the *s-fac* isomer was isolated in oxidation state III.[14] Dc polarography indicated the presence of the same two reduction steps (including the maximum for the Co(II)/Co(0) step) as obtained in the previous cases. However, the $E_{1/2}$ for the Co(III) + $e^- \rightleftarrows$ Co(II) reduction step was +0.230 V vs. Ag|AgCl, 265 mV more positive than observed in the *s-fac*-$[\mathrm{Co^{III}(dien)_2}]^{3+}$ isomer. The half-wave potentials for the two-electron reduction step were the same for both *s-fac* complexes. Dc polarograms of the electrolysis products following a one-electron reduction were recorded. The $E_{1/2}$ values of these polarograms were the same as found for the *s-fac*-$[\mathrm{Co(medien)_2}]^{3+}$ starting material, indicative that in oxidation state II the *s-fac* isomer is the most stable species. Free ligand was also found as with the cobalt dien system. The electrolysis products were then oxidized. Dc polarograms gave no change in half-wave potential, again indicating that in oxidation state III the *s-fac* isomer as synthesized originally is produced.

Searle, Petkovic, and Keene[15] found that the stability of the cis isomers (facial) was increased at the expense of the trans (meridional) upon N-methylation of cobalt complexes containing the triethylenetetramine ligand. Clearly the N-methylation of the dien ligand in this instance is responsible for the large enhancement of the stability of the *s-fac* isomer. So extensive is this enhancement that, in both oxidation states II and III, neither the *mer* nor the *u-fac* isomer could be detected.

Registry No. *mer*-$[\mathrm{Co^{III}(dien)_2}]^{3+}$, 38318-06-8; *u-fac*-$[\mathrm{Co^{III}(dien)_2}]^{3+}$, 38318-05-7; *s-fac*-$[\mathrm{Co^{III}(dien)_2}]^{3+}$, 38318-04-6; *mer*-$[\mathrm{Co^{II}(dien)_2}]^{2+}$, 67145-46-4; *u-fac*-$[\mathrm{Co^{II}(dien)_2}]^{2+}$, 67145-47-5; *s-fac*-$[\mathrm{Co^{II}(dien)_2}]^{2+}$, 67145-48-6; *s-fac*-$[\mathrm{Co^{III}(medien)_2}]^{3+}$, 63544-39-8; *s-fac*-$[\mathrm{Co^{II}(medien)_2}]^{2+}$, 67113-81-9.

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(1) University of Melbourne.
(2) To whom correspondence should be addressed.
(3) University of Adelaide.
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Contribution from the Department of Chemistry, Howard University, Washington, D.C. 20059,
and the Department of Chemistry, The Catholic University of America, Washington, D.C. 20064

Synthesis and Further Characterization of Potassium (Ethylenediamine)dicarbonatocobaltate(III) and the Tetraaquo(ethylenediamine)cobalt(III) Ion

NANCY S. ROWAN,[1a] CARLYLE B. STORM,*[1a] and JOHN B. HUNT[1b]

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Potassium (ethylenediamine)dicarbonatocobaltate(III) has been prepared from the reaction of potassium tricarbonatocobaltate(III) with limiting amounts of $\mathrm{en{\cdot}2HClO_4}$. Solutions of this compound have absorption maxima at 394 (ϵ 164) and 567 nm (ϵ 159). Addition of excess $\mathrm{HClO_4}$ generates the tetraaquo(ethylenediamine)cobalt(III) ion, which has absorption maxima at 373 (ϵ 49) and 510 nm (ϵ 59). At pH >2, $\mathrm{Co(en)(H_2O)_4}^{3+}$ undergoes dimerization. The complex has a $\mathrm{p}K_\mathrm{a}$ value of ca. 3.7 and undergoes substitution reactions with chloride ion to form mono- and dichloro products, which have been characterized by their ^{1}H NMR spectra and behavior on cation-exchange resin. Substitution of the first $\mathrm{Cl^-}$ into $\mathrm{Co(en)(H_2O)_4}^{3+}$ is the rate-determining step for the formation of the mono- and dichloro complexes. This rate has an apparent first-order dependence on $[\mathrm{Cl^-}]$ and an inverse first-order dependence on $[\mathrm{H^+}]$. At 25.8 ± 0.2 °C in 1.00 M $\mathrm{Cl^-}$ and 0.40 M $\mathrm{H^+}$, the observed rate constant for the formation of the monochloro complex is $7.88 \times 10^{-5}\ \mathrm{s^{-1}}$. Under these same conditions, $E_\mathrm{a} = 29.2$ kcal/mol, $\Delta H^\ddagger = 28.8$ kcal/mol, and $\Delta S^\ddagger = 18.5$ cal/(mol deg). The equilibrium constants for $\mathrm{Co(en)(H_2O)_4}^{3+} + \mathrm{Cl^-} \rightleftarrows \mathrm{Co(en)(H_2O)_3Cl^{2+}}$ (K_1) and $\mathrm{Co(en)(H_2O)_3Cl^{2+}} + \mathrm{Cl^-} \rightleftarrows \mathrm{Co(en)(H_2O)_2Cl_2}^+$ (K_2) equilibria have been measured by spectrophotometry and by ^{1}H NMR. At 25 °C, $K_1 = 16 \pm 3$, measured at $\mu = 0.3$–0.5 M and pH 1, and $K_2 = 1.2 \pm 0.3$, measured at $\mu = 1.4$, pH 0.5.

Introduction

There has been considerable interest recently in the chemistry of the lower amine substituted members of the series $\mathrm{Co(NH_3)}_n\mathrm{(H_2O)}_{6-n}{}^{3+}$.[2-5] In the similar series of ethylenediamine (en) complexes, the simplest member containing only one en ligand has not been thoroughly characterized previously. Both $\mathrm{KCo(en)(CO_3)_2{\cdot}H_2O}$[6-8] and $\mathrm{Co(en)(H_2O)_4}^{3+}$[8] have been synthesized previously, but there was some doubt as to the form of the $\mathrm{Co(en)(CO_3)_2}^-$ ion. This paper presents a modified synthesis of $\mathrm{KCo(en)(CO_3)_2{\cdot}H_2O}$ and evidence that the fully chelated monomer has been produced. It describes the conditions for the production of the $\mathrm{Co(en)(H_2O)_4}^{3+}$ ion in solution and it examines the behavior of $\mathrm{Co(en)(H_2O)_4}^{3+}$ in acid solution and the anation of $\mathrm{Co(en)(H_2O)_4}^{3+}$ and $\mathrm{Co(en)(H_2O)_3Cl^{2+}}$ by $\mathrm{Cl^-}$.

Ethylenediamine complexes of Co(III) and their analogous ammonia complexes in general undergo substitution reactions at similar rates with similar activation parameters.[9,10] This is particularly true for complexes of the type $\mathrm{CoA_4X_2}$ where A = $^1/_2$en or $\mathrm{NH_3}$. In this paper, a comparison is made of the substitution rates for $\mathrm{Co(en)(H_2O)_4}^{3+}$ and $\mathrm{Co(NH_3)_2(H_2O)_4}^{3+}$.[3] It is also expected that the substitution rates for $\mathrm{Co(en)(H_2O)_4}^{3+}$ and $\mathrm{Co(en)(H_2O)_3OH^{2+}}$ will be faster than the corresponding rates for $\mathrm{Co(en)_2(H_2O)_2}^{3+}$ and $\mathrm{Co(en)_2(H_2O)(OH)^{2+}}$[11] but slower than those for $\mathrm{Co(H_2O)_6}^{3+}$ and $\mathrm{Co(H_2O)_5OH^{2+}}$.[12]

Experimental

Synthesis of $\mathrm{KCo(en)(CO_3)_2{\cdot}H_2O}$. A 23.8-g portion of $\mathrm{CoCl_2{\cdot}6H_2O}$ (0.1 mol) was dissolved in a solution containing 10 mL of water and 12 mL of 30% $\mathrm{H_2O_2}$. The bubbling solution was added dropwise to

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Table I. Spectral Properties of Newly Synthesized Complexes

complex	λ_{max}, nm	ϵ^a	λ_{max}, nm	ϵ^a	δ	multiplicity
$Co(en)(CO_3)_2^{-}$ [b]	567	159	394	164	2.67	AA′BB′
$Co(en)(H_2O)_4^{3+}$ [c]	510	59	373	49	2.83	singlet
$Co(en)(H_2O)_3Cl^{2+}$	535	45	397	41	2.72	multiplet
	600[d]	36				
$Co(en)(H_2O)_2Cl_2^{+}$	544	38	400	33	2.66	singlet
	620	37				

[a] Calculated from cobalt analysis of spectral solutions; ±3% error from analysis. [b] λ_{max} 570 nm, ϵ 148; λ_{max} 390 nm, ϵ 214, reported previously.[6,8] [c] λ_{max} 511 nm, ϵ 44; λ_{max} 367 nm, ϵ 32, reported previously.[8] [d] Shoulder.

an ice-cold stirred solution of 35 g of $KHCO_3$ (0.35 mol) in 300 mL of water. The green $K_3Co(CO_3)_3$ formed immediately.[13,14] After the addition, which took approximately 1 h, 50 mL of an aqueous solution which was 1 M in en (0.05 mol) and 2 M in $HClO_4$ was also added dropwise. The resulting solution was stirred at room temperature for 1 h and then heated at 40 °C for 2 h. The purple solution was cooled to room temperature and vacuum filtered to remove olive green unreacted $K_3Co(CO_3)_3$. The filtrate was concentrated to approximately 100 mL on a rotary evaporator and then passed over a Dowex 50-X2 column, 50–100 mesh, in the K^+ form. The red $Co(en)_2CO_3^+$ was retained on the column and the blue $Co(en)(CO_3)_2^-$ was washed through with distilled water. The eluate from the column was reduced in volume to ca. 25 mL with a rotary evaporator. The concentrate was cooled in ice and the precipitated $KHCO_3$ was filtered off. A 2-mL portion of dimethylformamide (DMF) was added to the filtrate and the solution cooled in ice for at least 1.5 h (overnight is preferable). More $KHCO_3$ precipitated and was filtered off. Successive additions of 2-mL portions of DMF followed by cooling and filtration usually gave alternating crops of $KHCO_3$ and blue-black $KCo(en)(CO_3)\cdot H_2O$ crystals. Higher purity was obtained if the crystals were allowed to grow for several days. Large additions of DMF led to oils and mixed $KHCO_3$–$KCo(en)(CO_3)_2$ precipitates. Relatively low yields of product were obtained.

The blue-black crystals of $KCo(en)(CO_3)_2\cdot H_2O$ were analyzed for C, H, and N[15] and Co[16] with the following results. Anal. Calcd: C, 16.20; H, 3.38; N, 9.45; Co, 19.9. Found: C, 16.09; H, 3.12; N, 9.68; Co, 19.4. See Table I for spectral data.

All UV–vis spectra were recorded on a Cary 15 spectrophotometer. The ^1H NMR spectra were obtained on a Varian HR 220 spectrometer in either the CW or FT mode. Chemical shifts are reported on the δ scale relative to trimethylsilylpropanesulfonic acid as an internal standard.

Synthesis and Characterization of $Co(en)(H_2O)_4^{3+}$. $Co(en)(H_2O)_4^{3+}$ was produced from an aqueous solution of $Co(en)(CO_3)_2^-$ by the addition of sufficient $HClO_4$ to give $[H^+] \geq 0.05$ M after the evolution of CO_2. $Co(en)(H_2O)_4^{3+}$ was never isolated in the solid form. The behavior of this ion on a 10-cm Dowex 50-X2, 100–200 mesh, column in the H^+ form was studied. The column elution characteristics had been calibrated with $Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(en)_2(NO_2)_2^+$. This column, in either the H^+ or the Na^+ form, was used for all column experiments in this work. The UV–vis and ^1H NMR spectra are reported in Table I.

pK_a Determinations. Initial attempts to determine the pK_a of $Co(en)(H_2O)_4^{3+}$ by direct titration were unsuccessful due to dimer and polymer formation[17] (see below). Since the pK_a could not be determined by direct titration, it was measured using a flow cell and the visible spectrum in the 510–540-nm region. Buffer solutions of either acetate, formate, or phosphate were mixed with equal amounts of acidic $Co(en)(H_2O)_4^{3+}$ solution using a syringe pump so that the absorbance could be measured within 10–15 s of mixing. Because the change in absorbance was small, the pK_a was determined by comparing the observed spectrum at pH 3.38 (formate buffer) to spectra calculated using the extinction coefficients of $Co(en)(H_2O)_4^{3+}$ and $Co(en)(H_2O)_3OH^{2+}$ and various assumed pK_a values. This procedure led to an estimate of pK_a = 3.8 ± 0.1 at μ = 1.0 M. The absorption spectrum of $Co(en)(H_2O)_4^{3+}$ was measured in 0.1 M $HClO_4$ and that of $Co(en)(H_2O)_3OH^{2+}$ in acetate buffer at pH 4.8, using the flow cell.

The pK_a was also determined using a Durrum D-110 stopped-flow spectrometer and measuring the transmittance of the buffer–complex solutions at 545 nm 1 s after mixing. Again, 0.05 M $HClO_4$ was used in the determination of the transmittance of the acidic form, acetate buffer for the basic form, and formate buffer for the mixed species. The pK_a determined by this method was 3.65 ± 0.13.

Table II. Spectral Data for Related Cobalt(III) Complexes

complex	λ_{max}, nm	ϵ	λ_{max}, nm	ϵ	ref
cis-$Co(en)_2(H_2O)_2^{3+}$	500	80	350	70	19, 20
$Co(en)_2C_2O_4^+$	500	113	360	143	19
$Co(en)_2CO_3^+$	514	135	361	124	21, 22
cis-$Co(en)_2Cl_2^+$	530	78	380	69	23, 24
	535	100	390	78	
trans-$Co(en)_2Cl_2^+$	625	25	385	44	24
	450	35			
$Co(en)(C_2O_4)_2^-$	540	95	384	172	21
cis-$Co(NH_3)_2(H_2O)_4^{3+}$	540	41	375	40	2, 3
trans-$Co(NH_3)_2(H_2O)_4^{3+}$	537	44	362	73	4
cis-$Co(NH_3)_2(C_2O_4)_2^-$	556	110	384	200	21
cis-$Co(NH_3)_2(CO_3)_2^-$	575	174	395	258	21
$Co(NH_3)_2(H_2O)_3Cl^{2+}$	604	38	395	45	4
$Co(NH_3)_2(H_2O)_2Cl_2^+$	645	50			4

Kinetics Experiments. Changes in absorbance during the reaction of $Co(en)(H_2O)_4^{3+}$ with Cl^- were followed at 320 nm on a Guilford 2000 spectrophotometer with a thermostated cell compartment. The ionic strength of all reaction solutions was maintained at 2.0 M with $NaClO_4$. Distilled, deionized water was used to prepare all reaction and stock solutions. Stock NaCl (0.40–2.00 M) and $NaClO_4$ (2.00–4.00 M) solutions were made by dissolving reagent grade solids in distilled water, filtering if necessary and diluting to volume with distilled water. Stock $HClO_4$ (4.043 M) was standardized against standard NaOH. At the beginning of a kinetic run, $Co(en)(H_2O)_4^{3+}$ was generated in situ by adding a weighed quantity of $KCo(en)(CO_3)_2\cdot H_2O$ to a (thermostated) $HClO_4$–$NaClO_4$ solution, and reaction with Cl^- was initiated by the addition of an appropriate quantity of stock NaCl solution. For the reactions at 26.0 and 35.6 °C, the cuvettes were rinsed with the reaction solution and then filled and placed in cell compartment, with the first data points being recorded 5 min later. At 44.5 °C, the filled cuvettes were partially immersed in the bath for 1 min and then dried and placed in the thermostated cell compartment, and the first data points were taken 2 min later. Rate constants were calculated from absorbance–time data using a nonlinear least-squares computer program and equations discussed below.

Reaction Product Characterization and Equilibrium Studies. The identity of products in reaction solutions which had reached equilibrium was determined from ^1H NMR spectra, and the product distribution as indicated by peak areas was used to calculate equilibrium constants. Reaction products were also separated on cation-exchange columns (Dowex 50-X2, H^+ form) at 4 °C. Spectra of the eluted bands were recorded immediately after elution, and product extinction coefficients were calculated using the Co analysis of each band (see Table I).

Equilibrium constants for the reaction with Cl^- were also calculated from infinite-time absorbance readings and the initial Co(III) concentrations from each kinetic run with a nonlinear least-squares program.

Results

Characterization of Species and Reaction Stoichiometry. $KCo(en)(CO_3)_2\cdot H_2O$.

The results of the C, H, N and Co analyses (given above) show that the blue-black crystals obtained in the synthesis of $KCo(en)(CO_3)_2$ are probably $KCo(en)(CO_3)_2\cdot H_2O$. The spectral data (Table I) indicate that the $Co(en)(CO_3)_2^-$ ion that is produced when the complex is dissolved in water is a monomer with both carbonates acting as bidentate ligands. This evidence comes primarily from the ^1H NMR spectrum, since the visible spectrum is not particularly sensitive to the difference between monodentate and bidentate oxygen donors. For example, $Co(en)_2(C_2O_4)^+$ and $Co(en)_2(H_2O)(OC_2O_3)^+$ have the same visible λ_{max} but different extinction coefficients.[18] Spectral data of complexes related to $Co(en)(CO_3)_2^-$ and others produced in this work are given in Table II. The ^1H NMR spectrum of the $Co(en)(CO_3)_2^-$ ion, which has C_2 symmetry if the carbonates are fully chelated, shows the multiplet expected for a AA′BB′ pattern

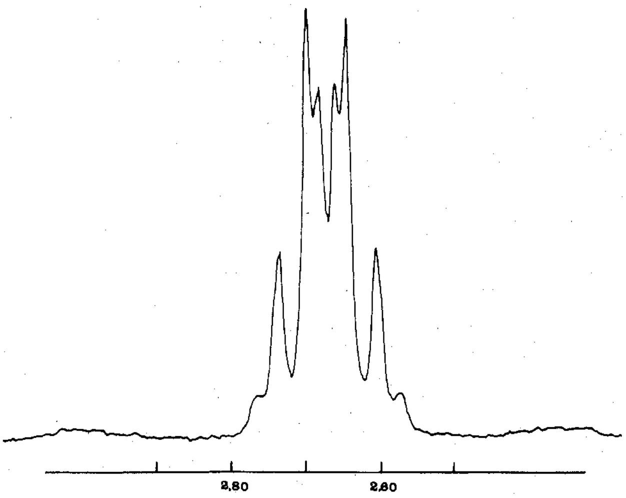

Figure 1. ^{1}H NMR spectrum at 220 MHz of the ethylenediamine protons of the $Co(en)(CO_3)_2^-$ ion in D_2O.

for the methylene protons of the ethylenediamine, centered at δ 2.67 (Figure 1).

$Co(en)(H_2O)_4^{3+}$. Acidification with $HClO_4$ of the solution of $Co(en)(CO_3)_2^-$ causes the evolution of CO_2 and yields a pink solution of $Co(en)(H_2O)_4^{3+}$. To confirm this identification, the pink solution was separated on a calibrated cation-exchange column, yielding a single colored band behaving as expected for a 3+ charge and containing all of the Co (±5%) originally added as $KCo(en)(CO_3)_2 \cdot H_2O$. In addition to a resonance peak at δ 6.51 due to the NH_2 protons of the coordinated ethylenediamine, the ^{1}H NMR spectrum of $Co(en)(H_2O)_4^{3+}$ has a single sharp peak at δ 2.83 for the methylene protons, as expected for its C_{2v} symmetry (Table I). The UV–visible spectrum of $Co(en)(H_2O)_4^{3+}$ is similar to that reported earlier by Davies and Yung,[8] except that our values of extinction coefficients are substantially higher (Table I).

In preliminary studies of the anation of $Co(en)(H_2O)_4^{3+}$ by halide ions, it was found that I^- reduces the complex instantaneously, Br^- reduces it slowly, and Cl^- does not reduce it at all. Evidence of the reduction was the fading of the pink color of $Co(en)(H_2O)_4^{3+}$ and formation of a violet CCl_4 layer in I^--containing solutions and a yellow CCl_4 layer in Br^--containing solutions. With Cl^- present the solution changed from pink to purple. As the reaction between $Co(en)(H_2O)_4^{3+}$ and Cl^- occurs, or if $Co(en)(CO_3)_2^-$ is treated with HCl rather than $HClO_4$, two new peaks are observed in the ^{1}H NMR spectrum. The first of these is a multiplet at δ 2.77 and the second is a singlet at δ 2.66 (Figure 2). The first suspicion was that these peaks represented the two isomers of $Co(en)(H_2O)_3Cl^{2+}$. However, further investigation showed that the ratio of the two peaks was sharply dependent on the Cl^- concentration, suggesting the formation of a mixture of $Co(en)(H_2O)_3Cl^{2+}$ and $Co(en)(H_2O)_2Cl_2^+$. This assignment was confirmed by the separation of the 2+ and 1+ species on the cold ion-exchange column and observing their UV–vis spectrum and interconversion. The spectral data are reported in Table I.

The substitution of Cl^- on $Co(en)(H_2O)_4^{3+}$ then yields a mixture of species related by the equilibria

$$Co(en)(H_2O)_4^{3+} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(en)(H_2O)_3Cl^{2+}$$

$$Co(en)(H_2O)_3Cl^{2+} + Cl^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co(en)(H_2O)_2Cl_2^+$$

The equilibrium constants for these reactions obtained from integrated peak areas of the methylene protons in the ^{1}H NMR spectra are $K_1 = k_1/k_{-1} = 16$ and $K_2 = k_2/k_{-2} = 1.2$. Values for these equilibrium constants were also obtained from the absorbance at 320 nm of solutions from kinetics runs. At 320 nm the extinction coefficient of $Co(en)(H_2O)_4^{3+}$ is very small compared to those of the chloro complexes, so that the absorbance at equilibrium is closely approximated by

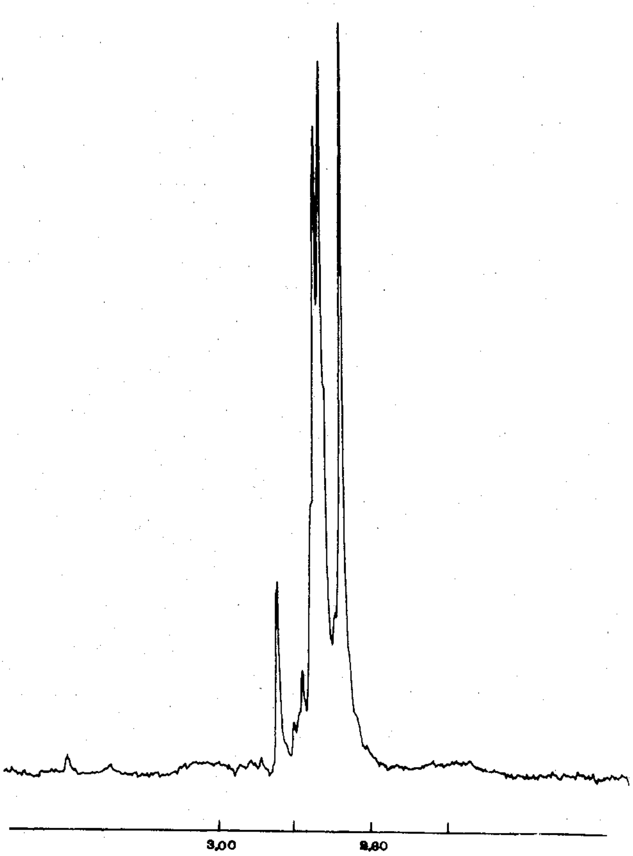

Figure 2. ^{1}H NMR spectrum at 220 MHz of the ethylenediamine protons of $Co(en)(H_2O)_4^{3+}$, $Co(en)(H_2O)_3Cl^{2+}$, and $Co(en)(H_2O)_2(Cl)_2^+$ in equilibrium at pH 0.7 in a 0.3 M Cl^- solution.

$$A = \frac{(\epsilon_2 + \epsilon_3 K_2[Cl^-])K_1[Cl^-]}{1 + K_1[Cl^-] + K_1K_2[Cl^-]^2}[Co(III)]_T$$

where ϵ_2 and ϵ_3 are the extinction coefficients of $Co(en)(H_2O)_3Cl^{2+}$ and $Co(en)(H_2O)_2Cl_2^+$, respectively, and $[Co(III)]_T$ is the total Co concentration. The equilibrium constants, obtained from the above expression by a nonlinear least-squares fit using the values $\epsilon_2 = 246 \pm 5$ and $\epsilon_3 = 506 \pm 10$, are $K_1 = 9$ and $K_2 = 2$. The values from the ^{1}H NMR spectra are probably more accurate because of a larger uncertainty in the weight of $KCo(en)(CO_3)_2 \cdot H_2O$ used in the kinetics runs.

No evidence of dimerization of $Co(en)(H_2O)_4^{3+}$ was observed for solutions of pH ≤1, but solutions adjusted to pH >3 with NaOH exhibited steadily increasing absorbance in the 290–340 nm region and a steadily declining pH, behavior characteristic of the formation of dimers and higher polymers.[17] Unlike the case of $Co(NH_3)_2(H_2O)_4^{3+}$, however, no precipitation or loss of N-containing ligand was observed at high pH, but readjustment of the solutions to pH 1 did not reverse the change in spectrum, even after several weeks at room temperature. Polymerization appears to be rapid at pH >7, since solutions of $Co(en)(H_2O)_4^{3+}$ adjusted to pH 7 or pH 9 and immediately placed on Dowex 50-X2 cation-exchange columns in the Na^+ form contained no species which could be eluted with 3 M $NaClO_4$, a solution which elutes 3+ ion from this resin. At pH 3.5 the polymerization reaction is sufficiently slow that immediate separation of a solution of $Co(en)(H_2O)_4^{3+}$ adjusted to this pH gave a major band be-

Table III. Kinetic Data for the Reaction of $Co(en)(H_2O)_4^{3+}$ with Cl^- at an Ionic Strength of 2.0 M

temp, °C	$[H^+]$, M	$[Cl^-]$, M	10^4k_{obsd}, s^{-1}
26.0 ± 0.2	0.10	1.0	2.57 ± 0.05
	0.20	0.2	0.237 ± 0.025
	0.20	0.4	0.668 ± 0.028
	0.20	0.5	0.922 ± 0.022
	0.20	0.7	1.03 ± 0.03
	0.20	0.8	1.05 ± 0.04
	0.20	0.8	1.34 ± 0.05
	0.20	1.0	1.33 ± 0.03
	0.20	1.0	1.38 ± 0.02
	0.40	1.0	0.762 ± 0.018
	0.40	1.0	0.893 ± 0.030
	0.80	1.0	0.622 ± 0.042
	0.80	1.0	0.503 ± 0.030
	1.00	1.0	0.478 ± 0.018
35.6 ± 0.02	0.10	1.0	13.7 ± 0.70
	0.20	0.2	2.23 ± 0.07
	0.20	0.5	4.80 ± 0.17
	0.20	0.8	6.05 ± 0.15
	0.20	1.0	8.75 ± 0.33
	0.20	1.0	6.75 ± 0.17
	0.40	1.0	3.98 ± 0.08
	0.40	1.0	3.97 ± 0.10
	0.80	1.0	2.42 ± 0.05
	1.00	1.0	2.18 ± 0.05
44.5 ± 0.2	0.10	1.0	41.5 ± 1.70
	0.20	0.2	8.45 ± 0.43
	0.20	0.5	17.8 ± 0.30
	0.20	0.8	24.3 ± 1.50
	0.20	1.0	22.7 ± 1.20
	0.20	1.0	24.3 ± 0.70
	0.40	1.0	14.4 ± 0.30
	0.40	1.0	14.4 ± 0.30
	1.00	1.0	7.95 ± 0.12

having as expected for an equilibrium mixture of $Co(en)(H_2O)_4^{3+}$ and $Co(en)(H_2O)_3OH^{2+}$, i.e., moving as if the charge were between 2+ and 3+. The solution immediately adjusted to pH 5.0 produced a large band (eluted with 0.3 M $NaClO_4$) which behaved as though it had a 1+ charge and two minor bands, one with a 3+ charge and one with a >3+ charge.

To avoid the interference of the polymerization reaction the pK_a of $Co(en)(H_2O)_4^{3+}$ was determined spectrophotometrically using the change in absorbance in the 510–545-nm region and using the stopped-flow method. The pK_a determined by these methods was 3.7 ± 0.2.

Kinetic Studies. Rate constants for the reaction of $Co(en)(H_2O)_4^{3+}$ with Cl^- were determined for solutions 0.2–1.0 M in Cl^-, 0.1–1.0 M in H^+, and $(0.8–1.3) \times 10^{-3}$ M in Co(III). In this range of acidity, there was no interference from the dimerization reaction during the time of the Cl^- substitution reaction. Plots of ln $(A_t - A_\infty)$ vs. time were linear for at 85% of the reaction. Values of the pseudo-first-order rate constant (k_{obsd}) are listed in Table III. The data at 26 °C have been used to construct Figure 3, a plot of k_{obsd} vs. $[Cl^-]$ which is linear within the precision of our data and has a positive intercept. A plot (Figure 4) of k_{obsd} vs. $1/[H^+]$ was also linear with a nonzero intercept, consistent with an acid-dependent and an acid-independent reaction path.

Since the equilibrium constant for the formation of $Co(en)(H_2O)_3Cl^{2+}$ from $Co(en)(H_2O)_4^{3+}$ is small, it was anticipated that k_{obsd} would be the sum of rate constants for the anation and aquation reactions. In order to derive the rate law for treatment of the kinetic data it was therefore important to know the relative rates of reactions of $Co(en)(H_2O)_4^{3+}$ and $Co(en)(H_2O)_3Cl^{2+}$ with Cl^-. A ^1H NMR experiment was set up with the $Co(en)(H_2O)_4^{3+}$ concentration at 0.053 M, $[Cl^-]$ at 4.41 M, pH at 0.68, and temperature at 22 °C. The half-life for the first substitution under these conditions is 15 h. The ratio of monochloro to dichloro complex was determined from the integrated area of the methylene protons of the ethylenediamine. The ratio was constant after the first quarter of a half-life of the reaction. These results demonstrate that the Cl^- substitution of the monochloro complex is rapid relative to the Cl^- substitution of the tetraaquo complex.

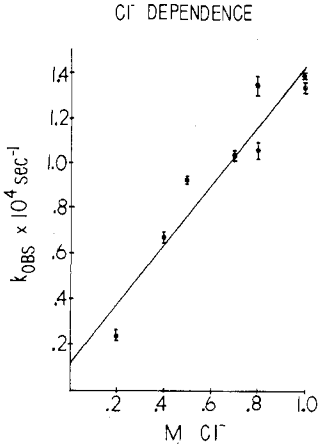

Figure 3. The Cl^- ion dependence of k_{obsd} at 26 °C in 0.20 M acid at μ = 2.0 M.

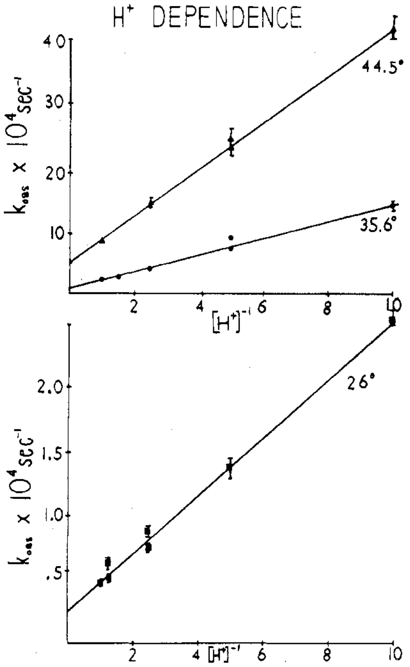

Figure 4. The H^+ ion dependence of k_{obsd} at the three reaction temperatures in 1.0 M Cl^- solutions with μ = 2.0 M.

Approximations for k_{-1}, k_2, and k_{-2} were obtained at 26 °C by observing the appropriate reactions of the species isolated with the cold ion-exchange column. By comparing these values with the rate constants (k_{obsd}) for the reaction of $Co(en)(H_2O)_4^{3+}$ + Cl^-, it was found that $k_{-1} \ll k_{obsd} \ll k_{-2}, k_2$ (Table IV) and that substitution of the first Cl^- in the $Co(en)(H_2O)_4^{3+}$ coordination sphere is the rate-determining step for the reaction. Consequently, the analysis of the kinetics of this system is similar to that for the monoacetylacetonate–copper(II) system in methanol and water studied by Pearson and Anderson.[25]

The system described here obeys the equation $(A_t - A_\infty) = (\text{const})e^{-\lambda_2 t} + (\text{const}')e^{-\lambda_3 t}$. λ_2 is important only for very short times and λ_3 reduces to $k_1[Cl^-] + k_{-1}/(1 + K_2[Cl^-])$, under conditions of constant acidity. In most cases, the contribution of λ_2 was over before the monitoring of the reaction began,

Table IV. Kinetic Data for Reactions of $Co(en)(H_2O)_3Cl^{2+}$ and $Co(en)(H_2O)_2Cl_2^+$ at 25.8 °C and Ionic Strength 1.4 M

reactions	initial $[Cl^-]$, M	$[H^+]$, M	k_{obsd}, s^{-1}
$Co(en)(H_2O)_3Cl^{2+} \rightarrow Co(en)(H_2O)_4^{3+}$	0.0	0.36	$6.25 \times 10^{-6} \pm 0.06$
$Co(en)(H_2O)_3Cl^{2+} + Cl^- \rightarrow Co(en)(H_2O)_2Cl_2^+$	0.5	0.36	$2.13 \times 10^{-3} \pm 0.10$
	1.0	0.36	$2.37 \times 10^{-3} \pm 0.08$
$Co(en)(H_2O)_2Cl_2^+ \rightarrow Co(en)(H_2O)_3Cl^{2+} + Cl^-$	0.0	0.36	$1.33 \times 10^{-3} \pm 0.33$
[a] $Co(en)(H_2O)_4^{3+} + Cl^- \rightarrow Co(en)(H_2O)_3Cl^{2+}$	1.0	0.40	$8.30 \times 10^{-5} \pm 0.70$

[a] Average value from Table III; $\mu = 2.0$.

so that only the first or second kinetics points, if any, show any curvature. Our k_{obsd} then equals $k_1[Cl^-] + k_{-1}/(1 + K_2[Cl^-])$.

Consistent with the kinetic data, the following mechanism for the substitution of the first Cl^- is suggested. It is similar to that proposed by Bodek, Davies, and Ferguson.[3]

$$\begin{tikzcd}
Co(en)(H_2O)_4^{3+} + Cl^- \arrow[r, shift left, "k_1'"] \arrow[d, shift left, "-H^+"] & Co(en)(H_2O)_3Cl^{2+} \arrow[l, shift left, "k_{-1}'"] \arrow[d, shift left, "-H^+"] \\
Co(en)(H_2O)_3OH^{2+} + Cl^- \arrow[r, shift left, "k_1''"] \arrow[u, shift left, "{K_h, +H^+}"] & Co(en)(H_2O)_2(OH)Cl^+ \arrow[l, shift left, "k_{-1}''"] \arrow[u, shift left, "{K_a, +H^+}"]
\end{tikzcd}$$

From this mechanism, we derive the relationships

$$k_1 = k_1' + k_1''K_h/[H^+]; \qquad k_{-1} = k_{-1}' + k_{-1}''K_a/[H^+]$$

$$k_{obsd} = (k_1' + k_1''K_h/[H^+])[Cl^-] + \frac{k_{-1}' + k_{-1}''K_a/[H^+]}{1 + K_2[Cl^-]}$$

At constant acidity the variation of k_{obsd} with $[Cl^-]$ reduces to $k_{obsd} = k_1[Cl^-] + k_{-1}/(1 + K_2[Cl^-])$. A plot of k_{obsd} vs. $[Cl^-]$, such as Figure 3, would then not be expected to be truly linear, since there is both a direct and an inverse dependence on $[Cl^-]$. However, it can be shown that the variation in the term $k_{-1}/(1 + K_2[Cl^-])$ is so small over the range 0–1 M Cl^- as to have a negligible (ca. 5%) effect on the slope of Figure 3. The intercept of Figure 3 provides a value of $k_{-1} = 1.2 \times 10^{-5}$ s^{-1}. Using the value $K_2 = 1.2$ M, we calculate a value of 5×10^{-6} s^{-1} for the term $k_{-1}/(1 + K_2[Cl^-])$ at $[Cl^-] = 1$ M so that this term decreases by 7×10^{-6} s^{-1} over the range 0–1 M Cl^-, compared to an increase of 1.3×10^{-4} in k_{obsd} (slope of Figure 3). The slope of Figure 3 is then a reasonably good measure of k_1. The measured value of k_{-1} from Table IV cannot be compared directly with that obtained from the intercept of Figure 3. However, if an inverse dependence of k_{-1} on $[H^+]$ is assumed, then the value of 6×10^{-6} s^{-1} obtained at $[H^+] = 0.4$ M (Table IV) would become 1.2×10^{-5} s^{-1} at $[H^+] = 0.2$ M, in good agreement with the intercept of Figure 3. At constant $[Cl^-]$, the variation of k_{obsd} with $[H^+]$ would reduce to $k_{obsd} = a/[H^+] + b$, where $a = k_1''K_h[Cl^-] + k_{-1}''K_a/(1 + K_2[Cl^-])$ and $b = k_1'[Cl] + k_{-1}'/(1 + K_2[Cl^-])$.

From the k_{obsd} vs. $1/[H^+]$ and $[Cl^-]$ plots at 26 °C, it is possible to put some limits on k_1', k_1'', k_{-1}', and k_{-1}''. For example, in 1.0 M Cl^-, $k_1'[Cl^-] + k_{-1}'/(1 + K_2[Cl^-]) = 2.6 \times 10^{-5}$ s^{-1}. At 0.2 M H^+, $k_1' + k_1''K_h[H^+] = 1.3 \times 10^{-4}$ s^{-1} M^{-1}. Therefore, the maximum value for k_1' is 0.3×10^{-4} s^{-1} M^{-1} and $k_1''K_h/[H^+]$ lies between 1.3×10^{-4} and 1.0×10^{-4} s^{-1}. If we use our approximate value for K_h of 2.0×10^{-4}, then if $k_1' = 0.3 \times 10^{-4}$ s^{-1} M^{-1}, $k_1'' = 0.10$ s^{-1} M^{-1}. As k_1' approaches zero, k_1'' approaches 0.13 s^{-1} M^{-1}.

In 1.0 M Cl^-, $k_1''K_h[Cl^-] + k_{-1}''K_a/(1 + K_2[Cl^-]) = 0.23 \times 10^{-4}$ s^{-1}. Using the minimum value for k_1'', $k_{-1}''K_a/(1 + K_2[Cl^-]) \leq 3 \times 10^{-6}$ s^{-1}. If $10^{-4} > K_a > 10^{-6}$, then k_{-1}'' will fall between 10 and 0.1 s^{-1}. At 0.2 M H^+ and 0 M Cl^-, $k_{-1}' + k_{-1}''K_a/[H^+] = 1.2 \times 10^{-5}$ s^{-1}. k_{-1}' is thus probably near 0.5×10^{-5} s^{-1}. Therefore, it appears that the first anation on cobalt is due primarily to the reaction of $Co(en)(H_2O)_3OH^{2+}$ with Cl^- in the $[Cl^-]$ and $[H^+]$ regions studied.

Table V. Substitution Rate Constants for $Co(en)(H_2O)_4^{3+}$ and Other Similar Complexes

complex	incoming ligand	rate const (25–26 °C)	ref
$Co(NH_3)_2(H_2O)_4^{3+}$	Cl^-	$k_1 \leqslant 7 \times 10^{-6}$ M^{-1} s^{-1}	3
$Co(NH_3)_2(H_2O)_3OH^{2+}$	Cl^-	$k_2 \geqslant 1 \times 10^{-2}$ M^{-1} s^{-1}	3
$Co(en)(H_2O)_4^{3+}$	Cl^-	$k_1' \leqslant 3 \times 10^{-5}$ M^{-1} s^{-1}	this work
$Co(en)(H_2O)_3OH^{2+}$	Cl^-	0.10–0.13 M^{-1} s^{-1}	this work
cis-$Co(en)_2(H_2O)_2^{2+}$	H_2O	7.5×10^{-6} s^{-1}	11
$Co(en)(H_2O)OH^+$	H_2O	5×10^{-4} s^{-1}	11
$Co(H_2O)_6^{3+}$	Cl^-	3 M^{-1} s^{-1}	32
$Co(H_2O)_5OH^{2+}$	Cl^-	1.23×10^4	32

The activation parameters for the reaction of Cl^- and $Co(en)(H_2O)_4^{3+}$ calculated from the data for 1.00 M Cl^- and 0.4 M H^+ are $E_a = 29.2$ kcal/mol, $\Delta H^\ddagger = 28.8$ kcal/mol, and $\Delta S^\ddagger = 18.5$ kcal/(mol deg).

Discussion

Our experimental data confirm that we have produced crystalline $KCo(en)(CO_3)_2 \cdot H_2O$, and solutions containing $Co(en)(H_2O)_4^{3+}$, $Co(en)(H_2O)_3Cl^{2+}$, and $Co(en)(H_2O)_2(Cl)_2^+$.

Our work shows that $Co(en)(H_2O)_4^{3+}$ has a pK_a of about 3.7 and that the complex dimerizes or polymerizes at pHs above 2. Since all of our experimental work was done at pH 1 or less, neither $Co(en)(H_2O)_3OH^{2+}$ nor $[Co_2(en)_2(H_2O)_2(OH)_3]^{3+}$ and related dimers or oligomers are present in appreciable concentrations in any of our reaction solutions. The pK_a of $Co(H_2O)_6^{3+}$ has been reported as 3.0[12,26] and the pK_a of $Co(en)_2(H_2O)_2^{3+}$ as 6.1.[20]

Our results are consistent with those found for the aforementioned complexes. Dimer formation as the pH is increased has also been observed for $Co(NH_3)_3(H_2O)_3^{3+}$[27,28] and other similar aquo systems.[27,29]

The reaction of $Co(en)(H_2O)_4^{3+}$ with Cl^- gives a mixture of chloro products and does not go to completion. Under the conditions in our kinetics experiments, the substitution of the first chloride into the first coordination sphere of the complex is the rate-determining step for the reaction. Once the monochloro complex is formed, the second chloride reacts rapidly and can also leave relatively easily. This behavior demonstrates that the monochloro complex is more labile than the tetraaquo complex and that the coordinated Cl^- labilizes a coordinated H_2O more easily than another coordinated H_2O molecule. These studies gave no indication which of the possible isomers was produced in either the mono- or dichloro case. Our limited studies on monochloro complex do not allow us to determine whether a hydroxychloro species is an important reaction intermediate for either the anation or aquation reaction. Due to the reduced charge on the complex, one would expect that $Co(en)(H_2O)_3Cl^{2+}$ would have a higher pK_a then $Co(en)(H_2O)_4^{3+}$. It has been reported that *cis*-$Co(en)_2Cl_2^+$[30] loses one chloride about 100 times more rapidly than *cis*-$Co(en)_2(H_2O)Cl^{2+}$.[9,31] Data for further comparisons can be found in Table V. Our system gives similar results at 26 °C and $[H^+] = 0.4$ M, $k_{-2}/k_{-1} = 200$. We also find under the same conditions, $k_2/k_{-1} \approx 350$ demonstrating that in the monochloro complex, the coordinated water is more labile than the coordinated chloride. Therefore, the system seems to prefer to maintain or lower its charge in solution and not to increase it.

In our detailed study of the reaction of $Co(en)(H_2O)_4^{3+}$ with Cl^-, we find that the $Co(en)(H_2O)_3OH^{2+}$ species is the more reactive of the two species in solution. Our estimates, $k_1' < 3 \times 10^{-5}$ M^{-1} s^{-1}, $k_1'' \approx 0.10$–0.13 M^{-1} s^{-1}, $k_{-1}' < .5 \times 10^{-5}$ s^{-1}, and $k_{-1}''K_a < 7 \times 10^{-6}$ s^{-1}, at 26.0 °C, agree reasonably well with those made for the $Co(NH_3)_2(H_2O)_4^{3+}$ system.[3] Our acid dependence appears to be slightly different. Because their observed rate constants are about 5 times greater than ours under the same conditions, their $k_2K_h[Cl^-] + k_{-2}K_a$ (notation from ref 3) term is much larger than ours so their $1/[H^+]$ vs. k_{obsd} plot may appear to have a zero intercept when it actually does not. Their reaction path involving $Co(NH_3)_2(H_2O)_3OH^{2+}$ is so much more rapid than the one for $Co(NH_3)_2(H_2O)_4^{3+}$ that the contribution from that path appears to be negligible. For both systems, $Co(en)(H_2O)_4^{3+}$ and $Co(NH_3)_2(H_2O)_4^{3+}$, the OH^- group has a labilizing effect. This effect could be due to the π bonding ability of OH^- in the transition state.[9] The increased reactivity of the hydroxy species has also been found in the $Co(en)_2(H_2O)_2^{3+}$ system.[11] The rate constants for the $Co(en)(H_2O)_4^{3+}$ reaction with Cl^- are between those found for the $Co(en)_2(H_2O)_2^{3+}$ and $Co(H_2O)_6^{3+}$ systems (see Table V). The activation parameters found in this work are consistent with those for other Co(III) substitution reactions.[9]

Our value of the equilibrium constant for the formation of the monochloro complex (K_1) is 16 at 26 °C, which is about 3 times as large as the value found for the diammine complex. The value for the diammine complex is based on a calculated spectrum, while the value in this work comes from weights, measured volumes, and peak areas in the ^1H NMR experiments with confirming spectrophotometric results. However, the equilibrium constants for the two systems were not measured at the same ionic strength, and this will affect the values to some extent. Since K_2 for the en system is 1.2, the amounts of dichloro and monochloro complex formed are about the same in solutions with high chloride concentrations. It is possible that the dichlorodiammine complex also forms in the reaction of $Co(NH_3)_2(H_2O)_4^{3+}$ with Cl^-, but it has not been mentioned by Bodek et al.[3] Even if it is present in their system, it is known to be relatively labile,[4] and as in our case, the rate-determining step would be the substitution of the first chloride. Consequently, their kinetic analysis would not be changed appreciably, but their equilibrium constant would be affected.

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Registry No. $KCo(en)(CO_3)_2$, 54992-64-2; $Co(en)(H_2O)_4^{3+}$, 67426-09-9; $Co(en)(H_2O)_3Cl^{2+}$, 67426-10-2; $Co(en)(H_2O)_2Cl_2^+$, 67426-11-3; $Co(en)(H_2O)_3OH^{2+}$, 67426-12-4; $K_3Co(CO_3)_3$, 15768-38-4.

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