Solvent Dependence of the Stereochemistry of Base-catalysed Solvolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+/2+}$ Ions in Dipolar Aprotic Solvents

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The preparation is described of *trans*-$[Co(NH_3)_4(^{15}NH_3)(OSO_2CF_3)][ClO_4]_2$ as a precursor for the synthesis of $^{15}NH_3$-labelled complexes *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+}$ with weakly co-ordinating neutral ligands X. The availability of these compounds makes it possible to study the stereochemistry of base-catalysed solvolysis of penta-amminecobalt(III) complexes in weakly co-ordinating dipolar aprotic solvents. For a number of cases the observed stereochemistry differs significantly from the results reported earlier for more strongly co-ordinating and protic solvents (around 50% retention). This difference in stereochemistry cannot be exclusively explained by solvational effects. Specific effects of the entering and leaving groups are shown to be important. The results are compatible with a mechanistic model involving a five-co-ordinate intermediate.

Recently, by using $^{15}NH_3$-labelled *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$, we showed the stereochemistry of its base-catalysed solvolysis to be solvent independent for water, methylamine, methanol, and aqueous mixtures of dimethyl sulphoxide and of methanol.[1] These results could be accommodated in the familiar conjugate-base mechanism† if it is assumed that dissociative activation produces a discrete five-co-ordinate intermediate in the rate-determining step. This in contrast with a more dynamic picture of immediate capture of a solvent molecule before bond angles in the intermediate can equilibrate. The last model is closer to an I_d mode of activation.[3,4] In the previous study, the use of chloride as leaving group made it necessary to limit the range of incoming groups to strongly co-ordinating donor solvents. By coincidence these solvents (water, CH_3OH, and CH_3NH_2) are also protic and highly structured. It would therefore be interesting to investigate whether the constant stereochemistry is also maintained in less structured and more weakly co-ordinating dipolar aprotic solvents. This extension has recently been made possible by the availability of the trifluoromethanesulphonato-complexes, where the triflate ($CF_3SO_3^-$) ligand is O-bonded to the metal.[5] The synthesis of penta-amminecobalt(III) complexes with weakly co-ordinating ligands from the triflato-complex has increased the known range of reactivity of cobalt(III) ammine complexes in aquation and base hydrolysis.[6]

In this contribution we describe the synthesis of *trans*-penta-ammine(trifluoromethanesulphonato)cobalt(III) perchlorate from the labelled sulphito-compound, as precursor for the synthesis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+}$ complexes (X = dimethylformamide, dimethyl sulphoxide, or trimethyl phosphate). These compounds were used to study the stereochemistry of base-catalysed solvolysis in dimethylformamide (dmf), dimethyl sulphoxide (dmso), trimethyl phosphate (tmp), acetonitrile, and acetone.

Experimental

Materials.—The complex *trans*-$[Co(NH_3)_4(^{15}NH_3)(SO_3)]ClO_4$ was prepared as previously described,[1,7] using $^{15}NH_4ClO_4$ instead of $^{15}NH_4Cl$. (The presence of chloride must be avoided, as it competes effectively with $CF_3SO_3^-$.) The complex *trans*-$[Co(NH_3)_4(^{15}NH_3)(OSO_2CF_3)][CF_3SO_3]_2$ was prepared by adding *trans*-$[Co(NH_3)_4(^{15}NH_3)(SO_3)]ClO_4$ (0.5 g) slowly with vigorous stirring and cooling in an ice–salt bath (< -10 °C) to neat trifluoromethanesulphonic acid (2 cm^3) (CF_3SO_3H was used as supplied by Jansen Chim., Beerse, Belgium). The pink-red solution was then added dropwise to cold (< 10 °C) dry diethyl ether (25 cm^3). The triflato-complex was recovered and washed with dry ether and stored under nitrogen. The identity and purity of the complex ion followed from its ^1H n.m.r. spectrum [5] in neat CF_3SO_3H and elemental analysis. The solvent-co-ordinated complexes *trans*-$[Co(NH_3)_4(^{15}NH_3)X][ClO_4]_3$, with X = dmf, dmso, or tmp, were prepared as described [8] and identified as to isomeric purity by their ^1H n.m.r. spectra.

Base-catalysed Solvolysis.—The base hydrolysis reactions were done by dissolving the complex (20 mg) in NaOH (1 cm^3, 0.2 mol dm^{-3}). After 5 min the product was precipitated by adding an excess of concentrated $HClO_4$ with cooling.

For the base-catalysed solvolysis reactions in other solvents a general procedure was worked out. These reactions were performed in the purified and dried organic solvents.[9] These solvents were mixed with the non-co-ordinating base ethyldi-isopropylamine (90:10, v/v). The reaction was started by adding the penta-ammine (20 mg) to this mixture (1 cm^3). This less elegant method is unavoidable, as the large rate of background solvolysis excludes the usual procedure of predissolution of the compound.[6] After 5 min the reaction product was isolated as described for the spontaneous solvolysis.[8] For the reaction in tmp the reaction time had to be limited to 1 min to prevent subsequent isomerization.

In all experiments described, recovery of products after washing with ether and ethanol was done by centrifugation. The reaction products were dried *in vacuo* over P_2O_5 and characterized by ^1H n.m.r. spectroscopy (250 MHz). The *cis*/*trans* distribution was determined from the resonance areas and $^{15}NH_3$ peak heights.[1]

As the outcome of the reaction of the triflatopenta-ammine in acetonitrile was rather unexpected, we investigated the possibility of isomerizations before and after base-catalysed solvolysis and of competitive spontaneous solvolysis. To this end the reaction temperature was varied between -10 and 25 °C and the concentration of base between 1 and 20% (v/v). These variations did not affect the stereochemistry (63% *cis*) within the experimental error (±2%). Isolation of the triflato-compound after one half-life of base-catalysed solvolysis (at 1% base) showed this compound to be in the initial *trans* configuration; this excludes a base-catalysed re-arrangement of the starting product.

† For a recent survey of the mechanism of base hydrolysis see the review in ref. 2.

The triflatopenta-ammine was also subjected to base-catalysed solvolysis in an aqueous mixture of acetonitrile (30:70, v/v), wherefrom a mixture of the two possible solvent complexes could be isolated. The general procedure described above was doubtful for acetone as solvent, as the isolated acetonepenta-ammine invariably contained some aqua-complex, formed during isolation as a result of the extreme reactivity of the acetone complex. Therefore the reaction in acetone was stopped by adding acidified ($HClO_4$) water, followed by isolation of the aquapenta-ammine. Separately, by using direct ^1H n.m.r. monitoring in [$^2H_6$]acetone, we proved that the spontaneous aquation of the acetone complex proceeded with full retention. Thus, a solution of *trans*-[$Co(NH_3)_4(^{15}NH_3)(OSO_2CF_3)$][$CF_3SO_3$]$_2$ (10 mg) in [$^2H_6$]acetone (0.5 cm^3) at 25 °C initially has δ_H (250 MHz; standard, sodium 3-trimethylsilylpropane-1-sulphonate) 4.72 (12 H, s, 4 *cis*-NH_3) and 3.23 [3 H, d, $J(^{15}NH)$ 70 Hz, 1 *trans*-NH_3]. In time this spectrum changes to that of the *trans*-acetonepenta-ammine, with δ_H 4.67 (12 H, s, 4 *cis*-NH_3) and 3.47 [3 H, d, $J(^{15}NH)$ 70 Hz, 1 *trans*-NH_3]. After addition of a few drops of ^2H_2O the spectrum is characteristic of the *trans*-aquapenta-ammine: δ_H 4.53 (12 H, s, 4 *cis*-NH_3) and 3.45 [3 H, d, $J(^{15}NH)$ 70 Hz, 1 *trans*-NH_3].

A direct ^1H n.m.r. monitoring of the base-catalysed reaction in [$^2H_6$]acetone was prohibited by the overlapping resonances of the added base.

N.M.R. Spectra.—Hydrogen-1 n.m.r. spectra of the $^{15}NH_3$-labelled compounds and reaction products were recorded on a Bruker WM 250 Fourier spectrometer as previously described.[1] Integrals of resonance areas were reproducible within 2%.

Results and Discussion

The synthetic method for the labelled triflato-compound uses reaction (1). Reaction (1) proceeds with predominant retention

$$trans\text{-}[Co(NH_3)_4(^{15}NH_3)(SO_3)]^+ + CF_3SO_3H \longrightarrow [Co(NH_3)_4(^{15}NH_3)(OSO_2CF_3)]^{2+} + HSO_3^- \quad (1)$$

of configuration, producing 92 ± 2% *trans* product. Employing literature procedures,[8] the triflate was then substituted by weakly co-ordinating ligands, with stereochemical retention. All results given here were corrected [1] for the percentage of *cis* isomer in the reagent, stemming from the 8% *cis* form of the triflato-intermediate, as established from the ^1H n.m.r. spectrum in neat CF_3SO_3H. The availability of the labelled ligandpenta-amminecobalt(III) complexes of weakly donating ligands extends the possibilities of studying solvent and medium effects on the conjugate-base mechanism.[2]

Table. Stereochemistry of base-catalysed solvolysis of complexes *trans*-[$Co(NH_3)_4(^{15}NH_3)X]^{3+\ 2+}$

X	Solvent	θ_c/°C	% *cis*[a]
$CF_3SO_3^-$	Water	25	47 ± 2
$CF_3SO_3^-$	dmf	25[b]	51 ± 2
$CF_3SO_3^-$	dmso	25	21 ± 3
$CF_3SO_3^-$	tmp	−10	46 ± 3
$CF_3SO_3^-$	Acetone	25	49 ± 2
$CF_3SO_3^-$	Acetonitrile	25[b]	63 ± 2
dmf	Water	25	0
dmso	dmf	25	65 ± 2

[a] Corrected for the percentage *cis* form of the reagent;[1] mean value from at least two independent measurements. [b] At −10 °C the same stereochemistry was observed.

Reaction conditions for the base-catalysed solvolysis were dictated by the demand that spontaneous solvolysis of the reagent and base-catalysed solvolysis of the product should not interfere. The relative rates of the processes involved were determined in separate experiments. The demand could not be met for the tmp complex. Stereochemical results for the base-catalysed reactions are given in the Table. In all cases, with the exception of base hydrolysis of the dmf compound, the reaction products were identified as the solvent-co-ordinated penta-ammine. The reaction product of the dmf complex consists mainly (90%) of *trans*-[$Co(NH_3)_4(^{15}NH_3)(O_2CH)]^{2+}$. This gives further support for the mechanism proposed for this reaction.[10]

The main body of stereochemical data in the Table coincides with the range of values previously found [1] (between 44 and 50% *cis* product) for a more limited range of solvents. The results for dmso as solvent, for this ligand as leaving group in dmf, and for the triflatopenta-ammine in acetonitrile, are at variance with the general picture. The reactions involving dmso may be complicated by redox reactions, in the way suggested by Swaddle and co-workers.[11]

An alternative explanation of the exceptional value (65% *cis*) found for the solvolysis of the *trans*-[$Co(NH_3)_4(^{15}NH_3)$-(dmso)]$^{3+}$ ion in dmf is to postulate a leaving-group effect of the dmso ligand. We have reported a similar exception for protic solvents.[1] Following Sargeson and co-workers,[12] we may then again ascribe this effect to the presence of the bulky leaving group dmso in the solvation shell of the transition state and the intermediate.[1]

Base-catalysed solvolysis in acetonitrile, however, presents a different perspective. The constancy of the stereochemistry with variation of either the temperature or the concentration of base excludes competing processes. In addition we could also exclude pre-solvolysis and post-solvolysis isomerization (see the Experimental section). A crucial experiment is the solvolysis in the mixed aqueous solvent (70:30, v/v), where the stereochemistry of the two product ions is different: 60 ± 3% *cis* for [$Co(NH_3)_4(^{15}NH_3)(NCCH_3)]^{3+}$ and 43 ± 3% *cis* for [$Co(NH_3)_4(^{15}NH_3)(H_2O)]^{3+}$. For either product the stereochemistry is exactly as found in the respective pure solvent. This means that the apparent solvational effect is in reality an entering-group effect. If this argument is accepted, it is interesting to compare the stereochemistry of competition experiments using the azide ion in the base hydrolysis of *trans*-[$Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$, where the [$Co(NH_3)_4(^{15}NH_3)$-$(N_3)]^{2+}$ formed is *ca.* 70% *cis*.[7] The reason for this parallel behaviour cannot be elaborated at the present time.

Finally the present study has brought to light new and unexpected data on the stereochemistry of base-catalysed solvolysis. The final conclusion of our previous study [1] on solvent effects on this stereochemistry can still be upheld. Essentially we argued that the constant stereochemistry indicates a discrete five-co-ordinate intermediate in base-catalysed solvolysis. This in contrast to a proposed [3,4] model for base hydrolysis in which the reactive five-co-ordinate species tends to react with the incoming group even before a relatively stable configuration is reached. Then the stereochemistry of the product will be dependent on the moment of entry and hence on the nature of the solvent. The predominantly constant stereochemistry found for the now extended range of solvents of widely differing structure and nucleophilicity seems to refute this dynamic model, at least for the structurally simple penta-ammines.

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