curve; if the values of cation–solvent distances have a great spread, their contributions to the $G(r)$ function are very broadened.

Obviously, this increase in disorder must be attributed to some anionic effect, for instance, to some tendency of the sulfate ion to compete with water molecules for the occupancy of hydration shell positions. This would be in keeping with the differences in the solid structures of the hydrates[16,17] of $CuSO_4$ and $Cu(ClO_4)_2$.[18] In the first case, sulfate ions enter the first coordination sphere of Cu^{2+} ions, while in the second case only water molecules envelop the central copper(II) ion. In this connection it is worth noting that, in a recent EXAFS[19] investigation on crystalline $CuSO_4{\cdot}5H_2O$, the distance Cu–w_{eq} were carefullly determined at 1.97 Å; on the contrary, poor evidence has been found for axial distances at 2.40 Å, which, according to neutron and X-ray diffraction studies, involve O atoms of the sulfate groups. This was explained on the basis of the remarkable degree of dynamic disorder of the bond Cu^{2+}–O_{ax}, which greatly affects the EXAFS signal. This hypothesis may be considered consistent with our interpretation.

Finally, we wish to emphasize that our observations on the $CuSO_4$ solution agree very well with the results of an X-ray diffraction investigation by Ohtaki et al.[20] on solutions of divalent transition-metal ions, including $CuSO_4$ and $Cu(ClO_4)_2$ solutions. While in the radial curve of the $Cu(ClO_4)_2$ solution two clear peaks indicate two distinct coordination distances of Cu^{2+} ions, in the $D(r)$ of the $CuSO_4$ solution, besides the peak at 2.00 Å of the pairs Cu^{2+}–w_{eq}, only a small hump is present at about 2.40 Å. However, the same coordination geometry was used in the interpretation of both data series.

As already mentioned in the Introduction, the existence of a distorted coordination polyhedron around Cu(II) ions was not evident in a neutron diffraction study[4] of a $Cu(ClO_4)_2$ solution. In this study the use of a "null" isotope of nickel rendered the isomorphic method favorable, but the assumption of isomorphism for the pair Cu(II)–Ni(II) indeed lacks chemical and structural evidence. In the light of the not neglibible differences between the distribution curves of Ni^{2+} and Cu^{2+} solutions (see Figure 5 in ref 4), the conclusion[4] that Ni^{2+} and Cu^{2+} have similar environments deserves to be reexamined.

In conclusion, the existence of a distorted arrangement of six water molecules around Cu^{2+} ions in $CuSO_4$ solution is supported by inspection of the distribution curve and direct fitting of the structure function. This coordination structure appears to be more disordered in $CuSO_4$ than in $Cu(ClO_4)_2$ solutions.

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Registry No. $CuSO_4$, 7758-98-7; $Cu(H_2O)_6{}^{2+}$, 14946-74-8.

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Equilibrium and Kinetics of the Extraction of Nickel with 7-Dodecenyl-8-quinolinol (Kelex 100)

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The equilibrium and kinetics of the extraction of nickel(II) ion with chloroform solutions of 7-dodecenyl-8-quinolinol (Kelex 100, HL) have been studied at an ionic strength of 0.1 and 25 °C. The extracted species was found to be NiL_2, and its extraction constant of $\log K_{ex} = -6.34 \pm 0.11$ was obtained. The measurement of the distribution equilibrium of Kelex 100 as a function of pH exhibited a dependence on stirring rates that suggests that the heterogeneous acid–base equilibrium is dramatically shifted by preferential interfacial adsorption of the anionic form of the ligand. The rate of extraction was found to be best described by a two-term expression, both of which are first order in nickel ion and HL concentrations. The first term has zero dependence on hydrogen ion concentration whereas the second is inversely first order with respect to hydrogen ion concentration. These results support the hypothesis that the rate-determining steps involve two concurrent reactions of nickel ion with neutral and anionic forms of Kelex 100 (HL and L^-). The first reaction takes place in the aqueous phase, whereas the one involving the anion occurs in the interface. This work represents strong evidence that, while the anion of Kelex 100 is surface active, the neutral species is not and demonstrates the feasibility of elucidating extraction systems involving surface-active components.

Introduction

Recent work in this laboratory[2a] has shown that the rates of extraction of metal ions with large chelating extractants, whose anions are surface active, are enhanced considerably under conditions that generate an extensive interfacial region by interfacial adsorption of ligand anions. The systems studied, alkylated dithizones, involved only ligand anions in the rate-determining step because the experiments were conducted in the pH regions close to their pK_a values. In the case of 8-quinolinols,[2b,3] however, where chelate formation occurs in a pH range much lower than the pK_a so that the concentration

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ratio of neutral to anionic ligand forms is very large, this is not the case. Hence, in the mechanism of the extraction of metal ions such as nickel ion, two reaction pathways, i.e. reactions with both neutral and anionic forms of the ligand, are concurrently active. For this reason, such systems would be useful in testing the hypothesis that the anion is interfacially active and forms a 1:1 chelate in an interfacial region, whereas the neutral ligand behaves normally in that the formation of the 1:1 chelate occurs in the bulk aqueous phase.

This report is devoted to the testing of this hypothesis using the system of the extraction of nickel ion with a chloroform solution of alkylated 8-quinolinol, Kelex 100.

Experimental Section

7-Dodecenyl-8-quinolinol (Kelex 100, HL) was kindly supplied in its undiluted form by Sherex Chemical Co. The reagent was purified as described previously.[4] All other chemials were of analytical grade. Chloroform was washed with water twice just before use. Phosphate buffer, sodium perchlorate, and sodium hydroxide solutions were washed with solutions of Kelex 100 in chloroform to remove the metal ion impurities. A 1.00×10^{-2} M nickel stock solution was prepared by dissolving nickel perchlorate in a 10^{-2} M perchloric acid solution and standardized by complexometric titration with EDTA. Distilled–deionized water was used throughout the experiments.

Apparatus. A Burrell Model BB wrist-action shaker with 280 oscillations/min. was used for the conventional (low-speed) extraction equilibrium study. A continuously monitoring, computer-controlled solvent extraction system previously developed in this laboratory[6,7] was used to determine the distribution ratio of Kelex 100 under high-speed stirring. The concentration of nickel in the aqueous phase was determined with a Varian AA-6 atomic absorption spectrophotometer at 232 nm with an air–acetylene flame. UV and visible absorbances were measured with a Gilford 2400 spectrophotometer. All pH measurements were made with an Orion 701 pH meter calibrated with use of standard buffer solutions of pH 4.00, 7.00, 10.00, and 12.45. The temperature of the reaction systems was controlled to 25 ± 0.1 °C with a Thermoelectric water bath.

Equilibrium Procedure. The distribution of nickel between the chloroform and aqueous phases was determined as functions of the concentration of Kelex 100 and pH. A 20-mL portion of an aqueous solution containing 2.00×10^{-4} M nickel ion, 0.01 M acetate buffer, and sodium perchlorate to maintain the ionic strength to 0.1 was placed into a 150-mL glass vial along with a 20-mL portion of a chloroform solution of Kelex 100. The vials were capped and shaken for 8 h to ensure that the equilibrium was achieved. After the phases separated, the equilibrium concentration of nickel in the aqueous phase was determined by means of atomic absorption spectrophotometry. The equilibrium concentration of nickel in the organic phase was calculated by subtracting the aqueous equilibrium concentration from the initial concentration.

Kinetic Procedure. The procedure was essentially similar to that described previously.[3,5] The kinetic runs were carried out under pseudo-first-order conditions, Kelex 100 in the organic phase being in large excess over nickel ion in the aqueous phase. The "plateau" region, where further increase of stirring speed had no effect on the rate of extraction, was chosen to carry out the kinetic experiments. The observed pseudo-first-order rate constants, k_{obsd}, were determined from

$$\ln ([Ni^{2+}]_{t=0}/[Ni^{2+}]_t) = k_{obsd}t \qquad (1)$$

where t is the reaction time and $[Ni^{2+}]_t$=0 and $[Ni]_t$ are the concentrations of nickel in the aqueous phase at reaction times zero and t.

Distribution of Kelex 100 under High-Speed Stirring. The apparatus and procedure were similar to those described previously.[2a,6] A 50-mL portion of chloroform containing 1.20×10^{-4} M Kelex 100 was placed into the distribution vessel together with a 50-mL portion of the aqueous phase, buffered with phosphate–sodium hydroxide or sodium hydroxide alone. After the absorbance reading of the organic phase at 330 nm, which is the wavelength of the absorption shoulder of Kelex 100, became steady, the high-speed stirrer was started and the absorbance change was continuously recorded. The apparent distribution ratio of Kelex 100, D', under high-speed stirring was obtained from

$$D' = \frac{A_0 - \Delta A}{\Delta A} \qquad (2)$$

where A_0 and ΔA are the initial absorbance of the organic phase and the absorbance decrease caused by stirring, respectively.[2a]

Table I. Summary of Equilibrium Data for the Extraction of Nickel with Kelex 100 at $\mu = 0.1$ and 25 °C

range of variables		slope of log D_{Ni} vs. log $[HL]_0$ or pH	
pH	$-\log [HL]_0$		$-\log K_{ex}$
3.80	1.00-1.60	2.00 ± 0.20	6.32 ± 0.09
4.35	1.00-2.00	1.98 ± 0.09	6.32 ± 0.06
4.75	1.00-2.60	1.98 ± 0.05	6.37 ± 0.05
3.80-5.41	1.60	1.91 ± 0.03	6.36 ± 0.04

Table II. Summary of Extraction Kinetics of Nickel by Kelex 100 at 25 °C, $[Ni^{2+}]_{t=0} = 1.00 \times 10^{-4}$ M, and $\mu = 0.1$

$10^3[HL]_0$, M	pH	$10^{-4}k_{obsd}$, s^{-1}	$10^3[HL]_0$, M	pH	$10^{-4}k_{obsd}$, s^{-1}
2.85	6.20	0.675	7.59	6.16	1.77
	6.67	1.13		6.67	3.24
	6.85	1.53		6.80	3.77
	7.02	1.90		7.02	5.81
	7.33	3.67	10.30	6.16	2.54
5.09	6.16	1.27		6.66	4.44
	6.68	1.99		6.80	6.16
	6.80	2.25		6.96	7.64
	6.96	3.06		7.06	8.63
	7.06	3.69			

Results and Discussion

Equilibrium of Nickel Extraction. The distribution ratio of nickel, D_{Ni}, for the extraction with a chloroform solution of Kelex 100 was measured at various Kelex 100 concentrations and pH. Plots of both log D_{Ni} vs. log $[HL]_0$ at constant pH and log D_{Ni} vs. pH at constant Kelex 100 concentration were linear with slopes of 2 as shown in Table I. Thus, it can be concluded that only a simple 1:2 chelate, NiL_2, was extracted into the organic phase. This result is in accord with a previous description.[7] The overall extraction reaction can be expressed as

$$Ni^{2+} + 2HL(o) \overset{K_{ex}}{\rightleftharpoons} NiL_2(o) + 2H^+ \qquad (3)$$

where the letter o refers to the species in the organic phase. The extraction constant was calculated to be log $K_{ex} = -6.34 \pm 0.11$ from the experimental data. The comparison of the value of log K_{ex} with that of the Cu–Kelex 100 chelate (log K_{ex} = 1.09[8]) indicates the ease of separation of copper from nickel with this extractant.

The extraction constant, K_{ex}, is a composite of the overall chelate formation constant, β_2, and the distribution constant of the chelate, K_{DC}, as well as of the reagent acid dissociation constant, K_a, and its distribution constant, K_{DR}; i.e.

$$K_{ex} = \beta_2 K_{DC}{}^2 K_a{}^2 / K_{DR} \qquad (4)$$

The heterogeneous equilibrium constant for eq 5, $\beta_2 K_{DC}$,

$$Ni^{2+} + 2L^- \rightleftharpoons NiL_2(o) \qquad (5)$$

can be evaluated to be log $(\beta_2 K_{DC})$ = 25.50 by employing the

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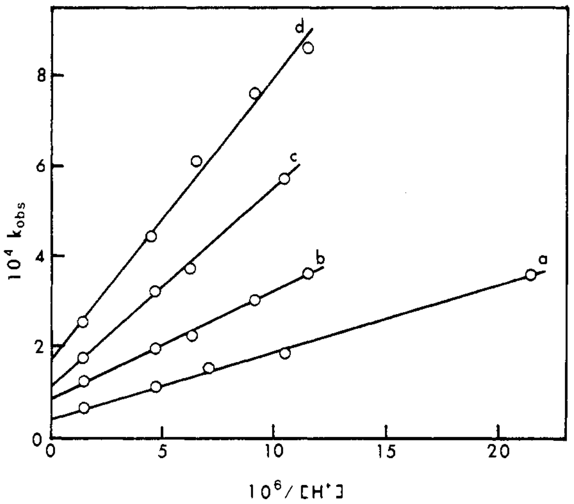


Figure 1. Rate of extraction of nickel with Kelex 100 as a function of $1/[H^+]$ at 25 °C and $\mu = 0.1$, with $[Ni^{2+}]_{t=0} = 1.00 \times 10^{-4}$ M and $[HL]_0$ ($\times 10^3$ M) = (a) 2.85, (b) 5.09, (c) 7.59, and (d) 10.30. Solid lines are obtained from a least-squares treatment of the data.

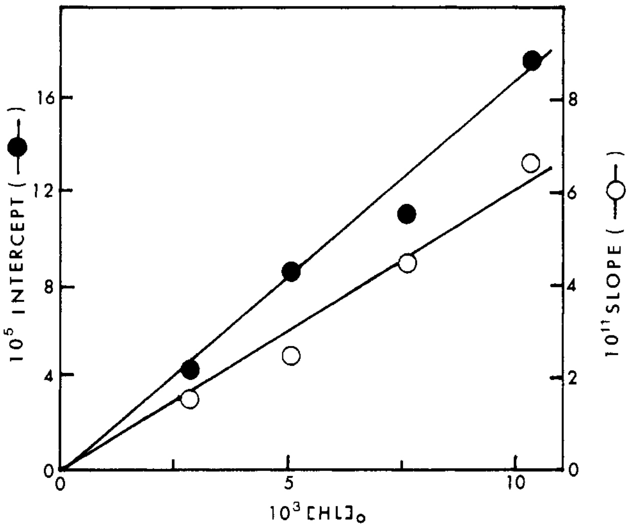


Figure 2. Slope and intercept of Figure 1 as a function of the concentration of Kelex 100 in the organic phase. Solid lines are obtained from a least-squares treatment of the data.

values of $pK_a = 10.40$ and $\log K_{DR} = 5.52$.[8] The higher value of $\log (\beta_2 K_{DC})$ of the present system than that of the parent ligand 8-quinolinol ($\log (\beta_2 K_{DC}) = 22.6$[9] can be almost entirely attributed to the greater K_{DC} value of the alkylated 8-quinolinol chelate.

Kinetics of Nickel Extraction. The rate of the extraction of nickel ion with Kelex 100 into chloroform was found to follow pseudo-first-order kinetics. The observed rate constants, k_{obsd}, are summarized in Table II.

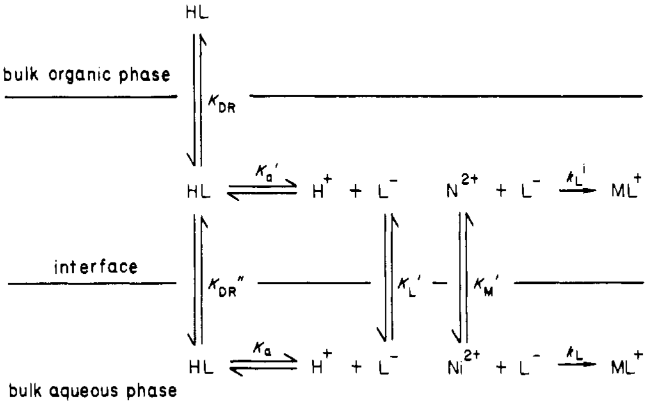
As shown in Figure 1, the plots of k_{obsd} against $1/[H^+]$ at various $[HL]_0$ are linear. The values of both the intercepts and the slopes of these lines are proportional to $[HL]_0$ as shown in Figure 2. These results are similar to those of nickel extraction with 8-quinolinol[2b] and 8-mercaptoquinoline,[3] which suggest that the rate-determining steps are concurrent reactions of nickel ion with neutral and anionic forms of Kelex 100.

Table III. Summary of Rate Constants for Nickel Extraction with Kelex 100 and Its Analogues at 25 °C and $\mu = 0.1$

extractant	$10^{-3}k_{HL}$, $M^{-1}\ s^{-1}$	k_L, $M^{-1}\ s^{-1}$
Kelex[a]	5.5 ± 0.8	$(5.3 \pm 0.9) \times 10^{7}$[d]
8-quinolinol[b]	3.6	5.4×10^5
8-mercaptoquinoline[c]	2.8 ± 0.4	$(2.7 \pm 0.7) \times 10^5$

[a] Present work. [b] Reference 2. [c] Reference 3. [d] This value is invalid. The value of k_L^i, $(8.3 \pm 2.9) \times 10^6\ M^{-1}\ s^{-1}$, is more relevant. See text.

Scheme I



If, in analogy to previously reported systems,[2b,3] the rate-determining reactions take place in the aqueous phase, the rate equation can be represented by eq 6, where k_{HL} and k_L are the rate constants of two rate-determining reactions represented by eq 7 and 8.

$$-\frac{d[Ni^{2+}]}{dt} = k_{obsd}[Ni^{2+}] = \left(k_{HL} + k_L\frac{K_a}{[H^+]}\right)\frac{[Ni^{2+}][HL]_0}{K_{DR}} \quad (6)$$

$$Ni^{2+} + HL \xrightarrow{k_{HL}} NiL^+ + H^+ \quad (7)$$

$$Ni^{2+} + L^- \xrightarrow{k_L} NiL^+ \quad (8)$$

The values of k_{HL} and k_L were obtained from the slopes of the lines in Figure 2 by using the relation of eq 6 and are listed in Table III along with the constants for 8-quinolinol and 8-mercaptoquinoline.

The value of k_{HL} for the present system is almost the same as that for the systems of the parent compound 8-quinolinol and its sulfur analogue, 8-mercaptoquinoline, as shown in Table III. The k_{HL} value is also close to the rate constants reported for reactions of nickel ion with neutral ligands in aqueous solution.[10,11] These facts clearly indicate that the 1:1 chelate formation reaction of the neutral form of Kelex 100, represented in eq 7, occurs in the aqueous phase.

The value of k_L, on the other hand, is more than 100-fold larger than the rate constants for nickel ion reactions with most of the ligands having a negative charge,[10] including 8-quinolinol and 8-mercaptoquinoline (see Table III) in aqueous solution. This large discrepancy suggests that the 1:1 chelate formation reaction of anionic Kelex 100, represented by eq 8, does not proceed by the aqueous-phase mechanism.

Recently, it was found in this laboratory that the rate of extraction of metal ions with alkyl-substituted dithizones, whose ionic forms exhibit surface activity, are enhanced considerably under high-speed stirring conditions, which

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generate an extensive interfacial region.[2a]

Since Kelex 100 has a large alkyl substituent at the 7-position, its anion is likely to have surface activity. If this is the case, the interfacial mechanism postulated previously[2a] (Scheme I) should be considered to apply to the 1:1 chelate formation reaction of the Kelex 100 anion.

According to Scheme I, the overall rate constant for the reaction of L, k_L', becomes

$$k_L' = \frac{K_a}{K_{DR}}\left(k_L + k_L^i K_M' K_L' \frac{Ad}{\bar{V}}\right) \qquad (9)$$

where k_L k_L^i are rate constants in the aqueous phase and the interfacial region, K_M' and K_L' are the distribution constants of nickel ion and anionic Kelex 100, L^-, between the interface and bulk aqueous phase, A is the total interfacial area in the extraction system, d is the thickness of the interfacial layer, and $\bar{V}$ refers to the volume of the aqueous phase.

Distribution of Kelex 100 at High-Speed Stirring and Intefacial Rate Constant. The apparent distribution ratio of Kelex 100 under conditions of high-speed stirring, D' (see eq 2), was studied as a function of pH, to clarify the interfacial mechanism referred to above. A significant decrease of D' with increasing pH was observed in the range of pH 11.7–12.4. The linear relation obtained between log D' and pH having a slope of −0.81 (correlation coefficient 0.990) yielded a $pH_{1/2}$ value of 14.1 ± 0.1, which is 1.8 pH units smaller than that obtained by conventional means.[8] This observation indicates that the interfacial region participated in a major way to the distribution of Kelex 100 under high-speed stirring conditions.

According to the previous paper,[2a] the following equation can be derived for the pH region much higher than the pK_a, where D is the distribution ratio obtained ordinarily, i.e. in the absence of stirring:

$$\log\left(\frac{D}{D'} - 1\right) = \log\left(10^{\Delta pH_{1/2}} - 1\right) = \log K_L' \frac{Ad}{\bar{V}} \qquad (10)$$

From eq 10, the $K'Ad/\bar{V}$ value for the present system was calculated to be (6.2 ± 1.6) × 10.

Although the perfect resolution of k_L into k_L and k_L^i terms is impossible, we can estimate the k_L^i value from eq 9 by assuming that the rate constant of 1:1 chelate formation of Kelex 100 anion with nickel ion in the aqueous phase is the same as that of its parent compound, 8-quinolinol, i.e., $k_L = 5.4 \times 10^5\ M^{-1}\ s^{-1}$,[2a] and the k_M' value is unity as assumed previously.[2a] The value of k_L' is obtained from Figure 2, and then k_L^i is calculated to be $(8.3 \pm 2.9) \times 10^6\ M^{-1}\ s^{-1}$. It is interesting that the ratio of $k_L^i/k_L = 15 \pm 5$ for the present system is quite close to that obtained for alkylated dithizonates ($k_L^i/k_L = 10^{1.3}$).[2a]

It can be noted that this study not only clarifies the mechanism of extraction of nickel with Kelex 100 but also confirms the hypothesis that, in a highly hydrophobic chelating extractant system, the ligand anion can exhibit surface activity while the neutral ligand does not. Hence, the 1:1 chelate formation reaction of the anionic form of the extractant occurs mainly in an interfacial region under high-speed stirring because of its surface activity, while that with the neutral ligand occurs in the bulk aqueous phase. We further demonstrate that extraction systems with surface-active components can be quantitatively explained using our automated extraction apparatus.[6]

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On the Bailar Inversion Reaction of $\Lambda(+)$-$[Co(en)_2Cl_2]^+$

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The steric course for the base hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ has been precisely determined (25 °C, 23.5% cis (16% Λ, 7.5% Δ), 76.5% trans; 0 °C, 18.5% cis (13.5% Λ, 5.0% Δ), 81.5% trans). This result differs significantly from an earlier value (0 °C, 37% cis (21% Λ, 16% Δ)). More importantly it is shown to be independent of $[OH^-]$, again contrary to previous reports. The steric course for the base hydrolysis of Λ-$[Co(en)_2(OH)Cl]^+$, where there are similar discrepancies, is recorded also (25 °C, 94.5% cis (92.5% Λ, 2.0% Δ), 5.5% trans; 0 °C, 95% cis (93.5% Λ, 1.5% Δ), 5% trans). By careful control of the conditions, a unique base-catalyzed pathway is established, a route by which Λ-$[Co(en)_2Cl_2]^+$ hydrolyzes with the simultaneous loss of both Cl^- ions. This remarkable reaction path leads to a substantiant net inversion for the *cis*-$[Co(en)_2(OH)_2]^+$ product (0 °C, 82% cis (12% Λ, 70% Δ), 18% trans), and the steric course for this route is shown to be independent of $[OH^-]$ also. The complete rate law for the base hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ is deduced: $-d[CoCl_2^+]/dt = k_1[OH^-] + k_2[OH^-]^n$ where $n \lesssim 2$; the first term corresponds to the normal S_N1CB base hydrolysis pathway (loss of the first Cl^- ion), and the second term, to the path in which both Cl^- ions are lost together. The mechanistic implications of the present results are discussed, and the conflicting results of the several previous reports on these reactions are evaluated.

Introduction

The base hydrolysis of resolved *cis*-$[Co(en)_2AX]^+$ invariably leads to rearrangement.[1,2] *cis*- and *trans*-$[Co(en)_2A(OH)]^+$ result, and the cis product is partly racemized. Furthermore, in every case studied save one, there is net retention (Λ > Δ) for the cis product. The apparent exception, $\Lambda(+)$-*cis*-$[Co(en)_2Cl_2]^+$, has been studied by different groups[3-6] with different results. Tobe and Chan[3] claimed net retention (21% Λ, 16% Δ) for the *cis*-$[Co(en)_2(OH)Cl]^+$ product of the first base hydrolysis step and net retention (61% Λ, 36% Δ) for the hydrolysis of this ion through to $[Co(en)_2(OH)_2]^+$. Thus overall there was retention, albeit ~99% of the original activity

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