Steric Changes at Labelled NH_2 Sites during the Base-catalysed Ammoniation of the *trans*-Azido(dimethyl sulphoxide)bis(ethylenediamine)cobalt(III) Ion

Sijbe Balt* and Hendrikus J. Gamelkoorn
Department of Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

A quantitative evaluation of the acid dependence of the kinetics of ammoniation of *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ (en = ethylenediamine, dmso =dimethyl sulphoxide) to give *trans* (70%)- and *cis* (30%)-$[CoN_3(en)_2(NH_3)][ClO_4]_2$ in liquid ammonia is presented. The reaction follows the normal conjugate-base mechanism, consisting of a fast pre-equilibrium, followed by the rate-determining elimination of dmso. Independent methods are presented for the assignment of the ^1H n.m.r. resonances of co-ordinated ethylenediamine in the *trans* complexes. The large difference in exchange rates of the protons at either side (near dmso or N_3) of the $Co(en)_2$ 'plane' make it possible to study the ammoniation reaction in liquid N^2H_3 of a complex selectively deuteriated at the N_3-side. In this complex the remaining hydrogens function as ^1H n.m.r. labels. In the *trans*-$[CoN_3(en)_2(NH_3)]^{2+}$ reaction product the position of the labels indicates inversion at the active amido-site and rotation of the chelate ring not involved in acid dissociation during the ammoniation. The results lead to a proposal for the stereochemistry of the five-co-ordinate intermediate involving N-donor π bonding.

The now well established conjugate-base mechanism [indicated as S_N1(c.b.), $D_{c.b.}$, or simply c.b.] is characterized by dissociative activation, involving a five-co-ordinate intermediate.[1] Ever since the pioneering paper of Pearson and Basolo[2] a trigonal bipyramidal structure for the intermediate has been favoured. A strong argument for this stereochemistry is the possibility of the amido-group (formed by deprotonation) to act as an effective π donor in a planar (sp^2) conformation. The mechanism predicts a stereochemical change at the amido-nitrogen during base hydrolysis. This proposition can be checked for appropriate optically-active complexes by looking at racemization at the active amido-site. The problem was first tackled by Buckingham *et al.*[3] in a study of the ion *sym*-$[Co(trenen)Cl]^{2+}$ [trenen = 1,8-diamino-3-(2′-aminoethyl)-3,6-diazaoctane]. The conclusion was negative as to the possibility of Co=N< π bonding *via* a sp^2 N centre *trans* to the leaving group. However, this *trans* centre was not unambiguously identified as the active amido-site,[4] so π bonding *via* an amido-group positioned *cis* to the leaving group is still possible. A different approach to the stereochemistry at the amido-site in the intermediate has been offered for the $[Co(dadn)Cl_2]^+$ system (dadn = 1,9-diamino-3,7-diazanonane) by Tobe and co-workers.[1,5] The appearance of the same product, *RS-trans*-$[Co(dadn)(OH)Cl]^+$, for the three isomers of the dichloro-compound, *RS-trans*, *RR*(*SS*)-*trans*, and *RR*(*SS*)-β-*cis*, could be interpreted as an indication for a common intermediate. The five-co-ordinate intermediate then should be trigonal bipyramidal with the remaining chloride in the trigonal plane, together with a planar secondary amido-nitrogen.[6] The claim in this study that the common results demonstrate the π stabilization of the amido-nitrogen has been challenged.[7]

Similarly to the above case, the complete racemization of optically-active $[Co(dien)(dapo)Cl]^{2+}$ (dien = diethylenetriamine; dapo = 1,3-diaminopropan-2-ol) on base hydrolysis is difficult to rationalize other than by assuming a planar amido-N π-donor trigonal bipyramidal intermediate.[8] In this case the active amido-site should be located *cis* to the leaving (and entering) ligand. But again there is no unambiguous determination of the active site.

In view of this state of affairs it seemed worthwhile to obtain direct evidence on stereochemical changes involved in the formation and reaction of the intermediate. This should be possible by using labelling of the acidic protons in an amine complex. In this paper we therefore present a study of base-catalysed ammoniation, where hydrogen labelling, combined with ^1H n.m.r. monitoring, unambiguously determined the site of active deprotonation and of reprotonation. Our experiments concern ammoniation of partly deuteriated *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ (en = ethylenediamine, dmso = dimethyl sulphoxide) in fully deuteriated liquid ammonia and our results can be interpreted in terms of inversion at the active amido-site.

In addition the fate of ^1H labels on ammoniation provides a more detailed picture of changes in the ethylenediamine chelate rings during the reaction.

Experimental

Materials.—*trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ was prepared according to Jackson and Begbie.[9] The identity and purity of the compound were confirmed from u.v.–visible and ^1H n.m.r. spectra (in $[^2H_6]$dmso) (Found: Cl, 14.4; Co, 12.0. Calc. for $C_6H_{22}Cl_2CoN_7O_9S$: Cl, 14.25; Co, 11.85%). In the region expected for co-ordinated ethylenediamine the ^1H n.m.r. spectrum [250 MHz, solvent acidified ^2H_2O, 5 °C, standard tsp (sodium 3-trimethylsilylpropane-1-sulphonate)] showed peaks at 4.99 and 5.18 (each 4 H). The perdeuteriated bis($[N,N,N',N'$-$^2H_4]$ethylenediamine) complex was prepared from the azidochloro-complex as described[9] for the non-deuteriated compound. *trans*-$[CoN_3([N,N,N',N'\text{-}^2H_4]en)_2Cl][ClO_4]$ was prepared by dissolving *trans*-$[CoN_3(en)_2Cl][ClO_4]$ (ref. 9) in ^2H_2O (10 mg cm^{-3}). The solution was kept at pD = 10.0 (NaO^2H) for 45 min. After rapid acidification to pH = 1 addition of solid $NaClO_4$ (60 mg cm^{-3}) and cooling in ice precipitated the azidochloro-complex, while a violet aqua-azido-complex, formed in a small amount by base hydrolysis, remained completely in solution. The complex was washed with dry ethanol and diethyl ether and dried *in vacuo*. ^1H N.m.r. indicated the degree of deuteriation to be $\geqslant$ 94%.

Selectively deuteriated *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ was prepared by dissolving 100 mg of either the perdeuteriated complex in acidified NH_3 or the non-deuteriated complex in N^2H_3 at −75 °C. The solvent was acidified with NH_4ClO_4 or $N^2H_4ClO_4$, respectively (to 1 mol kg^{-1}). The solvent was then rapidly evaporated *in vacuo*, which had to be maintained for more than 12 h to eliminate traces of moisture and ammonia completely. The residue was dissolved in the minimum amount of acidified (trifluoroacetic acid) anhydrous acetone, from which the cobalt complex was precipitated with anhydrous diethyl ether. The compounds prepared in this way contain some ammonium perchlorate. In the isolated compounds ^1H n.m.r. (250 MHz, ^2H_2O) spectra showed either the resonance at 4.99 (product prepared from non-deuteriated compound) or the one at 5.18 p.p.m. (perdeuteriated) [HN(en)] to be reduced to $<15\%$.

cis-$[CoN_3(en)_2(dmso)][NO_3][ClO_4]$ was prepared according to Jackson and Sargeson.[10] The complex was converted into the diperchlorate by routine treatment with $NaClO_4$. The identity was confirmed from u.v.–visible and ^1H n.m.r. spectra (Found: Cl, 14.4; Co, 11.8 Calc.: for $C_6H_{22}Cl_2CoN_7O_9S$: Cl, 14.25; Co, 11.85%).

cis- and *trans*-$[CoN_3(en)_2(NH_3)]Cl_2$ were prepared as described by Buckingham *et al.*[11] Conversion to the diperchlorate was done by routine treatment with $AgClO_4$. ^1H N.m.r. (250 MHz) of the isolated *trans* complex showed the presence of the *cis* isomer as expected.[12] Separation was achieved by ion-exchange chromotography [Bio-Rad Dowex (H^+) 50W-X2, 200—400 mesh, elution with 1 mol dm^{-3} $NaClO_4$]. The *trans* isomer was eluted first.

The preparation of N^2H_3 and the handling, purification, and storage of NH_3 and N^2H_3 were as described previously.[13]

Kinetics of Aquation.—The loss of dmso upon aquation of *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ was monitored on a Zeiss PM QII spectrophotometer in 1-cm quartz cells at 25.00 ± 0.05 °C and a complex concentration of 2×10^{-3} mol dm^{-3}. NH_4ClO_4 was added to the acidified (0.01 mol dm^{-3} $HClO_4$) solvent in the case of the non-deuteriated or perdeuteriated complexes in order to obtain the same medium as the partly deuteriated compounds that contain some ammonium perchlorate as a result of the method of preparation. In order to eliminate errors from absorbance changes resulting from the subsequent isomerization, the aquation was followed at 537 nm, the isosbestic wavelength of the *cis*/*trans*-$[CoN_3(en)_2(H_2O)]^{2+}$ equilibrium. In all kinetic runs a first-order rate law was strictly adhered to (within 1%) for over five half-lives. The rate constants could be reproduced within 1% and agree with the literature value.[9] From ^1H n.m.r. it was found that the dmso compounds aquate under retention of both the configuration and the labelled positions.

Kinetics of Ammoniation.—The ammoniation of *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ was monitored photometrically at 580 nm in a closed system under dry nitrogen. A detailed description of the apparatus and the data processing procedure has been given elsewhere.[13] Because of the rapidity of the reactions a special measuring cell was used, equipped with a mechanism to add solid complexes to the ammonia solution, previously brought to the desired temperature, by breaking thin-walled glass ampoules. The kinetic runs were performed at ambient pressure in a constant ionic medium of $[ClO_4]^-$ (0.20 mol kg^{-1}) by the addition of $KClO_4$. The complex concentration was fixed at 0.02 mol kg^{-1}; runs were performed at four ammonium perchlorate concentrations between 0.20 and 0.02 mol kg^{-1}. Individual rate constants could be reproduced within 3%. The temperature constancy was better than 0.1 °C.

N.M.R. Measurements of Solutions in Liquid Ammonia.—Hydrogen-1 n.m.r. spectra were recorded on a Bruker WM-250 spectrometer. Solutions were made up in 5-mm diameter tubes by condensing a known volume of liquid ammonia, enriched with 5% N^2H_3 as internal lock, or perdeuteriated ammonia onto a weighed amount of complex plus the salt to make up the reaction medium, at −75 °C. The stoppered sample tubes were then transferred into the n.m.r. probe, which had already been brought to the desired reaction temperature. For liquid ammonia, the solvent peak was saturated before acquisition. Chemical shifts are given relative to the solvent.

Table. Aquation rate constants (k_{aq} at 25 °C) of *trans*-$[CoN_3(en)_2(dmso)]^{2+}$

N_3^--side[a]	dmso-side[a]	$10^3k_{aq}/s^{-1}$
^1H	^1H	6.18
		6.21
		6.06[b]
^2H	^1H	6.24
		6.18
^1H	^2H	5.64
		5.66
^2H	^2H	5.62
		5.65

[a] Isotopic composition of HN (en) hydrogens relative to the $Co(en)_2$ plane. [b] Ref. 9.

^1H–^2H exchange kinetics were monitored by following peak heights and areas of the appropriate ^1H n.m.r. resonances as a function of time. In these experiments a Bruker WH-90 spectrometer was used, of which the probe and temperature control were adapted to ensure thermostatting within 0.2 °C for several hours.[13]

Results and Discussion

Proton N.M.R. Assignments.—*trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ has the following n.m.r. spectrum (all resonances are broad): δ_H (250 MHz, solvent NH_3 at −77 °C, standard NH_3) 1.8 [14 H, m, 4 $-CH_2-$ (en) and 2 CH_3(dmso)], 5.8 [4 H, s, 4 HN (en) at N_3-side*], and 6.4 p.p.m. [4 H, s, 4 HN (en) at dmso-side]. Assignments follow the general finding,[14] that $\delta_H[-CH_2-(en)] \leqslant \delta_H(NH_3) < \delta_H[HN\ (en)]$ in (amine)bis(ethylenediamine)cobalt(III) complexes. In addition a good start for assigning co-ordinated HN (en) resonances proves to be the assumption that the two ^1H [HN (en)] chemical shifts (for X-side and Y-side protons) of mixed complexes *trans*-$[CoXY(en)_2]^{n+}$ follow the order of this resonance in their symmetrical parent complexes.[15] In this way assignment of the resonance at 5.8 p.p.m. in the azido(dmso)-complex is based on the position of the HN (en) resonance (at $\delta_H = 5.64$ p.p.m.) in the symmetrical parent *trans*-$[Co(N_3)_2(en)_2][ClO_4]$. In view of the importance of this assignment for the mechanistic conclusions (see later), we further confirmed this assignment by a comparison of deuterium isotope effects on the aquation of selectively deuteriated azido(dmso)-compounds (Table). The reduction in rate on deuteriation is as expected.[16–18] Generally authors agree that this reduction must be explained by a change in solvation at the site of the leaving group.[16–18] A similar conclusion has been reached[19] from the stereochemical behaviour of the selectively *trans*-deuteriated ion $[Co(NH_3)_4(N^2H_3)Br]^{2+}$. The rate of aquation of the partially deuteriated *trans*-$[CoN_3(en)_2(dmso)]^{2+}$ complexes apparently is determined by the isotopic composition of –HN (en) at the

---

* Here and in the following 'side' means position relative to the bis(ethylenediamine)cobalt(III) plane of the complex. Differences in chemical shifts resulting from different en conformations are levelled out on the n.m.r. scale.

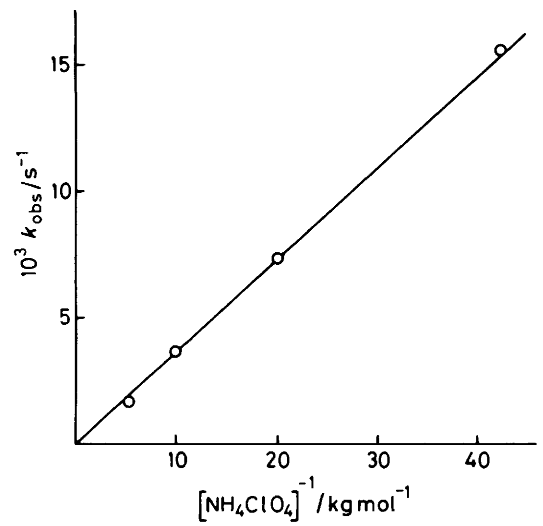


Figure 1. Observed rate constants for the ammoniation of *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ *versus* the reciprocal ammonium perchlorate concentration at −75.0 °C and I = 0.20 mol kg^{-1}

dmso-side. In view of the mechanistic picture of the influence of isotope effects on aquation, outlined above, this finding is a strong confirmation of our tentative assignment.

trans-$[CoN_3(en)_2(NH_3)][ClO_4]_2$ has the n.m.r. spectrum: δ_H (250 MHz, solvent NH_3 at −70 °C, standard NH_3) 1.7 [8 H, m, 4 $-CH_2-$ (en)], 2.2 (3 H, s, NH_3), 5.4 [4 H, s, 4 HN (en) at NH_3-side] and 5.7 p.p.m. [4 H, s, 4 HN (en) at N_3-side]. Confirmation of the assignment of the HN (en) resonances comes from the behaviour on addition of chloride (NaCl or NH_4Cl). Invariably for *trans*-bis(ethylenediamine)cobalt(III) complexes in liquid ammonia, this addition results in a downfield shift of the resonance at the side of the NH_3 ligand.[15] In the present case, successive addition of chloride resulted in a progressive downfield shift of the resonance at 5.4 p.p.m., until it was found below the insensitive resonance at 5.7 p.p.m.

Identification of Reaction Products.—The red product of ammoniation (at −40 °C) of *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ was identified by its ^1H n.m.r. spectrum (recorded at −70 °C) as a stable mixture of *cis*- and *trans*-$[CoN_3(en)_2(NH_3)]^{2+}$. *cis* and *trans* resonances could be distinguished from a comparison with the separately measured spectra of the pure *cis* and *trans* ammine(azido)-compounds. From the resonance integrals the ratio *cis*:*trans* = 30:70 (error 3% absolute) was calculated. Similarly ammoniation of *cis*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ gives a *cis*–*trans* isomeric mixture of the ammineazido-complex in the ratio *cis*: *trans* = 50:50.

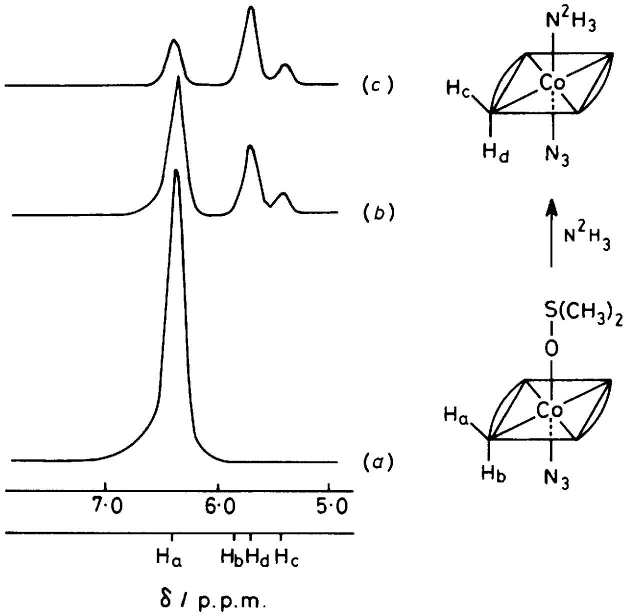


Figure 2. ^1H N.m.r. (250 MHz, reference solvent) spectra during the ammoniation in N^2H_3 of *trans*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ at (*a*) t = 0, (*b*) t = 10^3 s, and (*c*) t = 2 × 10^3 s. The expected chemical shift positions of hydrogen-1, at geometrically different sides relative to the $Co(en)_2$ plane, are indicated for reference

Kinetics and Labelling Experiment.—The kinetics of the first step of ammoniation of the title compound were studied at −75.0 °C (I = 0.20 mol kg^{-1}) [equation (1)].—The persistence

$$trans\text{-}[CoN_3(en)_2(dmso)][ClO_4]_2 + NH_3 \longrightarrow [CoN_3(en)_2(NH_3)][ClO_4]_2 + dmso \quad (1)$$

of two isosbestic points in the u.v.–visible spectrum, at 442 and 540 nm, during the reaction, and the absence of further ammoniation for more than 10 half-lives prove the single-step character. The medium dependence of the rate constant is diagnostic of the mechanism (see ref. 13 for a detailed treatment). In the present case, the observed first-order rate constant, $k_{obs.}$, as a function of the acid (ammonium perchlorate) concentration obeyed equation (2) [this is equation (7) of ref. 13] (see Figure 1), where $K^{c.b.}$ is the

$$k_{obs.} = K^{c.b.}k_2[NH_4ClO_4]^{-1} \quad (2)$$

equilibrium constant for the acid–base pre-equilibrium and k_2 is the rate constant for the rate-determining elimination of dmso to form the five-co-ordinate intermediate.

A least-squares fitting procedure to the $k_{obs.}$ values on the basis of equation (2) gave $K^{c.b.}k_2 = (3.8 \pm 0.1) \times 10^{-4}$ mol kg^{-1} s^{-1} (correlation coefficient r = 0.9999; intercept zero within the experimental error). This proves that reaction (1) proceeds by the 'normal' conjugate-base mechanism in the acidity range studied* [equations (3) and (4)]. Equation (4) is then followed

$$trans\text{-}[CoN_3(en)_2(dmso)][ClO_4]_2 + NH_3 \underset{\text{rapid}}{\overset{K^{c.b.}}{\rightleftharpoons}} trans\text{-}[CoN_3(en)(en - H)(dmso)][ClO_4] + NH_4ClO_4 \quad (3)$$

$$trans\text{-}[CoN_3(en)(en - H)(dmso)][ClO_4] \xrightarrow[\text{rate-determining}]{k_2} [CoN_3(en)(en - H)][ClO_4] + dmso \quad (4)$$

by a sequence of rapid reactions to form the ammineazido-complex of equation (1). The ammoniation reaction is too rapid to allow photometric monitoring at higher temperatures. Therefore the activation parameters are not available.

Next, the ammoniation reaction (1) was studied in fully-deuteriated liquid ammonia, at −66.6 °C ($[N^2H_4ClO_4]$ = 0.70 mol kg^{-1}, I = 1.00 mol kg^{-1}). Representative ^1H n.m.r. spectra, recorded during the ammoniation reaction, are presented in Figure 2. The ^1H n.m.r. spectrum at the start of the reaction showed only one HN (en) resonance, at 6.4 p.p.m., corres-

---

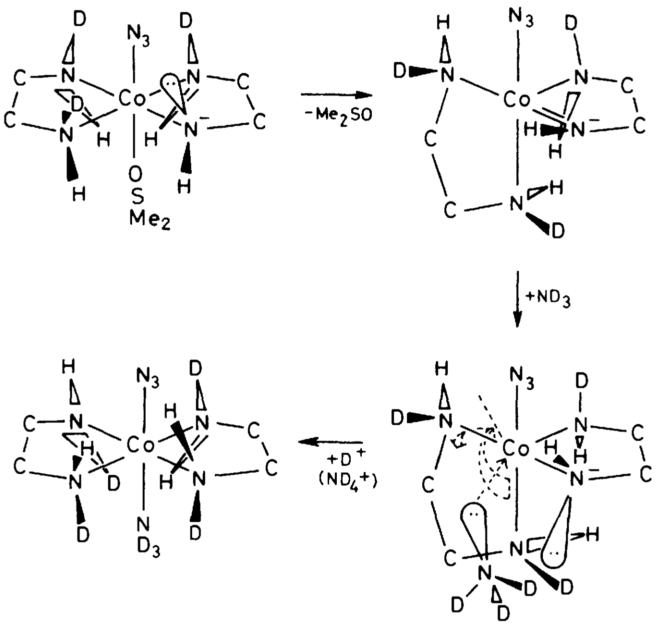
* There is a theoretical possibility that the mechanism is by rate-determining deprotonation, with $k_1{}^0$ (rate constant of deprotonation by NH_3)/$k_1{}^1$ (rate constant of deprotonation by $NH_2{}^-$) $\ll$ 1, but this would be in flagrant contradiction to the fact that the above ratio for cases having this mechanism in liquid ammonia is exceptionally large (> 1 000).[20]

ponding to 4 H (calibrated with reference to the $-CH_2-$ resonance). This indicates complete $^1H-^2H$ exchange of the HN (en) hydrogens at the N_3-side of the $Co(en)_2$ plane. The disappearance of this resonance obeyed a first-order rate law ($r = 0.998$), with $k_{obs.} = 1.1 \times 10^{-3}\ s^{-1}$ and appeared synchronous with the ammoniation. The latter conclusion could be verified quantitatively from a separate experiment, necessarily at a lower temperature (−77.6 °C), where the first-order rate constant for the disappearance of the resonance at 6.4 p.p.m. is $1.5 \times 10^{-4}\ s^{-1}$ ($[N^2H_4ClO_4] = 0.64\ mol\ kg^{-1}$). A value of $2.4 \times 10^{-4}\ s^{-1}$ is calculated from the value of $K^{c.b.}k_2$ obtained above and in equation (2). In view of the expected (but unknown) isotope effect the agreement is satisfactory.

As the reaction conditions are well within the region where the 'normal' c.b. mechanism was shown above to apply, rate-determining deprotonation is excluded. Consequently the active site for deprotonation must be the fully exchanged N_3-side. Therefore the non-exchanged hydrogens can be used as labels to follow the stereochemistry. It must be noted that a minor loss of labels on the time-scale of the ammoniation is not completely excluded. Fortunately, this will not bear on the conclusions (see later).

The ^1H n.m.r. spectrum shows that the ^1H label on ammoniation appears at both sides of the $Co(en)_2$ plane of the *trans*-$[CoN_3(en)_2(N^2H_3)]^{2+}$ reaction product.* During ammoniation the hydrogens of this *trans* product exchange, as Figure 2 [compare spectra (*b*) and (*c*)] makes clear. However, a separate experiment under similar reaction conditions (−66.6 °C, $[N^2H_4ClO_4] = 1.1\ mol\ kg^{-1}$) showed the $^1H-^2H$ exchange rates at the two sides of *trans*-$[CoN_3(en)_2(N^2H_3)]^{2+}$ to be nearly equal: k_H (N^2H_3-side) = $2.5 \times 10^{-4}\ s^{-1}$ and k_H (N_3-side) = $2 \times 10^{-4}\ s^{-1}$. Consequently the intensity ratio of the n.m.r. resonances of the ^1H labels at the two positions is a reliable datum. It must be noted that a small amount of $^1H-^2H$ pre-exchange not leading to ammoniation at the dmso-side cannot be excluded, as this reaction goes unnoticed in the ^1H n.m.r. spectrum. Fortunately, the intensity ratio is not influenced by the eventual presence of this reaction and will still give the distribution of the remaining labels over the two sets of equivalent hydrogen sites [at either side of the $Co(en)_2$ plane] of the *trans*-product. In addition, no complications arise from pre-ammoniation and post-ammoniation *trans–cis* rearrangements, as *cis*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ and both *cis*- and *trans*-$[CoN_3(en)_2(NH_3)][ClO_4]_2$ were found to be stable on the time-scale of the ammoniation reaction (1). The average value for the ^1H distribution from several experiments, where the reaction was followed up to three half-lives, gives 23 ± 3% of the ^1H labels appearing at the side of the entering group (NH_3-side).

Mechanistic Implications.—The $^1H-^2H$ distribution found means that *ca.* $\frac{3}{4}$ of the ^1H labels originally located at the N_3-side, after the ammoniation appear at the side of the $Co(en)_2$ plane, opposite to the N_3 ligand. This means that the reaction product has one ^1H label at the NH_3-side and three ^1H labels at the N_3-side (the total number of labelled positions is four). As a complete inversion of the position of all labels relative to the plane as a result of ammoniation is difficult to envisage, a combination of reaction routes (necessarily involving in one of the products a 0:4 ratio of the labels) is not very probable. The most straightforward proposition for the formation of the *trans*-ammine(azido)-ion is then a one-route mechanism, giving a 1:3 ratio for the labels. This distribution of odd numbers of labels in the product must necessarily involve a direct inversion at one of the amine nitrogens (if no bonds are broken). Our tentative mechanistic proposal therefore combines inversion at the active amido-site with a rotation of the Co(en) chelate ring that is not involved in acid dissociation. This is worked out in the Scheme (where for clarity ^2H is denoted as D). Capture of N^2H_3 by the five-co-ordinate intermediate and selective deuteriation at the side of the entering group produces the ^1H labels in the ratio 1:3.



Scheme. C ≡ CH_2

A few additional remarks are required. (1) The proposed structure of the intermediate is not expected to maximize π bonding with the central metal ion. For this the planar amido-nitrogen should have its plane perpendicular to the trigonal plane.[1,6] (2) Besides a planar amido-nitrogen, intramolecular proton exchange between the two bonding sites at the deprotonated nitrogen can also accommodate inversion at the amido-nitrogen. This mechanism is not very probable for the conjugate base,[7] but it may operate in the intermediate on account of its higher acidity.† (3) The position of entry in the intermediate can better be described as facial attack[21] than as the more generally postulated entry *via* an edge of the bipyramid. (4) In the present case reactive deprotonation occurs opposite the leaving group. This fact does not seem significant, as the analogous complexes *trans*-$[CoN_3(en)_2X]^+$ (X = Cl or Br) seem to have the reactive deprotonation at the side of the leaving group, but show similar stereochemistry.[12] (5) The indications about the steric course of ammoniation only pertain to the formation of the *trans* product. The *cis*-ammine(azido)-product may share the same intermediate with the *trans* compound or not. In addition the overall steric course of ammoniation of *cis*-$[CoN_3(en)_2(dmso)][ClO_4]_2$ is also clearly different from the *trans* analogue. Consequently no general predictions as to the steric course of ammoniation (or base hydrolysis) can be formulated.

In conclusion, our technique of following the fate of ^1H labels during ammoniation in perdeuteriated liquid ammonia has brought a clear indication of inversion (and consequently π bonding) at the active amido-site during base-catalysed

---

* The protons of the *cis* reaction product exchange immediately after its formation.

† A higher acidity of the transition state is concluded from the considerably higher solvolysis rates of the base-catalysed compared to the spontaneous reaction and their common *D* (dissociative) character. The expected similarity in structure and bonding between the transition state and the short-lived intermediate transfers this conclusion to the intermediate.

ammoniation. In addition progress has been made in understanding the steric course of this reaction.

References

1 For a recent review, see M. L. Tobe, in 'Advances in Inorganic and Bioinorganic Mechanisms,' ed. A. G. Sykes, Academic Press, London, 1983, vol. 2, p. 1.

2 R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, 1956, **78**, 4878.

3 D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1969, **8**, 1595.

4 Ref. 1, p. 54.

5 E. Ahmed and M. L. Tobe, *Inorg. Chem.*, 1974, **12**, 2956.

6 R. A. Henderson and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 2576.

7 W. G. Jackson and A. M. Sargeson, in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 2, pp. 273—378, especially p. 332.

8 P. Comba and W. Marty, *Helv. Chim. Acta*, 1980, **63**, 693.

9 W. G. Jackson and C. M. Begbie, *Inorg. Chim. Acta*, 1982, **60**, 115.

10 W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 1348.

11 D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1968, **90**, 6654.

12 S. Balt, H. J. Gamelkoorn, and S. Oosterink, *Inorg. Chem.*, in the press.

13 S. Balt, H. J. Gamelkoorn, H. J. A. M. Kuipers, and W. E. Renkema, *Inorg. Chem.*, 1983, **22**, 3072.

14 D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, 1967, **20**, 257.

15 S. Balt, H. J. Gamelkoorn, and K. R. Lammers, unpublished work.

16 A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

17 R. G. Pearson, N. C. Stellwagen, and F. Basolo, *J. Am. Chem. Soc.*, 1960, **82**, 1077.

18 S. C. Chan, *J. Chem. Soc.*, 1965, 418.

19 D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, 1967, **20**, 597.

20 H. J. A. M. Kuipers, Thesis, Free University, Amsterdam, 1983.

21 D. A. Buckingham, C. R. Clark, and T. W. Lewis, *Inorg. Chem.*, 1979, **18**, 1985.

Received 2nd October 1984; *Paper* 4/1706