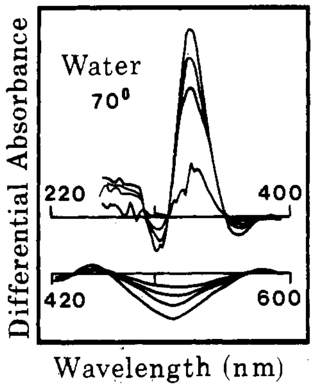


Figure 2. Decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in water at 70 °C: 0 (0.71), 135 (0.61), 350 (0.49), 1040 (0.25).[28]

lution, the pK_a for the dissociation having the value 4.9 ± 0.1 at room temperature. Thus, the loss of optical activity that is observed when aqueous solutions of $Co(HL)_3^{3+}$ are heated must be attributed to the decomposition of both ions, the rates for the thermolyses not necessarily being the same.

To determine the rate for each ion, thermolyses were carried out by using solutions with pH values of 3 and 8, at which A and B, respectively, are the predominant species. Thermolyses were also carried out with solutions in which the pH and the concentrations of A and B were determined only by the dissociation reaction (eq 1).

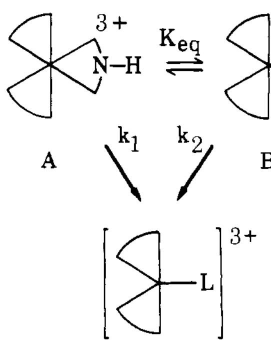
$$\underset{A}{Co(HL)_3^{3+}} = \underset{B}{Co(HL)_2L^{2+}} + H^+ \qquad (1)$$

The loss of optical activity during the thermolyses under these various conditions of pH, temperature, and ionic strength was characterized by the collapse of the CD spectra to the zero line. No shifts in absorption were observed, no new bands appeared, and the differential dichroic intensity curve always crossed the base line at the same wavelength (see Figures 1 and 2). The electronic absorption spectra, by contrast, changed during the course of the experiments in a very complicated way.

The inference drawn from these data is that both the A and the B ions undergo dissociation to five-coordinate species as a precursory step to further decomposition, one ligand becoming monodentate. Substitution and decomposition reactions of cobalt(III) complexes appear to occur by a dissociative mechanism rather than an associative one.[8,9] This five-coordinate species solvates rapidly to an aquo complex that then undergoes either fast racemization or fast substitution and racemization (see Scheme I).

It is important to note that whereas, in the A ion, the HL ligands are relatively strong acids, there is no indication of unusual acidity

Scheme I. Decomposition of $[Co(HL)_3](ClO_4)_3$ in Water[a]



[a] The five-coordinate intermediate undergoes either fast racemization or fast decomposition.

in the bis(HL) complexes of cobalt(III); (carbonato)bis(HL)cobalt(III) ion and peroxobis(HL)cobalt(III) ion show no evidence that the HL ligands are capable of acidic behavior. The tris(HL) complexes of rhodium(III) and iridium(III) also show no unusual or enhanced acidity associated with the bridging amine moiety.[10] The five-coordinate intermediates formed by dissociation of the B ion presumably scavenge protons in solution, causing the amide moiety to be protonated to HL. For this reason, only a single intermediate is shown in Scheme I.

The CD spectra of solutions of A and B in equilibrium are characterized by two fairly intense bands at 510 and 330 nm. The decay of these bands, as a function of time, was used to estimate the two first-order rate constants k_1 and k_2 of Scheme I.

The two rate constants were evaluated as follows. At low pH, the concentration of B is negligible, and the loss of optical activity is due to principally to the thermolysis of the A ion; at high pH, the reverse is true. The $[H^+]$ and $[OH^-]$ values remain constant during the thermolyses, and the rates of decomposition reduce to the simple first-order decay equations

$$d[A_T]/dt = -k_1[A] \qquad (2)$$

$$d[A_T]/dt = -k_2[B] \qquad (3)$$

at pH 3 and 8 respectively, and where

$$[A_T] = [A] + [B]$$

The differential dichroic absorbance can be written as

$$\delta(t) = \Delta\epsilon_A[A]_0 \exp(-k_1 t) \qquad (4)$$

at pH 3, and as

$$\delta(t) = \Delta\epsilon_B[A]_0 \exp(-k_2 t) \qquad (5)$$

at pH 8, where $\delta(t)$ is the observed differential absorbance, $\Delta\epsilon_A$ and $\Delta\epsilon_B$ are the differential dichroic extinction coefficients of A and B, respectively, and $[A]_0$ is the initial concentration of the complex. Treatment of the data by least-squares analysis gives $k_1 = (3.08 \pm 0.23) \times 10^{-5}\ s^{-1}$ and $k_2 = (5.95 \pm 0.35) \times 10^{-5}\ s^{-1}$.

In the experiments where the pH was determined by the equilibrium reaction 1, account should be taken of the rate of decay of both the A and the B ions. The differential equations for the decay of these two ions were solved by fourth-order Runge–Kutta integration,[11] but no definitive values for k_1 and k_2 were obtained; a trough exists in the surface of standard deviations as a function of k_1 and k_2. Only an average rate constant, k_{AB}, was obtainable for the loss of optical activity under these conditions. The values of k_{AB} at 60 and 70 °C were $(7.50 \pm 0.83) \times 10^{-6}$ and $(1.77 \pm 0.05) \times 10^{-5}\ s^{-1}$, respectively, and were calculated from the decay of $[A_T]$ as a function of time. From these values, the average activation enthalpy was calculated to be 93.3 kJ mol^{-1} (estimated error of ±15%), with an activation entropy of −63 eu (estimated

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Table I. First-Order Rate Constants for the Thermolysis of $[Co(HL)_3](ClO_4)_3$ in Water

T, °C	rate const and value $\times 10^6$, s^{-1}	
60	k_{AB}	7.50 ± 0.83
70	k_{AB}	17.7 ± 0.5
70	k_1	30.8 ± 2.3
70	k_2	59.5 ± 3.5

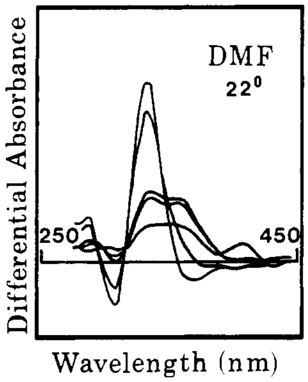


Figure 3. Decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in DMF at 22 °C: 0 (0.68), 1420 (0.57), 1460 (0.27), 1780 (0.25), 2845 (0.14).[28]

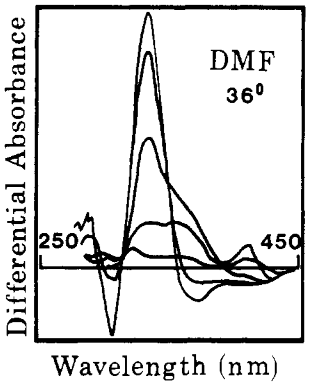


Figure 4. Decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in DMF at 36 °C: 0 (1.04), 120 (0.92), 270 (0.47), 353 (0.21), 550 (0.05).[28]

error of ±34%). The slight acceleration of the rate at pH 3 and pH 8, where there are larger concentrations of hydrogen and hydroxide ions, indicates that most probably the same mechanism for the loss of optical activity operates, although there may be some contribution from second-order mechanisms involving these ions. The results are summarized in Table I.

Thermolysis in DMF Solution. The decay of the CD spectra of the A and B ions in DMF solution show two important characteristics. First, an isosbestic point[12] is maintained for the first third of the duration of the reaction at all temperatures used (Figures 3–6); as the initial peak at 330 nm decays, a new peak grows in at 360 nm, the isosbestic point occurring at 346 nm. We refer to the complex responsible for the new peak as C.

Secondly, the rate of loss of differential dichroic absorbance at 330 nm and the rate of its growth at 360 nm increases as a function of time. The differential dichroic absorbance then shows a gradual decay to zero, with a new peak at 410 nm being generated about two-thirds of the way through the experiments, decaying to zero as the experiments end. The complex responsible for this peak is referred to as D.

The maintenance of an isosbestic point during the first or the last stages of a reaction require some special conditions. These

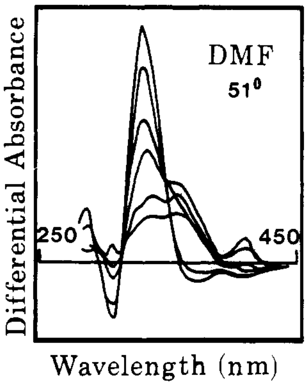


Figure 5. Decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in DMF at 51 °C: 0 (0.92), 45 (0.74), 60 (0.54), 75 (0.41), 90 (0.22), 105 (0.15).[28]

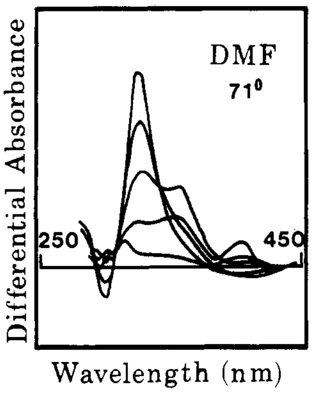
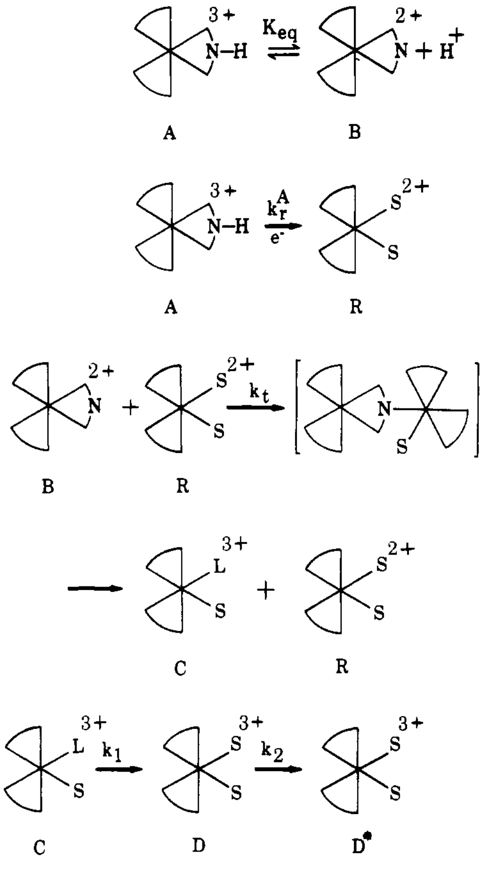


Figure 6. Decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in DMF at 71 °C: 5 (0.72), 20 (0.50), 40 (0.32), 55 (0.16), 70 (0.03).[28]

Scheme II. Simplified Reaction Scheme for the Decomposition of $[Co(HL)_3](ClO_4)_3$ in DMF Solution[a]



[a] D* represents either racemized D or its decomposition product. The reduction of C and D to R is not shown.

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(12) We do not dwell on the possible etymological conflict over the words "isobestic" and "isosbestic" but do note that many authors use both spellings with equal frequency in order to be incorrect only half of the time. We also note the preference of H. Bennett, in: "Concise Chemical and Technical Dictionary", Chemical Publishing House: New York, 1974. (Editor's Note: ACS style is isosbestic: Fieser, L.; Fieser, M. "A Style Guide for Chemists"; Reinhold: New York, 1960.)

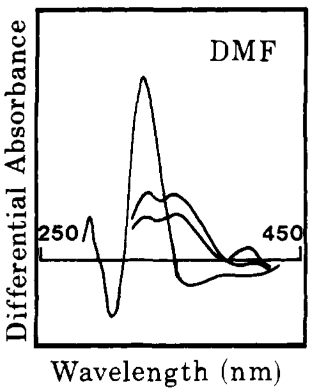

Figure 7. CD spectrum of $[Co(HL)_3](ClO_4)_3$ before and immediately after the addition of $[Co(HL)_3](ClO_4)_2$. The third curve shows the growth of the peak characteristic of complex D 200 min after the addition.

conditions have been discussed for situations in which isosbestic points occur at the end of a reaction.[13] Consider the simple reaction A → X + products. An isosbestic point will occur in the CD spectrum of the reaction mixture if the differential absorption bands of A and X cross one another. At the crossing point, where the differential absorbance is given by $\delta = \Delta\epsilon_A[A]_t + \Delta\epsilon_X[X]_t$, it can be shown that $\delta = \Delta\epsilon[A]_0$, where $[A]_0$ is the initial concentration of A and $\Delta\epsilon = \Delta\epsilon_A = \Delta\epsilon_X$.

The conditions for the maintenance of an isosbestic point in more complex reaction schemes can be evaluated as follows. Consider the following reaction sequence, which models the mechanism proposed in Scheme II:

$$A = B + H^+ \qquad K = [H^+][B]/[A]$$

$$B \rightarrow C \qquad C \rightarrow D$$

Write $[A_T]_t = [A]_t + [B]_t$; then $[A_T]_t = [A]_t(1 + K/[H^+]_t)$ and

$$\begin{aligned}[A]_0 &= [A]_t + [B]_t + [C]_t + [D]_t \\ &= [A_T]_t + [C]_t + [B]_t\end{aligned}$$

The differential absorbance is given by

$$\begin{aligned}\delta &= \Delta\epsilon_A[A]_t + \Delta\epsilon_B[B]_t + \Delta\epsilon_C[C]_t + \Delta\epsilon_D[D]_t \\ &= \Delta\epsilon_A(1 + \Delta\epsilon_B K/\Delta\epsilon_A[H^+]_t)[A]_t + \\ &\qquad \Delta\epsilon_C([C]_t + \Delta\epsilon_D[D]_t/\Delta\epsilon_C)\end{aligned}$$

During the first third of the thermolyses, negligible amounts of D are formed, and if it is noted that $[C]_t \simeq [A]_0 - [A]_t - [B]_t$, the expression for the differential absorbance becomes

$$\delta = \Delta\epsilon[A]_0 + \Delta\epsilon(\Delta\epsilon_B/\Delta\epsilon_A - 1)K[A]_t/[H^+]_t$$

$$\Delta\epsilon = \Delta\epsilon_A = \Delta\epsilon_C$$

The equilibrium constant, K, has a value on the order of 10^{-5}, the ratio $\Delta\epsilon_B/\Delta\epsilon_A$ is about 1.3, and the ratio $[A]/[H^+] < 1.0$. Thus, the values of the physical constant associated with this reaction are such that, as long as very little D has been formed, there will be an isosbestic point in the CD spectrum of the reaction mixture, and in fact, the isosbestic point disappears just before the peak associated with D appears.

Before presenting the proposed mechanism for the thermolysis of the A and B ions, it is propitious to discuss the results of a number of qualitative experiments. When an equilibrium solution of the A and B ions in DMF is treated with a DMF solution of tris(HL)cobalt(II) perchlorate, the CD spectrum changes intensity from that of the mixture to that typical of complex C (Figure 7). As is shown in Figure 7, complex C then continues to form complex D exactly as is observed in the thermolysis experiments. Moreover, the differential dichroic absorbance is the same as is observed during the thermolysis, indicating that no adduct between a cobalt(III) and a cobalt(II) ion is formed. We assume that the cobalt(II) ion converts the cobalt(III) ion completely and instantaneously to the complex C. Treatment of equilibrium solutions of the A and B ions in DMF separately with DMF solutions of cobalt(II) ion, HL, and tris(1,10-phenanthroline)cobalt(II) ion produces no instantaneous change in the CD spectra. A solution treated first with cobalt(II) ion and then with phen solution shows the same change as when treated with tris(HL)cobalt(II) ion, but the optical purity of complex C is much diminished. Treatment with a solution of iron(II) ion causes the immediate collapse of the CD spectrum and decomposition of the complex.

These results are summarized as follows:

$Co(HL)_2L^{2+} + Co^{2+} \rightarrow$ no immediate reaction

$Co(HL)_2L^{2+} + HL \rightarrow$ no immediate reaction

$Co(HL)_2L^{2+} + Co(phen)_3{}^{2+} \rightarrow$ no immediate reaction

$Co(HL)_2L^{2+} + Fe^{2+} \rightarrow$ instantaneous decomposition

$Co(HL)_2L^{2+} + Co(HL)_3{}^{2+} \rightarrow$
instantaneous, quantitative formation of C

$Co(HL)_2L^{2+} + Co^{2+}$, then phen $\rightarrow$
instantaneous reaction with some formation of C

It is concluded from the results of these experiments, and another experiment described below, that complex C is formed by a redox reaction from the B ion. The +3 oxidation state is not a particularly stable one for cobalt in solution, unless cobalt is coordinated to ligands that can stabilize it. The standard reduction potential of free cobalt(III) ion is +1.842 V in aqueous solution, and that for $Co(phen)_3{}^{3+}$ is +0.420 V;[14] this reflects the greater ligand field stabilization of d^6 ions relative to d^7 ions by strong ligands. Iron(III) has a standard reduction potential of +0.770 V and is relatively stable in aqueous solution. While Co^{2+} is incapable of reducing the B ion, Fe^{2+} can do so easily, but without the formation of any C ion.

The rate of reaction between the B ion and $Co(phen)_3{}^{2+}$ is particularly significant. The logarithm of the overall stability constant for this complex in aqueous solution, β, is nearly 20.[15] This means that there are negligible concentrations of partially solvated species such as $Co(phen)_2S_2{}^{2+}$, where the S indicates a solvent molecule. Thus, electron exchange between these ions can only occur by an outer-sphere process, with a rate that is negligible compared to the rates of the other exchange reaction discussed below. When phen is added to a solution of the A and B ions already containing free cobalt(II) ion, the complexes $Co(phen)S_4{}^{2+}$, $Co(phen)_2S_2{}^{2+}$, and finally $Co(phen)_3{}^{2+}$ are formed successively. It is clearly one of the first two complexes, most probably the second, taking account of its ligand field stabilization, that causes the observed reduction of B. The $Co(HL)_3{}^{2+}$ product apparently reacts with unreacted B to form the small quantity of C ion that is observed. $Co(HL)_3{}^{2+}$ is able to dissociate much more easily to a less substituted species than is $Co(phen)_3{}^{2+}$ ion, and its addition to solutions of the B ion causes instantaneous formation of the C ion. We assume that, in each of these reductions, electron transfer follows the formation of a bond between the negatively charged amide of the B ion and the metal ion in the reductant.

Solutions of (−)-$Co(HL)_3{}^{3+}$ in DMF saturated with dry hydrogen chloride gas show a zero-order decay of their CD spectra, the zero-order rate constant being $(2.0 \pm 0.1) \times 10^{-9}$ s^{-1} (Figures 8 and 9) at 22 °C. The product of this reaction is the cobalt(II) ion, this being determined spectroscopically by the identification in the visible spectrum of the product solution of absorption bands due to the $CoCl_4{}^{2-}$ ion.[16] The (−)-$Co(HL)_3{}^{3+}$ ion, the only ion present because of the high hydrogen ion concentration, undergoes

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Table II. Estimated Rate Constants for the Thermolysis of $[Co(HL)_3](ClO_4)_3$ in DMF

T, °C	k_r^a, M s^{-1}	$k_r^{C,D}$, M s^{-1}	k_t, M^{-1} s^{-1}	k_1, s^{-1}	k_2, s^{-1}	τ^a
36	6.7×10^{-14}	1.7×10^{-7}	1.1×10^{4}	5.7×10^{-5}	6.7×10^{-5}	0.85
51	5.0×10^{-13}	6.0×10^{-7}	3.3×10^{4}	2.0×10^{-4}	4.8×10^{-4}	0.36
71	1.3×10^{-12}	6.7×10^{-7}	6.7×10^{4}	3.3×10^{-4}	1.3×10^{-3}	0.60

[a] Fraction of run time for which agreement is good; see text.

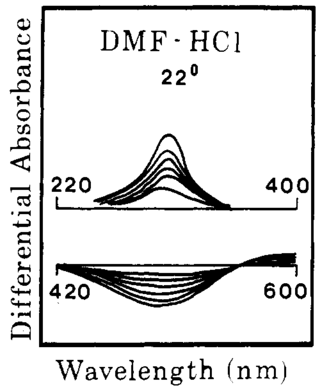

Figure 8. Zero-order decay of the CD spectrum of $[Co(HL)_3](ClO_4)_3$ in DMF saturated with dry HCl gas at 20 °C.

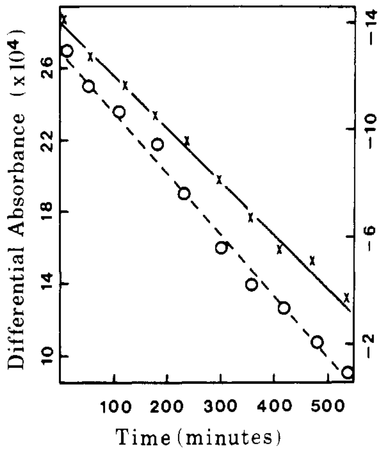

Figure 9. Plot of the differential dichroic absorbance vs. time for the data of Figure 8: O (refer to the left-hand ordinate), decay of the peak at 300 nm; × (refer to the right-hand ordinate), decay of the peak at 500 nm.

reduction at a rate that is apparently governed by the rate of production of electrons.

Scheme II presents the proposed mechanism for the thermolysis of solutions of (–)-$Co(HL)_3^{3+}$ ion in DMF. The A ion undergoes a very slow zero-order reduction to the cobalt(II) complex, R. The A and B ions may undergo direct thermolysis to the complex C, but the rate is negligible compared to that of the following redox process. The partially dissociated complex, R, forms an inner-sphere complex with the B ion, with ensuing rapid electron transfer. The inner-sphere complex then dissociates to form C, with proton scavenging as discussed earlier. The structure of complex R is unknown, but it is probably derived from complex A either by one HL ligand becoming monodentate or by the ligand dissociating off completely to give a bis-bidentate cobalt(II) complex. The same holds for complex C, it having one HL ligand monodentate either through a pyridine lone-pair or through the amide moiety by ligand transfer from R, shown as L in Scheme II. Complex C cannot be a disolvated bis-bidentate complex because it continues on to produce a new optically active complex, which most likely is the disolvated complex. The complex C then undergoes first-order decay to D, which then rapidly racemizes. We have not been able to synthesize the $Co(HL)_2(DMF)_2^{3+}$ ion and thus are not able to identify complex D positively as a bis-bidentate species. Complexes A and B are assumed not to racemize because any twist mechanism for these sterically restricted molecules is very unlikely. Complex C may racemize, but we assume the rate to be negligible compared to its conversion to the D ion, to keep the proposed scheme as simple as possible. Complexes A, C, and D all appear to undergo reduction to cobalt(II) with $k_r^C = k_r^D \gg k_r^A$ because C and D do not have as large a ligand field stabilization as A, and about 30% of the cobalt ends up as cobalt(II), this being determined by spectrophotometric methods. The rate of reduction of B to R must be negligible because the equilibrium mixture of A and B contains mostly the B ion, and for the first third of the reaction, more than 95% of the material is present as A, B, or C, as evidenced by the isosbestic point. This indicates that very little R is formed. If it is assumed that B does undergo reduction to R at a rate comparable to that of the A ion, the integration of the differential equations developed from Scheme II (see below) gives a poor profile of the change in the differential absorbance with time and does not allow the existence of the isosbestic point.

The postulated inner-sphere complex is formed by the binding of a cobalt(II) ion to the negatively charged bridging nitrogen atom of the B complex, permitting rapid electron transfer through the π-orbitals of the ligand. This electron transfer now renders the DPA^- moiety basic, and scavenging of proton occurs to give the two complexes C and R, as shown in Scheme II. The most important consequence of the postulated binuclear complex is that the electron-transfer process is almost 100% stereoselective, because the observed optical activity arises not from the original enantiomers of the A and B mixture but from the racemic cobalt(II) complex formed from the zero-order reduction of A. Although an earlier report of stereoselective electron-transfer processes between metals in different oxidation states has been proven wrong,[17,18] some recent work has shown that differential diastereomeric interactions are observable even in systems in which the interactions are very weak. Thus, the diastereomeric ion pair formation constants between optically active $[Co(en)_3]^{3+}$ ion and $[Co(ox)_2(gly)]^{3-}$ have been shown to have a ratio between 1.04 and 1.17.[19] Although this ratio is small, one must bear in mind that the process is merely ion pair formation in aqueous solution, a process that hitherto has never been shown to be stereoselective at all.

A number of examples of chiral discrimination in outer-sphere electron-transfer reactions have recently been reported,[20-26] in one case with 90% stereoselectivity.[20]

The differential equations for the changes in the concentrations of the various species in Scheme II can be written as

$$d[A_T]/dt = -k_r^A - k_t[B][R] \tag{6}$$

$$d[C]/dt = k_t[B][R] - k_1[C] - k_r^C \tag{7}$$

$$d[D]/dt = k_1[C] - k_2[D] - k_r^D \tag{8}$$

$$d[H^+]/dt = d[A_T]/dt(K(K + [H^+]_0)^2 + 4K[A_T])^{-1/2} \tag{9}$$

where $[A_T] = [A] + [B]$. To simplify the estimation of the various

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Table III. Least-Squares Analysis of the Temperature Dependence of the Rate Constants for the Thermolysis of $[Co(HL)_3](ClO_4)_3$ in DMF

	k_r^A	$k_r^{C,D}$	k_t	k_1	k_2
ΔH^*, kJ mol^{-1}	73.7	33.5	44.9	43.7	73.7
intercept[a]	−1.40	−2.28	26.9	7.41	19.3
R^2 [a]	0.94	0.77	0.97	0.92	0.94

[a] This intercept and correlation coefficient for the least-squares analysis of the data. Entropies of activation were not calculated.

rate constants, we assume that $k_r^C = k_r^D \gg k_r^A$ for the reasons given above. The differential dichroic absorbance as a function of time can be written as

$$\delta(t) = \Delta\epsilon_A[A]_t + \Delta\epsilon_B[B]_t + \Delta\epsilon_C[C]_t + \Delta\epsilon_D[D]_t$$

at any wavenumber for unit path length. Initial values for $\Delta\epsilon_A$ and $\Delta\epsilon_B$ were estimated from those observed in aqueous solution, i.e. about 60–70 units for $\Delta\epsilon_A$ and 80–100 units for $\Delta\epsilon_B$. $\Delta\epsilon_C$ was estimated from the experiment in which $Co(HL)_3^{3+}$ was reacted with $Co(HL)_3^{2+}$ to form C. Assuming a quantitative conversion with 100% stereoselectivity, the value for $\Delta\epsilon_C$ was calculated to be 30 units as a minimum. The value of $\Delta\epsilon_D$ is more difficult to estimate, but because the concentration of D is never very large, it was sufficient to consider it to be zero.

The rate equations above were solved as a function of time by fourth-order Runge–Kutta integration, and values for k_r^A, $k_r^C = k_r^D$, k_t, k_1, and k_2 were obtained by minimizing the sum of the squares of the deviations between the calculated and observed differential dichroic absorbance. The results are given in Tables II and III. Before discussing the results, it must be remembered that, to simplify the treatment of the data, it was assumed that complex C does not undergo racemization. Any loss of differential absorbance due to such racemization will be embedded in the data and will manifest itself through the value of k_r^C, which controls the loss of optical activity by reduction to the racemic cobalt(II) complex. For this reason the values of k_r^C will not be as accurately estimated as the other rate constants. Toward the end of the thermolysis runs, when the concentration of C is relatively large, failure to account for this racemization rate will lead to large deviations between the calculated and observed differential absorbance. The rate constants shown in Table II give good agreement between these values for the first two-thirds of the runs, after which the experimental values decay much more rapidly than does the calculated one. The fractions of the total run times for which the agreement is good are shown in Table II. The rate of reduction of A is seen to be extremely slow, but the rate of electron exchange between the complexes R and B is comparable in magnitude to other inner-sphere electron-transfer processes.[27] Despite the fact that Scheme II is a simplification of what occurs during these thermolyses, the sets of rate constants were treated by least-squares analysis to determine primarily the correlation coefficient and secondarily the activation enthalpies. The results (see Table III) indicate that k_r^A, k_t, k_1, and k_2 are reasonably significant quantities but that k_r^C and k_r^D are not, most probably for the reason discussed above. It remains to be seen if any advantage can be taken of the high stereoselectivity of this type of electron-transfer process to synthesize optically active complexes from lower valence racemic precursors.

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(28) The times in minutes and the differential absorbances in parentheses of the curves starting at the top of the band near 330 nm.

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Reactions of Chromium(II) with Fumaronitrile and Pentaamminecobalt(III)- and Pentaaquochromium(III)-Fumaronitrile Complexes

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The reaction of chromium(II) with the fumaronitrile complex of pentaamminecobalt(III) proceeds with transfer of fumaronitrile to the chromium(III) product and with a rate constant of $(1.9 \pm 0.2) \times 10^5$ M^{-1} s^{-1} (25 °C, 0.50 M $LiClO_4$–$HClO_4$). The chromium(III)–fumaronitrile complex undergoes further reduction by chromium(II), forming various organochromium(III) products. The reaction of chromium(II) with fumaronitrile was found to be $\sim 10^3$ times slower than that of the chromium(III) complex. With fumaronitrile, the main products are succinonitrile (~20%) and $(H_2O)_5Cr\text{-}CH(CN)\text{-}CH_2CN\text{-}Cr(OH_2)_5^{5+}$ (~70%), while with the chromium(III) complex, all the organic ligand appears as organochromium species of which the main product is $(H_2O)_5Cr\text{-}CH(CONH_2Cr)\text{-}CH_2CNCr(OH_2)_5^{8+}$ (~70%). The distribution and composition of the products are rationalized on the basis of a few simple principles.

This study began as a simple investigation of the electron-transfer kinetics between $(NH_3)_5Co(fumaronitrile)^{3+}$ and Cr^{2+} in order to compare fumaronitrile as a bridging ligand to analogues such as succinonitrile,[1] 1,4-dicyanobenzene,[2] and others.[3] Fumaronitrile is shown to provide a very facile electron-transfer pathway between chromium(II) and pentaamminecobalt(III). In addition it was noted that subsequent reactions between chromium(II) and fumaronitrile, either free or complexed to chromium(III), can complicate the product analysis and spectrophotometric observations. Although these are minor complications for the original goal, a thorough investigation of them was undertaken and constitutes the main portion of this work. This investigation was stimulated by the seemingly disparate results that have been obtained for the reduction of fumaric and maleic acids and their esters by chromium(II).[4-6] The nitrile presents

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