

# Thermodynamic and Kinetic Studies of the Equilibration between the Sulfur- and Carbon-Bonded Forms of a Cobalt(III) Complex with the Ligands 2-Aminoethyl-3-aminopropyl-sulfide and 1,1,1-Tris(aminomethyl)ethane

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A thermodynamic and kinetic study of the equilibration between the Co–S bonded complex  $\text{Co}(\text{tame})(\text{S-aeaps})^{3+}$  and the Co–C bonded complex  $\text{Co}(\text{tame})(\text{C-aeaps})^{2+}$  is reported (tame = 1,1,1-tris(aminomethyl)ethane, aeaps = 2-aminoethyl-3-aminopropylsulfide = 3-thiahexane-1,6-diamine and C-aeaps = 1,6-diamino-3-thiahexan-4-ide anion). Kinetic and thermodynamic data have been obtained using UV–VIS spectroscopy, IE-HPLC and  $^{13}\text{C}$  NMR ( $[\text{OH}^-] = 4 \times 10^{-5} - 1.0 \text{ M}$ ,  $T = 25.0 - 100^\circ\text{C}$ ,  $I = 1.0 \text{ M}$ ). The kinetic data have been interpreted in terms of different reactivity of ion pairs with perchlorate and hydroxide, respectively. Rate constants and activation parameters for the formation of the cobalt–alkyl complex from 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 data have been interpreted in terms of the intermediate formation of a carbanion, and this was strongly supported by  $^{13}\text{C}$  NMR CH/CD-exchange studies. The  $\text{Co}(\text{tame})(\text{aeaps})^{3+}$  cation exchanges one C–H proton, and only one, prior to the formation of the cobalt–alkyl complex. The subsequent reaction of the partially C-deuterated ( $-\text{N}-\text{CH}_2-\text{CH}_2-\text{CHD}-\text{S}^-$ ) cobalt–sulfur complex to form the cobalt–alkyl complex gave complete loss of deuterium. From the kinetic data it is estimated that the carbanion reacts with water 170 times faster than it is captured by cobalt(III).

It was previously shown<sup>1</sup> that the cobalt(III) complex  $\text{Co}(\text{aeaps})_2^{3+}$  (aeaps = 2-aminoethyl-3-aminopropyl sulfide = 3-thiahexane-1,6-diamine) reacts in aqueous basic solution forming a cobalt–alkyl complex  $\text{Co}(\text{aeaps})(\text{C-aeaps})^{2+}$  (C-aeaps = 1,6-diamino-3-thiahexan-4-ide-anion). The cobalt–alkyl complex was isolated as the dithionate salt and characterized by a single-crystal X-ray diffraction study.<sup>1</sup> Kinetic data for this reaction were reported, but a detailed mechanistic interpretation of the kinetic data was not achieved. More recently it was shown that the related complex in which one of the ligands in  $\text{Co}(\text{aeaps})_2^{3+}$  has been substituted with the inert tripodal ligand tacn (1,4,7-triazacyclononane) reacts similarly.<sup>2</sup> It was shown that in basic solution  $\text{Co}(\text{tacn})(\text{aeaps})^{3+}$  equilibrates fast

with its alkyl derivative  $\text{Co}(\text{tacn})(\text{C-aeaps})^{2+}$ . A detailed thermodynamic and kinetic study has been reported.<sup>3</sup> It was shown that  $\text{Co}(\text{tacn})(\text{aeaps})^{3+}$  exchanges one methylene proton, and only one, prior to the formation of the alkyl complex. The labile methylene proton is bound to the carbon atom which in the alkyl complex is bound to cobalt(III). From  $^{13}\text{C}$  NMR experiments in  $\text{D}_2\text{O}$  it was shown that the labile proton is lost when the alkyl complex is formed. Recently<sup>4</sup> the corresponding tame complex has been isolated,  $[\text{Co}(\text{tame})(\text{aeaps})]\text{Cl}_3 \cdot \text{H}_2\text{O}$ , and it reacts in base, as anticipated, to form the cobalt–alkyl complex, which was isolated as  $[\text{Co}(\text{tame})(\text{C-aeaps})](\text{ClO}_4)_2$  in high yield [tame = 1,1,1-tris(aminomethyl)ethane]. The tame alkyl complex was characterized by a crystal structure obtained from single-crystal diffraction data and preliminary thermodynamic and kinetic data were given. In the present

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paper 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.** [Co(tame)(aeaps)]Cl<sub>3</sub>·H<sub>2</sub>O and [Co(tame)(C-aeaps)]S<sub>2</sub>O<sub>6</sub> were prepared as described previously.<sup>4</sup> Deuterium oxide (99.8 atom % D) and sodium deuterioxide (40% solution in D<sub>2</sub>O, 99 atom % D) were obtained from Sigma. All other reagents were of analytical grade and CO<sub>2</sub>-free doubly deionized water was used for all measurements. Potentiometric pH measurements were made as described previously.<sup>2</sup> A Perkin-Elmer diode array spectrophotometer, LA 3048, and a Cary 3 spectrophotometer were used for spectral measurements. Ion-exchange high-performance liquid chromatography was performed using Waters IE-HPLC system connected to a diode array detector. A Waters Protein Pak SP-5PW cation exchanger was used with 0.19 M Na<sub>2</sub>SO<sub>4</sub> as eluent. The flow rate was normally 1.0 ml/min. All HPLC experiments were made at a column temperature of 25 °C. <sup>13</sup>C NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer equipped with a 5 mm probe. <sup>13</sup>C DEPT NMR spectra were used to study the CH/CD exchange reaction.

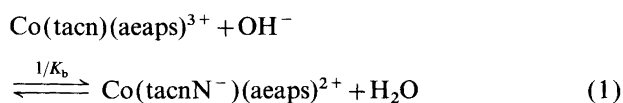
**Determination of the equilibrium constant  $K_f = K_1K_2$ .** Analysis by IE-HPLC of mixtures of the sulfur- and carbon-bonded species gave chromatograms with well separated peaks for the two cations. The chromatograms were monitored at 291 nm, since at this wavelength the molar absorbancies of the two species are similar. Equilibrium solutions were obtained by heating ammonia/ammonium buffer solutions of the sulfur-bonded species to 40.0, 60.0, 80.0 and 100.0 °C, respectively. The solutions were heated for different times and then analyzed by IE-HPLC. When additional heating did not change the chromatograms it was assumed that equilibrium had been attained. In one case this was further confirmed by the observation that the same chromatograms were obtained for solutions initially containing either [Co(tame)(aeaps)]Cl<sub>3</sub>·H<sub>2</sub>O or [Co(tame)(C-aeaps)]S<sub>2</sub>O<sub>6</sub>. The concentrations of the two species, [Co(tame)(aeaps)]<sup>3+</sup> and [Co(tame)(C-aeaps)]<sup>2+</sup>, were calculated from the relative peak areas as described previously.<sup>3,5</sup> The pH values of the equilibrium solutions were calculated using published pK<sub>a</sub> values for NH<sub>4</sub><sup>+</sup>.<sup>6</sup>

**Kinetic measurements.** The kinetic experiments were made using spectrophotometry as described previously.<sup>3,6</sup> The data were interpreted in terms of a single pseudo-first-order reaction. The pseudo-first-order rate constants,  $k_{\text{obs}}$ , were calculated on the basis of absorbances measured at 111 and 251 different wavelengths, respectively, in the region 240–350 nm ( $C_{\text{Co}} = 6 \times 10^{-5}$  M) or in the region 350–600 nm ( $C_{\text{Co}} = 4 \times 10^{-3}$  M). A kinetic experi-

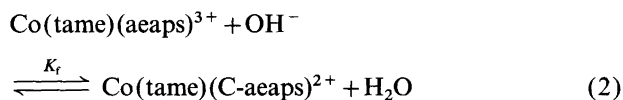
ment typically included 40–90 spectra recorded during seven half-lives. Most of the experiments were conducted under anaerobic conditions, i.e. the two solutions containing the cobalt(III) complex and the base, respectively, were flushed with nitrogen 1 h before mixing, and the reactant solution was then transferred to the cell under anaerobic conditions.

## Results

**Stoichiometry and thermodynamics of the equilibrium between the sulfur- and carbon-bonded species.** It was previously shown<sup>2</sup> that Co(tacn)(aeaps)<sup>3+</sup> in strong base is deprotonated at a coordinated amine, to give a reddish-purple aminato complex. The site of deprotonation is not known, but it is likely that the deprotonation occurs at one of the tacn amine groups, as indicated in eqn. (1).



The value  $K_b = 0.43$  M has been reported (25 °C).<sup>2</sup> The corresponding tame complex is a significantly weaker acid, and it was previously<sup>4</sup> shown that  $K_b > 20$  M. Deprotonation of an amine group in Co(tame)(aeaps)<sup>3+</sup> therefore does not play any stoichiometrically significant role at the conditions used in the present study of  $K_f$  ( $[\text{OH}^-] = 4 \times 10^{-5} - 10^{-4}$  M) and the stoichiometry of the equilibration reaction can be expressed as shown in eqn. (2).



A high concentration of hydroxide affords a quantitative formation of the alkyl complex, while lower hydroxide concentrations give a mixture of the two species as shown by analysis of the product solution using IE-HPLC. The equilibrium constant for eqn. (2) was determined by means of IE-HPLC analysis as described previously<sup>3</sup> (see Experimental). The results are given in Table 1.

**Table 1.** Thermodynamic data for the equilibrium in 1 M NaClO<sub>4</sub> between the sulfur- and carbon-bonded species, eqn. (2), determined by IE-HPLC.

T/°C	[OH <sup>-</sup> ]/M	$K_f^{\text{ClO}_4}$ (obs)/M <sup>-1</sup>	$K_f^{\text{ClO}_4}$ (calc) <sup>a</sup> /M <sup>-1</sup>
100.0	$4.0 \times 10^{-4}$	8200 <sup>b</sup>	7800
100.0	$4.0 \times 10^{-4}$	7200	7800
80.0	$4.2 \times 10^{-4}$	7300	6650
80.0	$4.0 \times 10^{-5}$	6000	6650
60.0	$4.4 \times 10^{-4}$	6300	5570
40.0	$4.6 \times 10^{-4}$	4000	4550

<sup>a</sup> The values of  $K_f^{\text{ClO}_4}$ (calc) have been calculated using the values for  $\Delta H^\circ$  and  $\Delta S^\circ$  given in Table 4. <sup>b</sup> In this case the experiment was made by starting with a solution of [Co(tame)(C-aeaps)]S<sub>2</sub>O<sub>6</sub>. In all the other experiments the starting material was [Co(tame)(aeaps)]Cl<sub>3</sub>·H<sub>2</sub>O.

**Kinetics of the equilibration reaction.** The kinetics of the equilibration reaction between the sulfur- and carbon-bonded forms were studied at 25.0, 46.8, 58.9 and 72.0 °C ( $I=1.00$  M). The reaction was followed spectrophotometrically in the UV and the VIS region. For both regions the change of the absorbance followed first-order kinetics and rate constants obtained on basis of UV and VIS data, respectively, were identical (Table 2). Reactant solutions were made by starting with  $[\text{Co}(\text{tame})(\text{aeaps})]\text{Cl}_3 \cdot \text{H}_2\text{O}$  and the hydroxide ion concentration was varied from 0.001–1.000 M. At these conditions the reaction gives the alkyl complex quantitatively or nearly quantitatively (99 and 92%, respectively, at  $[\text{OH}^-]=0.02$  and 0.002 M, 60 °C). The cobalt(III) alkyl complex is not stable in the presence of oxygen, in particular when the base concentration is large. In strong basic solutions ( $[\text{OH}^-]>0.5$  M) the rate by which the alkyl complex is formed is comparable with the rate by which it reacts with oxygen ( $2.6 \times 10^{-4}$  M  $\text{O}_2$ ). At lower  $[\text{OH}^-]$  the reaction with oxygen does not contribute significantly within the timescale for the formation of the alkyl complex. All experiments have therefore been performed using oxygen-free solutions, except for a few experiments with hydroxide concentrations less than 0.005 M. The formation of the alkyl complex is followed by the consumption of one mole of base per mole of cobalt(III) [eqn. (2)], but since the cobalt(III) concentration was kept small relative to hydroxide concentration, pseudo-first-order conditions can be assumed. In all experiments corrections for the minor consump-

tion of base were made by using  $[\text{OH}^-]=([\text{OH}^-]_0 + [\text{OH}^-]_{t,\infty})/2$  in the subsequent calculations.

**$^{13}\text{C}$  NMR CH/CD-exchange experiments.** It was previously<sup>3</sup> shown that  $[\text{Co}(\text{tame})(\text{aeaps})]^{4+}$  undergoes a fast CH/CD-exchange reaction before the formation of the cobalt-alkyl complex. During the equilibration reaction one specific hydrogen atom of the  $\text{CH}_2$  group remains on the carbon, while the other undergoes a deuterium for hydrogen exchange prior to the Co–C bond formation. In the present study we found, using  $^{13}\text{C}$  DEPT NMR spectroscopy, that the alkyl complex formed in 1 M NaOD does not have deuterium incorporated into the carbon chain of the aeaps ligand. This shows that the labile hydrogen atom is lost when the alkyl complex is formed, as was also reported for the corresponding tacn system.<sup>3</sup> The rate constant for the exchange reaction was previously determined by  $^{13}\text{C}$  NMR measurements at 25.0 °C in 1 M NaOD. In the present study this measurement has been repeated and supplemented with additional determinations made at 5.0, 15.0 and 40.0 °C as shown in Table 3.

**Interpretation of the kinetic data.** The kinetic data for low concentration of hydroxide are interpreted in terms of the reactions shown in Scheme 1. This gives the rate expression in eqn. (3) with  $k_f=K_1k_2$  and  $k_{-2}=k_f/K_f$  ( $K_f=K_1K_2=k_f/k_{-2}$ ).

$$k_{\text{calc}}=k_f[\text{OH}^-]+k_{-2} \quad (3)$$

The expression has been derived assuming that the acid–base equilibrium ( $K_1$ ) is much faster than the subsequent formation ( $k_2$ ) of the alkyl species. 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 in Scheme 1 in order to simplify the subsequent discussion. It is noted that eqn. (3) is consistent with the kinetic data, but only for  $[\text{OH}^-]$  less than 0.01 M. At higher concentrations the variation of  $k_{\text{obs}}$  with the concentration of hydroxide deviates from linearity and finally a decrease in  $k_{\text{obs}}$  with increasing  $[\text{OH}^-]$  is observed. A similar behaviour was observed for the corresponding tacn system and was interpreted in terms of different reactivities of the ion pairs of the reactants with perchlorate and hydroxide, respectively. Therefore, following the results for the tacn

Table 2. Kinetic data for the equilibration reaction at  $I=1.0$  M  $[\text{Na}(\text{OH},\text{ClO}_4)]$ .

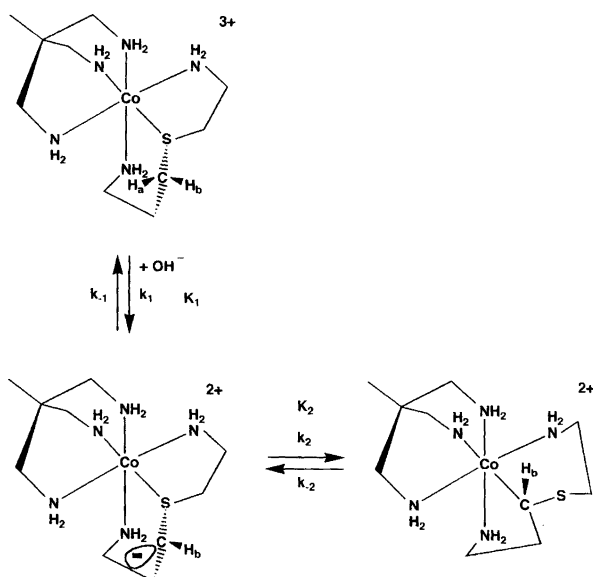
$T/^\circ\text{C}$	$[\text{OH}^-]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$k_{\text{calc}}^a/\text{s}^{-1}$
72.0	0.00597	0.00334 <sup>b</sup>	0.00312
72.0	0.00397	0.00198 <sup>b</sup>	0.00211
72.0	0.00197	0.00119 <sup>b</sup>	0.00109
58.9	0.998	0.00950 <sup>c</sup>	0.0105
58.9	0.498	0.0130 <sup>c</sup>	0.0152
58.9	0.198	0.0113 <sup>c</sup>	0.0116
58.9	0.0983	0.00785 <sup>c</sup>	0.00740
58.9	0.0483	0.00455 <sup>c</sup>	0.00419
58.9	0.00197	0.000197 <sup>b</sup>	0.000214
58.9	0.00097	0.000099 <sup>b</sup>	0.000115
46.8	0.998	0.00154 <sup>c</sup>	0.00130
46.8	0.498	0.00237 <sup>c</sup>	0.00200
46.8	0.198	0.00191 <sup>c</sup>	0.00175
46.8	0.100	0.00120 <sup>b</sup>	0.00125
46.8	0.0983	0.00116 <sup>c</sup>	0.00123
46.8	0.0500	0.000773 <sup>b</sup>	0.000768
46.8	0.0483	0.000709 <sup>c</sup>	0.000748
46.8	0.0200	0.000358 <sup>b</sup>	0.000356
46.8	0.00197	0.0000463 <sup>b</sup>	0.0000420
25.0	0.998	0.0000189 <sup>c</sup>	0.0000197
25.0	0.498	0.0000276 <sup>c</sup>	0.0000318
25.0	0.198	0.0000367 <sup>c</sup>	0.0000337

<sup>a</sup> Calculated using the expression in eqn. (4) and the parameters given in Table 4. <sup>b</sup> Kinetic data measured in the UV region. <sup>c</sup> Kinetic data measured in the VIS region.

Table 3. Kinetic data for the CH/CD-exchange reaction in 1 M NaOD determined by  $^{13}\text{C}$  DEPT NMR.

$T/^\circ\text{C}$	$k_{\text{ex}}(\text{obs})/\text{s}^{-1}$	$k_{\text{ex}}(\text{calc})^a/\text{s}^{-1}$
40.0	0.0219	0.0226
25.0	0.00361 <sup>b</sup>	0.00346
15.0	0.000907	0.000892
5.0	0.000203	0.000209

<sup>a</sup> The values of  $k_{\text{ex}}(\text{calc})$  have been calculated using the parameters given in Table 4. <sup>b</sup> In Ref. 4 the value 0.0028 s<sup>-1</sup> was reported.

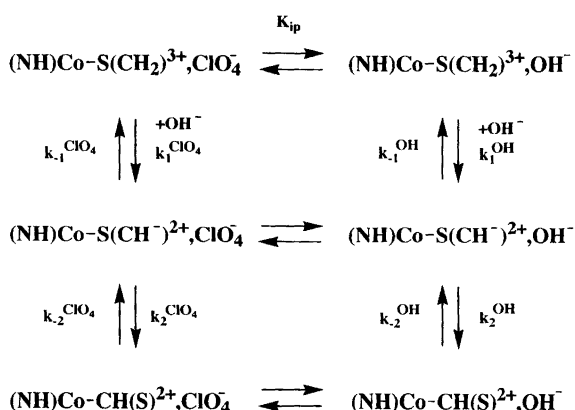


**Scheme 1.** Reaction scheme for the equilibration reaction at low hydroxide ion concentration. The hydrogens atoms here designated  $H_a$  and  $H_b$ , may also be characterized as axial and equatorial, respectively.  $H_a$  is the labile hydrogen atom.

system, we propose a reaction scheme for the present system as shown in Scheme 2, which is an extension of Scheme 1 with the additional assumption that all cationic coordination species are bound to either perchlorate or hydroxide anions as ion pairs. In the tacn system equilibria for the formation of species formed by deprotonation of one of the coordinated amine groups had to be included to the reaction scheme. Such equilibria are not required in the present system [ $K_b > 20$  M, viz. eqn. (1)]. This gives the expression in eqn. (4), where

$$k_{\text{calc}} = \frac{\{[\text{ClO}_4^-]k_f^{\text{ClO}_4} + [\text{OH}^-]K_{\text{ip}}k_f^{\text{OH}}\}[\text{OH}^-]}{[\text{OH}^-]K_{\text{ip}} + [\text{ClO}_4^-]} + k_{-2}^{\text{ClO}_4} \quad (4)$$

$k_f^{\text{ClO}_4} = K_1^{\text{ClO}_4}k_2^{\text{ClO}_4}$  and  $k_f^{\text{OH}} = K_1^{\text{OH}}k_2^{\text{OH}}$  are defined as



**Scheme 2.** Reaction scheme for the equilibration reaction. This scheme contains the same equilibria as shown in Scheme 1, but for each species it has been extended with equilibria between ion pairs with perchlorate and hydroxide, respectively.

before (Scheme 1), but are now referring to the ion pairs with perchlorate and hydroxide, respectively, as shown in Scheme 2. Equation (4) has four independent parameters  $k_f^{\text{ClO}_4}$ ,  $k_f^{\text{OH}}$ ,  $k_{-2}^{\text{ClO}_4}$  and  $K_{\text{ip}}$  (i.e. eight parameters when the temperature dependence is included). It is noted that only  $k_{-2}^{\text{ClO}_4}$  and not  $k_{-2}^{\text{OH}}$  contribute to the rate expression. The reason is that  $k_{-2}$  only contributes significantly at low hydroxide ion concentration where the concentration of hydroxide ion pairs is minimal. Since  $K_f^{\text{ClO}_4}$  has been determined (Table 1) the relation  $k_{-2}^{\text{ClO}_4} = k_f^{\text{ClO}_4}/K_f^{\text{ClO}_4}$  has been used to reduce the number of independent parameters in eqn. (4) from four to three. These parameters were then determined using the method of non-linear least-squares minimization, and the result is shown in Fig. 1 and Table 4. There is a good agreement between the observed and the calculated constants (Tables 2 and 4 and Fig. 1) and all constants are well defined (Table 4).

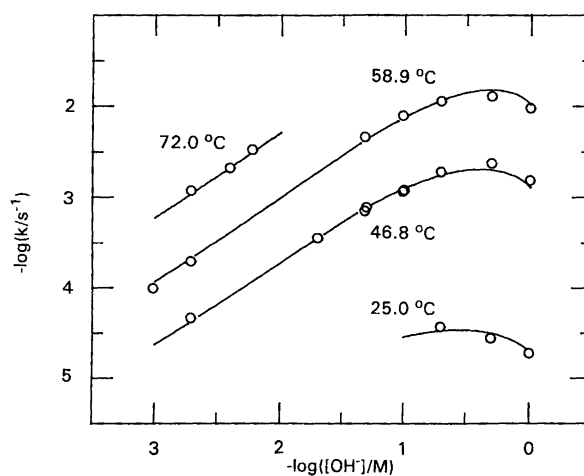
The rate constants determined for the CH/CD-exchange,  $k_{\text{ex}}$ , are interpreted as shown in eqn. (5)

$$k_{\text{ex}}(\text{calc}) = k_1^{\text{OD}}[\text{OD}^-] \quad (5)$$

and the activation parameters for the second-order rate constant  $k_1$  has been calculated using non-linear least-squares minimization as shown in Tables 3 and 4.

## Discussion

By coordination of a thioether sulfur atom to cobalt(III) the sulfur atom obtains sulfonium character by donation of electrons to the metal center.<sup>7</sup> The coordinated sulfur atom is therefore capable of stabilizing an adjacent carbanion much better than an uncoordinated thioether. Mechanistically this in part explains how coordinated thioethers facilitate the formation of cobalt-carbon complexes from Werner-type complexes.<sup>1,2,4</sup> A similar explanation is probably also relevant for the formation of cobalt(III)-carbon complexes in basic acetonitrile/



**Fig. 1.** Observed and calculated (solid lines) values of the pseudo-first-order rate constants for the equilibration reaction shown in Schemes 1 and 2.

Table 4. Summary of kinetic and thermodynamic data for the reactions of Co(L)(aeaps)<sup>3+</sup> at 25 °C and I = 1.0 M.

L = tame				L = tacn <sup>a</sup>		
Constant	Value	$\Delta H^\ddagger, \Delta H^\circ$ or $\Delta H^\ddagger - \Delta H^\circ$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger, \Delta S^\circ$ or $\Delta S^\ddagger - \Delta S^\circ$ /J mol <sup>-1</sup> K <sup>-1</sup>	Value	$\Delta H^\ddagger, \Delta H^\circ$ or $\Delta H^\ddagger - \Delta H^\circ$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger, \Delta S^\circ$ or $\Delta S^\ddagger - \Delta S^\circ$ /J mol <sup>-1</sup> K <sup>-1</sup>
$k_f^{\text{ClO}_4}/\text{M}^{-1} \text{s}^{-1, b}$	$7.4(12) \times 10^{-4}$	116(3)	86(10)	$8.2(4) \times 10^{-4}$	126(2)	118(5)
$k_f^{\text{OH}}/\text{M}^{-1} \text{s}^{-1, b}$	$2.0(2) \times 10^{-5}$	150(4)	169(12)	$4.1(3) \times 10^{-4}$	120(3)	93(9)
$k_{-2}^{\text{ClO}_4}/\text{s}^{-1}$	$1.9(4) \times 10^{-7}$	108(4)	-12(12)	$1.5(2) \times 10^{-7}$	110(2)	-9(5)
$k_1^{\text{OD}}/\text{M}^{-1} \text{s}^{-1}$	$3.46(7) \times 10^{-3}$	95(1)	25(4)	$3.2(2) \times 10^{-2}$	99(3)	59(12)
$K_f^{\text{ClO}_4}/\text{M}^{-1, c}$	$3.9(7) \times 10^3$	9(3)	98(7)	$5.6(7) \times 10^3$	16(2)	126(7)
$K_{\text{ip}}$	15(4)	-36(6)	-98(19)	0.84(36)	1(14)	1(42)

<sup>a</sup> From Ref. 3. <sup>b</sup>  $k_f = K_1 k_2$ . <sup>c</sup>  $K_f = K_1 K_2$ .

water mixtures from complexes with Schiff-base thioether ligands as recently reported by Chakravorty and coworkers.<sup>8,9</sup>

The kinetic and thermodynamic data for the present tame system are, as expected, similar to those reported for the tacn system as seen from Table 4. The thermodynamic parameters for the equilibrium between the C- and S-bonded species are similar. The kinetic parameters for the re-formation of the S-bonded species are, within the errors, identical for the two systems. There is a significant difference for the kinetic parameters  $k_f^{\text{ClO}_4}$  and  $k_f^{\text{OH}}$ , but since these are composite terms it is difficult to draw any conclusions.

In the discussion above the formation of the carbanion has been assumed to occur by a second-order reaction between hydroxide and Co(tame)(aeaps)<sup>3+</sup>. For the tacn system it was suggested that alternatively the carbanion may be formed by an intramolecular reaction in which the aminato species rearranges to the carbanion, possibly via a hydrogen-bonded water molecule, as shown in Fig. 2. If the reaction proceeds entirely by this path the rate constant for the intramolecular proton transfer,  $k_1^{\text{OD}}(\text{intra})$ , may be calculated from the relation  $k_1^{\text{OD}}(\text{intra}) = k_1^{\text{OD}} K_b(\text{ND})$ . Previously we obtained  $K_1^{\text{OD}}(\text{intra}) = 0.0084 \text{ s}^{-1}$  for Co(tacn)(aeaps)<sup>3+</sup>, and from the present data it is calculated that  $k_1^{\text{OD}}(\text{intra}) > 0.07 \text{ s}^{-1}$  for Co(tame)(aeaps)<sup>3+</sup>. The observation that  $k_1^{\text{OD}}(\text{intra})$  for the tame complex is significantly larger than  $k_1^{\text{OD}}(\text{intra})$  for the tacn complex corresponds well to the difference in basicity of the

aminato groups. The HN<sup>-</sup> group in the tame complex is at least 50 times stronger as a nucleophile than the N<sup>-</sup> group in the tacn complex. Although these results are in favour of an intramolecular mechanism (Fig. 2), we conclude that at present it is not possible to distinguish the two pathways and it is likely that they both play a significant role.

$K_{\text{ip}}$  is a measure of the stability of the ion pairs with hydroxide relative to those with perchlorate.  $K_{\text{ip}}$  in the present tame system is 20 times larger than that reported for the tacn system. This is very surprising, since the involved species have identical charges. A possible explanation could be a different degree of hydrogen bonding between hydroxide and coordinated NH or NH<sub>2</sub> groups, i.e. the tame complex forms stronger hydrogen bonds with hydroxide than the tacn complex does, and thereby its stability relative to perchlorate ion pairs is increased.

From the results above it may be concluded that it is the carbanion, formed during the initial CH/CD exchange reaction, which is the reactive species. It can also be concluded that the carbanion does not undergo inversion within the timescale of the experiment, since this would have resulted in CH/CD-exchange of both methylene protons. The question as to which of the two protons (H<sub>a</sub> and H<sub>b</sub> in Scheme 1) is exchanged was discussed previously for the tacn system. Following this discussion it is concluded that also in the present system it is H<sub>a</sub> which is the labile hydrogen atom, that the carbanion formed by dissociation of this proton does not undergo inversion and that it reacts with retention to give the alkyl species.

The composite term for the formation reaction,  $k_f^{\text{OH}} = k_1^{\text{OH}} k_2^{\text{OH}} / k_{-1}^{\text{OH}}$ , and the rate constant  $k_1^{\text{OD}}$  may be combined to estimate roughly for the ratio  $k_{-1}^{\text{OH}} / k_2^{\text{OH}}$  as shown in eqn. (6).

$$\frac{k_{-1}^{\text{OH}}}{k_2^{\text{OH}}} = \frac{k_1^{\text{OH}}}{k_f^{\text{OH}}} \approx \frac{k_1^{\text{OD}}}{k_f^{\text{OH}}} = 1.7 \times 10^2 \quad (25^\circ\text{C}) \quad (6)$$

It should be noted that this expression has been derived assuming that  $k_1$  is equal to  $k_1^{\text{OD}}$ , and therefore ignores solvent effects (H<sub>2</sub>O/OH<sup>-</sup> vs. D<sub>2</sub>O/OD<sup>-</sup>) and secondary isotope effects (NH vs. ND). These effects are likely to

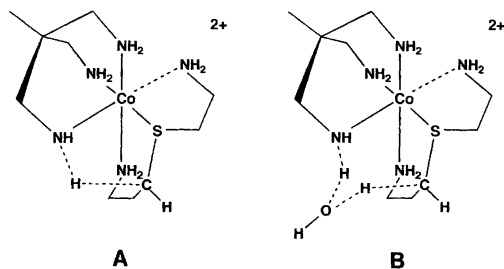


Fig. 2. Possible transition-state structures for the cases when the carbanion is formed by an intramolecular proton transfer between CH<sub>a</sub> and the aminato ligand by either a direct (A) or water-assisted (B) proton transfer.

be small in the present context. With these restrictions we therefore conclude that the carbanion reacts with water 170 times faster than it is captured by the cobalt(III) center. The value for the tacn system is 80.<sup>3</sup>

### Conclusions

The kinetic and thermodynamic data for the reaction of Co(tame)(aeaps)<sup>3+</sup> are very similar to those previously reported for the reaction of Co(tacn)(aeaps)<sup>3+</sup>. In both systems it is shown that the Co-S and Co-C bonded complexes 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. Also it is shown that at high [OH<sup>-</sup>] the different reactivity of ion pairs with perchlorate and hydroxide, respectively, plays an important role. The <sup>13</sup>C NMR CH/CD 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. The present data provide evidence in favour of a proposed intramolecular mechanism for the CH/CD exchange reaction. Co(tame)(C-aeaps)<sup>2+</sup> was found to be very unstable in the presence of oxygen at large [OH<sup>-</sup>], but at present no identification of the product(s) has been obtained.

A similar reaction was not observed for Co(tacn)(C-aeaps)<sup>2+</sup>.

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