

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

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The new cyclic thioether 1,4-diaza-7-thiacyclodecane, dathicd, has been synthesized and used for the preparation of the sulfur- and carbon-bonded cobalt(III) complexes: $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ and $[\text{Co}(\text{tacn})(\text{C-dathicd})](\text{ClO}_4)_2$ (tacn, 1,4,7-triazacyclononane; C-dathicd, 1,4-diamino-7-thiacyclodecan-8-ide anion). A thermodynamic and kinetic study of the equilibration between these coordination compounds has been performed using UV–VIS absorption spectroscopy, IE–HPLC and ^{13}C NMR ($[\text{OH}^-] = 10^{-5} - 1.0 \text{ M}$, $T = 25.0^\circ\text{C}$, $I = 1.0 \text{ M}$). In basic solution $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ deprotonates at one of the coordinated amine groups and the base dissociation constant has been determined to $K_b(\text{NH}) = 0.311(32) \text{ M}$. The equilibrium constant for the reaction of $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ with hydroxide ions to give $\text{Co}(\text{tacn})(\text{C-dathicd})^{2+}$ has been determined to $K_f = 1.8 \times 10^5 \text{ M}^{-1}$ at 25°C . The kinetic data have been interpreted in terms of the intermediate formation of a carbanion and this was strongly supported by ^{13}C NMR CH/CD-exchange studies. It was shown that $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ exchanges one methylene proton, and only one, prior to the formation of the 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 alkyl complex gave 100% loss of deuterium. It is 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 270 times faster than it is captured by cobalt(III).

It was previously shown¹ that $\text{Co}(\text{S-aeaps})_2^{3+}$ reacts in base forming an alkyl complex $\text{Co}(\text{S-aeaps})(\text{C-aeaps})^{2+}$ (for abbreviations see Experimental). Kinetic data for this reaction were reported, but a detailed mechanistic interpretation was not achieved. More recently it was shown that the related complexes in which one of the ligands in $\text{Co}(\text{S-aeaps})_2^{3+}$ has been substituted with the inert tripodal ligands tacn or tame react similarly.^{2–5} It was shown that in basic solution $\text{Co}(\text{tacn})(\text{S-aeaps})^{3+}$ equilibrates fast with its alkyl derivative $\text{Co}(\text{tacn})(\text{C-aeaps})^{2+}$, and a similar result was obtained for $\text{Co}(\text{tame})(\text{S-aeaps})^{3+}$. Detailed thermodynamic and kinetic studies have been reported for the two systems.^{3,5} It was shown that the sulfur-bonded complexes exchange one methylene proton, and only one, prior to the formation of the alkyl complex. The labile methylene proton

is bound to the carbon group which in the alkyl complex is bound to cobalt(III). From ^{13}C NMR experiments in D_2O it was shown that it is the labile proton which is lost when the alkyl complex is formed. The equilibration reaction is presumed to occur via a carbanion intermediate and from the kinetic data it was estimated that the carbanion from $\text{Co}(\text{tacn})(\text{S-aeaps})^{3+}$ and $\text{Co}(\text{tame})(\text{S-aeaps})^{3+}$, respectively, reacts with water 80 and 170 times faster than it is captured by cobalt(III).^{3,5} In the present paper we report the synthesis of the analogous complexes with tacn and the new cyclic thioether dathicd (1,4-diaza-7-thiacyclodecane) and a study of their equilibration reaction.

Experimental

Abbreviations. aeaps, aminoethyl aminopropyl sulfide = 3-thiahexane-1,6-diamine; C-aeaps, 1,6-diamino-3-thia-

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hexan-4-ide anion; aeapsts₂, *N,N'*-di(*p*-toluenesulfonyl)-2-aminoethyl-3-aminopropylsulfide; daes, di(aminoethyl) sulfide = 3-thiapentane-1,5-diamine; dathicd, 1,4-diaza-7-thiacyclodecane; dathicdts₂, 1,4-di(*p*-toluenesulfonyl)-1,4-diaza-7-thiacyclodecane; *C*-dathicd, 1,4-diaza-7-thiacyclo-decan-8-ide anion; dmf, dimethylformamide; dmsO, dimethyl sulfoxide; tacn, 1,4,7-triazacyclononane; tame, 1,1,1-tris(aminomethyl)ethane; tsCl, *p*-toluenesulfonyl chloride; ts, *p*-toluenesulfonyl.

Materials and instruments. Co(tacn)Cl₃,⁶ 2-aminoethyl-3-aminopropylsulfide (aeaps)⁷ and 1,2-di(*p*-toluenesulfonyloxy)ethane⁸ were made by literature methods. 33% hydrogen bromide in acetic acid was purchased from Aldrich Co. Deuterium oxide (99.8 atom % D), sodium deuteroxide (40% solution in D₂O, 99 atom % D), deuterium chloride (35% solution of D₂O, 99 atom % D) and acetonitrile-d₃ (99 atom % D) were obtained from Sigma. ND₄ Cl was made as reported previously.³ All other reagents were of analytical grade and CO₂-free doubly deionized water was used for all measurements. A Cary 3 spectrophotometer was used for spectral measurements. Ion-exchange high-performance liquid chromatography was performed using a Waters IE-HPLC system connected to a diode-array detector. A Waters Protein Pak SP-5PW cation-exchanger was used and 0.19 M Na₂SO₄ 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. ¹³C NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer equipped with a 5 mm probe. Deuterated solvents were used to provide a deuterium lock. ¹³C NMR spectra were obtained on a 14286 Hz spectral window with a digital resolution of 0.872 Hz per point. ¹³C DEPT NMR spectra were used to achieve differentiation of CH, CH₂ and CH₃ groups. An additional line-broadening of 1 Hz was employed before Fourier transformation to improve the signal-to-noise ratio. ¹³C chemical shift values (δ) are reported in ppm relative to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; δ = 0, 17.66, 21.74 and 57.02 ppm) for D₂O solutions, tetramethylsilane (TMS; δ = 0 ppm) for acetonitrile-d₃ solutions.

Syntheses. *N,N'*-di(*p*-toluenesulfonyl)-2-aminoethyl-3-aminopropylsulfide, aeapsts₂. To a solution of aeaps (14 ml, 102 mmol) and NaOH (10 g, 0.25 mol) in water (85 ml) was dropwise added a solution of *p*-toluenesulfonyl chloride (51 g, 267 mmol) in diethyl ether (400 ml) during 4 h. with vigorous stirring at room temperature. The mixture was stirred for another 2 h. The precipitate was filtered off, washed with water (2 × 100 ml), diethyl ether (2 × 100 ml) and dried in the air. Yield 44.2 g (98%). M.p. 89.7(2) °C. Analytical data: Calculated for C₁₉H₂₆N₂O₄S₃: C, 51.56; H, 5.92; N, 6.33. Found: C, 51.39; H, 5.90; N, 6.23.

1,4-Di(p-toluenesulfonyl)-1,4-diaza-7-thiacyclodecane, dathicdts₂. NaH (2 g, 50 mmol, 55–65% in oil) was

added in small portions to a solution of aeapsts₂ (9.0 g, 20 mmol) in dmf (240 ml) under N₂. The mixture was stirred at room temperature for 1.5 h. The mixture was heated to 70 °C and stirred for another 1.5 h to complete the reaction. This gave a white precipitate of the sodium salt of deprotonated aeapsts₂ and unreacted NaH.

Following the published procedures,⁸ unreacted NaH should be removed by filtration, as excess hydride may cause reduction of the tosyl ester. In the present case this is not possible, owing to the precipitation of the sodium salt of deprotonated tosyl amide. The excess NaH was therefore kept to a minimum. The mixture was then heated to 105 °C and a solution of 1,2-di(*p*-toluenesulfonyloxy)ethane (8.0 g, 21 mmol) in dmf (150 ml) was added dropwise during 3 h. This gave a brown–orange solution. The solution was evaporated to 1/3 volume, and then slowly poured into an ice–water mixture (800 ml). This gave a white precipitate, which was filtered off, washed with ethanol (2 × 150 ml) and diethyl ether (200 ml). The product was dried in the air. Yield 7.7 g (82%). M.p. 251(3) °C. Analytical data: Calculated for C₂₁H₂₈N₂O₄S₃: C, 53.82; H, 6.02; N, 5.98. Found: C, 53.60; H, 6.00; N, 5.95.

1,4-Diaza-7-thiacyclodecane dihydrobromide, dathicd·2-HBr. A solution of dathicdts₂ (1.0 g, 2.1 mmol) and phenol (1.5 g) in 33% HBr in CH₃ COOH (20 ml) was placed in a glass ampoule and heated at 70 °C for 3 days. The dark-brown product solution was poured into a vigorously stirred mixture of diethyl ether (88 ml) and ethanol (12.5 ml) and a sticky brown solid separated. The solid was dissolved in water (10 ml) and active charcoal (ca. 1 g) was added. The solution was boiled for 5 min and filtered. Evaporation of the filtrate gave a colourless oil. Yield 0.63 g (90%). The product was identified by its ¹³C NMR spectrum (Table 1).

1,4-Diaza-7-thiacyclodecane, dathicd. To a solution of dathicd·2HBr (2 g, 6.2 mmol) in water (5 ml) was added, with cooling in ice, solid NaOH to basic reaction (pH ca. 13). The solution was then extracted three times with CHCl₃ (200 ml). The organic extracts were dried with Na₂SO₄. The filtered solution was then evaporated to give an yellow oil of pure dathicd. Yield 0.9 g (90%). The product was identified by its ¹³C NMR spectrum (Table 1).

[Co(tacn)(S-dathicd)]Cl₃·5H₂O. To a solution of Co(tacn)Cl₃ (1.5 g, 5.1 mmol) in dry dmf (35 ml) was added dathicd (1 g, 6.3 mmol) at 110 °C with stirring. After 5 min another portion of dathicd (0.5 g, 3.1 mmol) was added. The mixture was stirred at 110 °C for further 15 min, during which the mixture changed colour from green–brown to red–brown. Cooling to room temperature gave a brown precipitate, which was filtered off, washed with dmf (5 ml) and 96% ethanol (10 ml). The precipitate was dissolved in water (50 ml), filtered and evaporated to dryness. This gave 2 g of a crude product. IE–HPLC showed the presence of two main components:

Table 1. ^{13}C NMR δ -values for cobalt(III) coordination compounds with tacn and dathicd at 300 K.

Compound	tacn		dathicd										
			C2	C3	C5	C6	C8	C9	C10				
dathicd			47.7	48.2	47.6	36.4	28.9	34.0	46.2				
dathicd·2HBr			46.5	49.0	45.2	33.8	25.3	30.4	43.1				
[Co(tacn)(S-dathicd)]Cl ₃ ·5H ₂ O	57.8	57.0	56.7	56.3	55.7	51.8	51.5	51.6	51.1	35.3	28.6	18.9	47.2
[Co(tacn)(C-dathicd)](ClO ₄) ₂	56.8	55.6	53.7	52.3	52.2	51.4	50.9	50.9	46.7	23.2	40.9	39.8	49.4
[Co(tacn)(C-dathicd)](ClO ₄) ₂ ^a	55.1	53.9	52.4	50.6	50.3	49.9	49.4	49.4	45.2	21.6	39.6	38.1	47.7

^a In acetonitrile-d₃. All others in D₂O.

Co(tacn)(S-dathicd)³⁺ and Co(tacn)₂³⁺ in the ratio 3 : 1. The crude product was separated using cation exchange (Sephadex C-25, 0.3 M Na₂SO₄ as eluent). The second main band was absorbed on a cation exchange resin SP 1080 GR, and the column was washed with water and then with 0.5 M HCl. The complex was eluted with 6 M HCl and the eluent was evaporated to dryness. The solid was recrystallized from water and ethanol to give an orange product of pure [Co(tacn)(S-dathicd)]Cl₃·5H₂O. Yield 1.3 g corresponding to 47% based upon Co(tacn)Cl₃ and 25% based upon dathicd. Analytical data: Calculated for C₁₃H₄₁N₅O₅SCoCl₃: C, 28.66; H, 7.58; N, 12.85; S, 5.88; Cl, 19.52. Found, C, 28.92; H, 7.58; N, 12.65; S, 7.08; Cl, 19.62. Cyclic voltammetry gave [0.1 M (CH₃)₄NCl in water]: E° = -0.187 V (vs. NHE).

[Co(tacn)(C-dathicd)](ClO₄)₂. [Co(tacn)(S-dathicd)]Cl₃·5H₂O (0.65 g, 1.19 mmol) was dissolved in 2 M NaOH (6 ml) at 40 °C. The violet-red solution was stirred at 40 °C for 90 min, during which the color changed from violet-red to dark orange. NaClO₄ (5 g) was added in small portions to the solution at room temperature. The mixture was stirred for 15 min at room temperature and then cooled at 10 °C for 15 min. The precipitate was filtered off, washed with 50% ethanol, then with 98% ethanol and dried in the air. This gave 0.64 g of a pure product (98%). Analytical data: Calculated for C₁₃H₃₀N₅O₈SCoCl₂: C, 28.58; H, 5.53; N, 12.86; S, 5.87; Cl, 12.98. Found: C, 28.27; H, 5.52; N, 12.74; S, 5.83; Cl, 12.81. Cyclic voltammetry gave (0.1 M tetrabutylammonium hexafluorophosphate in dmf): E° = -1.270 V (vs. NHE).

Determination of the equilibrium constant K_f = K₁K₂. Analysis by IE-HPLC of mixtures of the sulfur- and carbon-bonded species gave chromatograms with well separated peaks for the two components. The chromatograms were monitored at 219 and 295.8 nm, since at each of these wavelengths the molar absorbancies of the two species are practically identical. Equilibrium solutions were obtained by heating ammonia/ammonium buffer solutions of the sulfur-bonded species to 60.0, 70.0 and 80.0 °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. It was further confirmed that same chromatograms were obtained for solutions initially containing either [Co(tacn)(S-dathicd)]Cl₃·5H₂O or [Co(tacn)(C-dathicd)](ClO₄)₂. The concentrations of the two species, Co(tacn)(S-dathicd)³⁺ and Co(tacn)(C-dathicd)²⁺, were calculated from the relative peak areas.⁹ The pH-values of the equilibrium solutions were calculated using published pK_a values for NH₄⁺.¹⁰

Kinetic measurements. The kinetic experiments were made using spectrophotometry as described previously.^{3,10} The data were interpreted in terms of a single pseudo-first-order reaction. The pseudo-first-order rate constants, k_{obs}, were calculated on basis of absorbancies measured at 101 and 451 different wavelengths, respectively, in the regions 250–350 nm (C_{Co} = 2 × 10⁻⁴ M) and 350–800 nm (C_{Co} = 2 × 10⁻³ M). A kinetic experiment typically includes 20–35 spectra recorded within seven half lives. CH/CD-exchange experiments were performed using ¹³C NMR as previously described.³

Results and discussion

Synthesis and spectroscopic characterizations. The N₂S 10-membered macrocyclic thioether, 1,4-diaza-7-thia-cyclodecane (dathicd), was synthesized from aeaps and 1,2-ethanediol by the methods of Richman and Atkins¹¹ with the modification that the sodium salt of the tosyl amide was made *in situ* by reaction with sodium hydride.^{8,12} Detosylation was made at 70 °C using phenol in a mixture of hydrogen bromide and acetic acid.¹³ It was found that detosylation at 70 °C gave an optimal yield, whereas higher temperatures resulted in lower yields due to decomposition of the amine (10% yield at 100 °C). The yields of pure dathicd·2HBr and pure dathicd, respectively, were 73 and 66% based upon aeaps. Reaction of Co(tacn)Cl₃ with the free ligand dathicd in dmf (115 °C) gave a 3:1 mixture of Co(tacn)(S-dathicd)³⁺ and Co(tacn)₂³⁺, which could be separated by cation exchange chromatography. Orange crystals of pure [Co(tacn)(S-dathicd)]Cl₃·5H₂O were isolated in an yield of 25% based upon dathicd. Attempts to synthesize [Co(tacn)(S-dathicd)]³⁺ using dmso as solvent, as reported² for [Co(tacn)(S-aeaps)]³⁺, failed for unknown reasons. [Co(tacn)(S-dathicd)]³⁺ reacts with strong base

in aqueous solution and orange crystals of the Co–C bonded complex, $[\text{Co}(\text{tacn})(\text{C-dathicd})](\text{ClO}_4)_2$, was isolated in a yield of 98%.

The absorption spectra of $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ and $\text{Co}(\text{tacn})(\text{C-dathicd})^{2+}$ are shown in Fig. 1. The position of the first visible absorption band of the two compounds, respectively, are 477 and 465 nm. As expected these values are nearly identical to those reported² for the corresponding compounds $\text{Co}(\text{tacn})(\text{S-aeaps})^{3+}$ and $\text{Co}(\text{tacn})(\text{C-aeaps})^{2+}$, respectively, for which the values are 476 and 464 nm. As noted previously² the position of the first band of the two alkyl complexes are close to that reported for $\text{Co}(\text{tacn})_2^{3+}$ (460 nm) indicating that that the coordinated carbanion has ligand field properties similar to those of an amine.

The ^{13}C resonance signals of the free ligand, dathicd, are given in Table 1. The C5–C10 signals may be assigned in analogy with aeaps,^{2,4} whereas C2 and C3 presumably have the highest resonance frequencies. The ^{13}C DEPT NMR spectrum of a 0.2 M solution of $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ is shown in Fig. 2a. The spectrum contains 13 resonance signals as expected. Upon coordination the ^{13}C resonance frequencies of the ligands undergoes a coordination shift.^{2,4} Based on the expected coordination shifts, the ^{13}C resonance signals of $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ have been assigned as shown in Table 1. The six signals at higher frequency in Fig. 2a are attributed to the six carbon atoms in the tacn ligand² and the seven signals at lower frequencies are attributed to the coordinated dathicd ligand. It is characteristic that the middle carbon (C9) in a six-membered chelate ring has a large negative shift upon coordination ($\Delta\delta =$

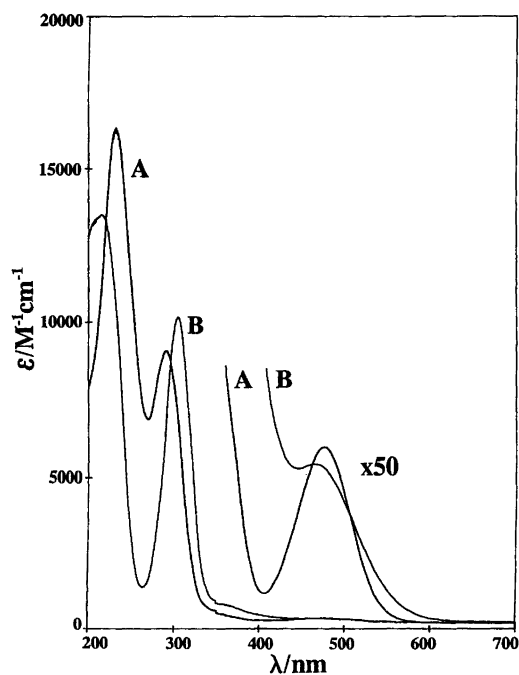


Fig. 1. Absorption spectra of $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ in 1 M NaClO_4 (A) and $\text{Co}(\text{tacn})(\text{C-dathicd})^{2+}$ in 1 M NaOH (B) at 25 °C.

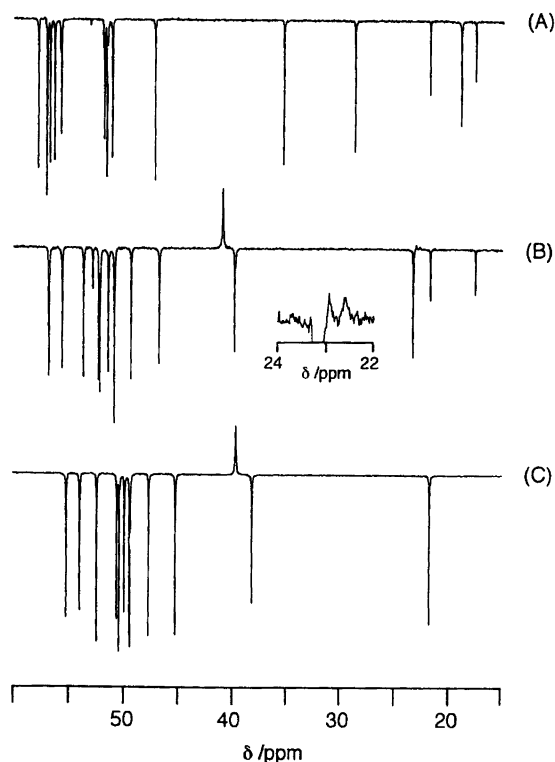


Fig. 2. ^{13}C NMR spectra of $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ in D_2O (A), $\text{Co}(\text{tacn})(\text{C-dathicd})^{2+}$ in 1 M NaOD (B, see text) and $[\text{Co}(\text{tacn})(\text{C-dathicd})](\text{ClO}_4)_2$ in acetonitrile- d_3 (C).

–15.1 ppm). The carbon atoms bonded to sulfur (C6 and C8) have very small coordination shifts, –1.1 and –0.3 ppm, respectively. The resonance signal at 28.6 ppm in $[\text{Co}(\text{tacn})(\text{S-dathicd})]^{3+}$ can unambiguously be assigned to C8, as this methylene group undergoes a rapid deuterium for hydrogen exchange in basic solution prior to the formation of the carbon-bonded species (see below). The coordination shift of the carbon atom (C10) bonded to a secondary nitrogen in the six-membered ring is small (1.0 ppm), whereas those in the five-membered rings are larger (3.4–3.8 ppm). This is in accordance with earlier observations.^{2,4} It should be noted, however, that the resonance signals above 50 ppm can not be unambiguously assigned as belonging to the tacn ligand or to C2 or C3 of the dathicd ligand.

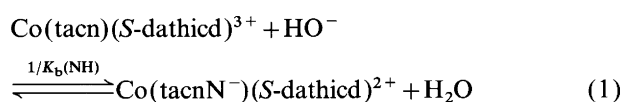
The ^{13}C DEPT NMR spectrum of 0.2 M $[\text{Co}(\text{tacn})(\text{C-dathicd})]^{2+}$ in 1 M NaOD is shown in Fig. 2b. This sample was made by adding a solution of NaOD to a solution of $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ in D_2O , and the spectrum was recorded after 8 h. The spectrum is identical to that of $[\text{Co}(\text{tacn})(\text{C-dathicd})](\text{ClO}_4)_2$ in D_2O . Since the resonance signal at 40.9 ppm is the only one that is positive, it is assigned to the cobalt-bonded carbon atom (C8), as it is the only possible CH group. The existence of a CH group is direct evidence that the alkyl compound exists in aqueous solution, as demonstrated earlier for the aeaps ligand.^{2,4}

We have previously found^{2,4} that the presence of a coordinating carbon atom does not affect the coordina-

tion shifts of the remaining carbon atoms. The signal at 23.2 ppm is the middle carbon atom (C6) of the six-membered ring in $[\text{Co}(\text{tacn})(\text{C-dathicd})]^{2+}$. It has a large negative coordination shift (-13.2 ppm) and can unambiguously be assigned to C6 due to the incorporation of deuterium in the methylene group. This is evidenced by the small positive triplet caused by coupling between ^{13}C and deuterium in the CHD group, Fig. 2 (B, insertion). The shift to lower ^{13}C resonance frequency upon exchange of hydrogen with deuterium is characteristic.^{3,14} Deuterium for hydrogen exchange in a methylene group bonded to a coordinated thioether sulfur atom in a five-membered ring have previously been observed¹⁴ in $\text{Co}(\text{tacn})(\text{daes})^{2+}$. Upon the formation of the alkyl complex the CH/CD-exchange at the C6 methylene group is stopped. The C9 carbon atom in $\text{Co}(\text{tacn})(\text{C-dathicd})^{2+}$ has a coordination shift of 5.8 ppm, which is similar to the coordination shift of methylene groups bonded to a secondary amine in a five-membered ring. The C5 has a small negative coordination shift (-0.9 ppm) as often found for carbon bonded to nitrogen in a six-membered ring.²

The ^{13}C DEPT NMR spectrum of $[\text{Co}(\text{tacn})(\text{C-dathicd})](\text{ClO}_4)_2$ in acetonitrile- d_3 exhibits the same pattern as the spectrum obtained in aqueous solution as shown in Fig. 2(C), and the resonance signals may be assigned in the same manner. In particular, the spectrum displays a CH group, confirming the existence of an alkyl-cobalt(III) compound in solution.

Stoichiometry and thermodynamics of the equilibrium between the sulfur- and carbon-bonded species. $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ reacts in strong base by deprotonation at a coordinated amine to give a reddish-purple aminato complex. The site of deprotonation is not known and for simplicity we assume that the deprotonation occur at one of the amine groups of tacn, as indicated in eqn. (1):



From measurements of the absorption spectra $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ in 1 M $\text{Na}(\text{OH}, \text{ClO}_4)$ with $[\text{OH}^-] = 10^{-5} - 1.0$ M the value $K_b(\text{NH}) = 0.31$ M was determined as described previously.² Similarly, in D_2O the value $K_b(\text{ND}) = 0.13$ M was obtained. The UV and VIS absorption spectra of $\text{Co}(\text{tacnN}^-)(\text{S-dathicd})^{2+}$ was calculated from the value of $K_b(\text{NH})$ and the observed spectra of $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ in 1 M NaClO_4 and 1 M NaOH , respectively. The calculated spectrum of $\text{Co}(\text{tacnN}^-)(\text{S-dathicd})^{2+}$ is shown in Fig. 3 together with the spectrum of $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$. The deprotonation reaction in eqn. (1) is followed by a slow formation of the C-bonded complex [eqn. (2)]:

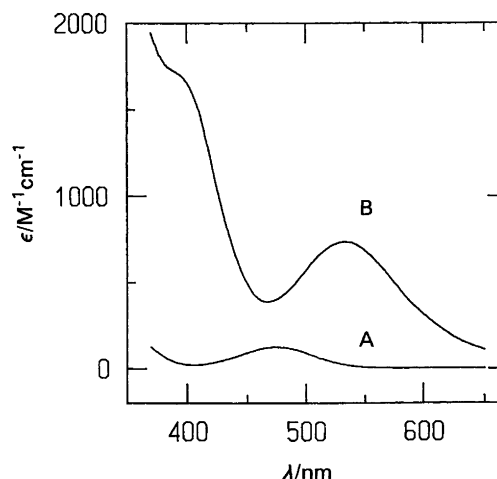
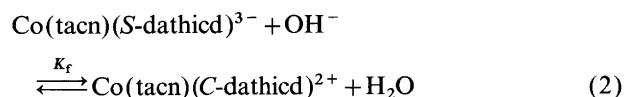


Fig. 3. Absorption spectra of $\text{Co}(\text{tacn})(\text{S-dathicd})^{3+}$ in 1 M NaClO_4 (A) and the calculated spectrum of $\text{Co}(\text{tacnN}^-)(\text{S-dathicd})^{2+}$ (B) at 25°C.

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 solutions by IE-HPLC analysis. The equilibrium constant for eqn. (2) was determined by means of IE-HPLC analysis as described previously³ (see also Experimental). These equilibrium experiments have been performed at a low hydroxide ion concentration ($2 \times 10^{-5} - 4 \times 10^{-5}$ M) for which the deprotonation in eqn. (1) does not play any stoichiometrically significant role. The results are given in Tables 2 and 3.

Kinetics of the equilibration reaction. The kinetics of the equilibration reaction between the sulfur- and carbon-bonded forms were studied at 25.0°C ($I = 1.00$ M). The reaction was followed spectrophotometrically in the UV region. The change of the absorbance followed strictly first-order kinetics. Reactant solutions were made by starting with $[\text{Co}(\text{tacn})(\text{S-dathicd})]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ and the hydroxide ion concentration was varied from 0.0024 to 1.000 M. At these conditions the alkyl complex is formed quantitatively. 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.

The kinetic data for the formation of the Co-C complex from the Co-S complex in base are primarily interpreted in terms of the reactions shown in Scheme 1. The pathway $k_1(\text{intra})$ is ignored in the following, but is discussed later. This gives the rate expression in eqn. (3) in which $k_f = k_2 K_1$ and $k_{-2} = K_f/k_2$:

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

The expression, eqn. (3), has been derived assuming that

Table 2. Determination of the equilibrium constant K_f in 1 M NaClO₄ by IE-HPLC.

Starting species ^a	T/°C	[OH ⁻] ^b /M	$K_f(\text{obs})/\text{M}^{-1}$	$K_f(\text{obs})^{\text{average}}/\text{M}^{-1}$	$K_f(\text{calc})^c/\text{M}^{-1}$
Co-S	60.0	3.90×10^{-5}	2.52×10^5	2.39×10^5	2.42×10^5
Co-S	-	1.91×10^{-5}	2.12×10^5		
Co-C	-	4.15×10^{-5}	2.54×10^5		
Co-S	70.0	3.80×10^{-5}	2.66×10^5	2.64×10^5	2.60×10^5
Co-S	-	1.86×10^{-5}	2.16×10^5		
Co-C	-	4.04×10^{-5}	3.11×10^5		
Co-S	80.0	3.69×10^{-5}	2.68×10^5	2.76×10^5	2.78×10^5
Co-S	-	1.79×10^{-5}	2.25×10^5		
Co-C	-	4.10×10^{-5}	3.36×10^5		

^a The equilibrium solutions were made by starting with a solution of [Co(tacn)(S-dathicd)]Cl₃·5H₂O or [Co(tacn)(C-dathicd)](ClO₄)₂.

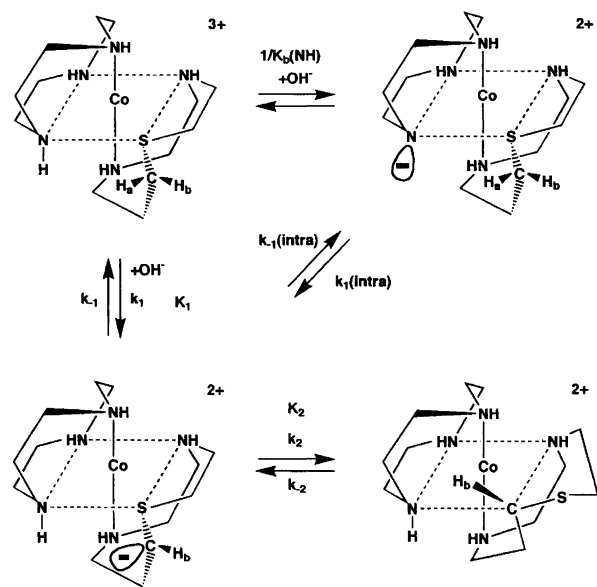
^b Hydroxide ion concentrations were kept nearly constant using NH₃/NH₄ClO₄ buffer solutions; corrections due to consumption or production of hydroxide during the equilibration have been made.

^c Calculated from the thermodynamic data given in Table 3.

Table 3. Thermodynamic data for the equilibrium constant K_f at 25 °C.

Constant	Value		
	Co(tacn)(S-aeaps) ³⁺ , ^a	Co(tame)(S-aeaps) ³⁺ , ^b	Co(tacn)(S-dathicd) ³⁺
K_f/M^{-1}	$5.6(7) \times 10^3$	$3.9(7) \times 10^3$	$1.80(15) \times 10^5$
$\Delta H^\circ/\text{kJ mol}^{-1}$	16(2)	9(3)	6.9(14)
$\Delta S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	126(7)	98(7)	124(4)

^a From Ref. 3. ^b From Ref. 5.



Scheme 1. Proposed reaction scheme for the equilibration reaction ignoring ion pair formation (see Scheme 2). 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.

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 at this stage in order to simplify the subsequent discussion. It

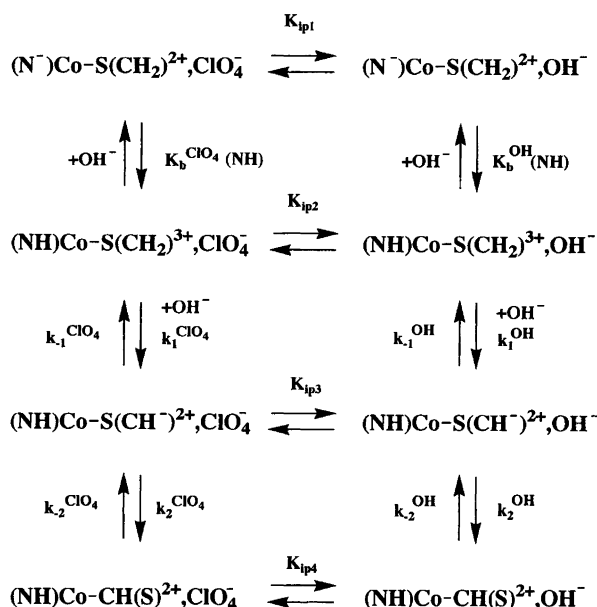
is noted that eqn. (3) is consistent with the kinetic data, but only for $[\text{OH}^-] < \text{ca. } 0.1 \text{ M}$. At high concentration of hydroxide the dependence of k_{obs} of the $[\text{OH}^-]$ deviate from eqn. (3) and a decrease in k_{obs} with increasing $[\text{OH}^-]$ is found. A similar behaviour was observed for the corresponding $\text{Co}(\text{tacn})(\text{S-aeaps})^{3+}$ and $\text{Co}(\text{tame})(\text{S-aeaps})^{3+}$ complexes. Detailed thermodynamic and kinetic studies of these systems have been reported and were interpreted in terms of different reactivities of the ion pairs of the reactants with perchlorate and hydroxide (less reactive), respectively.^{3,5} The complete reaction scheme is shown in Scheme 2 which is an extension of Scheme 1 with the additional assumption that all coordination cations are bound to either perchlorate or hydroxide anions as ion pairs. Following the same arguments as presented previously³ for $\text{Co}(\text{tacn})(\text{S-aeaps})^{3+}$ it is assumed that $K_b^{\text{ClO}_4}(\text{NH}) = K_b^{\text{OH}}(\text{NH}) = K_b(\text{NH})$ and that $K_{\text{ip}1} = K_{\text{ip}2} = K_{\text{ip}}$. These approximations simplify the interpretation of the kinetic data significantly and the rate expression for the equilibration reaction is shown in eqn.(4)–(6). It is noted that eqn. (4)

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

$$k_f^{\text{ClO}_4} = k_2^{\text{ClO}_4}K_1^{\text{ClO}_4} \quad (5)$$

$$k_f^{\text{OH}} = k_2^{\text{OH}}K_1^{\text{OH}} \quad (6)$$

contains only one term for the back-reaction, $k_{-2}^{\text{ClO}_4}$. The contribution from the k_{-2}^{OH} path can be ignored,



Scheme 2. Extension of Scheme 1 with the inclusion of ion pairs.

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 pair is negligible. In fact, the contribution of $k_{-2}^{\text{ClO}_4}$ to k_{calc} is negligible for the present conditions. Using the known values for $K_b(\text{NH})$ and $K_f^{\text{ClO}_4}$ together with the relation $k_{-2}^{\text{ClO}_4} = k_f^{\text{ClO}_4} / K_f^{\text{ClO}_4}$ the number of independent unknown parameters in eqns. (4)–(6) are three: $k_f^{\text{ClO}_4}$, k_f^{OH} and K_{ip} . These parameters were determined from the kinetic data using the method of non-linear least-square minimization and the result is shown in Fig. 4 and Tables 4 and 5. There is good agreement between the observed and the calculated rate constants and all parameters are

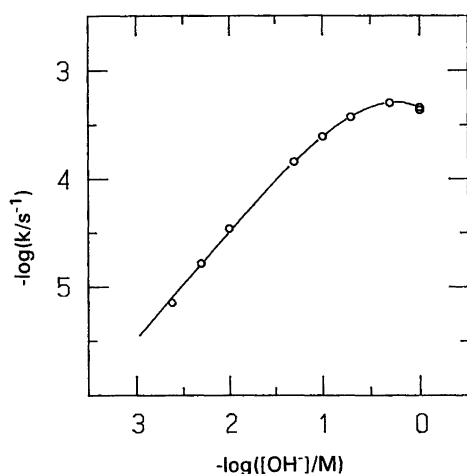


Fig. 4. Observed (circles) and calculated (solid line) values of the pseudo-first-order rate constant for the equilibration reaction shown in Schemes 1 and 2 and studied spectrophotometrically at $I = 1.0 \text{ M}$ and 25°C .

Table 4. Kinetic data at 25°C for the equilibration reaction in Scheme 1, $I = 1.0 \text{ M}$ $[\text{Na}(\text{OH}, \text{ClO}_4)]$.

$[\text{OH}^-]/\text{M}$	$10^5 k_{\text{obs}}/\text{s}^{-1}$	$10^5 k_{\text{calc}}/\text{s}^{-1}$
1.000	43.3	44.4
1.000 ^a	45.6	44.4
0.500	50.4	50.6
0.200	37.5	37.6
0.100	24.6	24.5
0.0499	14.4	14.2
0.0099	3.50	3.23
0.0049	1.66	1.63
0.0024	0.72	0.80

^a From measurements in the region 350–800 nm. All other rate constants have been obtained from measurements in the region 250–350 nm.

well defined. From the relation $k_{-2}^{\text{ClO}_4} = k_f^{\text{ClO}_4} / K_f^{\text{ClO}_4}$ the value for $k_{-2}^{\text{ClO}_4}$ is calculated (Table 5).

¹³C NMR CH/CD-exchange experiments. In basic solution $\text{Co}(\text{tacn})(S\text{-dathid})^{3+}$ undergoes a fast CH/CD exchange reaction preceding the formation of the alkyl complex. A similar behaviour has previously been reported for the analogous $\text{Co}(\text{tacn})(S\text{-aeaps})^{3+}$ and $\text{Co}(\text{tame})(S\text{-aeaps})^{3+}$ complexes.^{3–5} During the equilibration reaction one specific hydrogen atom of the C8 methylene group remains on the carbon, while the other undergo a deuterium for hydrogen exchange prior to the Co–C bond formation and is subsequently lost when the alkyl complex is formed. The reaction of $\text{Co}(\text{tacn})(S\text{-dathid})^{3+}$ in 1 M NaOD during the early reaction stage was followed by ¹³C NMR. It was readily established that the CHD-deuterated isomer of $\text{Co}(\text{tacn})(S\text{-dathid})^{3+}$ is formed quantitatively prior to the formation of the alkyl complex. Since the exchange reaction is fast ($t_{1/2} = 12.3 \text{ s}$ at 25°C) compared to the time required to obtain a good quality spectrum the reaction was studied by quenching of the basic product solutions by addition of an excess of ND_4Cl .³ In 1 M NaOD the negative resonance signal for CH_2 disappears and at the same time a resonance signal (positive triplet) for CHD appears. The exchange is more than 100 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 constant was calculated to $k_{\text{ex}} = 0.056(2) \text{ s}^{-1}$ (1.0 M NaOD, $C_{\text{Co}} = 0.2 \text{ M}$, 25°C). The rate constant determined for the CH/CD-exchange, k_{ex} , may be interpreted as shown in eqn. (7).

$$k_{\text{ex}}(\text{obs}) = \frac{k_1^{\text{OD}}[\text{OD}^-]K_b^{\text{OD}}(\text{ND})}{[\text{OD}^-] + K_b^{\text{OD}}(\text{ND})} \quad (7)$$

Since the exchange experiments has been made using 1 M NaOD in D_2O , the constants in eqn (7) are those referring to ion pair with OD^- exclusively. The rate constant k_1^{OD} is defined similarly to k_1^{OH} and $K_b^{\text{OD}}(\text{ND})$

Table 5. Summary of kinetic and thermodynamic data for Co(tacn)(S-aeaps)³⁺, Co(tame)(S-aeaps)³⁺ and Co(tacn)(S-dathicd)³⁺ (25 °C and I = 1.0 M).^a

	Value		
	Co(tacn)(S-aeaps) ³⁺	Co(tame)(S-aeaps) ³⁺	Co(tacn)(S-dathicd) ³⁺
$k_f^{\text{ClO}_4}/\text{M}^{-1} \text{ s}^{-1}$	$8.2(4) \times 10^{-4}$	$7.4(12) \times 10^{-4}$	$3.38(9) \times 10^{-3}$
$k_f^{\text{OH}}/\text{M}^{-1} \text{ s}^{-1}$	$4.1(3) \times 10^{-4}$	$2.0(2) \times 10^{-5}$	$1.87(8) \times 10^{-3}$
$k_{-2}^{\text{ClO}_4}/\text{s}^{-1}$	$1.5(2) \times 10^{-7}$	$1.9(4) \times 10^{-7}$	$1.9(6) \times 10^{-8}$
$k_1^{\text{OD}}/\text{M}^{-1} \text{ s}^{-1}$	$3.2(2) \times 10^{-2}$	$3.46(8) \times 10^{-3}$	0.50(5)
$K_f^{\text{ClO}_4}/\text{M}^{-1}$	$5.6(7) \times 10^3$	$3.9(7) \times 10^3$	$1.80(15) \times 10^5$
K_{ip}	0.84(36)	15(4)	0.96(42)
$K_b(\text{NH})/\text{M}$	0.433(13)	> 20	0.311(32)
$K_b(\text{ND})/\text{M}$	0.266(13)	—	0.130(15)

^a The values for Co(tacn)(S-aeaps)³⁺ and Co(tame)(S-aeaps)³⁺ have been taken from Refs. 2 and 3 and Ref. 5, respectively.

(the base dissociation constant in D₂O) have been determined in this study (Table 5). The actual concentration of OD⁻ was calculated from the solution stoichiometry using the value of $K_b^{\text{OD}}(\text{ND})$. The rate constant k_1^{OD} was then calculated from eqn. (7). This gave $k_1^{\text{OD}} = 0.50 \text{ s}^{-1}$.

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 timescale 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 or H_b) is exchanged has been addressed in previous studies,^{3,5} and following these discussions it seems likely that the labile proton is the axial proton, designated H_a in Scheme 1.

The composite term for the formation reaction, $k_f^{\text{OH}} = k_2^{\text{OH}}K_1^{\text{OH}} = k_1^{\text{OH}}k_2^{\text{OH}}/k_{-1}^{\text{OH}}$, and the rate constant, k_1^{OD} , may now be combined to calculate a rough estimate for the ratio $k_{-1}^{\text{OH}}/k_2^{\text{OH}}$ (referring to the hydroxide ion pair, only) as shown in eqn. (8):

$$\frac{k_{-1}^{\text{OH}}}{k_2^{\text{OH}}} = \frac{k_1^{\text{OH}}}{k_f^{\text{OH}}} \approx \frac{k_1^{\text{OD}}}{k_f^{\text{OH}}} = 2.7 \times 10^2 \text{ (25 °C)} \quad (8)$$

It should be noted that this expression has been derived assuming that $k_1^{\text{OH}} = k_1^{\text{OD}}$, and therefore ignores solvent effects (H₂O/OH⁻ vs. D₂O/OD⁻) and secondary isotope effects (NH vs. ND). These effects are likely to be small in the present context. With these restrictions we therefore conclude that the carbanion reacts with water 270 times faster than it is captured by the cobalt(III) center.

Intramolecular pathway for the carbanion formation [k_1 (intra) in Scheme 1]. As shown in Scheme 1, the carbanion may be formed either by a second-order reaction, k_1 , between hydroxide and Co(tacn)(S-dathicd)³⁺ or by an intramolecular reaction k_1 (intra) in which the aminato species rearranges by an intramolecular proton transfer from CH₂ to N⁻. The site of the lone pair in the aminato ion is not known, but it has been suggested³ that it is placed at the triazacyclononane ligand. The observation

that the two tacn aminato complexes have similar $K_b(\text{NH})$ values (0.31 and 0.43 M) and that they are much weaker bases than the tame aminato complex [$K_b(\text{NH}) > 20 \text{ M}$] seems to support this proposal strongly. In Scheme 1 the lone-pair has been placed on an arbitrarily chosen nitrogen ligator, but it seems reasonable to assume that the aminato species should be correctly described in terms of an equilibrium mixture between all three possible monodeprotonated species. In one of these aminato species the lone-pair has a direction toward the labile methylene proton, H_a, and it seems possible that the carbanion could be formed by an intramolecular proton transfer from CH₂ to N⁻, as illustrated in Fig. 5, which shows a suggested³ transition state structure for this reaction. A similar reaction is not possible for the other proton, H_b, and thereby this mechanism explains in a simple way the very large reactivity difference between the two methylene protons.

If it is assumed that the reaction entirely proceeds via the intramolecular path the rate constant, $k_1^{\text{OD}}(\text{intra})$, may be calculated from $k_1^{\text{OD}}(\text{intra}) = k_1^{\text{OD}}K_b(\text{ND})$. This gives $k_1^{\text{OD}}(\text{intra}) = 0.065 \text{ s}^{-1}$. The corresponding values for Co(tacn)(S-aeaps)³⁺ and Co(tame)(S-aeaps)³⁺, respectively, have been reported^{3,5} to be $k_1^{\text{OD}}(\text{intra}) = 0.0084 \text{ s}^{-1}$ and $k_1^{\text{OD}}(\text{intra}) > 0.07 \text{ s}^{-1}$. As mentioned previously⁵ the observation that $k_1^{\text{OD}}(\text{intra})$ for Co(tame)(S-aeaps)³⁺ is significantly larger than $k_1^{\text{OD}}(\text{intra})$ for Co(tacn)(S-aeaps)³⁺ corresponds to the difference in basicity of the aminato groups, since the

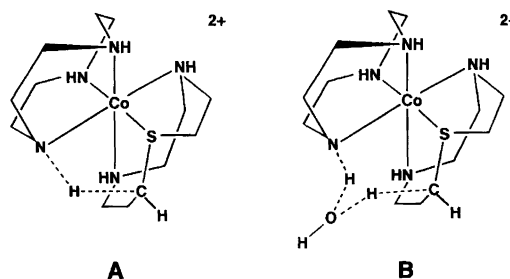


Fig. 5. Suggested transition state structures for the intramolecular transfer of a proton from CH₂ to N⁻.

N^- group in the tame complex is a much stronger nucleophile than the N^- group in the tacn complex. For the two tacn complexes we find that $Co(tacn)(S\text{-aeaps})^{3+}$ reacts slower than $Co(tacn)(S\text{-dathicd})^{3+}$, and this difference may be ascribed to differences in the thioether containing ligands.

Conclusions

The kinetic and thermodynamic properties of $Co(tacn)(S\text{-dathicd})^{3+}$ are very similar to those reported for the analogous complexes $Co(tacn)(S\text{-aeaps})^{3+}$ and $Co(tame)(S\text{-aeaps})^{3+}$. For all three species the Co-S bonded complex (and its *N*-deprotonated aminato base form) and the Co-C bonded complex form an equilibrium with no significant production of other species. The kinetic data unambiguously show that the equilibration occur via an intermediate formation of a carbanion. Also it is shown that at high $[OH^-]$ the different reactivity of ion pairs with perchlorate and hydroxide, respectively, plays an important role for all three systems. The ^{13}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. From kinetic data it is estimated that the carbanion reacts with water 80, 170 and 270 times faster, respectively, than it is captured by cobalt(III) for the three complexes $Co(tacn)(S\text{-aeaps})^{3+}$, $Co(tame)(S\text{-aeaps})^{3+}$ and $Co(tacn)(S\text{-dathicd})^{3+}$.

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