Thermodynamic and Kinetic Studies of the Equilibration between the Sulfur- and Carbon-Bonded Forms of the Cobalt(III) Complex with the Ligands 2-Aminoethyl-3-aminopropylsulfide and 1,4,7-Triazacyclononane

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A thermodynamic and kinetic study of the equilibration between the Co–S bonded complex $Co(tacn)(aeaps)^{3+}$ (and its N-deprotonated amido base) and the Co–C bonded complex $Co(tacn)(C-aeaps)^{2+}$ is reported (tacn = 1,4,7-triazacyclononane, aeaps = 1,6-diamino-4-thiahexane and C-aeaps = 1,6-diamino-3-thia-4-hexanide).
    Kinetic and thermodynamic data have been obtained using UV–VIS spectroscopy, HPLC and ^{13}C NMR spectroscopy. At large [OH⁻] the rate constants showed an unexpected decrease with increasing [OH⁻], which is explained in terms of different reactivity of ion pairs with perchlorate and hydroxide, respectively. Rate constants for the formation of the alkyl complex for ion pairs with perchlorate and hydroxide, respectively (composite terms), and for the re-formation of the cobalt–sulfur complex from ion pairs with perchlorate are given, together with thermodynamic data.
    The kinetic data have been interpreted in terms of the intermediate formation of a carbanion complex. It was shown that $Co(tacn)(aeaps)^{3+}$ exchanges one C–H, and only one, prior to the formation of the alkyl complex. The subsequent reaction of the partially C-deuterated (–N–CH2–CH2–CHD–S–) cobalt–sulfur complex to form the alkyl complex gave 100 % loss of deuterium. The same partially C-deuterated complex was also obtained when $Co(tacn)(aeaps)^{2+}$ was reformed from $Co(tacn)(C-aeaps)^{2+}$ using D_2O as solvent, and it reacted similarly. It is therefore concluded that the labile methylene proton is bound to the carbon atom, which in the alkyl complex is bound to cobalt(III). From the kinetic data it is estimated that the carbanion reacts with water 80 times faster than it is captured by cobalt(III).
    Neither in $Co(tacn)(aeaps)^{3+}$ nor in $Co(tacn)(C-aeaps)^{2+}$ was an exchange of any other C–H observed within the timescale for equilibration.

It was previously shown[1] that the cobalt(III) complex $Co(aeaps)_2^{3+}$ (aeaps = *a*minoethyl *a*minopropyl *s*ulfide = 1,6-diamino-4-thiahexane) surprisingly reacts in base forming an alkyl complex. The alkyl complex was isolated as the dithionate salt and characterized in an X-ray diffraction study. Kinetic data for this reaction were also reported. It was shown that the formation of alkyl complex occurs via at least two consecutive reactions and that the final equilibrium solution contains at least three species, one of which is the isolated alkyl species. In addition it was found that all three unsymmetrical facial isomers of $Co(aeaps)_2^{3+}$ produce the same equilibrium solution. A detailed mechanistic interpretation of the kinetic data was not achieved. The complex behaviour of this system probably arises partially from the fact that both aeaps ligands may undergo reactions (cleavage of the cobalt–sulfur bond may give Co–C as well as Co–OH bonded species) and that the different isomers of $Co(aeaps)_2^{3+}$ apparently isomerize fast in basic solutions. The latter complication would clearly be

eliminated by substitution of one of the aeaps ligands with an inert tripodal ligand such as 1,4,7-triazacyclononane (tacn). As described recently, we were successful in preparing [Co(tacn)(aeaps)]Cl₃ · H₂O and found, as anticipated, that this complex readily forms an alkyl complex which was isolated as [Co(tacn)(C-aeaps)](ClO₄)₂ in high yield (C-aeaps = 1,6-diamino-3-thia-4-hexanide).[2] Both cations were characterized by X-ray single-crystal diffraction analysis and by their ¹H, ¹³C and ⁵⁹Co NMR spectra as well as UV–VIS spectra. In this paper we demonstrate that the reactions between the sulfur bond ligand and the carbon bond ligand are reversible. A detailed study of the thermodynamics and kinetics of the equilibration reactions of the Co–S and Co–C bonded species is reported.

Experimental

Materials and instruments. The salts [Co(tacn)(aeaps)]-Cl₃ · H₂O and [Co(tacn)(C-aeaps)](ClO₄)₂ were prepared as described previously.[2] Deuterium oxide (99.8 atom % D), sodium deuteroxide (40 % solution in D₂O, 99 atom % D)

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Table 1. Thermodynamic data for $K_b(ND)$ in 1 M NaClO$_4$ in D$_2$O.[a]

T/°C	$K_b(obs)/M^{-1}$	$K_b(calc)^b/M^{-1}$
25.0	0.275	0.266
14.9	0.340	0.352
1.5	0.530	0.527

[a]See Scheme 1. [b]Calculated using the parameters in Table 5.

and deuterium chloride (35 % solution in D$_2$O, 99 atom % D) were obtained from Sigma. ND$_4$Cl was made by dissolving NH$_4$Cl in D$_2$O, evaporating to dryness and repeating this procedure twice. All other reagents were of analytical grade, and CO$_2$-free doubly deionized water was used for all measurements. Potentiometric pH measurements were made as described previously.[2]

A Perkin–Elmer diode array spectrophotometer, LA 3048, was used for spectral measurements. Ion-exchange high-performance liquid chromatography (IE-HPLC) was performed using a Waters HPLC system connected to a diode array detector. A Waters Protein Pak SP-5PW cation exchanger was used; 0.23 M Na$_2$SO$_4$ was used as eluent in all experiments and the flow was normally 1.0 ml min^{-1}. All HPLC experiments were made at 25 °C. NMR spectra were measured at 5.87 T on a Bruker AC 250 MHz NMR spectrometer equipped with a 5 mm probe for ^{13}C NMR measurements.

Carbon-13 magnetic resonance spectra. Deuterated solvents were used to provide a deuterium lock. Quadrature detection and quadrature phase cycling were always used. ^{13}C NMR spectra were obtained on a 14286 Hz spectral window with a digital resolution of 0.872 Hz per point. ^{13}C DEPT NMR spectra were used to distinguish CH and CH$_2$ carbon atoms. The DEPT pulse sequence given by Doddrell *et al.*[3] was used to achieve a clear differentiation of CH, CH$_2$ and CH$_3$ groups.

The type of compound investigated here has coupling constants J_{CH} of about 135 Hz, and therefore a delay time $\tau = 3.7$ ms was used. The ^{13}C DEPT NMR spectra shown in this paper were all obtained using $\theta = 3\pi/4$, and the phase of the spectra was adjusted in order to make ^{13}C NMR signals from CH and CH$_3$ groups positive and those from CH$_2$ groups negative. Inverse gated ^{1}H decoupling was used to obtain ^{13}C NMR spectra suitable for integration of the resonance signals. An additional line-broadening of 1 Hz was employed to the ^{13}C NMR spectra before Fourier transformation to improve the signal-to-noise ratio.

^{13}C chemical shift values (δ) are reported in ppm relative to internal 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; $\delta = 0$ ppm, 17.66 ppm, 21.74 ppm and 57.02 ppm) for D$_2$O solutions, or tetramethylsilane (TMS; $\delta = 0$ ppm) for DMSO-d$_6$ and acetonitrile-d$_3$ solutions.

The spectrum of the CDH deuterated isomer of Co(tacn)(aeaps)$^{3+}$ was obtained as follows. The alkyl compound (0.1 M) was dissolved in 1 M ND$_4^+$/ND$_3$ buffer (D$_2$O) at pH 7.3. The solution was kept at 60 °C for 60 h. Thereafter the pH of the solution was adjusted to 7 with diluted DCl; it was kept at 60 °C for another 60 h, and then the ^{13}C DEPT NMR spectrum was recorded.

Determination of the equilibrium constant $K_f = K_1K_2$ *(Scheme 1).* Mixtures of the sulfur- and carbon-bonded isomer gave well separated elution curves when analyzed by IE-HPLC. Using mixtures of the two complexes having a known content of each component, it was shown that the relative peak areas can be used to determine the molar ratio of the two species with great accuracy. The determinations were initially shown to be independent of the wavelength. In most experiments elution curves monitored at 288 and 302 nm were used, since at these wavelengths the molar absorbances of the two species are similar. The following result illustrates the high accuracy of the method: analysis of a mixture containing 44.5 and 55.5 % of the sulfur- and carbon-bonded species, respectively, gave the values 45.4 and 54.6 %, respectively.

Equilibrium solutions were obtained by heating ammonia/ammonium buffer solutions of the cobalt(III) species to 60 °C. The solutions were analyzed by IE-HPLC at different times, and when the same IE-HPLC curves were obtained for solutions initially containing either [Co(tacn)(aeaps)]Cl$_3 \cdot$ H$_2$O or [Co(tacn)(C-aeaps)](ClO$_4$)$_2$ it was assumed that equilibrium had been attained. This was, in each case, further confirmed by the observation that additional heating did not give different HPLC curves. The concentrations of the two species, [Co(tacn)(aeaps)]Cl$_3 \cdot$ H$_2$O and [Co(tacn)(C-aeaps)](ClO$_4$)$_2$, were calculated from the relative peak areas (see also Refs. 4 and 5). The pH-values of the buffer solutions were calculated using published pK_a-values for NH$_4^+$ and trisH$^+$.[6]

Kinetic measurements. Reactant solutions were made by dissolving [Co(tacn)(aeaps)]Cl$_3 \cdot$ H$_2$O or [Co(tacn)(C-aeaps)](ClO$_4$)$_2$ directly in the solvent or by adding base/buffer to an aqueous neutral solution of the salt. For the

Table 2. Thermodynamic data for the equilibrium between the sulfur- and carbon-bonded species, eqn. (2), determined by IE-HPLC at 60 °C and in 1 M NaClO$_4$.

Starting species[a,b]	[OH$^-$]/M	$K_f(obs)/M^{-1}$
Co–C[a]	4.13×10^{-5}	1.25×10^4
Co–S[b]	4.13×10^{-5}	1.26×10^4
Co–C[a]	7.84×10^{-4}	1.22×10^4
Co–S[b]	7.84×10^{-4}	1.08×10^4

K_f(average) = 1.18(8)×10^4 M^{-1}

[a,b]The equilibrium solutions were made by starting with a solution of [a][Co(tacn)(C-aeaps)](ClO$_4$)$_2$ or [b][Co(tacn)(aeaps)]Cl$_3 \cdot$ H$_2$O. The hydroxide ion concentrations were kept constant using NH$_3$/NH$_4$ClO$_4$-buffer solutions (see also Fig. 1).

Table 3. Kinetic data for the equilibration reaction at $I = 1.0$ M [Na(OH,ClO$_4$)].

Method	[OH$^-$]/M	$k_{obs}/10^{-5}$ s^{-1}	$k_{calc}{}^c/10^{-5}$ s^{-1}
$T = 25.0\,°C$			
Spec.^{a}	1.000	11.7	12.4
"	0.750	12.8	14.5
"	0.500	15.0	14.7
"	0.100	6.27	6.39
"	0.010	0.83	0.81
$T = 40.1\,°C$			
Spec.^{a}	1.000	119	102
"	0.750	139	127
"	0.500	149	138
"	0.200	111	107
"	0.100	67	71
"	0.020	17.5	18.6
"	0.005	5.26	5.01
$T = 59.4\,°C$			
Spec.^{a}	1.000	1040	1102
"	0.750	1320	1489
"	0.500	1810	1724
"	0.250	1694	1625
"	0.100	1040	1081
"	0.050	641	672
"	0.020	292	313
"	0.010	174	166
"	0.005	81	86
"	0.002	39.0	36.0
$T = 60.0\,°C$			
HPLC^b	7.84×10^{-4}	18.2	16.5
"	4.13×10^{-5}	2.16	2.48
"	3.56×10^{-6}	1.77	1.77
Spec.^{b}	4.13×10^{-6}	1.77	1.78
"	3.56×10^{-7}	1.89	1.71
HPLC^b	3.95×10^{-7}	1.68	1.71
$T = 80.0\,°C$			
Spec.^{b}	3.92×10^{-6}	17.2	18.0
"	4.08×10^{-7}	17.8	17.0
$T = 100.0\,°C$			
Spec.^{b}	3.75×10^{-6}	142	142
"	4.60×10^{-7}	133	133

^{a}Starting with Co(tacn)(aeaps)$^{3+}$. ^{b}Starting with Co(tacn)(C-aeaps)$^{2+}$. ^{c}Calculated using the expressions in eqns. (5)–(7) and the parameters given in Table 5.

experiments with long half-lives, each kinetic run was based on different portions of the same batch solution, kept separately in glass ampoules in the dark. The faster reactions were measured using spectrophotometry by traditional repetitive scans of the same solution, combined with the use of a flow cell, in order to minimize the time interval from the mixing of the reactant to the first measurement (typically 20–30 s). The concentration of the cobalt(III) complex was 5×10^{-5} M in all the spectrophotometric measurements and 10^{-2} M in the HPLC studies. The pH

was adjusted either by using a large excess of NaOH (>0.002 M) or by using a buffer (ca. 0.1 M).

Most of the kinetic experiments were made using spectrophotometry. The pseudo first-order rate constants, k_{obs}, were calculated on basis of absorbances measured at 160–190 different wavelengths in the region 210–400 nm. the method for calculating rate constants and activation parameters has been described previously.[6] A few kinetic runs (re-formation of the sulfur-bonded species) were made by analyzing the reactant solutions at different times using IE-HPLC as described above and calculating the rate constant by standard procedures.

Results

Stoichiometry and thermodynamics of the equilibrium between the sulfur- and carbon-bonded species. It was previously shown[2] that Co(tacn)(aeaps)$^{3+}$ in strong base is deprotonated at a coordinated amine, to give a reddish-purple amido complex. The site of deprotonation is not known, but it is likely that the deprotonation occurs at one of the triazacyclononane amine groups, as indicated in eqn. (1). The thermodynamic parameters for this reaction

$$\text{Co(tacn)(aeaps)}^{3+} + \text{OH}^- \underset{1/K_b}{\overset{}{\rightleftharpoons}} \text{Co(tacnN}^-\text{)(aeaps)}^{2+} + \text{H}_2\text{O}$$

(1)
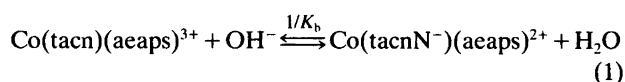
were previously determined in 1 M Na(OH,ClO$_4$) (using

Volume/ml
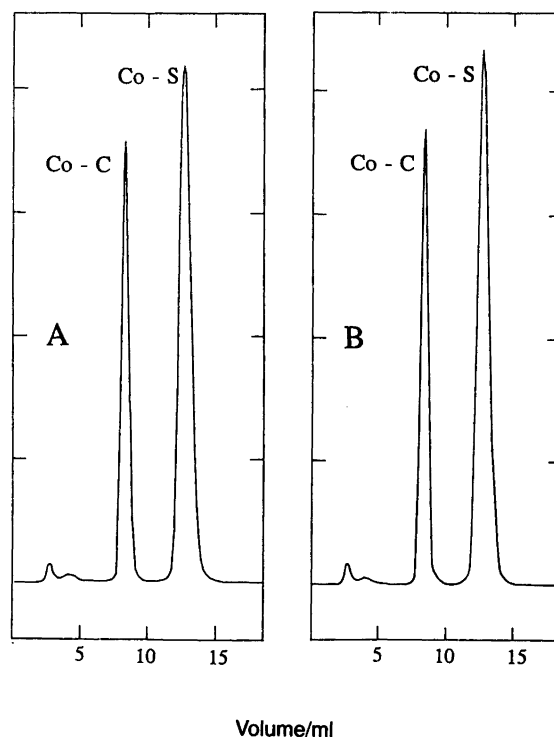
Fig. 1. IE-HPLC curves for a solutions of [Co(tacn)(aeaps)]Cl$_3 \cdot$ H$_2$O (A) and a solution of [Co(tacn)(C-aeaps)](ClO$_4$)$_2$ (B) in 0.1 M NH$_3$, 0.1 M NH$_4$ClO$_4$, 0.9 M NaClO$_4$ after heating to 60 °C for 180 h. The first elution curve represents the carbon-bonded species and the last the sulfur-bonded one.
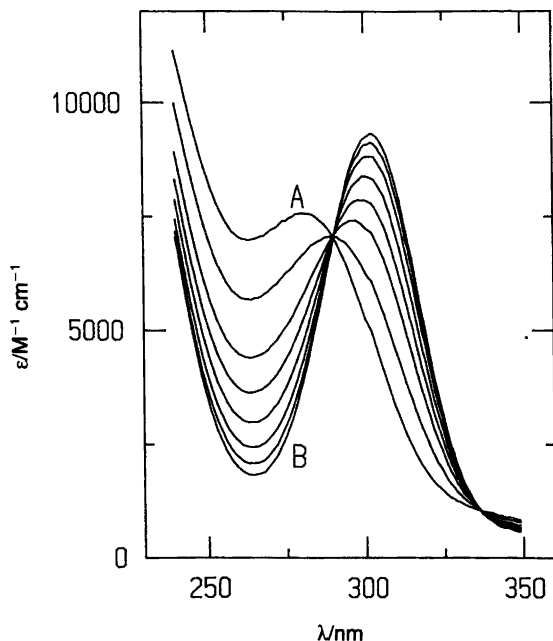
Fig. 2. The reaction of Co(tacn)(aeaps)$^{3+}$ (A) in 1 M NaOH at 25 °C yields Co(tacn)(C-aeaps)$^{2+}$ (B) quantitatively.

H_2O as solvent), and additional measurements were made in this study using D_2O as solvent (Tables 1 and 5). The decrease of K_b by a factor 2 on going from H_2O to D_2O is within the expected region.[7] In the following the nomenclature K_b(NH) and K_b(ND) have been used for the two values of K_b determined in H_2O and D_2O, respectively.

The initial and fast acid–base reaction of Co(tacn)-(aeaps)$^{3+}$ is followed by a relatively slow reaction, eqn. (2),

$$Co(tacn)(aeaps)^{3+} + OH^- \overset{K_f}{\rightleftharpoons} Co(tacn)(C\text{-}aeaps)^{2+} + H_2O$$

(2)
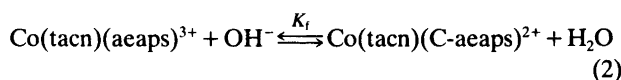
which at high concentration of hydroxide affords a quantitative formation of the alkyl complex shown by analysis of the product solution using UV–VIS spectroscopy, ^{13}C NMR spectroscopy and IE-HPLC analysis. For example, the UV–VIS spectra of the final solutions did not show any significant variation for [OH$^-$] varying from 0.01 to 1.0 M, and they were identical to that of [Co(tacn)(C-aeaps)](ClO$_4$)$_2$ in 1 M NaOH.

The equilibrium constant for eqn. (2) was determined by means of IE-HPLC analysis as described in the Experimental section. As shown in Fig. 1, the equilibrium solutions contain only two components, which were identified as Co(tacn)(aeaps)$^{3+}$ and Co(tacn)(C-aeaps)$^{2+}$, respectively, by their spectra and by comparison with the elution curves of the authentic species. The equilibrium constant K_f was then calculated from the relative peak areas obtained in experiments with [OH$^-$] = 4 × 10^{-5} and 8 × 10^{-4} M (Table 2). Similar experiments at low pH (tris-buffer, [OH$^-$] = 4 × 10^{-7} M) showed that the carbon-bonded

species re-forms the sulfur-bonded species quantitatively in this pH region.

Kinetics of the equilibration reaction. The kinetics of the equilibration reaction between the sulfur- and carbon-bonded forms were studied at five temperatures in the region 25–100 °C (I = 1.00 M). The reaction was followed spectrophotometrically (Figs. 2 and 3) and in a few cases also by using IE-HPLC analysis. Reactant solutions were made by starting either with [Co(tacn)(aeaps)]Cl$_3$ · H$_2$O or with [Co(tacn)(C-aeaps)](ClO$_4$)$_2$, depending on the pH. The reactions starting with the sulfur-bonded species were all studied spectrophotometrically. In these experiments the hydroxide ion concentration was varied from 0.002 to 1.00 M. At these conditions the reaction gives the alkyl complex quantitatively (100 % at [OH$^-$] = 1.0 M) or nearly quantitatively (96 % at [OH$^-$] = 0.002 M and 60 °C). In the reactions starting with the alkyl complex the hydroxide concentration was varied from 4 × 10^{-7} to 8 × 10^{-4} M using buffer solutions. At low pH complete re-formation of the sulfur complex will occur, while the more basic region will result in an equilibrium mixture (e.g. [OH$^-$] = 4 × 10^{-5} M yields 69 and 31 %, respectively, of the sulfur- and carbon-bonded species at 60 °C). The reactions are followed by consumption or production of base [up to one mole of base per mole of cobalt(III)], but since the cobalt(III) concentrations were kept small relative to concentrations of NaOH or buffer, pseudo first-order conditions can be assumed. The rate constants determined spectrophotometrically were in good agreement with those determined using IE-HPLC (60 °C; Fig. 7 and Table 3).

In all the spectrophotometric experiments, well defined isosbestic points were observed for the formation as well as
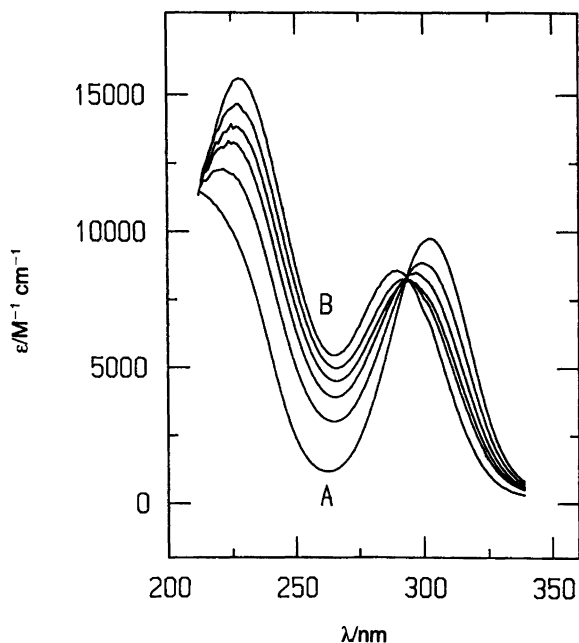

Fig. 3. The reaction of Co(tacn)(C-aeaps)$^{2+}$ (A) in NH$_3$/NH$_4^+$ buffer with [OH$^-$] = 4 × 10^{-6} M at 60 °C yields Co(tacn)(aeaps)$^{3+}$ (B) nearly quantitatively.
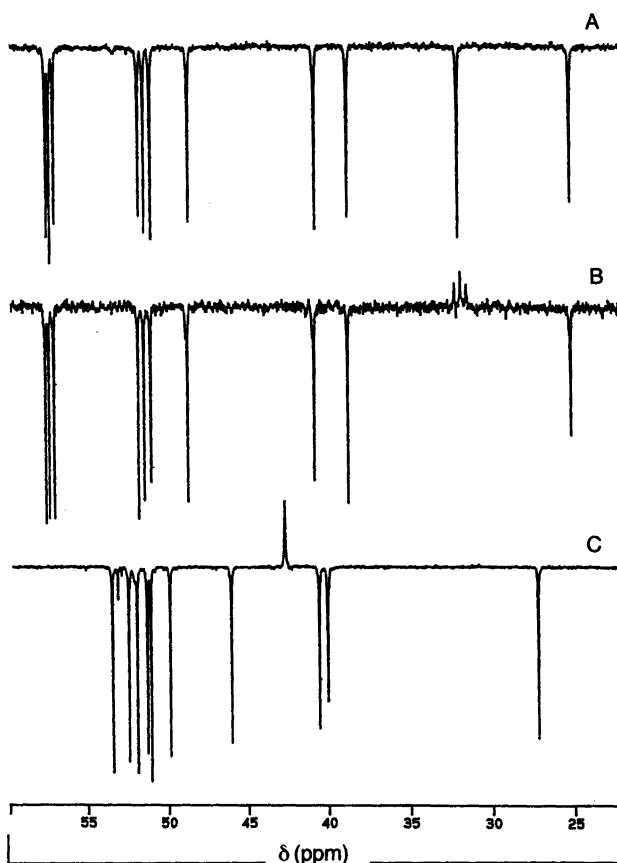
Fig. 4. ^{13}C DEPT NMR spectra. (A) Co(tacn)(aeaps)Cl$_3$ in D$_2$O.
(B) Co(tacn)(aeaps-d$_1$)$^{3+}$ in ND$_4^+$/ND$_3$ buffer (ca. pH 7) (C)
Co(tacn)(C-aeaps)$^{2+}$ in 1 M NaOD. All spectra were measured
at 25 °C.

for the re-formation reactions, which clearly indicates that
no significant amounts of intermediates (or by-products)
are formed (Figs. 2 and 3). This was supported by the fact
that IE-HPLC analyses made during the reaction un-
ambiguously showed the presence of only two species. The
stoichiometry can therefore be expressed by eqns. (1)
and (2).

Experiments at ionic strength 5 M (25 °C, 5 M NaNO$_3$)
were also made, and gave similar results (Fig. 8).

^{13}C NMR H/D-exchange experiments. The ^{13}C DEPT NMR
spectra of 0.2 M solutions of [Co(tacn)(aeaps)]Cl$_3$ · H$_2$O
and of [Co(tacn)(C-aeaps)](ClO$_4$)$_2$ in D$_2$O are shown in
Fig. 4. Both spectra show 11 resonance signals as expected.
For each spectrum the six resonances at higher frequency
may be assigned to the six carbon atoms in the tacn ligand,
and the remaining five resonance lines may be assigned to
the carbon atoms of the sulfur ligand, as discussed in
Ref. 2. It is of particular relevance to the present study that
the resonance signal for Co(tacn)(aeaps)$^{3+}$ at 31.8 ppm has
been assigned to the sulfur-bonded methylene carbon (C4)
in the propylene ring and that the resonance signal for
Co(tacn)(C-aeaps)$^{2+}$ at 42.60 ppm has been assigned to the
cobalt-bonded methine carbon. This resonance signal is the
only one that is positive, and thereby it is unambiguously

assigned to a CH group (see Experimental). This was fur-
ther established by using $\theta = \pi/2$ in the DEPT pulse se-
quence. This experiment suppresses all other ^{13}C NMR
signals except those from CH groups, and gives the ex-
pected result.

Formation of the alkyl complex in 1 M NaOD in D$_2$O
gave a product with a spectrum identical to that shown in
Fig. 4C. This shows that no deuterium is incorporated into
the carbon chain of the C-aeaps ligand.

At low pH the alkyl complex re-forms the sulfur-bonded
species as described above. This reaction was also made
using D$_2$O as solvent, and the ^{13}C NMR spectrum of the
product solution (Fig. 4) is identical to that of the original
Co(tacn)(aeaps)$^{3+}$, except that the resonance line at 31.80
ppm is now positive and splits up into a triplet, slightly
shifted to lower frequency (31.72 ppm). This is evidence for
a CHD group, since CH will give a positive signal (deute-
rium will not affect the phase of the ^{13}C resonance signal
because there are no pulses with the resonance frequency
of deuterium) and the triplet is caused by scalar coupling to
deuterium (spin $I = 1$). Deuterium has a rather small
quadrupole moment ($Q = 0.28 \times 10^{-30}$ m^2), and therefore a
splitting due to scalar coupling is usually seen. This means
that a CHD group is now introduced to the aeaps ligand:
NH$_2$CH$_2$CH$_2$S–CHD–CH$_2$CH$_2$NH$_2$ (aeaps-d$_1$). It should be
noted that the resonance frequency of the CHD carbon
atom confirms the assignment in Ref. 2 of the C4 carbon
atom. The experiment shows that the reaction is reversible,
and that the re-formation of the sulfur species is followed
by a stereospecific deuteration of the aeaps ligand.

The formation of the alkyl complex in 1 M NaOD using
D$_2$O, described above for Co(tacn)(aeaps)$^{3+}$, was repeated
using the CHD isomer, Co(tacn)(aeaps-d$_1$)$^{3+}$, and the ^{13}C
DEPT NMR spectrum was found to be equal to that of the
alkyl compound made from the undeuterated species, i.e.
no difference in the amplitudes of the cobalt-bound carbon
atom could be observed. Since the amplitude of a CD
group is zero in a ^{13}C DEPT NMR spectrum, it can be
concluded that a deuteron, and not a proton, is lost when
Co(tacn)(aeaps-d$_1$)$^{3+}$ reacts to give the alkyl compound.

In summary, these experiments show that during the
equilibration reaction *one specific* hydrogen atom of the
CH$_2$ group *remains* on the carbon; the other C–H bond is
broken when the alkyl complex is formed, and the same
C–H bond is re-formed when the reaction goes back. These
experiments, however, do not distinguish between a fast
exchange reaction preceeding the alkyl formation and a
simultaneous C–H bond-breaking and Co–C bond-making
reaction. The former situation was shown to be the case, as
described in the following.

The reaction of Co(tacn)(aeaps)$^{3+}$ in 1 M NaOD during
the early reaction stage was followed by ^{13}C NMR. It was
readily established that the CHD-deuterated isomer of
Co(tacn)(aeaps)$^{3+}$ is formed quantitatively and prior to the
formation of the alkyl complex. The exchange reaction is
fast ($t_{1/2} = 111$ s^{-1} at 25 °C) compared to the time required
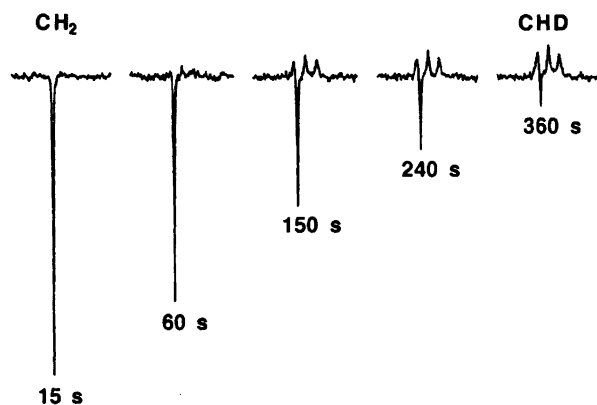to obtain a good quality spectrum; therefore the reaction

CH₂

CHD

360 s

240 s

150 s

60 s

15 s

Fig. 5. Exchange of H⁺ with D⁺ at the C4 carbon atom in the coordinated aeaps ligand (N–C1–C2–S–C4–C5–C6–N): ^{13}C DEPT NMR spectrum of 0.2 M Co(tacn)(aeaps)Cl₃ in 1 M NaOD at 25 °C as a function of time.

was studied by quenching of the basic product solutions by addition of an excess of acid. The change of the ^{13}C DEPT NMR spectra with time is shown in Fig. 5. It is seen that the resonance line for CH_2 disappears and that at the same time a resonance line for CHD appears. The exchange is 80 times faster than the formation of the alkyl compound, and the minor amount of the latter formed during the exchange reaction can therefore be ignored. The intensities of the resonance lines were taken as a measure of the relative concentrations, and the rate constants were calculated (Fig. 6 and Table 4). These data and additional measurements in 0.5 M NaOD, 0.5 M NaNO₃ are discussed in the following section.

Finally, no other proton in Co(tacn)(aeaps)³⁺ exchanges within the time scale for the formation of the alkyl compound, as shown from integrated ^{13}C NMR spectra and ^{13}C DEPT NMR spectra, and similarly, no proton exchange could be observed within one week for a solution of the alkyl compound in 1 M NaOD at 25 °C.

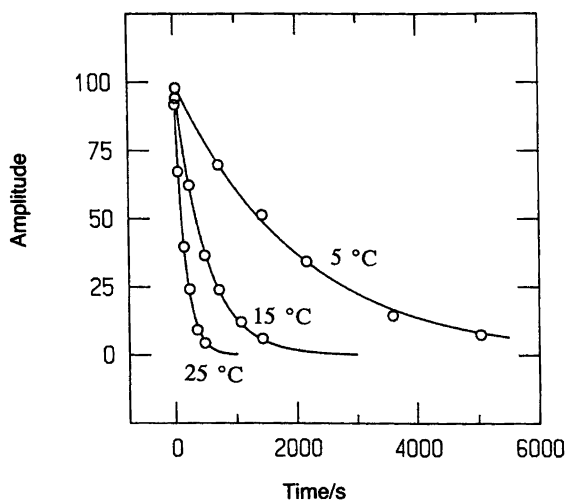*Interpretation of the kinetic data.* As discussed in the pre-

Fig. 6. Determination of the pseudo first-order rate constant, k_{ex}, for the exchange reaction in Fig. 5. See also Table 4.

Table 4. Kinetic data for the exchange reaction C–H/C–D in 1 M NaOD determined by ^{13}C NMR spectroscopy.

$T/°C$	$[OD^-]^a/M$	$k_{ex}(obs)/s^{-1}$	$k_{ex}(calc)^b/s^{-1}$
25.0	0.836	0.006 21	0.006 39
15.0	0.847	0.002 01	0.001 90
5.0	0.861	0.000 495	0.000 509

^{a}The concentrations of deuteroxide were calculated using K_b given in Table 5. ^{b}The values of k_{ex}(calc) have been obtained by non-linear regression analysis using eqn. (8), which gave the kinetic data for k_1^{OD} in Table 5.

vious sections, the stoichiometry of the reaction is expressed by eqns. (1) and (2). Initially, the reaction was studied only at low $[OH^-]$ in order to eliminate possible complications due to ion-pair formation between the cationic sulfur complex and hydroxide ions. This goal was apparently achieved, since we found that the dependence of k_{obs} on the hydroxide concentration in this region followed a simple expression shown in eqn. (3). This was

$$k_{calc} = \frac{a[OH^-]}{b + [OH^-]} + c \tag{3}$$

interpreted in terms of two acid–base pre-equilibria followed by a rate-determining equilibration between the sulfur- and carbon-bonded species as shown in Scheme 1, which leads to eqn. (4), which is of the same form as that in eqn. (3).

$$k_{calc} = \frac{k_2 K_1 K_b(NH)[OH^-]}{[OH^-] + K_b(NH)} + k_{-2} \tag{4}$$

Eqn. (4) has been derived assuming that both acid–base equilibria are much faster than the subsequent formation of the alkyl species. For the sake of simplicity the formation of the carbanion has been formulated as arising from the sulfur-bonded amine complex, rather than a rearrangement of the sulfur-bonded amido complex, which would lead to the same kind of expression as that in eqn. (4). The inclusion of the equilibrium involving the carbanion is *not* required to obtain an expression of the form in eqn. (3), but since it is postulated later we include it at this stage in order to simplify the subsequent discussion. Alternative mechanisms are discussed at the end of this section.

However, in order to study the possible influence by ion pairing we extended our measurements to include high concentrations of hydroxide, and now found that the increase in k_{obs} with increasing $[OH^-]$, is followed, at large $[OH^-]$, by a dramatic decrease in k_{obs}. For each ionic strength ($I = 1.0$ and 5.0 M) it was found that the maximum k_{obs} value occurs for $[OH^-] \sim [X^-]$ as shown in Figs. 7 and 8 (X^- is the anion of the electrolyte used to keep a constant salt-medium, ClO_4^- or NO_3^-). Preliminary kinetic data using 2 M NaClO₄ likewise gave a maximum k_{obs} for $[OH^-] \sim [ClO_4^-]$. The similarity in behaviour in these different solvents strongly indicates that the decrease in rate is
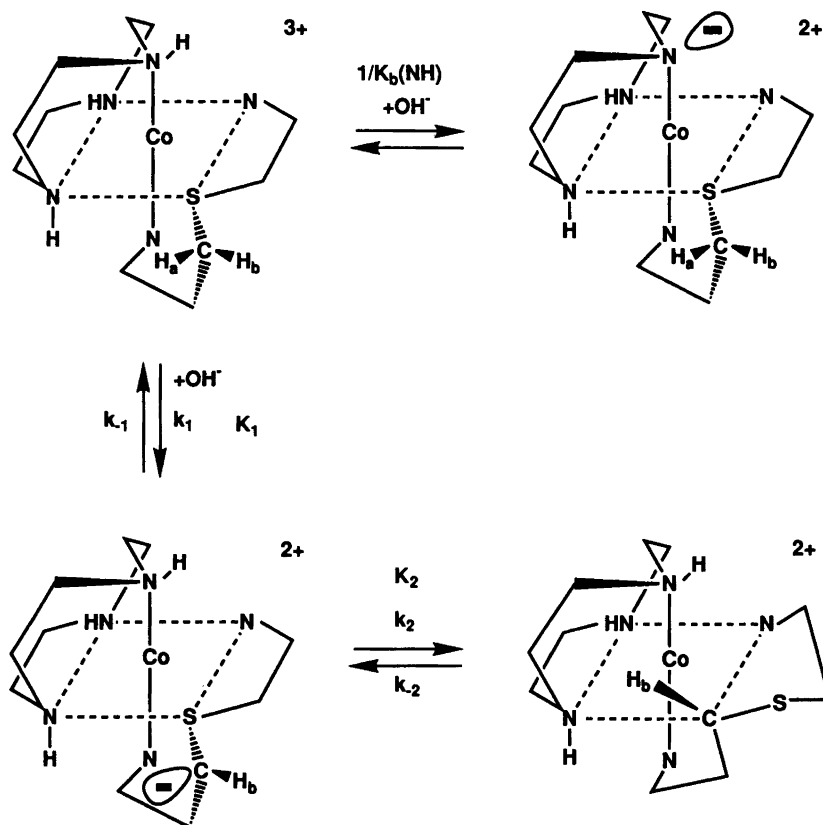
Scheme 1. Simplified reaction scheme for the equilibration reaction. The site for deprotonation of the amine is not known, but is here assumed to be one of the tacn nitrogens. The hydrogen atoms here designated H_a and H_b may also be characterized as axial and equatorial, respectively. H_a is the labile hydrogen atom.

due to a competition between OH^- and X^-, and ion pairing offers a simple explanation for this phenomenon. This is shown in Scheme 2, which is an extension of Scheme 1 supplemented with the possible ion pairs. It is noted that
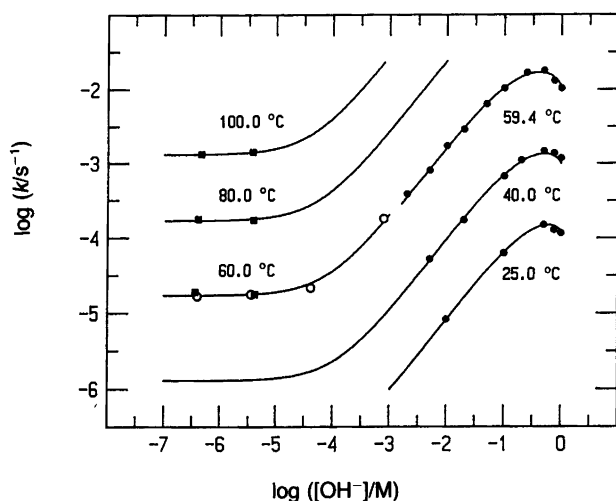
the reaction scheme contains only ion-paired complex cations. A model similar to that shown in Scheme 2, but with unpaired and hydroxide ion-paired cations as the reactive species (i.e. with the perchlorate ion pair ignored), was rejected on the grounds that, in the following calculations, it gave a negative value for one of the rate constants. Although two acid–base equilibria, $K_b^{ClO_4}(NH)$ and $K_b^{OH}(NH)$, are postulated in Scheme 2, the spectroscopic

Fig. 7. Observed and (solid lines) values of the pseudo first-order rate constant for the equilibration reaction shown in Schemes 1 and 2 and studied at $I = 1.0$ M determined spectrophotometrically starting with the sulfur-bonded complex (●) and determined spectrophotometrically (■) or by IE-HPLC (○) starting with the carbon-bonded complex.

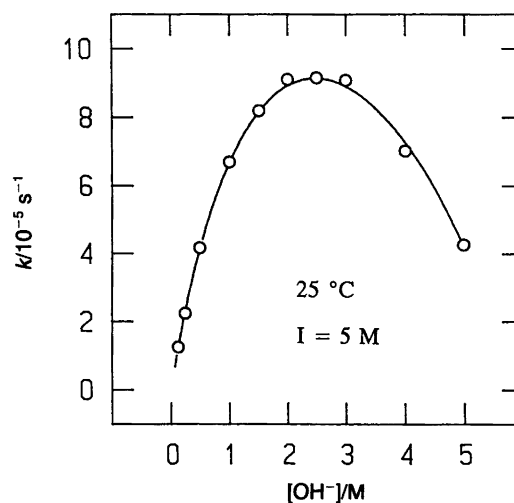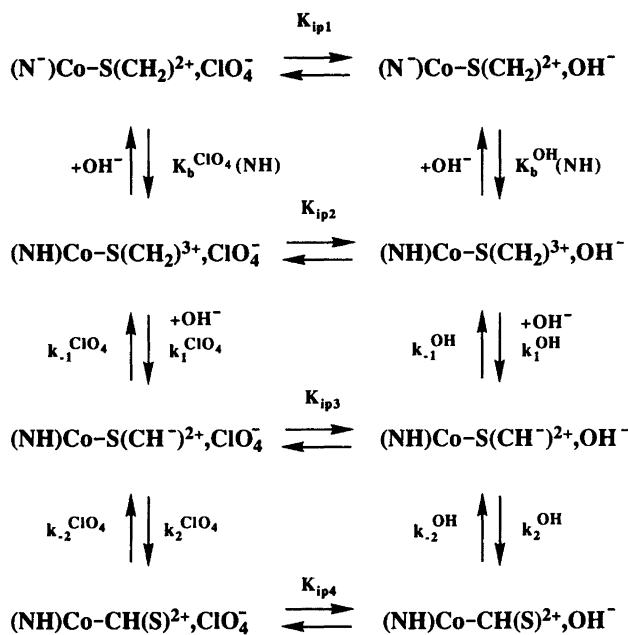*Fig. 8.* Observed (○) and calculated (solid line) values for the formation of the alkyl complex in 5 M $NaNO_3$ at 25 °C.

1155

$$K_{ip1}$$

$(N^-)Co-S(CH_2)^{2+},ClO_4^-$ ⇌ $(N^-)Co-S(CH_2)^{2+},OH^-$

$+OH^-$ ↕ $K_b^{ClO_4}(NH)$ $+OH^-$ ↕ $K_b^{OH}(NH)$

$$K_{ip2}$$

$(NH)Co-S(CH_2)^{3+},ClO_4^-$ ⇌ $(NH)Co-S(CH_2)^{3+},OH^-$

$k_{-1}^{ClO_4}$ ↕ $k_1^{ClO_4}$ k_{-1}^{OH} ↕ k_1^{OH}

$$K_{ip3}$$

$(NH)Co-S(CH^-)^{2+},ClO_4^-$ ⇌ $(NH)Co-S(CH^-)^{2+},OH^-$

$k_{-2}^{ClO_4}$ ↕ $k_2^{ClO_4}$ k_{-2}^{OH} ↕ k_2^{OH}

$$K_{ip4}$$

$(NH)Co-CH(S)^{2+},ClO_4^-$ ⇌ $(NH)Co-CH(S)^{2+},OH^-$

Scheme 2. Proposed reaction scheme for the equilibration reaction. It is noted that this scheme contains the same reactions as shown in Scheme 1, but for each complex ion extended with equilibria between ion pairs with hydroxide and perchlorate, respectively.

data could be interpreted in terms of one single acid–base equilibrium, and gave a well defined equilibrium constant, K_b. This means that there cannot be a significant difference between the former constants, and it is therefore assumed that $K_b^{ClO_4}(NH) = K_b^{OH}(NH) = K_b(NH)$.

From the relation $K_b^{ClO_4}(NH)K_{ip2} = K_b^{OH}(NH)K_{ip1}$ it then follows that $K_{ip1} = K_{ip2} = K_{ip}$. These approximations simplify the interpretation of the kinetic data significantly, and the rate-expression for the equilibration reaction is shown in eqns. (5)–(7). It is noted that eqn. (5) contains

$$k_{calc} = \frac{\{[ClO_4^-]k_f^{ClO_4} + [OH^-]K_{ip}k_f^{OH}\}[OH^-]K_b(NH)}{\{K_b(NH) + [OH^-]\}\{[OH^-]K_{ip} + [ClO_4^-]\}} + k_{-2}^{ClO_4}$$

(5)

$$k_f^{ClO_4} = k_2^{ClO_4}K_1^{ClO_4}$$

(6)

$$k_f^{OH} = k_2^{OH}K_1^{OH}$$

(7)

only one term for the back-reaction, $k_{-2}^{ClO_4}$. The contribution from the k_{-2}^{OH} path can be ignored, since re-formation of the sulfur-bonded complex will only contribute significantly to the rate expression at low pH, where the concentration of hydroxide ion pairs is negligible.

Eqns. (5)–(7) have four unknown, independent parameters: $k_f^{ClO_4}$, k_f^{OH}, $k_{-2}^{ClO_4}$ and K_{ip} [i.e. eight parameters when the temperature dependence is included; $\Delta H°(K_b)$ and $\Delta S°(K_b)$ have been determined previously]. These parameters were then determined from the kinetic data at $I = 1.0$ M, using the method of non-linear least-square minimization, and the result is shown in Fig. 7 and Tables 3

Table 5. Summary of kinetic and thermodynamic data for the reactions in Scheme 2 at 25 °C and $I = 1.0$ M.[a]

Constant	Value	$\Delta H^{\ddagger}$, $\Delta H°$ or $\Delta H^{\ddagger} - \Delta H°$ / kJ mol^{-1}	$\Delta S^{\ddagger}$, $\Delta S°$ or $\Delta S^{\ddagger} - \Delta S°$ / J mol^{-1} K^{-1}
$k_f^{ClO_4}/M^{-1}$ s^{-1} [b]	8.22(42)×10^{-4}	125.8(16)	117.8(49)
k_f^{OH}/M^{-1} s^{-1} [b]	4.11(30)×10^{-4}	120.2(27)	93.3(85)
$k_{-2}^{ClO_4}/s^{-1}$	1.47(15)×10^{-7}	109.5(18)	−8.6(51)
k_1^{OD}/M^{-1} s^{-1}	3.17(21)×10^{-2}	99.1(34)	58.9(119)
$K_f^{ClO_4}/M^{-1}$ [c]	5.59(67)×10^3	16.3(24)	126.4(72)
K_{ip}	0.84(36)	0.7(135)	1(42)
$K_b(NH)^d$	0.433(13)	−19.7(9)	−73(3)
$K_b(ND)^e$	0.266(13)	−19.8(16)	−77(6)

[a] The numbers in parentheses in this and the following tables are the standard deviation given in units of the last digit.
[b] $k_f = k_2K_1$ and $\Delta H = \Delta H^{\ddagger}(k_2) - \Delta H°(K_1)$. [c] $K_f = K_1K_2$. [d] In H$_2$O, from Ref. 2. [e] In D$_2$O, this work.

and 5. There is good agreement between the observed and calculated rate constants (Table 3 and Fig. 7), and all rate constants are well defined, while the parameter K_{ip} has a relatively large standard deviation (Table 5). From the rate constants referring to perchlorate ion pair it is now possible to determine the equilibrium constant $K_f^{ClO_4} = K_1K_2 = k_f^{ClO_4}/k_{-2}^{ClO_4}$ and its parameters $\Delta H°$ and $\Delta S°$ (Table 5). It is seen that there is excellent agreement between the thermodynamically determined value $K_f^{ClO_4} = 1.18 \times 10^4$ M^{-1} (60 °C) (determined independently of the kinetic data using IE-HPLC, Table 2) and the value calculated here from the kinetic data, $K_f^{ClO_4} = 1.11 \times 10^4$ M^{-1} (60 °C). The value K_f^{OH} cannot be determined, since the rate term k_{-2}^{OH}, as mentioned, does not contribute significantly to the kinetic data at any pH.

The kinetic data for $I = 5.0$ M were obtained only for one temperature (25 °C), and in all experiments the hydroxide ion concentrations were so large that the formation of the alkyl complex was nearly quantitative (>99 %), i.e. k_{-2} can be ignored. With the relevant modifications these data were then treated as described above, which gave the rate constants shown in Table 6. Also in this case there is good agreement between the observed and calculated rate constants (Fig. 8), and all constants are seen to be well defined (Table 6).
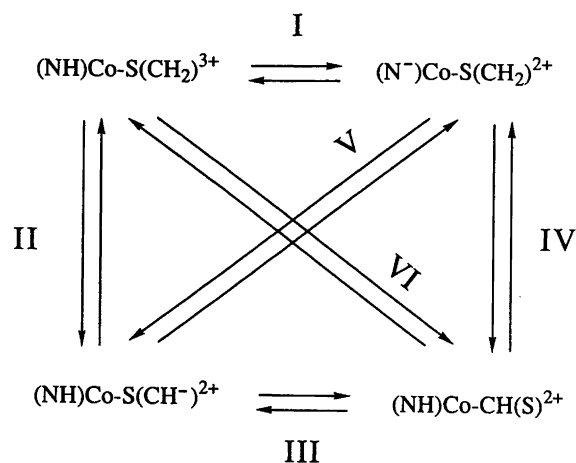
As mentioned at the beginning, it is not possible alone on the basis of the kinetic data shown in Fig. 7 (and 8) to

Table 6. Kinetic and thermodynamic data for the formation of the alkyl complex in 5 M NaNO$_3$ at 25 °C.

Constant[a]	Value
$k_f^{NO_3}/M^{-1}$ s^{-1}	1.05(13)×10^{-4}
k_f^{OH}/M^{-1} s^{-1}	2.61(6)×10^{-5}
K_{ip}/M	0.63(4)
$K_b(NH)/M^b$	2.38(22)

[a] Defined analogously to the corresponding constants in Table 5.
[b] In 5 M NaNO$_3$, from Ref. 2.

I

$$(NH)Co\text{-}S(CH_2)^{3+} \rightleftharpoons (N^-)Co\text{-}S(CH_2)^{2+}$$

$$\begin{array}{cc} II & IV \end{array}$$

$$(NH)Co\text{-}S(CH^-)^{2+} \rightleftharpoons (NH)Co\text{-}CH(S)^{2+}$$

III

Scheme 3. Summary of possible reaction pathways for the equilibration reaction.

exclude other reaction schemes. However, the additional kinetic information obtained by the ^{13}C NMR deuterium-exchange experiments provides strong evidence that the mechanism in Scheme 2 is correct as discussed in the following. The reaction mechanisms considered are combined in Scheme 3, and for the sake of simplicity no discrimination between different ion pairs has been made. The limiting cases may be divided into those where the carbanion is a reactive intermediate and those where the carbanion does not react further. In the latter cases, the alkyl complex is formed either by the rearrangement reaction (IV) or by a concerted mechanism (VI), and neither of these seems very probable: it is not very likely that a carbanion complex should be less reactive than the amido comples as a precursor to the alkyl complex, and a concerted mechanism is rejected, since it seems difficult to rationalize this path in a mechanistic way. Therefore, it is assumed that the reactive intermediate is a carbanion species. This leaves us with mechanisms involving paths (I)–(III) and (V) in Scheme 3, and two limiting cases will give a rate-expression of the observed form: (i) a rapid pre-equilibrium [(I) and (II)] followed by a rate-determining rearrangement of the carbanion to form the alkyl species (III); (ii) a slow, rate-determining formation of the carbanion [paths (II) and/or (V)] followed by a rapid formation of the product [path (III)]. The latter mechanism implies that the carbanion is captured by the cobalt (III) center much faster than it reacts with water (or D_2O), which is in conflict with the deuterium exchange results, and therefore this mechanism can be ignored completely. In contrast, mechanism (i) requires all C–H$_a$ (Scheme 1) to be exchanged before any significant amount of the product has been formed, which is in agreement with the ^{13}C NMR exchange experiments. The exchange reaction, which takes place via the formation of carbanion (which is formed in stoichiometrically negligible amounts) may occur either by direct deprotonation of C–H by reaction with OH$^-$ [path (II)] or by rearrangement of the amido complex [path (V)].

From the present data it is impossible to distinguish these two pathways, and in principle they could both contribute to the exchange reaction. In the following we shall, for the sake of clarity, discuss the results in terms of path (II), i.e. the mechanism shown in Scheme 2, and then later return to the alternative pathway, (V).

The rate constants determined for the C–H/C–D exchange, k_{ex}, may now be interpreted as shown in eqn. (8).

$$k_{ex}(calc) = \frac{k_1^{OD}[OD^-]K_b^{OD}(ND)}{[OD^-] + K_b^{OD}(ND)} \tag{8}$$

Since the exchange experiments have been made using 1 M NaOD in D_2O, the constants in eqn. (8) are those referring to ion pair with OD$^-$ exclusively. The rate constant k_1^{OD} is defined similarly to k_1^{OH}, and $K_b^{OD}(ND)$ is the base dissociation constant in D_2O defined similarly to $K_b^{OH}(NH)$. It is noted that k_1^{OD} and $K_b^{OD}(ND)$ both refer to the reactions of the fully N-deuterated cobalt(III) complex. The base dissociation constant $K_b^{OH}(ND)$ and its associated thermodynamic parameters have been determined in this study (Tables 1 and 5). The rate constant k_1^{OD} and its activation parameters were then calculated from the three values of k_{ex} determined at 5.0, 15.0 and 25.0 °C, using eqn. (8) and non-linear regression analysis (see Tables 4 and 5). The actual concentration of OD$^-$ given in Table 4 was calculated from the solution stoichiometry and the value of $K_b^{OD}(ND)$.

A single experiment at lower [OD$^-$] gave the value $k_{ex} = 3.49 \times 10^{-3}$ s^{-1} (25 °C, 0.5 M NaOD, 0.5 M NaNO$_3$), which is very close to the value 4.92×10^{-3} s^{-1} calculated from eqn. (8), and thereby supports the proposed reaction scheme. A minor deviation is expected because of a possible different reactivity of hydroxide and nitrate ion pairs. Sodium nitrate was used in this experiment due to a low solubility of the cobalt(III) species in perchlorate media.

Following the discussion above it is possible to obtain only upper limit estimates for second-order rate constants for the base-catalyzed dissociation of the less reactive C–H groups in Co(tacn)(aeaps)$^{3+}$, $k < 10^{-5}$ M^{-1} s^{-1}, and for those of the alkyl complex, $k < 10^{-8}$ M^{-1} s^{-1}. The establishment of the former of these estimates is restricted by the fact that the complex in the basic solution undergoes conversion into the alkyl complex, thereby limiting the time-scale for studying a possible exchange of the less acidic protons.

From the results above it may be concluded that it is the carbanion, formed during the initial exchange reaction, which is the reactive species. Also it can be concluded that the carbanion does not undergo inversion within the time-scale of the experiment, since this would have resulted in exchange of both methylene protons. The question as to which of the two protons (H$_a$ and H$_b$) that is exchanged is discussed below.

The carbanion formed by dissociation of H$_a$ (Scheme 1) has the proper geometry for formation of an alkyl species with the configuration found in the crystal structure. In
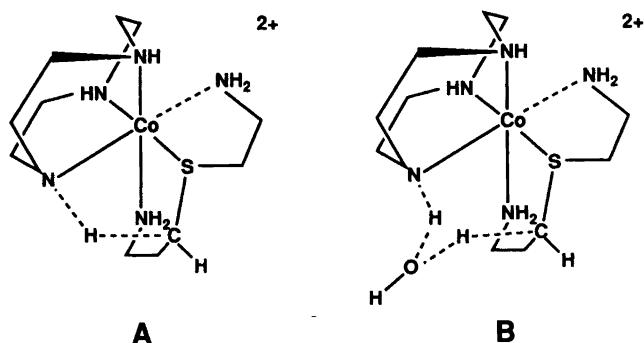
Fig. 9. Possible transition-state structure for the case when the carbanion is formed by an intramolecular proton transfer between CH_a and the amido ligand [reaction (V) in Scheme 3] by either a direct (A) or a water-assisted (B) proton transfer. The distance between C and N is 3.5 Å in $Co(tacn)(aeaps)^{3+}$ as calculated from the crystallographic data in Ref. 2.

contrast, the carbanion formed by dissociation of H_b leads to an alkyl species which has a configuration different from that observed in the crystal structure; also it is noted that this structure is sterically hindered. As pointed out above, it is certain that the carbanion itself does not undergo inversion, but a hypothetical reaction involving dissociation of H_b with concomitant inversion to form the alkyl complex cannot be rejected on the basis of the experimental facts. However, in this case the lone pair of the carbanion points away from the cobalt(III) center, and it seems difficult to find the driving force for such a reaction.

The simplest and most straightforward interpretation, in complete agreement with all experiment facts, therefore seems to be that the labile proton is the axial proton, designated H_a in Scheme 1, and that the carbanion formed by dissociation of this proton does not undergo inversion and reacts with retention to give the alkyl species.

The dissociation of the labile proton (H_a) in the Co–S species may be compared with base-catalyzed dissociation of the two glycine methylene protons (H_a and H_b) in $Co(en)_2(gly)^{2+}$. In this case both protons have been reported to dissociate with almost equal rate, $k = 3.2 \times 10^{-2}$ and $2.8 \times 10^{-2} M^{-1} s^{-1}$, respectively (25 °C).[8] The specificity in the glycine case is negligible compared with that observed in the present case (k_{H_a}/k_{H_b} being 1.04 and >80, respectively), and may, at least in part, be ascribed to the difference in stereochemistry: in the glycine complex the glycinato chelate is nearly planar and hence the two hydrogen atoms are nearly identical, while in the aeaps complex the trimethylene ring is puckered and the two hydrogen atoms are different, and may clearly be assigned as axial (H_a) and equatorial (H_b), respectively. The two rate constants reported for the glycine complex are only slightly larger than the value for the aeaps complex. Considering the charge differences of the cations, this strongly indicates that the labilizing effect of coordinated carboxylate is greater than that of a coordinated sulfur group. The labilizing effect of COO groups upon the acidity of CH groups is well known. Sulfur groups exhibit a similar effect and this may

be illustrated by the fact that Me_3S^+ exchanges protons 2×10^7 times faster than Me_4N^+.[9,10] Since nitrogen is more electronegative than sulfur, the large difference in the latter case cannot be explained by an inductive effect, and has been attributed to hyperconjugation, i.e. donation of electrons from carbon to empty, low-lying d-orbitals at sulfur.[9] In a cobalt(III) complex the sulfur attains sulfonium character by donation of electrons to the metal center and the labilizing effect may thus be explained by donation of electrons from carbon to p-orbitals at the sulfonium group. It seems likely that the influence upon the axial and equatorial hydrogen atoms would be different, thereby providing an explanation for the observed stereospecificity, as discussed further in Ref. 2.

The composite term for the formation reaction, $k_f^{OH} = k_2^{OH} K_1^{OH} = k_1^{OH} k_2^{OH}/k_{-1}^{OH}$, and the rate constant k_1^{OD} may now be combined to calculate a rough estimate for the ratio k_{-1}^{OH}/k_2^{OH} (referring to the hydroxide ion pair, only) as shown in eqn. (9). It should be noted that this expression

$$\frac{k_{-1}^{OH}}{k_2^{OH}} = \frac{k_1^{OH}}{k_f^{OH}} \sim \frac{k_1^{OD}}{k_f^{OH}} = 77 \ (25\,°C) \tag{9}$$

has been derived assuming that k_1^{OH} is equal to k_1^{OD}, and therefore ignores solvent effects (H_2O/OH^- versus D_2O/OD^-) and secondary isotope effects (NH versus ND). These effects are likely to be small in the present context. With these restrictions we therefore conclude that the carbanion reacts with water 80 times faster than it is captured by the cobalt(III) center.

Alternative pathway for the carbanion formation, path (V) in Scheme 1. In the above discussion the formation of the carbanion has been assumed to occur by a second-order reaction between hydroxide and $Co(tacn)(aeaps)^{3+}$, but, as mentioned, it is not possible on the basis of the present data to distinguish this pathway from an intramolecular reaction in which the amido species rearranges to the carbanion [(V) in Scheme 3]. In the following the latter possibility will be discussed.

The site of the lone pair in the amido ion is not known, but it has been suggested[2] that it is placed at the triazacyclonane ligand. In Scheme 1 the lone pair has been placed on an arbitrarily chosen nitrogen ligator, but it seems reasonable to assume that the amido species should be correctly described in terms of an equilibrium mixture between all three possible monodeprotonated species (at tacn, and possibly also including the species formed by monodeprotonation of the aeaps ligand).

In one of these amido species the lone pair has a direction toward the labile proton, CH_a, and it seems possible that the carbanion could be formed by an intramolecular proton transfer from CH to N^-, as illustrated in Fig. 9, which shows two possible transition-state structures for this reaction. A similar reaction is not possible for the other proton, CH_b, and thereby this mechanism explains in a simple way the very large reactivity difference between the

two methylene protons. The rate constant for the intramolecular reaction of the amido complex to form the carbanion (k_1') is obtained from the data in Table 5 using the relation $k_1' = k_1 K_b(\text{ND}) = 8.4 \times 10^{-3} \text{ s}^{-1}$ at 25 °C (for OD⁻ ion-pairs).

Summary

Our previous study of the reactions of Co(aeaps)$_2^{3+}$ gave a very complicated set of kinetic data. In order to simplify the kinetics we initiated a study of the more simple system obtained by substitution of one of the aeaps ligands with 1,4,7-triazacyclononane. The present study shows that this goal has been achieved.

It is shown that the Co–S bonded complex (and its N-deprotonated amido base) and the Co–C bonded complex form an equilibrium with no significant production of other species. The kinetic data unambiguously show that the equilibration occurs with an intermediate formation of a carbanion complex. Also it is shown that at high [OH⁻] the different reactivity of ion pairs with perchlorate and hydroxide, respectively, plays an important role.

The ¹³C NMR H/D-exchange studies unambiguously show that the equilibration reaction involves a stereospecific C–H bond cleavage and bond formation of only one of the two methylene protons on the carbon atom which participate in the Co–C bond. From kinetic data it is estimated that the carbanion reacts with water 80 times faster than it is captured by cobalt(III).

Neither in Co(tacn)(aeaps)$^{3+}$ nor in Co(tacn)(C-aeaps)$^{2+}$ was exchange of other C–H observed within the timescale for the equilibration reaction.

We conclude that the most simple reaction scheme which describes the kinetics of the equilibration reaction and the NMR exchange experiments is that shown in Scheme 2. However, the model is approximative in the sense that the assumption that $K_b^{\text{ClO}_4}(\text{NH}) = K_b^{\text{OH}}(\text{NH})$ ($K_{ip1} = K_{ip2}$) is probably not strictly correct. The good agreement between

experiment and model, however, indicates that the error is small. The ambiguity concerning the two different reaction paths, (II) and (V), for the formation of the carbanion has not been eliminated. In the first part of the discussion above (Schemes 1 and 2 and Table 5) we have assumed that the carbanion is formed exclusively as a second-order reaction between Co(tacn)(aeaps)$^{3+}$ and hydroxide ions. In the last part of the discussion, however, it is shown that formation of the carbanion by rearrangement of the amido ion might offer an explanation for the large difference in reactivity of the two methylene protons H$_a$ and H$_b$ (Fig. 9). Independently of the mechanism for the formation of the carbanion it was previously shown that the electronic properties of sulfur-bonded species may explain the different reactivities of the two protons.[2]

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