minimal evolution of H_2 at 25 °C. Equation 7, with millimole

$$\begin{array}{ccccccc} 2(\mathrm{CHF_2})_2\mathrm{PH} & + & \mathrm{B_2H_6} & \to & 2\mathrm{H_2} & + & 2(\mathrm{CHF_2})_2\mathrm{PBH_2} \\ 0.950 & & 0.491 & & 0.602 & & (0.53?) \\ -0.419 & & -0.163 & & & & \text{oil} \\ \hline 0.531 & & 0.328 & & & & \end{array} \qquad (7)$$

stoichiometry, describes the result. Here the excess consumption of B_2H_6 (0.0625 mmol), yielding 0.071 mmol of excess H_2, may be due to decomposition of B_2H_6.

The oil might be a mixture of $(CHF_2)_2PBH_2$ oligomers, none of which could be distilled off under high vacuum at 100 °C. However, it did absorb 0.455 mmol of $(CH_3)_3N$ during 20 min at 100 °C—a result possibly analogous to the formation of the monomer complex $(CH_3)_3N{\cdot}(CF_3)_2PBH_2$ (and longer chains) from $(CH_3)_3N$ and $[(CF_3)_2PBH_2]_3$.[14] This subject seems worthy of further study.

Possible $(CHF_2P)_n$ Oligomers. A 0.690-mmol sample of CHF_2PI_2 was completely consumed by repeated distillation at minimal pressure over droplets of mercury. There was no product appreciably volatile at 25 °C, but a slight sublimate came off under high vacuum at 100 °C; this could be $(CHF_2P)_n$ with n minimal. Action upon the whole product by HI produced volatile material, converted by HI and Hg to 0.324 mmol of nearly pure CHF_2PH_2, just as expected if the initial product were $(CHF_2P)_n$.

Acknowledgment. Thanks are due to Allan Kershaw for the ^{13}C NMR spectra and to Dr. K. L. Servis for good advice.

Registry No. $(CHF_2)_3P$, 94110-53-9; $(CHF_2)_2PI$, 97523-67-6; CHF_2PI_2, 97523-68-7; CHF_2I, 1493-03-4; P, 7723-14-0; $(CHF_2)_2PH$, 97523-69-8; $P_2(CHF_2)_4$, 97523-70-1; $(CHF_2)_2PCl$, 94110-56-2; $HgCl_2$, 7487-94-7; CHF_2PH_2, 97523-71-2; CHF_2PCl_2, 97523-72-3; $(CHF_2)_2P$-$P(CF_3)_2$, 97523-73-4; $P_2(CF_3)_4$, 2714-60-5; $(CF_3)_2PH$, 460-96-8; $(CF_3)_2PCl$, 650-52-2; $(CHF_2)_2PH{\cdot}BH_3$, 97551-00-3; B_2H_6, 19287-45-7; $(CHF_2)_3P{\cdot}BH_3$, 97523-75-6; $P_2(CHF_2)_4{\cdot}BH_3$, 97523-76-7; $(CHF_2)_3PO$, 97523-74-5; $(CF_3)_3P$, 432-04-2; $(CF_3)_3PO$, 423-01-8; $(CHF_2CO)_2O$, 401-67-2; $CHF_2OC(O)CHF_2$, 2002-63-3; $AgCO_2CHF_2$, 383-88-0; $Hg_2(CO_2CHF_2)_2$, 97523-77-8.

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Ammoniation Reactions of *cis*- and *trans*-$[Co(en)_2XY]^{n+}$ Complexes in Liquid Ammonia, Related to the Bailar Inversion Reaction

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Base-catalyzed ammoniation is described for a number of complexes from the series *cis/trans*-$[Co(en)_2XY]^{n+}$ (X, Y = Cl^-, Br^-, Me_2SO, DMF), where both X and Y are readily substituted ligands. Some members of the series with trans configuration have rate-limiting deprotonation (X, Y = Cl^-, Cl^-; Br^-, Br^-; Cl^-, Me_2SO). ^1H NMR spectra of the products, directly recorded in the reaction medium, established, besides the normal two-step ammoniation reaction, the presence of an additional pathway involving the simultaneous loss of both ligands X and Y. The percentage of double substitution varies from 23% (X, Y = Cl^-, DMF) to 65% (Br^-, Br^-). The $[Co(en)_2(NH_3)_2]^{3+}$ formed is a mixture of cis and trans isomers. The percentage of double substitution seems to depend primarily on the nature of the most strongly bound of the ligands X and Y, whereas the percentage of the trans complex in the diammine depends on the weakest bound ligand. The product distribution is independent of pH and temperature. For the Λ-(+)-$[Co(en)_2Br_2]^+$ ion, the double substitution leads to a net inversion for the *cis*-diammine reaction product. By the use of deuterated ammonia as reaction medium, information was collected on the fate of specific proton sites during the reaction. Arguments are presented that the double-ligand-loss pathway originates in an attack of a solvent molecule on the five-coordinate intermediate of the traditional dissociative conjugate-base mechanism.

Introduction

Recently a reinvestigation of the Bailar inversion reaction[1] by Jackson and Begbie[2] has established a unique base-catalyzed route, by which Λ-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) hydrolyzes with the simultaneous loss of both Cl^- ligands. These authors suggested[2] that both *cis*- and *trans*-$[Co(en)_2XY]^{n+}$ complexes with two readily substituted ligands X and Y could behave similarly to Λ-$[Co(en)_2Cl_2]^+$. To us, it seemed that some of the missing information on these systems, required to formulate a detailed reaction pathway, could be obtained from liquid-ammonia studies. The reason is that some of the systems expected to exhibit double substitution also are in the category for rate-limiting deprotonation[3] in liquid ammonia.[4] This makes it possible to establish the number and position of deprotonations leading to the reactive intermediate(s). In addition, systems showing the normal mechanism of base-catalyzed ammoniation often have widely differing rates of ^1H–^2H exchange at either side of the $Co(en)_2$ plane, which opens up the possibility to use ^1H labels in liquid N^2H_3 to follow the steric course.[5] Finally, the product distribution can be determined directly in liquid ammonia by ^1H NMR.[6]

We present here a study of the ammoniation of a number of *cis*- and *trans*-$[Co(en)_2XY]^{n+}$ complexes, with X, Y = Br^-, Cl^-, Me_2SO (dimethyl sulfoxide), DMF (dimethylformamide), which have as one of the reaction pathways a route involving the concerted loss of both X and Y.

Experimental Section

Materials. *cis*- and *trans*-$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$,[7] *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$,[8] Λ-(+)-$[Co(en)_2Cl_2](ClO_4)$ and Λ-(+)-$[Co(en)_2Br_2](ClO_4)$,[8] and *trans*-$[Co(en)_2BrCl](ClO_4)$[9] were prepared according to published methods. The identity and isomeric purity of the complexes followed from UV–visible, ORD, and ^1H NMR spectra. Analysis results were satisfactory. The cis and trans isomers of the compounds $[Co(en)_2Cl_2](ClO_4)$, $[Co(en)_2Br_2](ClO_4)$, $[Co(en)_2(NH_3)Cl](ClO_4)_2$, and $[Co(en)_2(NH_3)Br](ClO_4)_2$ were used from previous

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studies.[10,11] *cis*- and *trans*-$[Co(en)_2(DMF)Cl](ClO_4)_2$ were kindly supplied by Prof. W.G. Jackson.

Liquid ammonia, perdeuterated liquid ammonia, perdeuterated ammonium perchlorate, and other electrolytes were prepared and used as described previously.[4] All solids were thoroughly dried before use.

Kinetic Measurements. The ammoniations of *trans*-$[Co(en)_2Br_2](ClO_4)$ and *cis*-$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$ were followed photometrically in a closed system under dry nitrogen gas. A detailed description of the apparatus and the data processing procedures has been given elsewhere.[4] All kinetic runs were performed at a constant ionic medium[6] of 0.20 mol kg^{-1} perchlorate, by the addition of calculated amounts of potassium perchlorate. From repetitive scan spectra it was clear in both cases that one single-step ammoniation reaction could be followed, without interference from subsequent reactions. The disappearance of the dibromo complex was monitored at 355 nm at complex concentrations between (1–5) × 10^{-3} mol kg^{-1}; the ammoniation of the $[Co(en)_2(Me_2SO)Cl]^{2+}$ complex at 513 nm at a complex concentration of 7 × 10^{-3} mol kg^{-1}. The mean deviation of the fit of the observed absorbancies as a function of time to a first-order rate law was in all cases better than 0.5%. Individual rate constants could be reproduced in independent measurements within 2%. The accuracy of the temperature was better than ±0.05 °C.

NMR Measurements. ^1H NMR spectra were recorded in liquid NH_3 and N^2H_3 on a Bruker WH-90 or a Bruker WM-250 spectrometer. The low temperatures made a special adjustment of the probe necessary.[4] For solutions in NH_3 the solvent peak was saturated before acquisition and 5% N^2H_3 was added as internal lock. Solutions were made up by condensing the solvent onto the cobalt(III) complex at −78 °C.[4]

Identification of Reaction Products. The steric course of the ammoniation reactions was determined directly in the reaction medium from peak heights and integrated ^1H resonances of the NMR spectra, recorded on a Bruker WM-250 instrument. The reaction temperature was varied between −70 and −40 °C; the spectra were recorded at −70 °C in order to minimize line broadening from proton exchange between the complex and the irradiated solvent. The ammonium perchlorate concentration was varied between 0.001 and 2 mol kg^{-1}. The product distribution obtained could be reproduced within an error of 2% absolute. Optical rotatory dispersion (ORD) spectra of the dichloro and the dibromo complexes were recorded in a 2 × 10^{-3} M solution in DMF. Reaction products of the ammoniation of Λ-(+)-$[Co(en)_2Cl_2](ClO_4)$ and Λ-(+)-$[Co(en)_2Br_2](ClO_4)$ were obtained by dissolving 40 mg of the complex in 1 mL of liquid ammonia, kept at constant temperature (±3 °C) in a cryostat. In one control experiment ammonium perchlorate was added. Immediately after completion of the reaction (5 min (−40 °C) and 15 min (−70 °C), visible from a color change to yellow-brown) the solid $[Co(en)_2(NH_3)_2]X_2(ClO_4)$ products were obtained by evaporation of the solvent at its boiling point. The ORD spectra of the products were recorded in 4 × 10^{-3} M aqueous solutions on a Perkin-Elmer MC-241 spectropolarimeter, equipped with 10-cm tubes. For the reaction products the estimated error in the molar rotation is 5%.

Results

Kinetics and Mechanism of Ammoniation. In a previous paper[4] the complete CB reaction scheme for the base-catalyzed ammoniation reaction in liquid ammonia has been worked out. For the substitution of a single ligand X, the essential steps, omitting charges and counterions (in the medium employed the complex cations are completely ion associated), are

$$[Co(en)_2YX] + NH_3 \underset{k^0_{-1}}{\overset{k^0_1}{\rightleftharpoons}} [Co(en)(en\text{-}H)YX] + NH_4 \qquad (1)$$

$$[Co(en)_2YX] + NH_2 \underset{k^1_{-1}}{\overset{k^1_1}{\rightleftharpoons}} [Co(en)(en\text{-}H)YX] + NH_3 \qquad (2)$$

$$[Co(en)(en\text{-}H)XY] \xrightarrow{k_2} [Co(en)(en\text{-}H)Y]X \qquad (3)$$

Reactions 1–3 are followed by a fast reaction with the solvent to form $[Co(en)_2(NH_3)Y]$. en-H denotes deprotonated ethylenediamine.

Qualitative ^1H–^2H exchange experiments on the *cis*-$[Co(en)_2(Me_2SO)Cl]^{2+}$ complex, monitored by ^1H NMR in N^2H_3, revealed that the four HN< (en) hydrogens that resonate at higher field exchange instantaneously on dissolution of the complex, while the other four hydrogens exchange slower, but still several orders of magnitude faster than the base-catalyzed ammoniation (eq 3) under similar conditions. This means that the normal conjugate-base mechanism applies: a fast acid–base preequilibrium (reactions 1 and 2), followed by the rate-determining elimination of the leaving group (reaction 3).[4] This is also evident from the acid dependence of the pseudo-first-order rate constant of ammoniation (Figure 1) that obeys the linear eq 4, as expected.[4,6]

$$k_{obsd} = k_2K^{CB}[NH_4ClO_4]^{-1} \quad K^{CB} = k^0_1/k^0_{-1} \qquad (4)$$

The [acid] independence of the rate of ammoniation of the *trans*-$[Co(en)_2Br_2]^+$ ion (Figure 2) suggests rate-determining deprotonation by a solvent molecule (NH_3; forward reaction 1, rate constant k^0_1), the main pathway found for the *trans*-dichloro

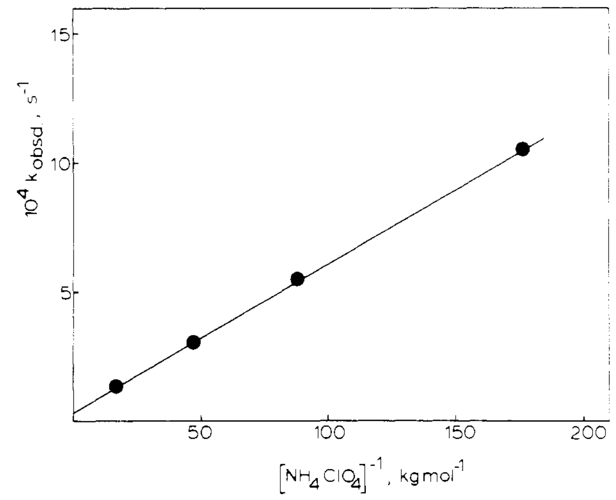

Figure 1. Observed rate constant for the ammoniation of *cis*-$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$ vs. the reciprocal ammonium perchlorate concentration at −65.0 °C and a constant ionic medium of 0.20 mol kg^{-1}.

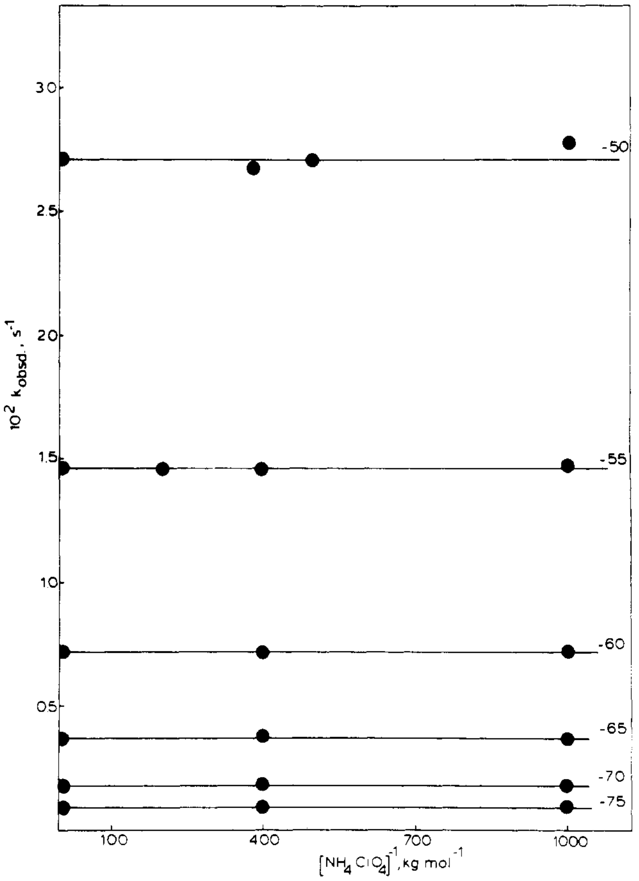

Figure 2. Observed rate constant for the ammoniation of *trans*-$[Co(en)_2Br_2](ClO_4)$ vs. the reciprocal ammonium perchlorate concentration at a constant ionic medium of 0.20 mol kg^{-1}.

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Table I. Stereochemistry of Reaction Products on Ammoniation of $[\text{Co(en)}_2\text{YX}]^{n+}$ Complexes in Liquid Ammonia

confign[a]	Y[b]	X[b]	*t*,[c] °C	$[\text{NH}_4\text{ClO}_4]$,[c] *m*	yield of *trans*-(Y,NH_3),[d] %	yield of *trans*-(X,NH_3),[d] %	yield of $(\text{NH}_3,\text{NH}_3)$,[d] %	yield of *trans*-$(\text{NH}_3,\text{NH}_3)$,[d,e] %
t	Cl	Cl	−70/−40	10^{-3}–1	71		29	30
c	Cl	Cl	−40	10^{-3}–1	⩽71		⩾29	28
t	Br	Br	−70	1	35		65	23
c	Br	Br	−40	10^{-3}–1	⩽35		⩾65	22
t	Cl	Br	−70	1	65		35	24
t	Cl	Me_2SO	−70	1	63	10	27	20
c	Cl	Me_2SO	−50	10^{-3}–(4×10^{-2})	68	?	32	21
t	Cl	DMF	−70	1	62	15	23	24
c	Cl	DMF	−40	2×10^{-2}	72	?	28	24
c[f]	Me_2SO	Me_2SO	−70	1	43		35	19
c	NH_3	Cl	−40	10^{-3}–0.5				25
t	NH_3	Cl	−40	10^{-3}–0.5				27
c	NH_3	Br	−40	10^{-3}–0.5				19
t	NH_3	Br	−40	10^{-3}–0.5				22

[a] Configuration of the reagent: c = cis; t = trans. [b] Reagent. [c] Reaction conditions. [d] Reaction products, % of total, accuracy ±2% absolute. [e] % of total $(\text{NH}_3,\text{NH}_3)$. [f] Reaction product *cis*-$(\text{Me}_2\text{SO},\text{NH}_3)$ = 22%.

analogue.[10,11] Then the averages of the rate constants in Figure 2 give the rate constant $k^0{}_1$ for reaction 1.

The values obtained were as follows: 27.3 (−50.00 °C); 14.6 (−55.00 °C); 7.2 (−60.00 °C); 3.67 (−65.00 °C); 1.81 (−70.00 °C); 0.79 (−75.00 °C) ($k^0{}_1$ in units of 10^{-3} s^{-1}). A weighted least-squares activation analysis gave $\Delta H^\ddagger = 50 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -48 \pm 7$ J K^{-1} mol^{-1}. The low $\Delta H^\ddagger$ value is characteristic for the mechanism by rate-determining deprotonation.[3,12]

^{1}H NMR Assignments. ^{1}H NMR provides an excellent means of distinguishing between cis and trans isomers of $[\text{Co(en)}_2\text{XY}]^{n+}$ complexes and between symmetric (X = Y) and asymmetric complexes.[13] In general liquid ammonia gives a good resolution of the chemical shifts. As the conformation equilibrium of coordinated ethylenediamine is leveled out on the NMR time scale, the number of resonances observed comes close to the theoretical expectation value. This property was used in product identification by means of "fingerprint" NMR spectra. Complete assignments for the cis complexes are now becoming possible, when special techniques are used,[14] but the spectra of the more symmetric trans complexes can be assigned straightforwardly.[13] A complete table of ^{1}H NMR spectra and assignments of the compounds used in this study and their reaction products is available as supplementary material.

Reaction Products. Table I gives the initial product distribution on ammoniation. All reaction products entered in Table I are stable at least for the time required for the recording of the NMR spectrum. To realize this, subsequent reactions had to be slowed down by adding ammonium perchlorate and working at low temperatures. Where temperature and acidity could be varied, the product distribution proved invariant to these parameters. For the comparatively inactive cis complexes the temperature had to be raised or the ammonium perchlorate concentration lowered to get a reaction. As a consequence, the condition of unreactivity of the products was no longer completely met for the *trans*-(NH_3,X)[15] products. Concretely this means that the absence of *trans*-$(\text{Me}_2\text{SO},\text{NH}_3)$ in the ammoniation of *cis*-$(\text{Cl},\text{Me}_2\text{SO})$ and of *trans*-(DMF,NH_3) in the ammoniation of *cis*-(Cl,DMF) may be caused by further reaction of these trans products. For both *cis*-(Cl,Cl) and *cis*-(Br,Br) it is clear that the diammine is immediately formed on ammoniation. Qualitatively the percentages of diammine complex seemed to be a little larger than for the trans analogues. The haloammine reaction products however are too reactive to allow a reliable quantitative product analysis. The isomeric composition of the diammine formed by direct substitution follows from the invariance of the cis/trans ratio of this product until the ammoniation is complete.

It is remarkable that, with the only exception of *cis*-$(\text{Me}_2\text{SO},\text{Me}_2\text{SO})$, no *cis*-$(\text{NH}_3,\text{X}$ or Y) reaction product was observed. Using previously determined rate constants,[11,16] we calculated that the *cis*-(NH_3,Cl) and the *cis*-(NH_3,Br) complexes should be stable under the conditions of Table I. Qualitative measurements on the other possible *cis*-$(\text{NH}_3,\text{X}$ or Y) reaction products lead to the same conclusion.

For the four haloammine complexes that are potential candidates to appear as intermediates in the reactions entered in Table I (i.e. *cis*- and *trans*-(NH_3,Cl) and -(NH_3,Br)), it was checked that all HN< (en) hydrogens exchange completely before ammoniation. This means that double substitution via route 5 is excluded. The essence of this reaction pathway is elimination

$$[\text{Co(en)}_2\text{X}_2]^+ \xrightarrow{-\text{H}^+} [\text{Co(en)(en-H)X}_2] \xrightarrow{-\text{X}^-} [\text{Co(en)(en-H)X}]^+ \xrightarrow{+\text{NH}_3} [\text{Co(en)(en-H)(NH}_3)\text{X}]^+ \xrightarrow{-\text{X}^-} [\text{Co(en)(en-H)(NH}_3)]^{2+} \xrightarrow{+\text{NH}_3} [\text{Co(en)(en-H)(NH}_3)_2]^{2+} \xrightarrow{+\text{H}^+} [\text{Co(en)}_2(\text{NH}_3)_2]^{3+} \quad (5)$$

of the second X before reprotonation of the conjugate base, which should lead to rate-limiting deprotonation in $[\text{Co(en)}_2(\text{NH}_3)\text{X}]^{2+}$, unless the rate of deprotonation at this particular site is too small to compete with other possible reaction pathways.

As the entries in Table I show a slight dependence on the nature of the leaving group, the ammoniation of the bromo complexes was repeated in the presence of 0.7 mol kg^{-1} NH_4Cl to check if the observed dependence is caused by the presence of the liberated chloride ion. No change in product distribution was observed.

It is interesting to note that rigid *trans*-dichlorotetraaminecobalt(III) complexes, like *trans*-dichloro[(*R*,*S*)-1,9-diamino-3,7-diazanonane]cobalt(III) and *trans*-dichloro[(*R*,*S*)-1,10-diamino-4,7-diazadecane]cobalt(III) in liquid ammonia yield only the *trans*-chloroammine complex (100%) in the first ammoniation step and from that the *trans*-diammine complex in the second step,[17,18] without any trace of double-ligand loss.

Inversion on Double Substitution. As the Bailar inversion reaction in aqueous solution involves a substantial net inversion,[1,2] it would be interesting to study this phenomenon in liquid ammonia. To do this we reacted Λ-(+)-$[\text{Co(en)}_2\text{Br}_2](\text{ClO}_4)$ in liquid ammonia, until all cobalt(III) was converted to the diammine. After isolation of the products in the solid state, the ORD spectra were recorded in aqueous solution at 25 °C, giving the molar

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Table II. Product Distribution in the Double-Substitution Route

temp, °C	$[M]^{25}{}_{589}$,[a] deg M^{-1} m^{-1}	% (−)cis[b]	cis[c] % Δ	cis[c] % Λ	% trans[d]
		Λ-(+)-$[Co(en)_2Br_2](ClO_4)$			
−40	−37	26	58	19	23
−40	−37	26	59	20	21
−40[e]	−56	39	69	9	22
−40[e]	−54	37	68	11	21
−40[f]	−34	24	58	21	21
−70	−43	30	62	15	23
−70	−43	30	63	16	21
		Λ-(+)-$[Co(en)_2Cl_2](ClO_4)$			
−60	−7	5	45	28	27
−50		10[g]	54	19	27

[a] Referring to the total amount of diammine. [b] Percentage of (−)cis complex above the racemic mixture, referring to the total amount of diammine. [c] Estimated error 5% absolute. [d] Estimated error 2% absolute. [e] Added NH_4ClO_4: 5×10^{-2} mol kg^{-1}. [f] Kept at the reaction temperature for 1 h. [g] Approximate value from ref 21.

rotation at the sodium D line: $[M]^{25}{}_{589}$. Combined with the value given by Mathieu[19,20] for the molar rotation of Λ-(+)-$[Co(en)_2(NH_3)_2]^{3+}$ ($[M]^{25}{}_{589} = +145°$ M^{-1} m^{-1}) the value of % (−)cis (the percentage of the optically active form above the racemic mixture[8]) was calculated: % (−)cis = $-100[M]^{25}{}_{589}$(product)/145 (Table II). For the dibromo complex the product distribution seems to vary slightly with the acidity but does not depend on the reaction temperature or the extent of the reaction. The latter observation excludes postreaction isomerization of the diammine; the same conclusion has been drawn from photometric studies.[11] The cis/trans distribution was obtained from the ^1H NMR spectrum of the reaction product in Me_2SO-d_6, accuracy 2% absolute. If it is now assumed that the percentage reaction via double halide loss for the *cis*-dihalo complex equals the value found for the *trans*-dihalo complex, the isomeric distribution in the diammine produced by double-halide loss can be calculated. In view of the accumulation of errors in obtaining the final product distribution in Table II, the results must be taken as a qualitative indication of net inversion in the formation of the cis product. As a comparison one experiment was done with Λ-(+)-$[Co(en)_2Cl_2](ClO_4)$. Because of the small contribution of the double-chloride-loss pathway (29%), the result is less reliable, but again net inversion is clearly indicated. The older approximate data of Archer and Bailar[21] are in agreement with this conclusion.

Ammoniations in N^2H_3. Reactions in perdeuterated liquid ammonia may give information on the site of deprotonation on the route to the reactive conjugate base[6] and about structural changes during ammoniation.[5] This approach is limited to the trans complexes, as the cis members of the series presented here all exchange their hydrogens completely, prior to ammoniation. We studied the trans isomers of the complexes (Br,Br), (Me_2SO,Cl), and (DMF,Cl).

trans-$[Co(en)_2Br_2](ClO_4)$ was reacted in N^2H_3 at the lowest temperature possible (<−70 °C) and high acid concentration (2.5 mol kg^{-1} $N^2H_4ClO_4$) to slow down the ^1H–^2H exchange of the diammine reaction product (the ammoniation of the dibromo complex itself is [acid] independent; Figure 2). Even under these conditions the exchange at the reaction products, especially the *trans*-diammine, is not negligible. Reliable back-extrapolation of this exchange is not possible, as the temperature control of the probe of the 250-MHz spectrometer, necessary for a distinct resolution of the ^1H resonances involved, takes a large part of the reaction time to adjust. Three independent experiments showed that after completion of the first stage of the ammoniation reactions (as given in Table I) 15 ± 2% of the integrated total of HN< (en) resonances (calibrated with reference to the HC< (en) resonances) had disappeared. In view of the discussion above, this sets an upper limit of 1.2 ± 0.2 ^1H protons exchanged per molecule of *trans*-(Br,Br) in the ammoniation.

trans-$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$ reacts instantaneously on dissolution in liquid ammonia, even at low temperature and high acidity. Therefore the mechanism cannot be concluded from medium effects on the photometric rate of ammoniation. The reaction was studied in N^2H_3 to determine the mechanistic mode of the reaction and the site of reprotonation. The information comes from the ^1H distribution over the two sets of inequivalent hydrogen sites (at the N^2H_3 or the Cl^- side) in the *trans*-$[Co(en)_2(N^2H_3)Cl]^{2+}$ reaction product. The respective resonances appear at 5.68 ppm and 5.36 ppm (δ_H relative to bulk NH_3; in the presence of chloride ions).[5,11,22] The HN< (en) resonances of the *trans*-diammine products of double substitution overlap with these positions.

We found that by adding $N^2H_4ClO_4$ up to 1 mol kg^{-1}, immediately after dissolution of the *trans*-(Me_2SO,Cl) complex in liquid N^2H_3 at −70 °C, the hydrogen exchange at the HN< (en) positions of *trans*-(N^2H_3,Cl) could be sufficiently stopped for the time necessary for the complete exchange of the *trans*-(N^2H_3,N^2H_3) hydrogens. Via calibration on the HC< (en) resonances, a comparison with the same experiment in NH_3 gave the number of hydrogens per molecule of *trans*-(N^2H_3,Cl) formed (results from three independent measurements): 3.0 ± 0.2 at the N^2H_3 side and 3.8 ± 0.2 at the Cl^- side. This means that the complex is formed by a mechanism of rate-determining deprotonation and that deuteration of the conjugate base takes place at the side of the entering group.

The experiment described above was repeated with the less reactive *trans*-$[Co(en)_2(DMF)Cl](ClO_4)_2$. Immediately after dissolution of the complex, at −70 °C, in liquid ammonia containing 2 mol kg^{-1} NH_4ClO_4, the ^1H NMR spectrum did not show appreciable reaction. Only one HN< (en) resonance (8 H), at 5.9 ppm (relative to NH_3), was observed. In N^2H_3, however, the 5.9 ppm resonance was instantaneously halved on dissolution of the complex, indicating complete exchange of hydrogen at one side of the $Co(en)_2$ plane. As a result of ammoniation all four remaining hydrogens reappeared in the *trans*-(N^2H_3,Cl) reaction product, distributed over both sides of the $Co(en)_2$ plane, as follows: 1.0 ± 0.2 (N^2H_3 side) and 2.9 ± 0.2 (Cl^- side) (four independent measurements). The mechanism in this case apparently is by a rapid preequilibrium (the "normal" CB mechanism).

Discussion

From the NMR analysis of the reaction products of ammoniation (Table I), it is clear that the phenomenon of concerted double-ligand loss is not restricted to the published[2] case of the *cis*-$[Co(en)_2Cl_2]^+$ ion in aqueous solution but plays an important role in the ammoniation in liquid ammonia of a number of bis(ethylenediamine)cobalt(III) complexes with two easily substituted ligands, in both the cis and the trans configuration. It seems reasonable to assume that the double-substitution pathway has a similar mechanism for all the reactions in liquid ammonia reported here. Then, the elucidation of the mechanism may combine results from different systems. In addition, parallels in the mechanism must exist between water and ammonia as solvent systems.

First, it must be decided, whether the two ammoniation routes, of single- and double-ligand loss, have an initial common route, diverting after the rate-determining step, or there are parallel, completely independent pathways. In the present case, the product distribution seems to be independent of acid concentration and temperature. Moreover, the rate equation for the present systems seems to be the same as for the normal stepwise mechanism. Consequently double-ligand loss does not seem to be an additional pathway, as suggested by Jackson and Begbie[2] for base hydrolysis of *cis*-$[Co(en)_2Cl_2]^+$. In this case the concerted mechanism is thought to show up most likely as a second-order term in $[OH^-]$.

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(20) The older value given by Mathieu is qualitatively confirmed by ORD spectra published later: Brushmiller, J. G.; Amma, E. L.; Douglas, B. E. *J. Am. Chem. Soc.* **1962**, *84*, 3227. MacDermott, T. E.; Sargeson, A. M. *Aust. J. Chem.* **1963**, *16*, 334.

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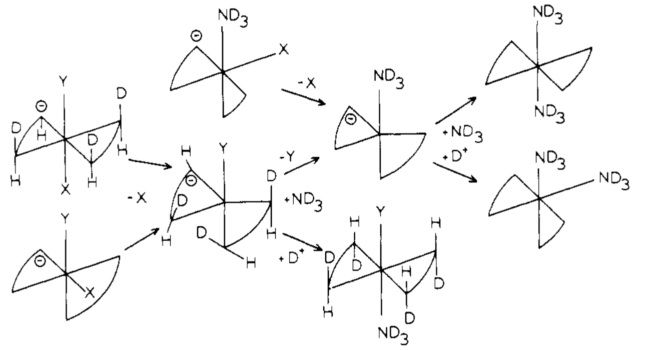
Scheme I



This conclusion was reached from the dependence of the product composition on $[OH^-]$. However, the results are also fully compatible with the mechanism propagated by us.[23]

The number of protons lost additively in both the pathways can only be reliably inferred from a system that reacts by rate-limiting deprotonation and has a substantial contribution of double substitution. In the present case the dibromo complex qualifies excellently for this job. The result obtained, 1.2 ± 0.2 H^+ lost per molecule, must be compared with the calculated number of 1 H^+ for a shared initial step in the normal mechanism and $0.35 + 2 \times 0.65 = 1.65$ H^+ for a parallel-route mechanism, involving double-H^+ loss for double-ligand loss (as a possible suggestion from the results in aqueous solution[2]). The result comes closest to the first mechanism.

When, in view of the above conclusions, it is tried to construct a mechanism with competitive routes after an initial rate-determining step, it must be realized that all imaginable six-coordinate intermediates were shown under Results to be too inert for this role. It then seems reasonable that the two pathways split at a five-coordinate intermediate. The double-ligand loss can then be imagined as an attack on the intermediate by NH_3 in liquid ammonia, contrasted to an attack by OH^- in water, explaining the change in medium dependence of the product composition.[23]

A remarkable fact in the reactions is the near equality of product distributions for geometrical isomers. The difference in rate law for the two dichloro[10] and dibromo[11] isomers, which changes the reactivity order in the available acidity range, excludes a preammoniation isomerization as an explanation.[10,11,24] Therefore it seems that isomeric cis and trans complexes of the present series react via the same intermediate. This conclusion is certainly limited to liquid ammonia.

As to the influence of the substituted ligands X and Y on the reaction course, the general picture of Table I is that the percentage of double substitution is primarily dependent on the nature of the less easily substituted of the leaving groups, Y, and, to a smaller extent, on X. The dependence on X is comparable to the leaving-group dependence of the second step of ammoniation (i.e. the ammoniation of the haloammine complexes). This kind of leaving-group effect has been explained by Jackson and Begbie[25] from the presence of this ligand in the solvent sheet of the substrate, which stays essentially intact during the formation and reaction of the five-coordinate intermediate in a predominantly dissociative activation.

We have been able to extend this explanation to ammoniation of asymmetric *trans*-$[Co(en)_2YX]^{n+}$ complexes with one easily substituted ligand X.[6] The experiments on the fate of ^1H labels on ammoniation of *trans*-$[Co(en)_2(Me_2SO)Cl]^{2+}$ and *trans*-$[Co(en)_2(DMF)Cl]^{2+}$ can be put together in one mechanism, if it is assumed that the reactive conjugate base is formed by deprotonation at the side of the nonleaving ligand (Cl^-) and that the *trans*-(NH_3,Cl) complex formed has been reprotonated at the side of the entering NH_3. For the DMF complex this mechanism in addition requires effective rotation of the ethylenediamine ring not involved in acid dissociation. This brings the ^1H distribution to 1/3 NH_3 side to Cl^- side. This is exactly the distribution that we have found[5] for the formation of *trans*-$[Co(en)_2N_3(NH_3)]^{2+}$ in the ammoniation of *trans*-$[Co(en)_2N_3(Me_2SO)]^{2+}$. Of course, the ring rotation will go unnoticed in the *trans*-(Me_2SO,Cl) complex. The structure and reaction geometry of the five-coordinate intermediate may then be adopted from the mechanism worked out for the azido–Me_2SO complex.[5]

All conclusions about the mechanism of double-ligand loss in liquid ammonia have been summarized in Scheme I, which gives the main reaction pathways. (For clarity ^2H is denoted as D (deuterium); charges are omitted.) The finding that double-ligand loss from the Λ-(+)-*cis*-$[Co(en)_2Br_2]^+$ produces *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ under net inversion is accommodated in the reaction scheme.

In conclusion the ammoniation reactions have brought a more detailed understanding of the pathways in double-ligand loss. Although some suggestions have been considered about electronic factors responsible for the mechanism,[2,26] these have been described as not especially compelling.[2] The data presented here do not seem to bring this problem closer to a solution. The same may be said in general about the intrinsic conjugate-base mechanism, that remains obscure, even after so many recorded attempts of explanation.

Acknowledgment. Prof. W. G. Jackson is thanked for a gift of *cis*- and *trans*-$[Co(en)_2(DMF)Cl](ClO_4)_2$. H. Bulthuis has assisted in the preparation of the cobalt complexes.

Registry No. NH_3, 7664-41-7; *trans*-$[Co(en)_2Cl_2](ClO_4)$, 14407-65-9; *cis*-$[Co(en)_2Cl_2](ClO_4)$, 23791-80-2; Λ-(+)-$[Co(en)_2Cl_2](ClO_4)$, 23791-81-3; *trans*-$[Co(en)_2Br_2](ClO_4)$, 15352-29-1; *cis*-$[Co(en)_2Br_2](ClO_4)$, 97704-66-0; Λ-(+)-$[Co(en)_2Br_2](ClO_4)$, 65760-53-4; *trans*-$[Co(en)_2ClBr](ClO_4)$, 15352-55-3; *trans*-$[Co(en)_2Cl(Me_2SO)](ClO_4)_2$, 77403-02-2; *cis*-$[Co(en)_2Cl(Me_2SO)](ClO_4)_2$, 15618-10-7; *trans*-$[Co(en)_2Cl(DMF)](ClO_4)_2$, 97704-67-1; *cis*-$[Co(en)_2Cl(DMF)](ClO_4)_2$, 15618-08-3; *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$, 14781-36-3; *cis*-$[Co(en)_2Cl(NH_3)](ClO_4)_2$, 15280-85-0; *trans*-$[Co(en)_2Cl(NH_3)](ClO_4)_2$, 71380-87-5; *cis*-$[Co(en)_2Br(NH_3)](ClO_4)_2$, 62301-87-5; *trans*-$[Co(en)_2Br(NH_3)](ClO_4)_2$, 97731-52-7.

Supplementary Material Available: A table containing the ^1H NMR chemical shifts (250 MHz) of the $[Co(en)_2XY]^{n+}$ perchlorates in liquid ammonia (1 page). Ordering information is given on any current masthead page.

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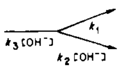
[23] If for base hydrolysis the scheme is



with k_3 rate determining, then the rate law is $k_{obsd} = k_3[OH^-]$. The product distribution is determined by the ratio $k_1/k_2[OH^-]$, which leads to a product distribution consistent with the data forwarded in ref 2.

[24] Preisomerization of *cis*-(NH_3,Cl) to the more reactive trans isomer is also excluded, because the reaction product of the optically active *cis*-(NH_3,Cl) in liquid ammonia still shows optical activity.[19,21]

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