Solvent Dependence of the Stereochemistry of Base-catalyzed Solvolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+/2+}$ (X = Me_2SO or Cl) Ions

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The *cis–trans* product ratio for the base-catalyzed solvolysis of the $^{15}NH_3$ labelled *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$ ion has been determined as a function of the solvent. The solvents used were H_2O–CH_3OH and H_2O–dmso (dimethyl sulphoxide) mixtures, as well as anhydrous CH_3OH and CH_3NH_2. The *trans*-$[Co(NH_3)_4(^{15}NH_3)(dmso)]^{3+}$ ion was included also in the study. The base hydrolysis results do not show any solvent or leaving-group dependence, within experimental error (2%). All *trans* systems give (44 ± 1)% rearrangement. Small, significant differences are shown by the penta-amminechloro-complex in CH_3NH_2 (50% rearrangement) and by the dmso complex (48% rearrangement in H_2O and 46% in CH_3OH). The results are interpreted as indicating the adequacy of a mechanistic model involving a five-co-ordinate intermediate.

Stereochemical change in base hydrolysis is still to a large extent an unsolved problem [1] in the conjugate base (c.b.) mechanism. This mechanism generally consists of a fast proton transfer pre-equilibrium, followed by the rate-determining dissociative elimination of the leaving group.[2,3] Early stereochemical theories assumed the five-co-ordinate intermediate, inherent in the dissociative activation, to have a fixed geometry. This idea was combined with that of a stereospecific entry of the incoming ligand, directed by the amido-group.[4,5] Recent results on the ' red ' s and p (secondary and primary) isomers of the $[CoL(NH_3)X]^{3+/2+}$ ion [L = 2,2′-diamino-2″-methylaminotriethylamine, X = Cl, Br, N_3, or NH_3], bearing on the lifetime of the intermediate,[6,7] have been interpreted as indicating that the five-co-ordinate species do not relax towards a common trigonal-bipyramidal structure, although this process would require only a small change in bond angle. The resulting more dynamic picture is the immediate capture of a solvent molecule, before bond angles can equilibrate.

If indeed the process of capture of the entering group by the five-co-ordinate species competes in rate with angle equilibration and solvent structure rearrangement,[6,7] relative rates and consequently product stereochemistry should be affected by the nature of the solvent. This conclusion does not seem consistent with the fact that experiments in our laboratory revealed a close agreement in product stereochemistry for the base-catalyzed reactions of $[Co(en)_2XY]^{2+/+}$ (en = ethylenediamine; X = Cl, Br, or dmso; Y = Cl, NCS, NO_2, N_3, or NH_3) complexes in liquid ammonia and in aqueous solution.[8,9] In this report we investigate the solvent dependence in the base-catalyzed solvolysis reaction of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+/2+}$ (X = dmso or Cl) ions, a reaction for which a fixed five-co-ordinate intermediate seems to explain [5] aqueous stereochemical results [10] well.

Experimental

Materials.—$[Co(NH_3)_5(SO_3)]Cl$ was prepared according to Siebert and Wittke.[11] The purity of the product proved to be sufficient for the synthesis.

trans-$[Co(NH_3)_4(OH)(SO_3)]$ was prepared as described in the literature,[10] with some modifications to improve the purity of the product. $[Co(NH_3)_5(SO_3)]Cl$ (5 g) was dissolved in a 3% aqueous solution of lithium hydroxide (125 cm^3). After 5 min stirring, Amberlite MB-3 cation–anion exchange resin (25 cm^3) was added and after another 2 min stirring, the solution was filtered. The hydroxosulphito-complex was precipitated from the filtrate by adding 96% ethanol (150 cm^3). Subsequent centrifuge recovery, washing with ethanol and diethyl ether, and vacuum drying yielded tetra-ammine(hydroxo)sulphitocobalt(III). This compound was used as a starting material for the synthesis of the *trans*-substituted complex.

For *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl][ClO_4]_2$, the method of Buckingham *et al.*[10] was followed, using a more strict pH control than indicated by these workers. A solution of $^{15}NH_4Cl$ (1 g) (VEB Berlin-Chemie) in water (10 cm^3) was brought to pH 9.7 with solid lithium hydroxide monohydrate. Freshly prepared tetra-ammine(hydroxo)sulphitocobalt(III) (1.25 g) was then dissolved in this solution; after 5 min stirring the resulting precipitate was filtered off. After readjusting the pH to 9.7, another 1.25 g of complex were added and this last procedure repeated once. The brown-yellow product was washed with ethanol and dried *in vacuo*. This *trans*-$[Co(NH_3)_4(^{15}NH_3)(SO_3)]Cl$ was converted into the chloro-complex by boiling in concentrated hydrochloric acid saturated with lithium chloride, and converted into the perchlorate salt by treatment with silver perchlorate in solution. The anhydrous complex was obtained by heating for 1 h *in vacuo* at 100 °C, yield 70%. The purity of the compound was checked by n.m.r. spectroscopy.[10]

$[Co(NH_3)_4(^{15}NH_3)(dmso)][ClO_4]_3$ (dmso = dimethyl sulphoxide) was prepared from *trans*-$[Co(NH_3)_4(^{15}NH_3)(H_2O)][ClO_4]_3$ according to Piriz Mac-Coll and Beyer,[12] and recrystallized from acidified aqueous solution. The aqua-complex was obtained from the mercury(II)-catalyzed aquation of *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl][ClO_4]_2$.[10] This procedure yielded a mixture of *cis* and *trans* dmso complex, the composition of which (determined by ^1H n.m.r. spectroscopy) depended on the reaction temperature. A reaction at room temperature during 10 d gave a 90% pure *trans* complex.

The other reagents and solvents used were purchased as analytical grade and purified further, and when necessary dried by routine methods.[13]

Base-catalyzed Solvolysis of the $^{15}NH_3$ *Labelled Penta-ammines.*—Penta-amminechlorocobalt(III) perchlorate was subjected to base-catalyzed solvolysis at 25 °C in water, water–methanol mixtures, and water–dmso mixtures (up to 40% v/v dmso; higher percentages of dmso decomposed the complex) by dissolving the complex (200 g) in the (mixed) solvent (10 cm^3), followed by the addition of sodium hydroxide (1 cm^3, 2 mol dm^{-3}). After 5 min, an excess of concentrated perchloric acid was added to precipitate the penta-ammine-aqua-complex. This complex was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*. The dmso complex in water was treated analogously. The reactions of $[Co(NH_3)_4(^{15}NH_3)X]^{3+/2+}$ (X = dmso or Cl) in anhydrous methanol were performed in a closed system under dry nitrogen. The perchlorate salt (100 mg) was dissolved in dried methanol (25 cm^3) in which metallic sodium (0.25 g) had been dissolved previously. After 30 min, the slightly turbid solution was filtered and an excess of concentrated perchloric acid was slowly added with cooling in ice. The pink complex, $[Co(NH_3)_4(^{15}NH_3)(CH_3OH)][ClO_4]_3$, crystallizing from the solution, was filtered off, washed with ethanol and diethyl ether, dried, and kept *in vacuo*.

The penta-amminechloro-complex was dissolved in methylamine by condensing methylamine at −70 °C on to the perchlorate salt (200 mg) in a closed system. On warming to −10 °C the reaction started and was complete (yellow solution) in 30 min. The reaction product was isolated by evaporating the solvent. The resulting solid $[Co(NH_3)_4(^{15}NH_3)(CH_3NH_2)][ClO_4]_2Cl$ was converted into the perchlorate by treatment with $AgClO_4$, washed with cold ethanol and diethyl ether, and dried *in vacuo*.

In none of the cases studied was a subsequent rearrangement of the products observed.

N.M.R. Spectra.—Hydrogen-1 n.m.r. spectra of the $^{15}NH_3$ labelled compounds were recorded on a Bruker WM 250 or 500 Fourier spectrometer. Solutions were made up in 5-mm diameter tubes, using acidified (trace of D_2SO_4) [$^2H_6$]dmso as solvent. Chemical shifts are in p.p.m. relative to sodium 3-trimethylsilylpropane-1-sulphonate (tsp) as internal reference. The chemical shifts of cobalt(III) amine complexes are susceptible to medium effects.[14] We found these effects to be minimal for the perchlorates (<0.02 p.p.m.). The chloride salts consistently show a downfield shift of the ammine resonances compared to the perchlorates and are more prone to medium effects. Integrals of resonance areas were reproducible within 2%.

Results

Hydrolysis in Water and Aqueous Mixtures.—For aqueous solutions and the solvent mixtures entered in the Table the main products of the base-catalyzed reactions after acidification are *cis*- and *trans*-$[Co(NH_3)_4(^{15}NH_3)(H_2O)][ClO_4]_3$.* The products were identified from the ^1H n.m.r. spectrum. The two geometric isomers have clearly separated $^{15}NH_3$ resonances: a characteristic doublet [$J(^{15}N–H)$ = 70 Hz] of comparatively narrow lines, its centre coinciding with the broad $^{14}NH_3$ resonance at 2.81 p.p.m. ($^{15}NH_3$ *trans* to H_2O) or at 3.83 p.p.m. (*cis*). The resonance of co-ordinated H_2O was found at 5.72 p.p.m. These positions agree with published spectra.[10] The *cis–trans* product distribution was calculated from the $^{14}NH_3$ peak areas and the $^{15}NH_3$ peak areas or peak heights. The results are given in the Table.

Reaction in Methanol.—In the product of base-catalyzed solvolysis in anhydrous methanol the aqua-resonances were completely absent. The identification of the final product as the $[Co(NH_3)_4(^{15}NH_3)(CH_3OH)]^{3+}$ ion is evident from the methanol exchange of this compound in D_2O [16] and the ^1H n.m.r. spectrum. Resonances were found at 2.81 p.p.m. [*trans*-$^{14}NH_3$ and the *trans*-$^{15}NH_3$ doublet, $J(^{15}N–H)$ = 70 Hz], 4.01 p.p.m. (*cis*-NH_3), 2.86 p.p.m. [co-ordinated CH_3OH triplet, J(H–H) = 7 Hz], and 6.74 p.p.m. (co-ordinated CH_3OH). Again the *cis–trans* product distribution followed from the resonance areas and peak heights.

Table. Product distribution of base-catalyzed solvolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+/2+}$ complexes in water–co-solvent mixtures and pure solvents at 25 °C

X	Co-solvent	Percentage co-solvent (v/v) [a]	Percentage *cis* [b]
Cl	—	—	50 [c]
Cl	—	—	44
Cl	CH_3OH	10	45
Cl	CH_3OH	40	45
Cl	CH_3OH	50	45
Cl	CH_3OH	70	43
Cl	CH_3OH	100	44
Cl	dmso	20	44
Cl	dmso	40	44
Cl	CH_3NH_2 [d]	100	50
dmso	—	—	48
dmso	CH_3OH	100	46

[a] If no co-solvent is indicated, the reaction medium is pure water. [b] Estimated error in percentage of *cis* product is 2%. The entries are averaged over at least two independent measurements. [c] From ref. 10, error 5%. [d] At −10 °C.

Reaction in Methylamine.—The solvolysis reaction was done without the addition of base, as reactions in liquid ammonia [17] and amines [18] have been shown to follow the c.b. mechanism, even when no base is added; no spontaneous reaction route is detected. In addition, the presence of amide ions must be avoided, as it induces polymerization and condensation reactions.[19] The product of the reaction could be identified as $[Co(NH_3)_4(^{15}NH_3)(CH_3NH_2)][ClO_4]_2Cl$ by ^1H n.m.r., i.r., and u.v.–visible spectra.[20] In addition, a minor amount (<1%) of the unreacted substrate and some $^{15}NH_3$-containing hexa-ammine (<5%) was invariably detected. Because of the small difference in ligand field strength between ammonia and methylamine, ammine hydrogens *cis* and *trans* with respect to co-ordinated methylamine in the complex are expected to show a very small difference in chemical shift. The resonances could only be clearly resolved in the 500-MHz spectrum of the triperchlorate, where they appeared as two narrow doublets [$J(^{15}N–H)$ = 70 Hz] of equal intensity, the centre of each coinciding with the broad *cis*-$^{14}NH_3$ (3.36 p.p.m.) or *trans*-$^{14}NH_3$ (3.38 p.p.m.) signals. The assignment of the lower field resonances to *trans*-NH_3 follows from the relative intensities. It does not agree [21] with the lower effective ligand field of methylamine compared to ammonia in cobalt(III) complexes.[22–24] Additional broader bands were found at 4.17 p.p.m. (CH_3NH_2, unresolved quartet) and 1.91 p.p.m. [CH_3NH_2, triplet, J(H–H) = 7 Hz]. The spectrum is displayed in the Figure.

Base Hydrolysis of $[Co(NH_3)_4(^{15}NH_3)(dmso)][ClO_4]_3$.—Because no pure *trans*-$^{15}NH_3$ compound could be synthesized, the percentage rearrangement on base hydrolysis was calculated from the *cis–trans* product distribution (determined by 250-MHz ^1H n.m.r.) in the initial mixture and the product, using the formula for the experimental fraction x of *cis* isomer in the penta-ammineaqua-product, $x = ab + (1 - b)(1 - 0.25a)$, with a as the fractional rearrangement in the base hydrolysis of the original *trans* compound and b as the initial fraction of *trans* in the starting compound. Experimentally we found for $b = 0.65$ that $x = 0.60$ and for $b = 0.82$ that $x = 0.55$, giving $a = 0.44$ and 0.48 respectively. The isomerically

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* Due to incomplete precipitation the relative amount of methanol complex in the precipitates was smaller than expected [15] in the $H_2O–CH_3OH$ solutions. No co-ordinated dmso was observed. We assume isotopic effects on the solubility to be negligible.

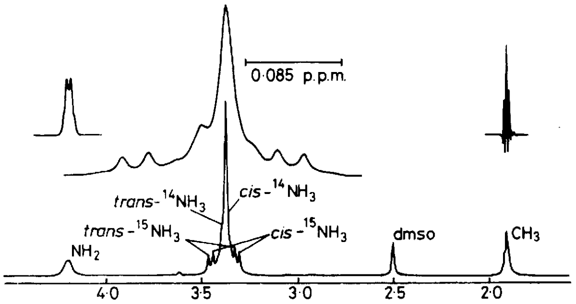

Figure. ^{1}H N.m.r. (500 MHz, in [^{2}H$_6$]dmso, reference tsp) spectrum of the *cis-trans*-[Co(NH$_3$)$_4$(^{15}NH$_3$)(CH$_3$NH$_2$)][ClO$_4$]$_3$ reaction product. The upper lines show the resonances on an enlarged scale. For the NH$_2$ and the CH$_3$ signals, the resolution-enhanced spectrum (using Gaussian deconvolution) is displayed also

most pure compound contained 92% of the *trans* isomer (b = 0.92) and yielded 51% of the *cis* aqua-isomer; the calculated *cis–trans* ratio for this most accurate case is given in the Table (a = 0.48). Agreement with the results from the less isometrically pure samples is satisfactory and illustrates the correctness of the calculation.

Reaction of the 92% *trans* compound in anhydrous methanol gave 49% of the *cis*-[Co(NH$_3$)$_4$(^{15}NH$_3$)(CH$_3$OH)]$^{3+}$ isomer (a = 0.46).

Discussion

The product distribution of base-catalyzed solvolysis of the *trans*-[Co(NH$_3$)$_4$(^{15}NH$_3$)Cl]$^{2+}$ ion in various solvents (with the exception of methylamine), as displayed in the Table, is remarkably independent of the nature of the solvent. In fact the percentage rearrangement (percentage of *cis*, Table) has an average of 44 ± 1. The reaction product in methylamine shows a small but significant deviation from this average. The cause may be the difference in reaction temperature (35 °C).

It has been convincingly argued[7] that the lifetime of the five-co-ordinate intermediate is so short that this situation is on the border of the possibility of a thermodynamic distinction[25] between transition state and intermediate. In this picture, which has been obtained from studies of polychelate complexes, the stereochemistry of base hydrolysis will be strongly influenced by the fact that the five-co-ordinate species tends to react with the incoming group even before an easily accessible and expectedly stable configuration is reached. Then the position of entry of the incoming solvent molecule will be dependent on the moment of entry, as the processes of bond angle adjustment and solvent entry are thought to be comparable in rate.[6,7]

If this situation is also accepted for the penta-amminechlorocobalt(III) ion, the considerable steric rearrangement, observed on base hydrolysis, will in all probability depend on the solvent. This will then certainly be shown in the range of solvents used here, as these have widely different structure and different nucleophilicity (H_2O, CH_3OH, CH_3NH_2) and, probably even more important for the fast reactions involved, different stereochemical properties. The absence of a solvent effect on the product distribution is a strong indication that the position of entry of the neutral solvent molecule occurs at an approximately fixed position on the reaction co-ordinate. The mechanistic possibility of other positions of entry (and consequently other *cis–trans* product ratios) is confirmed by the results of anion competition studies,[10] and the present results on the solvolysis of the dmso–penta-ammine complex. Our conclusion may be expressed more specifically as indicating the presence of a definite intermediate (or intermediates), in which the directive effects are not much affected by the solvation sphere. This interpretation is along the lines of that postulated in the now classic model of Nordmeyer.[5] However, this model needs to be refined, as the *cis–trans* product ratio differs significantly from the predicted 50–50 ratio.

The results on the stereochemical course of base hydrolysis of the [Co(NH$_3$)$_4$(^{15}NH$_3$)(dmso)]$^{3+}$ ion fit this picture. The small but solvent-independent (H_2O,CH_3OH) leaving-group effect, which is on the border of significance, can be explained by the presence of the leaving dmso in the solvation shell of the transition state and the intermediate.[15] It is then reasonable to assume that this bulky group will influence the relative ease of entering of the solvent. In addition, the difference in cationic charge between the chloro– and the dmso–penta-ammine complexes will influence the composition of the solvent sheet of the substrate. If it is accepted that this solvent sheet is inherited in the five-co-ordinate intermediate, it may thus affect the product distribution. The latter explanation follows the exposition of charge dependence of competition results for the [Co(NH$_3$)$_5$X]$^{n+}$ series by Sargeson and co-workers.[15] These authors have rejected the assumption of an interchange mechanism to explain the exceptional position of especially dmso as leaving group in anion competition results.[26]

The results obtained in this study can be interpreted to imply that for base hydrolysis of cobalt(III) amine complexes the existence of one or more discrete intermediate(s) of reduced co-ordination number is still a reasonable assumption, at least for the simple monodentate amine complexes. The analogous stereochemical behaviour of bis(ethylenediamine)-cobalt(III) complexes in water and liquid ammonia[8,9] makes the extension of this conclusion to these compounds reasonable. However, this contradicts the results obtained with some polychelate complexes that are now being studied extensively. Of course the simplicity of the complexes of the present report makes it difficult to reach more detailed conclusions.

Finally, it must be emphasised again that the independence of the solvent and consequently that of the entering group on the steric course, demonstrated by the results presented here, is restricted to neutral entering groups. An anionic ligand such as the azide ion, used in competition experiments, does change the steric course of the reaction.[10] Another restriction on the present conclusion is the choice of the leaving group. In view of the competition results it would be interesting to extend this study to more reactive and to less reactive penta-amminecobalt(III) complexes than those reported here.

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