# Substitution Behaviour of an Alkylcobaltamine Complex − Evidence for a Limiting Dissociative Mechanism

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The substitution behaviour of pentaamminemethylcobalt(III) with ethylenediamine (en) was studied in detail in aqueous ammonia solution. The displacement of four ammonia ligands by two ethylenediamine (en) chelates was followed by a subsequent slow *cis* to *trans* rearrangement of the bis(ethylenediamine)(amine)methyl complex. The dependence of the substitution reaction on [en], [$NH_3$], temperature and pressure was studied, and the observed kinetic traces could be fitted to the sum of two exponentials. The rate law for both reaction steps showed saturation kinetics with respect to [en] and [$NH_3$], and the activation parameters confirmed the operation of a limiting dissociative reaction mechanism under all conditions. For the first substitution reaction, $k_{sat.}(en)_{10\ °C}$ = 1.8 ± 0.4 $s^{-1}$, $k_{sat.}(NH_3)_{10\ °C}$ = 1.7 ± 0.3 $s^{-1}$ and $\Delta V^{\#}_{15\ °C}$ = +14 ± 1 $cm^3 \cdot mol^{-1}$, for the second substitution reaction, $k_{sat.}(en)_{10\ °C}$ = 0.55 ± 0.12 $s^{-1}$, $k_{sat.}(NH_3)_{10\ °C}$ = 0.58 ± 0.10 $s^{-1}$ and $\Delta V^{\#}_{15\ °C}$ = +24 ± 1 $cm^3 \cdot mol^{-1}$. The subsequent isomerization reaction was also studied in detail, and a complete set of activation parameters confirm the operation of a dissociative mechanism for the *cis* to *trans* rearrangement for which $k_{iso25\ °C}$ = (1.48 ± 0.07) × $10^{-3}$ $s^{-1}$; $\Delta H^{\#}$ = 115 ± 5 $kJ \cdot mol^{-1}$; $\Delta S^{\#}$ = + 86 ± 16 $J \cdot K^{-1} \cdot mol^{-1}$and $\Delta V^{\#}$ = +14.2 ± 0.6 $cm^3 \cdot mol^{-1}$.

## Introduction

The lability and substitution mechanism of $Co^{III}$ complexes can largely be controlled by the nature of spectator ligands. In terms of a classical example involving complex-formation reactions of $[Co(NH_3)_5H_2O]^{3+}$, displacement of the four in-plane coordinated ammonia ligands by a porphyrin macrocycle, results in a large increase in lability of the coordinated solvent molecule in the axial position *trans* to the remaining amine ligand.[1] Such a modification not only enhances the lability of coordinated water, but also causes a changeover in the ligand substitution mechanism from a dissociative interchange ($I_d$) to a limiting dissociative (D) mechanism. Similarly, the introduction of a strong σ-donor ligand, such as a methyl group, *trans* to the coordinated solvent molecule is also expected to cause a significant increase in lability, and maybe even a changeover in substitution mechanism. [2−7]

Such effects have been observed in the past for model $Rh^{III}$ complexes of the type *trans*-$[Rh(dmg)_2(R)(L)]$ (dmg = dimethylglyoximate; R = Me, $CH_2Cl$, $CH_2CF_3$; L = $H_2O$), which exhibit different substitution rates and substitution mechanisms depending on the σ-donor properties of R.[3] The introduction of several metal−carbon bonds through a ligand such as Cp* (pentamethylcyclopentadienyl) on aquated $Rh^{III}$ not only causes an increase in the water exchange rate constant for $[Rh(Cp^*)(H_2O)_3]^{2+}$ by 11 orders of magnitude relative to $[Rh(H_2O)_6]^{3+}$, but also a changeover from an $I_a$ water exchange mechanism for the hexaqua ion to an $I_d$ mechanism for the Cp* complex, as supported by the significantly different volumes of activation reported for the water exchange reactions.[2,8]

Cobalt complexes with a metal−carbon σ-bond can mimic the reactivity and mechanistic behaviour of $B_{12}$ coenzymes. Compounds that have been studied include *trans*-$[Co(dmg)_2(R)(L)]$ (R = $CH_3$, *i*-$C_3H_7$, 5′-deoxyadenosyl; L = $NH_3$, pyridine (py), 2-$NH_2$py, 5,6-dimethylbenzimidazole, MeOH, $Me_2S$, etc.) and many Schiff base complexes.[4,5,7,9−26] The simplest model for the $B_{12}$ coenzyme was recently synthesized by Kofod and consists of a $Co^{III}$ metal centre surrounded by five ammonia ligands and one methyl group.[27] The X-ray structure shows a large increase in the length of the Co−N bond *trans* to the metal−carbon bond compared to those of the equatorial positions.[28] An interesting question is to what extent the introduction of a single metal−carbon σ-bond affects the substitution behaviour of this $Co^{III}$ complex.

We have undertaken a detailed kinetic study of the reaction of $[Co(NH_3)_5(CH_3)]^{2+}$ with ethylenediamine (en), and could identify the rapid stepwise formation of *cis*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ and the subsequent slower isomerization to the stable *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ complex. All rate and activation parameters could be resolved and strongly support the operation of a limiting dissociative (D) mechanism for all reaction steps.

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## Results and Discussion

### Preliminary Observations

The pentaamminemethyl complex is stable in solution only in the presence of a large excess of $NH_3$ (>3 M). In less concentrated ammonia, the complex undergoes slow decomposition due to hydrolysis and Co−C bond breakage, accompanied by the formation of the hexaammine complex and $Co^{III}$ hydroxides. It was also observed that the pentaamminemethyl complex is sensitive to light and easily undergoes a photo-induced cleavage of the Co−C bond.

Experiments with monodentate ligands such as thiourea and derivatives, various substituted amines and thiocyanate, did not show significant spectral changes under the selected conditions, indicating that only weak complex formation occurred with these nucleophiles in the presence of the high concentration of ammonia. This is most probably due to the strong *trans* labilizing effect of the cobalt−carbon bond and the competition with the excess ammonia in solution. The reaction with cyanide leading to the formation of $[Co(CN)_5(CH_3)]^{3-}$ was recently reported by Kofod,[28] but the reaction was not studied kinetically. We therefore employed bidentate ligands that would lead to thermodynamically more stable products as a result of the chelate effect. Preliminary experiments were successful with bipyridine, phenanthroline or ethylenediamine (en). Of these, only en was soluble enough in water to perform kinetic measurements under pseudo-first-order conditions.

Important to note is that the pH had to be higher than 9.3, the p$K_a$ of $NH_4^+$. At lower pH, protonation of ammonia reduces its coordination ability and therefore the stability of the complex. A pH of ca. 11 proved to be most convenient, since ethylenediamine then acts simultaneously as a nucleophile and as a buffer.

Application of the rapid scan technique revealed an increase in absorbance between 250 and 620 nm (Figure 1), and absorbance−time plots at several wavelengths exhibited good fits for the sum of two exponentials. Following this fast reaction, a slow subsequent step could be observed which then led to the final UV/Vis spectrum of *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ (see Figure 2). Important to note is that in the presence of a high $NH_3$ concentration in solution, the formation of the amine complex was observed in the UV/Vis spectra, but when the $NH_3$ concentration was systematically decreased, the shoulder around 300 nm, which was assigned to the *trans*-amine complex,[28] disappeared. The final spectrum of the slower reaction at low $[NH_3]$ was identical to that of the *trans*-$[Co(en)_2(H_2O)(CH_3)]^{2+}$.[28] Only at high $[NH_3]$ (ca. 3 M) can the equilibrium be shifted to form the *trans* amine complex. This finding clearly demonstrates the high degree of *trans*-labilization caused by the methyl group at this position. The observed spectral changes (Figure 2) can be explained in terms of the *cis* to *trans* isomerization of $[Co(en)_2(NH_3)(CH_3)]^{2+}$, which followed the fast ligand-substitution reactions.

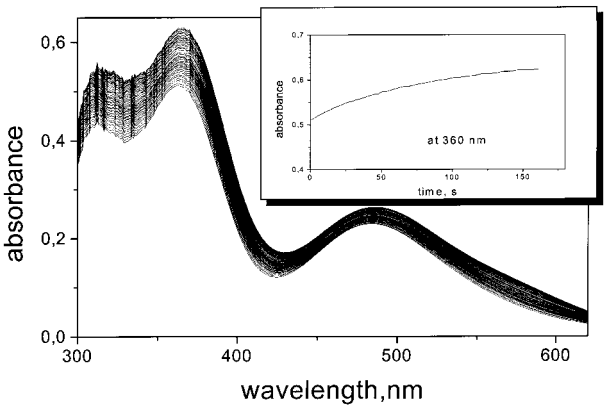



Figure 1. Repetitive-scan spectra for the reaction of $[Co(NH_3)_5(CH_3)]^{2+}$ with ethylenediamine; conditions: $[Co^{III}]$ = 2.5 mM, [en] = 0.2 M, $[NH_3]$ = 0.3 M, integration time for each spectrum 20 ms, total time 163.8 s, time between two spectra 2.64 and 4.64 s (two time bases), pH = 11 (not buffered); inset: the absorbance vs. time trace at 360 nm at room temperature

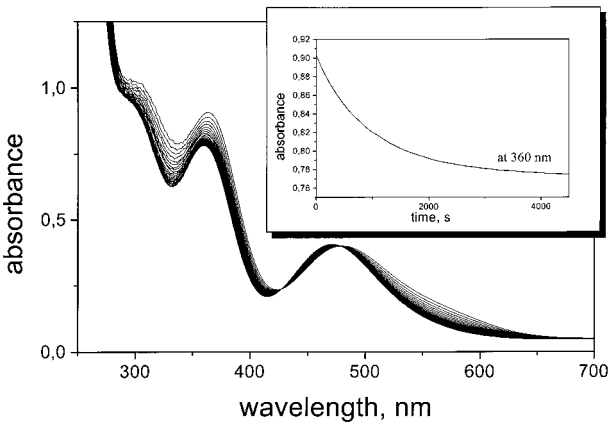



Figure 2. Repetitive-scan spectra recorded for the *cis* to *trans* isomerization of $[Co(en)_2(NH_3)(CH_3)]^{2+}$; conditions: [en] = 0.2 M, $[NH_3]$ = 0.3 M, 20.0 °C, time between two spectra 120 s, total time 38 min, pH ≈ 11(not buffered); inset: the absorbance vs. time trace at 360 nm

### Ligand Substitution Mechanism

A study of the ethylenediamine concentration dependence of the fast reactions at a fixed 3 M ammonia concentration, revealed a decrease in $k_{obs}$ for both reaction steps with increasing [en] as shown in Figure 3. Limiting rate constants of 1.8 ± 0.4 and 0.55 ± 0.12 $s^{-1}$ at 10 °C were found for the first and second reaction steps, respectively, at high ethylenediamine concentrations. Under these conditions ([en] = 0.9 M) the effect of the ammonia concentration on the observed rate constants was studied (see Figure 4), and the values of $k_{obs(1)}$ again decreased with increasing $[NH_3]$ to reach a limiting value of 1.7 ± 0.3 $s^{-1}$ (at 10 °C) at high ammonia concentration. The value of $k_{obs(2)}$ remains practically constant over the selected concentration range with a value of 0.58 ± 0.10 $s^{-1}$ at high ammonia concentration. These limiting values are in excellent agreement with those reported for the dependence on [en] in Figure 3. At low

$[NH_3]$, the kinetic traces can only be fitted with a single exponential and no value for $k_{obs(2)}$ could be determined.

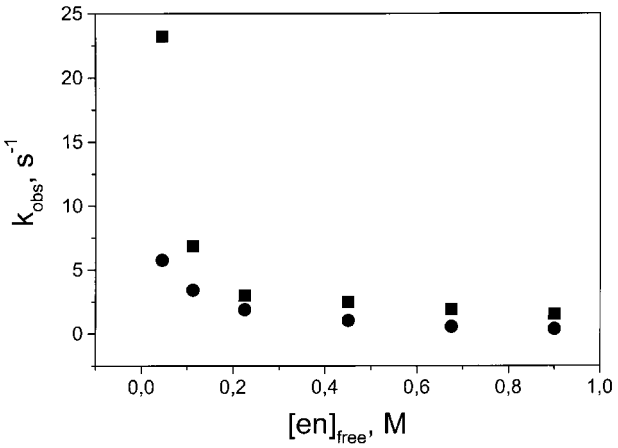



Figure 3. Plot of the observed rate constant ($k_{obs}$) vs. [en] at a constant $[NH_3]$ of 3 M at 10 °C, pH = 11, $I$ = 0.5 M ($NO_3^-$ medium); the filled squares are for the first ($k_{obs(1)}$) and the filled circles for the second ($k_{obs(2)}$) substitution reactions, respectively; $[en]_{free}$ is given as total [en] − $[enH^+]$

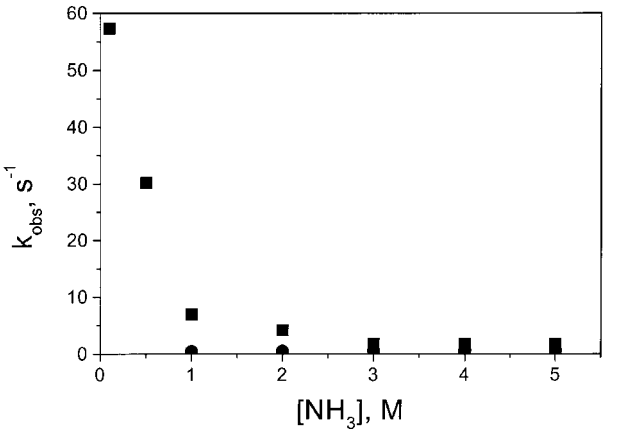



Figure 4. Plot of the observed rate constant ($k_{obs}$) vs. $[NH_3]$ at a constant [en] of 2 M at 10 °C, pH = 11, $I$ = 0.5 M ($NO_3^-$ medium); the filled squares are for the first ($k_{obs(1)}$) and the filled circles for the second ($k_{obs(2)}$) substitution reactions, respectively; $[NH_3]$ is given as total concentration

The temperature dependence of the reactions was measured under limiting concentration conditions, i.e. high concentrations of en and $NH_3$, over a rather limited temperature range due to the high ammonia concentration present in solution. The activation parameters could not be determined accurately and are therefore not reported. The pressure dependence of the reactions was measured under similar conditions and the results are summarized in Figure 5. Both $k_{obs(1)}$ and $k_{obs(2)}$ decrease significantly with increasing pressure. All rate and activation parameters are summarized in Table 1. The observed concentration dependences, as well as the reported activation volumes, strongly support the operation of a dissociative mechanism for both subsequent ligand-substitution processes. The unusual dependence of $k_{obs}$ on $[NH_3]$ and [en] was also found by Malin et al. and Henderson et al. for substitution reactions of iron complexes, and a dissociative character was proposed for the mechanisms.1[29−31]

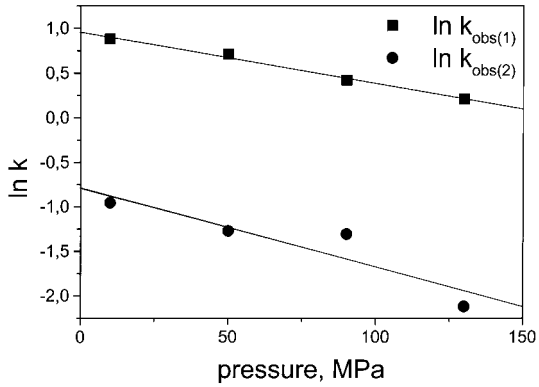
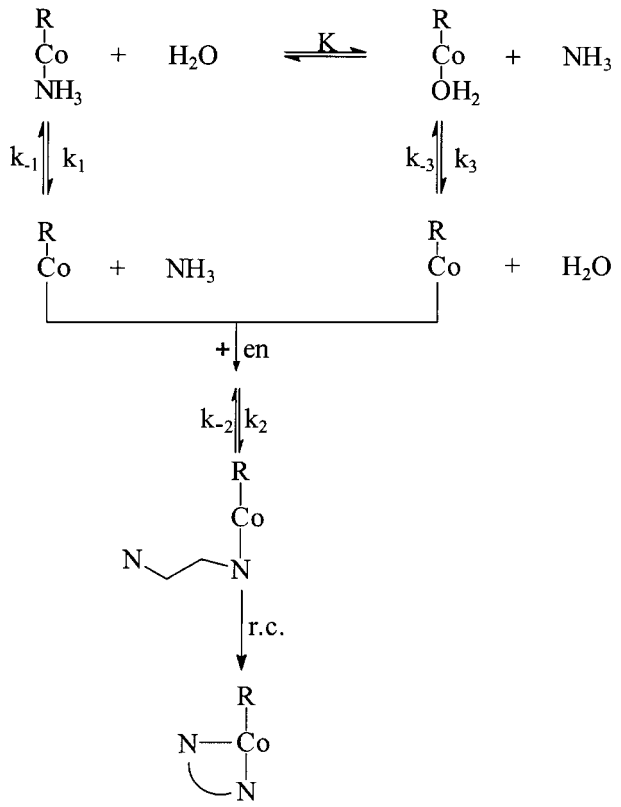



Figure 5. Pressure dependence of the observed rate constants for the two complex formation reactions $[Co(NH_3)_5(CH_3)]^{2+}$ with ethylenediamine, measured under limiting concentration conditions; conditions: [en] = 0.9 M, $[NH_3]$ = 3 M, temp. 15 °C, pH = 11, $I$ = 0.5 M ($NO_3^-$ medium)




Scheme 1

The first substitution reaction can be described by the mechanism outlined in Scheme 1.

As mentioned in the introduction, it is generally accepted that the metal−carbon bond in $[Co(NH_3)_5(CH_3)]^{2+}$ will induce a significant *trans*-labilization effect and cause a rapid spontaneous aquation reaction. The aquation equilibrium will be controlled by the concentration of ammonia in solution, for which the overall equilibrium constant can be ex-

Table 1. Rate and activation parameters for the reaction of $[Co(NH_3)_5(CH_3)]^{2+}$ with ethylenediamine (en) in ammonia solution

| | $k$ ($\times 10^3$) [$s^{-1}$] | $k_{sat}(NH_3)$[a] [$s^{-1}$] | $k_{sat}(en)$[a] [$s^{-1}$] | $\Delta H^{\#}$ [$kJ \cdot mol^{-1}$] | $\Delta S^{\#}$ [$J \cdot mol^{-1}K^{-1}$] | $\Delta V^{\#}_{15\,°C}$ [$cm^3 \cdot mol^{-1}$] |
|---|---|---|---|---|---|---|
| $k_1$ | – | 1.7 ± 0.3 | 1.8 ± 0.4 | – | – | +14 ± 1 |
| $k'_1$ | – | 0.58 ± 0.10 | 0.55 ± 0.12 | – | – | +24 ± 1 |
| $k_{iso}$[b] | 1.48 ± 0.07 | – | – | 115 ± 5 | +86 ± 16 | +14.2 ± 0.6 |

[a] $k_{sat}$ was measured under limiting conditions, i.e. for $k_{sat}(NH_3)$, $[NH_3]$ = 5 M and [en] = 2 M; for $k_{sat}$(en), $[NH_3]$ = 3 M and [en] = 2 M at 10 °C; pH = 11, $I$ = 0.5 M ($NO_3^-$ medium). – [b] $k_{iso}$ was measured at 25 °C in nonbuffered solution.

pressed by $K = [Co-H_2O][NH_3]/[Co-NH_3]$. It has been suggested that this equilibration involves the five-coordinate $[Co(NH_3)_4(CH_3)]^{2+}$ species, which can react with either water or ammonia in the absence of another nucleophile. In the presence of ethylenediamine, the five-coordinate intermediate can be scavenged by en to form the 1:1 *trans*-$[Co(NH_3)_4(en)(CH_3)]^{2+}$ product species. This species is stabilized by a ring-closure reaction of ethylenediamine, accompanied by the loss of an amine ligand. The operation of a limiting D mechanism was also supported by the presence of five-coordinate species that are stabilized by the Co–C bond among the $Co^{III}$ complexes of bis(salicylaldehyde)ethylenediamine and bis(acetylacetonato)ethylenediamine prepared by Costa and co-workers [9,32,33] and among the $Co^{III}$ porphyrin pentacoordinated complexes.[34] Application of steady-state conditions to the five-coordinate intermediate $[Co(NH_3)_4(CH_3)]^{2+}$, results in the following expression for $k_{obs}$, where $f_{Co-NH3} = [NH_3]/(K+[NH_3])$ and $f_{Co-H2O} = K/(K+[NH_3])$.

$$k_{obs} = \frac{k_1 k_2 f_{Co-NH_3}[en] + k_3 k_2 f_{Co-H_2O}[en] + k_{-1} k_{-2}[NH_3] + k_{-2} k_{-3}[H_2O]}{k_{-1}[NH_3] + k_{-3}[H_2O] + k_2[en]}$$

This rate law can account for the decrease in $k_{obs}$ with increasing $[NH_3]$ and [en].[29–31] The [en] dependence in Figure 3 was studied at a fixed and high $[NH_3]$, under which conditions this equation simplifies to

$$k_{obs} = \frac{k_1 k_2 f_{Co-NH_3}[en] + k_3 k_2 f_{Co-H_2O}[en] + k_a}{k_b + k_2[en]}$$

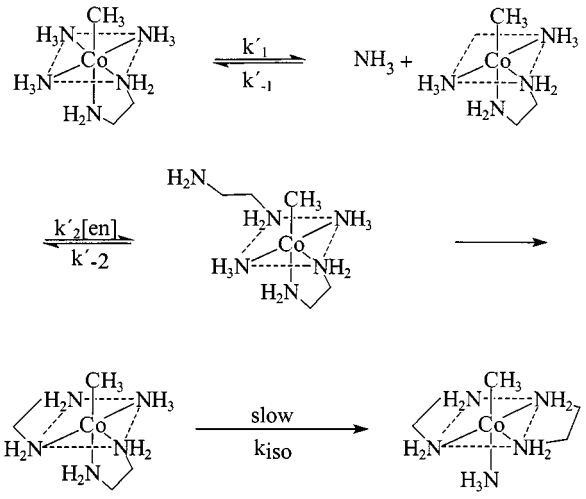
and reaches the limiting value

$$k_{obs} = k_1 f_{Co-NH_3} + k_3 f_{Co-H_2O} = \frac{k_1[NH_3] + k_3 K}{K + [NH_3]}$$

at high [en]. At high $[NH_3]$, this expression simplifies to $k_{obs} = k_1$. Furthermore, this expression can also account for the $[NH_3]$ dependence studied at high [en] (see Figure 4), from which the limiting rate constant found at high $[NH_3]$ must again be $k_1$. Thus under limiting conditions of high $[NH_3]$ and [en], the rate-determining step involves the dissociation of $NH_3$ from $[Co(NH_3)_5(CH_3)]^{2+}$. This accounts for the decrease in $k_{obs}$ with increasing $[NH_3]$, since the aqua complex is expected to be much more labile than the corresponding amine complex. Extrapolation to $[NH_3] = 0$ results in $k_{obs} = k_3 \geq 60\ s^{-1}$, i.e. at least 50 times larger than $k_1$.

It follows that the suggested reaction mechanism and the given rate law can, in a qualitative way, account for the observed concentration dependences and the limiting rate constants reached at high $NH_3$ and en concentrations. A detailed fit of the data is limited by the complexity of the rate law. The activation parameters in Table 1 determined under limiting concentration conditions also support the dissociative nature of the substitution process.

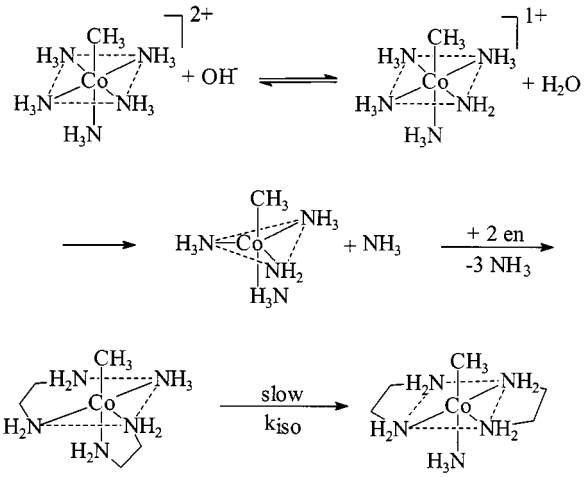
The subsequent formation of the 1:2 complex *cis*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ is about three to five times slower than the formation of the 1:1 complex, and it was more difficult to extract accurate data from the kinetic traces. The overall observed trends are very similar to those of the first substitution process, and we therefore suggest a similar mechanism for the attack of the second en ligand. This reaction must involve the displacement of a *cis* ligand, i.e. one of the three remaining amine ligands, since the *trans* position is occupied by en. The *cis*-labilization effect of the methyl group is expected to be much smaller, and therefore also the release of $NH_3$ in this position should also be slower than in the first reaction. The weaker labilization may also account for the absence of a clear $[NH_3]$ dependence, i.e. a lower $[NH_3]$ is still sufficient to stabilize the amine complex such that the equilibration with the aqua complex (see Scheme 1) does not have to be included in this case. The reaction steps can be summarized as shown in Scheme 2, from which it follows that $k'_1$ will be the rate-determining step under limiting [en] conditions and repre-




Scheme 2

sents the dissociation of an equatorial amine ligand. The five-coordinate intermediate rapidly reacts with a second en ligand, followed by a ring-closure reaction to produce *cis*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$. The reported activation volume for the second substitution process (Table 1) also supports the operation of a limiting dissociative mechanism. Subsequently, the slow *cis* to *trans* isomerization of the latter complex occurs (see further Discussion).

The volumes of activation found for the subsequent substitution reactions under limiting concentration conditions, viz. +14 ± 1 and +24 ± 1 $cm^3 \cdot mol^{-1}$, are significantly positive in line with a limiting D mechanism. The value for the first reaction is close to the value reported for the dissociation of $NH_3$ in various octahedral complexes.[35–37] Since the *trans* influence of the methyl group already labilizes the Co–$NH_3$ bond in the ground state, as seen from X-ray structure analysis,[28] the volume increase required to dissociate $NH_3$ in the transition state will be significantly smaller than the partial molar volume of ammonia, viz. 24.85 $cm^3 \cdot mol^{-1}$.[38,39] The significantly higher value found for the second reaction step is surprising. This value may suggest that not only ammonia is labilized in the *cis* position, but also the ethylenediamine chelate. Partial ring-opening could, along with the dissociation of ammonia, account for the larger volume of activation. Alternatively, the more positive volume of activation found for the second substitution reaction may be due to the operation of a conjugate-base mechanism under the selected conditions. Earlier studies have demonstrated that base hydrolysis reactions proceeding by means of a conjugate base mechanism are characterized by large positive volumes of activation as a result of conjugate base formation and the subsequent ligand dissociation step.[40–44] For this reason we have checked the base concentration dependence of the substitution reactions, and the results are reported in Figure 6. The first substitution process is significantly accelerated by base, whereas the second substitution reaction hardly shows any base concentration dependence. The suggested conjugate base mechanism which could account for the acceleration observed for the first substitution process is outlined in Scheme 3.




Scheme 3

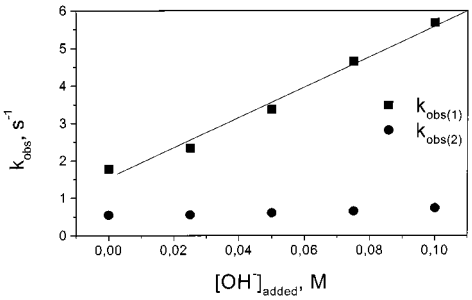



Figure 6. Plot of the observed rate constant ($k_{obs}$) vs. added [$OH^-$] for the reaction of $[Co(NH_3)_5(CH_3)]^{2+}$ with ethylenediamine; conditions: [en] = 0.9 M, [$NH_3$] = 3 M, temp. 10 °C, pH ≈ 11, $I$ = 0.5 M ($NO_3^-$ medium)

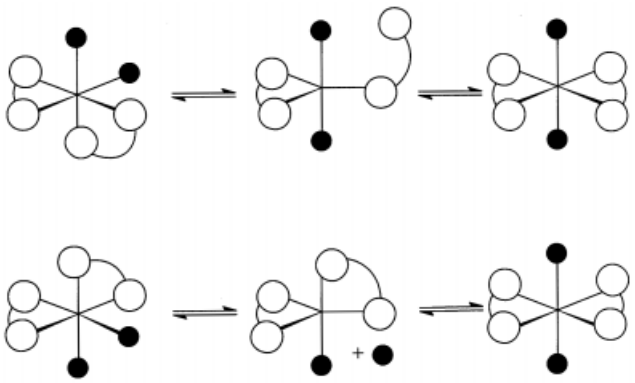
It follows from the data in Figure 6 that under the experimental conditions (pH ≈ 11, [en], [$NH_3$]) selected for the pressure dependence study, no significant contribution from base catalysis exists, and we can therefore rule out this possible explanation for the larger activation volume for the second substitution process.

### *cis*–*trans* Isomerization Mechanism

The third and slower reaction step was assigned to the formation of the *trans* complex. The isomerization was followed as a subsequent reaction of the *cis*-complex rapidly produced on dissolving the pentaammine complex in a solution of en and $NH_3$. It was characterized by UV/Vis spectra with sharp isosbestic points at 427 and 492 nm, new bands formed at 358 and 466 nm, and a shoulder at 290 nm (see Figure 2). The positions of these bands shifted slightly to 363 and 470 nm when $[Co(NH_3)_5(CH_3)](NO_3)_2$ was dissolved in water without the addition of $NH_3$. This suggests that a water molecule occupies the trans position in the absence of $NH_3$.

The final spectrum is identical to the one published for the isolated and X-ray characterized *trans*-$[Co(en)_2(NH_3)(CH_3)](S_2O_6)$ complex.[28] The rate of the isomerization reaction was studied over a [en] range of 0.3 to 2.2 M, at a fixed [$NH_3$] of 0.2 M. Absorbance–time traces were recorded and could be fitted with a single exponential. The rate of the *cis*–*trans* rearrangement was found to be independent of [en], with an average value of (1.48 ± 0.07) × $10^{-3}$ $s^{-1}$ for $k_{iso}$ at 25 °C. The solutions were not buffered during these measurements. The activation parameters measured in the unbuffered solution, $\Delta H^{\#}$(iso) = 115 ± 5 $kJ \cdot mol^{-1}$, $\Delta S^{\#}$(iso) = 86 ± 16 $J \cdot mol^{-1} \cdot K^{-1}$ and $\Delta V^{\#}$(iso) = +14.2 ± 0.6 $cm^3 \cdot mol^{-1}$, are all consistent with a limiting dissociative mechanism.

As known from a series of *cis*-*trans* isomerization reactions of cobalt complexes of the type $Co(en)_2XY$, the mechanism is in most cases a mixture of D or I type of reactions. In earlier papers isomerization mechanisms were discussed in terms of the possible reactions outlined in Scheme 4.[40,45]



Scheme 4

The main question that arises from Scheme 4 is how to distinguish between the two possible reaction paths that both involve ligand dissociation and will result in a positive volume of activation. It is not clear whether a square pyramidal or a trigonal bipyramidal intermediate is involved. On the one hand, we have the strong *trans* influence on the coordination site opposite to the carbon atom, as seen in the bond lengths of the solid state structure of $[Co(NH_3)_5(CH_3)](NO_3)_2$ [28] and in the fast $Co^{III}$ substitution kinetics on the stopped-flow time scale. On the other hand, there are also the *cis* effects of both the methyl and the bidentate ligand which will weaken the $Co-NH_3$ bond and can therefore open another reaction path. It was necessary to keep the $[NH_3]$ at a low level in these reactions. At higher $[NH_3]$, the reaction was suppressed and the *cis* to *trans* rearrangement could no longer be observed. This is in line with the suggested rate-determining dissociation of $NH_3$. At high $NH_3$ concentration, the vacant coordination site will again be readily occupied by ammonia, and isomerization will be prevented. At low $[NH_3]$, competition between the free dangling end of en and $NH_3$ as entering ligands is at play. Once the second nitrogen donor of en is bound to the Co centre, the chelate effect prevails and stabilizes the *trans* product. The volume of activation data are also typical for the dissociation of $NH_3$ in the rate determining step.[35–37]

Under these circumstances we favour the reaction path involving the dissociation of $NH_3$ and the formation of the trigonal bipyramidal intermediate, since it readily provides the correct path for the isomerization reaction. The dissociation (ring-opening) of the en ligand may occur on a rapid time scale, but does not lead to isomerization of the complex due to an efficient ring-closure reaction.

This suggestion differs from what was suggested earlier for the isomerization of $[Co^{III}(en)_2(L)H_2O]$ complexes, where L is $NH_3$, $Cl^-$, $Br^-$ or $OH^-$. The authors found that the reaction path is influenced by the strength of the Co–L bond relative to the strength of the Co–en bond.[45] However, in these studies the strong *trans* effect of the carbon donor, which will labilize any bond in that position, was not present.

To rule out the possible participation of a conjugate base mechanism during the *cis* to *trans* isomerization, the added base concentration was varied in a series of experiments. Only the loss of the isosbestic points and a general decrease in absorbance could be observed, suggesting that other processes interfere under such conditions.

## Conclusions

The mechanism of ligand substitution in $[Co(NH_3)_5(CH_3)]^{2+}$ is strictly dissociative. The large volume increase found when going to the transition state can be accounted for in terms of only intrinsic volume effects. The high values of either $+14\ cm^3 \cdot mol^{-1}$ for the first or $+24\ cm^3 \cdot mol^{-1}$ for the second step strongly support the limiting dissociative character of the substitution process.

The $[Co(NH_3)_5(CH_3)]^{2+}$ cation is not favoured to be used as model for $B_{12}$ chemistry due to the necessary presence of high ammonia concentrations and an unfavourable pH. The mechanistic understanding of the labilizing *trans* effect is important in terms of recent reports in the literature describing an interest in the activation of inert metal centres such as $Co^{III}$, $Rh^{III}$, and $Ir^{III}$ complexes.[2,3,8,46–49] One major interest is the understanding of the electronic vs. steric tuning effects in simple substitution reactions, to enhance the understanding of catalytic cycles, and to synthesize specially designed complexes to be used as highly reactive and selective catalysts. In that respect, the final product of the substitution process reported here, *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$, may be a potential model for the vitamin $B_{12}$ coenzyme and related systems.

## Experimental Section

Methylhydrazine, cobalt(II) nitrate hexahydrate, ethylenediamine (en), sodium nitrate and ammonia solutions were all purchased from Aldrich or Merck and used as received, except for en which was distilled and stored under nitrogen before use. Pentaamminemethylcobalt(III) nitrate was prepared according to the method of Kofod,[27] but oxygen was bubbled through the reaction mixture for 4 h instead of exposure to air. The complex was stored under nitrogen in the dark. The purity of the complex was checked by elemental analysis and $^1H$ NMR and UV/Vis spectroscopy.[27,28] – All solutions for the kinetic measurements were freshly prepared with Millipore water in the dark before use. 10% of the total concentration of en was protonated with nitric acid to use en-enH$^+$ as buffer. – The NMR measurements were performed on a Bruker Avance DRX 400 WB NMR spectrometer. – UV/Vis spectra were recorded on either a Cary 1 or a Shimadzu UV-2101PC spectrophotometer. – Kinetic measurements for the fast substitution reactions were performed on an Applied Photophysics BioSX 18 MV instrument connected to a diode-array detector (TIDAS 200–620 nm, J&M, Aalen, Germany) to measure complete spectra on a ms time scale. The *cis* to *trans* rearrangement was followed as a subsequent slower step after mixing the complex and en solutions in a tandem cuvette or a pill box cell. In this case, no buffer was used. Kinetic measurements at elevated pressure were performed on a home-made high-pressure stopped-flow apparatus for the fast reactions or in a home-made high-pressure cell combined with a Shimadzu UV-2101PC spectrophotometer for the slower isomerization step.[50,51]

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