A Kinetic NMR Study of the Stereospecific Exchange of the Protons on C2 and C4 of 3-Thiapentane-1,5-diamine in the (1,4,7-Triazacyclonane)(3-thiapentane-1,5-diamine)cobalt(III) Ion

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The deuterium-for-hydrogen exchange rates in the (1,4,7-triazacyclononane)(3-thiapentane-1,5-diamine)cobalt(III) ion, $Co(tacn)(daes)^{3+}$, have been studied by ^{13}C nuclear magnetic resonance spectroscopy. In basic solution the protons of the sulfur-bonded methylene groups exchange orders of magnitude faster than the other methylene protons. One kind of methylene proton (H_a) was found to exchange one order of magnitude faster than the other protons (H_b): $(CH_aH_b-S-CH_aH_b)$. The observed pseudo-first-order rate constants are: $k_{ex}(H_a) = 7.4(7) \times 10^{-5}$ s^{-1} and $k_{ex}(H_b) = 0.28(12) \times 10^{-5}$ s^{-1} (1 M NaOD, 25°C). Secondary kinetic isotope effects were within experimental error, i.e. it is assumed that the exchange rate for a specific proton is independent of the degree of deuteration. In strongly basic solution the $Co(tacn)(daes)^{3+}$ ion deprotonates to an aminato complex, probably by deprotonation of one of the coordinated secondary amine groups of the tacn ligand. The base dissociation constant in water, K_b, was previously determined to be 0.51 M [25°C, 1 M Na(OH,ClO$_4$)]. In this study K_b was determined in deuterium oxide, $K_b = 0.27$ M [25°C, 1 M Na(OD,ClO$_4$)]. From this value and the observed k_{ex}-values the second-order rate constants for base-catalyzed dissociation of the CH_2-S protons of $Co(tacn)(daes)^{3+}$ were calculated to be $k_H(H_a) = 3.6 \times 10^{-4}$ M^{-1} s^{-1} and $k_H(H_b) = 0.13 \times 10^{-4}$ M^{-1} s^{-1}. The different reactivity of the two CH_2-S protons may be explained by differences in the extent of $p\pi-d\pi$ interaction in the two carbanions and by dissociation of the most labile proton assisted by an intramolecular hydrogen bond.

In a recent study we found that the complex Co(tacn)-(aeaps)$^{3+}$ in basic solution equilibrates with an alkyl-cobalt(III) compound [tacn = 1,4,7-triazacyclononane and aeaps = (2-aminoethyl)(3-aminopropyl)sulfide = 3-thiahexane-1,6-diamine].[1] An important result of this study was the observation that the axial and equatorial protons of the methylene group linked to sulfur (C–C–CH$_2$–S) undergo deuterium-for-hydrogen exchange with very different rates.[2] The labile axial hydrogen atom, which is the proton lost when the alkylcobalt(III) compound is formed, is exchanged by deuterium with a second-order rate constant k_H(axial) = 3.17 × 10^{-2} M^{-1} s^{-1} (1 M NaOD, 25°C). The rate of exchange of the equatorial proton is so small that no exchange has been observed and we therefore judged it to be at least one order of magnitude smaller than the rate of formation of the

alkylcobalt(III) compound, i.e. k_H(equatorial) being $< 10^{-4}$ M^{-1} s^{-1}.

In order to explore further this stereospecificity we decided to study the H/D exchange reactions of the methylene protons of the daes ligand in the related complex, Co(tacn)(daes)$^{3+}$. [daes = 3-thiapentane-1,5-diamine = di(2-aminoethyl)sulfide]. An alkylcobalt(III) compound derived from this complex were to contain a most unstable four-membered ring, $\overline{-Co-N-C-C-}$. It was therefore expected that the study of the exchange reactions of this species might not be complicated by a concomitant formation of the alkyl species. The initial experiments verified our expectations but, rather surprisingly, also showed that the daes ligand is eliminated relatively fast in basic solution. It was therefore decided to study this hydrolysis reaction prior to a further study of the H/D exchange reactions, and the result of this study has been published recently.[3,4] This paper describes our study of
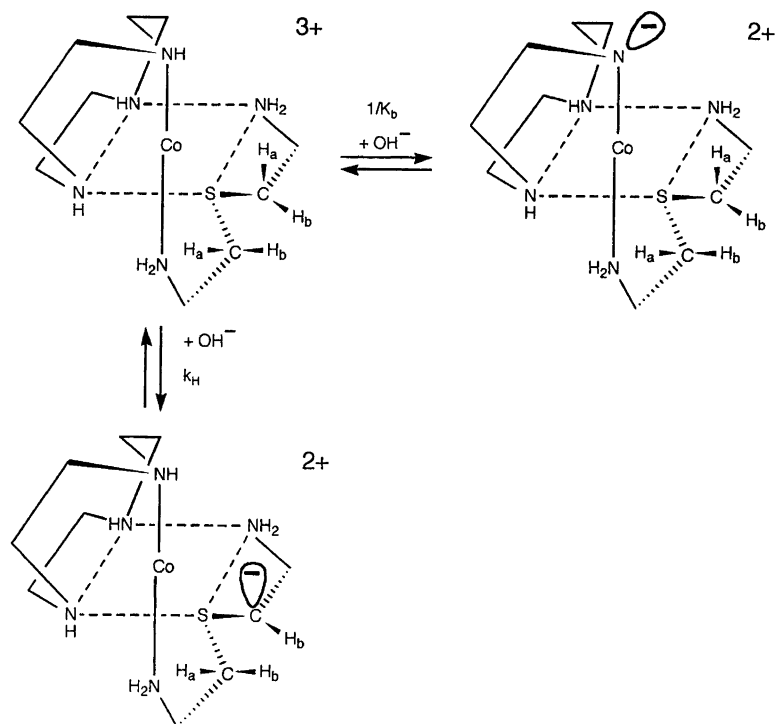
Scheme 1. Deprotonation of Co(tacn)(daes)$^{3+}$.

the H/D-exchange reactions of [Co(tacn)(daes)] Cl$_3$·H$_2$O in strongly basic solution.

Experimental

Materials and instrumentation. [Co(tacn)(daes)] Cl$_3$·H$_2$O, [(tacn)Co(OH)$_3$Co(tacn)](ClO$_4$)$_3$·4H$_2$O, Co(tacn)Cl$_3$ and solutions of Co(tacn)(OH)$_3$ were prepared as described previously.[2,5,6] Deuterium oxide, 99.8 atom % D; sodium deuteroxide, 40% solution in D$_2$O, 99+ atom % D; deuterium chloride, 35% solution in D$_2$O, 99 atom % D, were all obtained from Sigma. ND$_4$Cl were made by dissolving NH$_4$Cl in D$_2$O, evaporating to dryness and then repeating this procedure twice.

Ion-exchange high-performance liquid chromatography (IE-HPLC) was performed using a Waters IE-HPLC system connected to a diode array detector as described previously.[2,7] Visible absorption spectra, recorded on a Perkin-Elmer diode array spectrophotometer (LA 3048), were used for the determination of the base dissociation constant in D$_2$O of the aminato[†] complex of Co-(tacn)(daes)$^{3+}$ as described earlier.[1,2]

NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer. All measurements were per-

formed at 25°C. ^{13}C DEPT NMR was used to distinguish between CHD and CH$_2$ groups.[8] The phases of the spectra were corrected in order to make ^{13}C NMR signals from CH and CH$_3$ groups positive and those from CH$_2$ groups negative. ^{13}C chemical shift values (δ) are reported in ppm relative to internal 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; $\delta = 0$, 17.66, 21.74 and 57.02 ppm).

Kinetic measurements. To a solution of Co(tacn)(daes)Cl$_3$ (0.25 M) in D$_2$O at 25.0°C was added a solution of NaOD in D$_2$O to give a reaction mixture which was 0.2 M in complex and 1 M in OD$^-$. After an appropriate time the proton exchange reaction was quenched by adding the same volume 0.9 M DCl, 1 M ND$_4$Cl. The reaction time was varied from 1 min to 45 h. For reaction times longer than 10 h (up to 168 h), ^{13}C NMR was also measured directly on the basic reaction mixture.
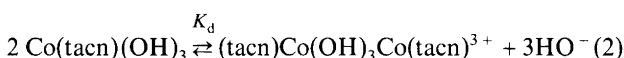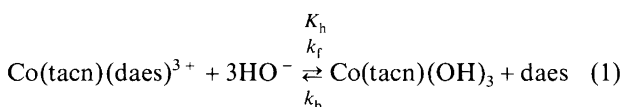
^{13}C NMR spectra of these samples were measured by the DEPT pulse technique. The carbon–hydrogen coupling constant of the C2 carbon atom in the coordinated daes ligand was measured to be $J_{CH} = 146.5$ Hz. The delay time in the DEPT pulse sequence was therefore chosen to be 3.41 ms in order to facilitate comparison of the amplitude of the ^{13}C NMR signal from the CH$_2$ group with the amplitude of the signal from the CHD group. For $\theta = 3\pi/4$ and $\tau = 1/(2 J_{CH})$ the amplitude of the signal due to CH$_2$ is $2\cos(3\pi/4)$ times larger than that of the CH group.[9]

[†] IUPAC recommends the name aminato for a coordinating R–NH$^-$ group instead of the commonly used name amido; Leigh, G. J., Ed., *Nomenclature of Inorganic Chemistry*, Blackwell, London 1990, p. 156.

Results

Reactions in basic solution. In strongly basic solution $Co(tacn)(daes)^{3+}$ is deprotonated to give an aminato complex, probably by deprotonation of one of the secondary amine groups of the tacn ligand as shown in Scheme 1. The base dissociation constant in water, K_b, was previously[1] determined to be 0.51 M [25°C, 1 M $Na(OH,ClO_4)$]. In this study K_b was determined in deuterium oxide, $K_b = 0.27$ M [25°C, 1 M $Na(OD,ClO_4)$]. Concomitant with the deprotonation of an amine group, $Co(tacn)(daes)^{3+}$ also forms a carbanion, as demonstrated by H/D-exchange of the sulfur-bonded methylene protons (Scheme 1).

Preliminary ^{13}C NMR measurements of $Co(tacn)(daes)^{3+}$ in 1 M NaOD at 25°C showed that all CH_2-S protons exchange within one week. During this time no measurable exchange of the other methylene protons of the daes or tacn ligands occurs and no NMR signals indicating the formation of a cobalt(III) carbon bond were observed. The kinetics of the exchange reaction, however, was disturbed by a hydrolysis reaction giving $Co(tacn)(OH)_3$ which underwent dimerization to $(tacn)Co(OH)_3Co(tacn)^{3+}$ as shown in eqns. (1) and (2).

$$Co(tacn)(daes)^{3+} + 3HO^- \underset{k_b}{\overset{K_h \atop k_f}{\rightleftharpoons}} Co(tacn)(OH)_3 + daes \quad (1)$$

$$2\,Co(tacn)(OH)_3 \overset{K_d}{\rightleftharpoons} (tacn)Co(OH)_3Co(tacn)^{3+} + 3HO^- (2)$$

These equilibria were recently established[3] for reactions at low cobalt(III) concentrations, $Co(III) < 0.005$ M. The following rate and equilibrium constants were determined: $K_h = k_f/k_b = 0.08(2)$ M^{-2}, $k_f = 1.02(2) \times 10^{-3}$ s^{-1}, and $K_d = 17(3)$ M^2 (59°C, 1 M NaOH). For reactions at higher cobalt(III) concentrations, 0.8 M, other products

are formed, and an equilibrium involving a new triaminato-bridged species has been described.[4]

In this study we have found that the hydrolysis reaction of 0.2 M $Co(tacn)(daes)^{3+}$ in 1 M NaOH at 25°C is slow relative to the exchange of the first methylene proton. After 2 h reaction time the content of $Co(tacn)(daes)^{3+}$ was approximately 97% of the original amount and the dominant product species was $Co(tacn)(OH)_3$. This was estimated from the NMR experiments and by analysis of the reaction mixture using HPLC. By quenching of the reaction mixture after 2 h by addition of an excess of ND_4Cl or NH_4ClO_4 (pH 8), $Co(tacn)(daes)^{3+}$ was quantitatively reformed. This was verified by NMR measurements and by HPLC analysis.

After 64 h reaction time the concentration of $Co(tacn)(daes)^{3+}$ had decreased to approximately 80% of the initial concentration, and after quenching with NH_4ClO_4 only partial reformation of $Co(tacn)(daes)^{3+}$ was observed. At this stage minor concentrations of other products than those shown in eqns. (1) and (2) were observed by the ^{13}C NMR spectra of the basic solutions as well as in the HPLC analysis of the quenched solutions. This confirms the previous observation that other products than those shown in eqns.(1) and (2) are formed at high cobalt(III) concentrations.[4]

^{13}C NMR H/D-exchange experiments. Since $Co(tacn)(daes)^{3+}$ has a plane of symmetry the ^{13}C NMR spectrum of this coordination compound consists of five resonance signals (Table 1). The three signals at higher frequency may be assigned to the carbon atoms in tacn. The signals at 46.5 and 39.1 ppm may, from a comparison with the free ligand, be assigned to the nitrogen-bound carbon atom and to the sulfur-bound carbon atom of daes, respectively. The H/D exchange reaction in basic solution was established by following the decay of the $S-CH_2$ group (negative singlet) and the formation of a
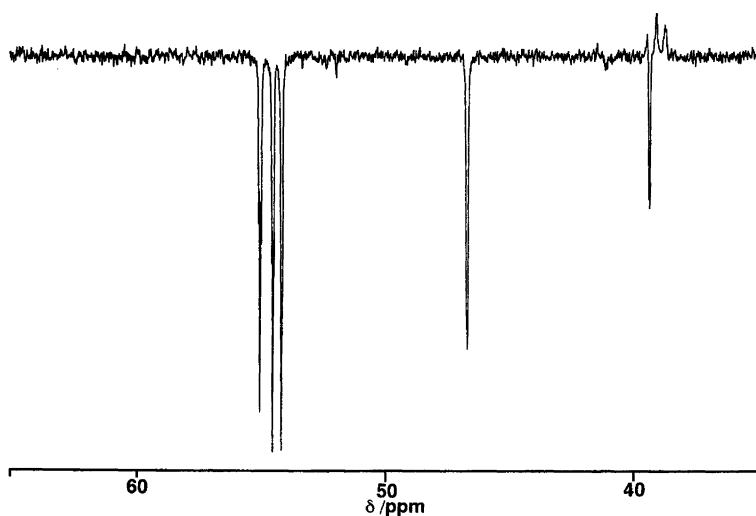

Fig. 1. ^{13}C DEPT NMR spectrum of 0.2 M $Co(tacn)(daes)Cl_3$ after a reaction time of 3 h in 1 M NaOD at 25°C. The reaction was quenched before measuring the NMR spectrum (see text).

Table 1. ^{13}C NMR chemical shift data for tacn·3HCl, daes and Co(tacn)(daes)Cl$_3$ in D$_2$O. The ligand daes is numbered by N-C1-C2-S-C4-C5-N.

|	δ(ppm) in Co(tacn)(daes)$^{3+}$	δ(ppm) in free ligand
daes C1, C5	46.5	42.4
C2, C4	39.1	36.2
tacn	53.8	43.7
	54.1	
	54.7	

CDH group (positive triplet) in the ^{13}C DEPT NMR spectrum as shown in Fig. 1. The positive triplet subsequently decayed slowly due to exchange of the second proton giving a CD$_2$ group.

The exchange of the first methylene proton is fast compared to the time required to obtain a ^{13}C NMR spectrum, and this part of the reaction was therefore monitored by NMR measurements on quenched solutions. The formation of Co(tacn)(OH)$_3$ is negligible at this stage. The exchange rate can be measured by normalizing the CH$_2$ amplitudes relative to the tacn methylene signals and to the daes N–CH$_2$ resonance signals.

The subsequent exchange of the second proton is much slower, and is associated with the formation of significant amounts of the hydroxo complex and the trihydroxobridged species [and minor amounts of other Co(III) species] and free daes ligand. This stage was monitored by measuring directly on the basic solutions. In this way it was possible to distinguish Co(tacn)(daes)$^{3+}$ from the other species. By normalizing the CH$_2$ amplitudes relative to the tacn methylene signals and to the daes N–CH$_2$ signal of Co(tacn)(daes)$^{3+}$ a good measure of the exchange rate was obtained without interference by the hydrolysis reaction.

The reformation reaction of the Co(tacn)(daes)$^{3+}$ [k_b in eqn. (1)] does not contribute significantly during the fast exchange reaction; it may, however, contribute to a minor extent during the second and slow exchange reaction. This possible contribution has been ignored in the following calculations. It was found that the free ligand daes does not undergo any H/D exchange of methylene protons during 7 days in 1 M NaOD, and the error generated by ignoring the reformation reaction will therefore be small in any case.

Kinetic model. The H/D-exchange reaction is assumed to proceed according to Scheme 2. Under the present conditions [OH$^-$] is negligible compared to [OD$^-$] and the exchange reaction does not consume base. Being a secondary deuterium effect, the difference between the observed rate constants k_{ex}^{11} and k_{ex}^{22} is expected to be very small. Similar considerations are valid for k_{ex}^{12} and k_{ex}^{21}. It is therefore assumed that $k_{ex}^{11} = k_{ex}^{22}$ and $k_{ex}^{12} = k_{ex}^{21}$, leading to expressions (3) and (4), where [A] and [B] are defined in eqns. (5) and (6), respectively.
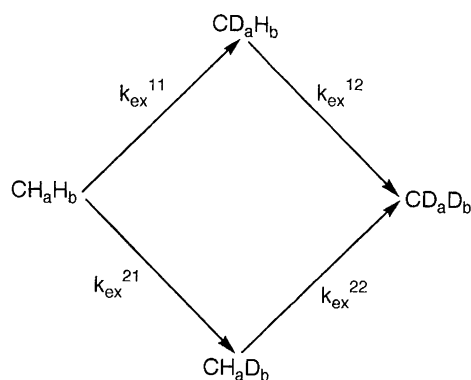
Scheme 2. Kinetic model for the stereospecific H/D-exchange reaction of a methylene group.

$$[A] = A_0 \exp[-(k_{ex}^{11} + k_{ex}^{12})t]$$ (3)

$$[B] = A_0\{\exp(-k_{ex}^{12}t) + \exp(-k_{ex}^{11}t) - 2\exp[-(k_{ex}^{11} + k_{ex}^{12})t]\}$$ (4)

$$[A] = 2[CH_2-S-CH_2] + [CH_2-S-CHD]$$ (5)

$$[B] = [CH_2-S-CHD] + 2[CHD-S-CHD] + [CD_2-S-CHD]$$ (6)

A_0 is [A] at $t = 0$. In eqn. (5) [CH$_2$–S–CH$_2$] denotes the concentration of the initial thioether cobalt(III) compound. For clarity the above definitions of [A] and [B] have been written without distinction between CH$_a$D$_b$ and CD$_a$H$_b$. The CH$_a$H$_b$ group gives a negative singlet in the ^{13}C DEPT NMR spectrum, and the relative concentration [A] can be determined by the amplitude (integral). The CD$_a$H$_b$ group and the CH$_a$D$_b$ group both give a positive triplet with a total amplitude proportional to [B].

Surprisingly, the ^{13}C DEPT NMR spectra show *two* negative singlets from the CH$_2$ groups of the C2 carbon atom. The two signals have a 2.25 Hz difference in frequency. The signal at highest frequency decreases from a full amplitude at $t = 0$ to zero amplitude, whereas the second signal increases from zero amplitude at $t = 0$ to a maximum (negative) amplitude at $t \approx t_{1/2,obs}$, after which the amplitude decreases to zero. This may be explained by assuming the resonance frequencies of the ^{13}C nuclei of the CH$_2$ group to be different, depending on whether a CH$_2$ group or a CHD group is present next to the sulfur atom. A similar but smaller influence on the resonance frequency is apparent for the C1 carbon atom in daes and even for the ^{13}C nuclei in tacn.

Calculation of rate constants. The relative concentrations of the CH$_2$ group and the CHD group were determined from the amplitudes of the ^{13}C resonance signals. Since the two negative singlets and the positive triplet overlap, it was necessary to simulate the spectra in order to determine the amplitudes. The spectra were simulated as a
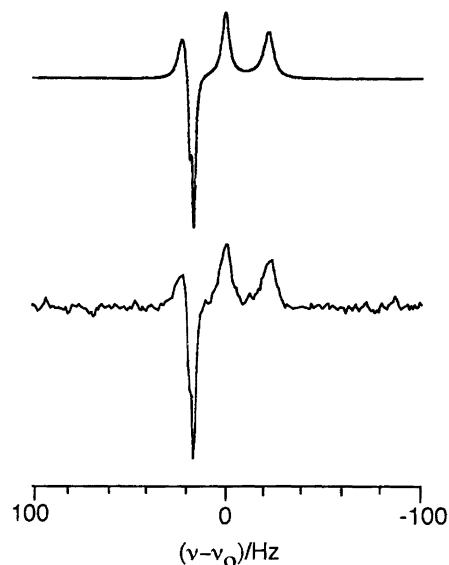
Fig. 2. Simulated (top) and measured (bottom) ^{13}C DEPT NMR spectrum of the C2 carbon atom in 0.2 M Co-(tacn)(daes)Cl_3 after a reaction time of 270 min in 1 M NaOD at 25°C. The reaction mixture was quenched before measuring the NMR spectrum.

Fig. 3. The amplitude the ^{13}C NMR signals from the CH_2 group (●) and the CDH group (◆) (the C2 carbon atom) in 0.2 M Co(tacn)(daes)Cl_3 as a function of time in 1 M NaOD at 25°C. The reaction was quenched before measuring the NMR spectrum (see text).

sum of three contributions, i.e. two Lorentz curves ($T_2 = 0.16$ s) with negative amplitudes and a 2.25 Hz difference in frequency, and a positive triplet with a 18.25 Hz difference in frequency to the high-frequency singlet. The triplet was calculated according to Pyper[10] with $I = 1$. Additional line broadening was accounted for by adding $1/T^*_{2,C}$ to the diagonal elements in the relaxation matrix.[10] The triplet was simulated using the parameters $J_{CD} = 22.5$ Hz, $T_{1,D} = 0.04$ s and $T^*_{2,C} = 0.25$ s.

These three spectra were added proportionally in order to give the best fit to the experimental spectra. An example of this is given in Fig. 2. The amplitudes of the simulated spectra were then normalized against the amplitude of the C1 carbon atom in the coordinated daes ligand. In this way the amplitudes of the CH_2 group (i.e. the sum of the two Lorentz curves) and the CDH group were determined. A CD_2 group does not give any signal in the ^{13}C DEPT experiment. Fig. 3 shows the amplitude of the CH_2 group and of the CDH group as function of
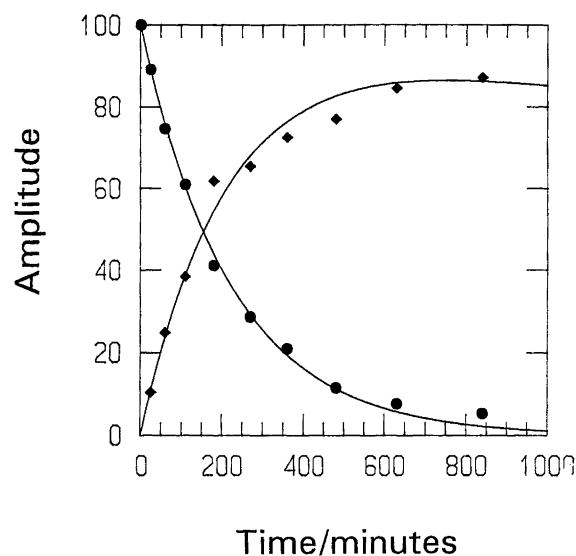
time. From the decay of the CH_2 signal the sum $k^{11}_{ex} + k^{12}_{ex} = 7.59(45) \times 10^{-5}$ s^{-1} was determined by a least-squares fit of eqn. (3) to the amplitude of the CH_2 signal.

The amplitude of a CH group in a ^{13}C DEPT NMR spectrum is smaller than that of a CH_2 group.[9] The amplitudes of the CDH group should be multiplied by a factor of $2\cos(3\pi/4)$ before comparing them with a CH_2 group. The actual amplitude factor may deviate from the theoretical value. We have therefore chosen to determine the amplitude factor together with the observed rate constants k^{11}_{ex} and k^{12}_{ex} simultaneously by a least-squares fit of eqn. (4) to the amplitudes of the CDH groups. This fit gave an amplitude factor for the CHD group relative to the CH_2 group of $- 1.3$, fairly close to the theoretical value, $- 1.41$. The observed rate constants were $k^{11}_{ex} = 7.4(7) \times 10^{-5}$ s^{-1} and $k^{12}_{ex} = 0.28(12) \times 10^{-5}$ s^{-1}. The sum $k^{11}_{ex} + k^{12}_{ex}$ is equal to the value measured from the decay of the CH_2 group when taking into account the experimental uncertainty.

Table 2. Rate constants for the base-catalyzed dissociation of CH_2 protons in cobalt(III) complexes at 25°C and $I = 1.0$ M.

Complex	Methylene group(s)	Assignment	$k_H/M^{-1}s^{-1}$
Co(tacn)(aeaps)$^{3+}$	N–CH_2–C or N–C–CH_2	All	$< 10^{-6}$
Co(tacn)(aeaps)$^{3+}$	S-CH_2–C–C–N	H_a	3.17×10^{-2}
Co(tacn)(aeaps)$^{3+}$	S–CH_2–C–C–N	H_b	$< 10^{-4}$
Co(tacn)(aeaps)$^{3+}$	S–CH_2–C–N	H_a and H_b	$< 10^{-4}$
Co(tacn)(daes)$^{3+}$	N–CH_2	All	$< 10^{-6}$
Co(tacn)(daes)$^{3+}$	S–CH_2	H_a	3.6×10^{-4}
Co(tacn)(daes)$^{3+}$	S–CH_2	H_b	0.13×10^{-4}
Co(en)^2(gly)$^{2+}$ ^{a}	CH_2–COO	H_a	2.7×10^{-2}
Co(en)^2(gly)$^{2+}$ ^{a}	CH_2–COO	H_b	2.2×10^{-2}
Co(tacn)(C-aeaps)$^{3+}$	CH or CH_2	All	$< 10^{-8}$

^{a}Presumed second-order rate constants based on observed rate constants[11] and $[OD^-] = 1.39 \times 10^{-2}$ M.

Owing to the poor signal-to-noise ratio the decay of the triplet from the CDH group was difficult to measure by this technique. Measurements performed directly on the basic reaction mixture were within experimental error, in agreement with the value for k_{ex}^{12} as given above.

The second-order rate constants k_H for the CH/CD exchange may be calculated[2] from the observed rate constants k_{ex} according to eqn. (7).

$$k_{ex} = \frac{k_H[OD^-]K_b}{[OD^-] + K_b} \tag{7}$$

[OD^-] can be estimated from $K_b = 0.27$ M determined in deuterium oxide. The calculation gives $k_H^{11} = 3.6 \times 10^{-4}$ $M^{-1} s^{-1}$ and $k_H^{12} = 0.13 \times 10^{-4}$ $M^{-1} s^{-1}$. Table 2 summarizes the present data together with the published data for Co(tacn)(aeaps)$^{3+}$,[2] Co(tacn)(C-aeaps)$^{3+}$,[2] and Co(en)$_2$(gly)$^{2+}$.[11]

Discussion

It is well known that attachment of a sulfur atom to a carbon atom causes an increase in carbanion stability.[12] This is frequently attributed to pπ–dπ interaction between the unshared electron pair of the carbanion and an empty sulfur d-orbital. This suggestion is supported by theoretical calculations.[13] The stabilizing effect of sulfur, however, has also been attributed to other causes.[14]

To our knowledge there are no known examples of thioethers that undergo base-catalysed hydrogen isotope exchange in aqueous solution. Hydrogen isotope exchange in trialkylsulfonium ions occurs with much more ease, reflecting an enhanced carbanion stabilizing capability of a sulfonium group relative to the sulfur atom in thioethers. By coordination of the thioether sulfur atom to cobalt(III) the sulfur attains sulfonium character by donation of electrons to the metal center. It is therefore expected that H/D exchange in thioethers is significantly promoted by coordination to a metal ion.

The five-membered ring of the coordinated daes may exist as two conformers with little energy difference.[15] A model of Co(tacn)(daes)$^{3+}$ shows that the two hydrogen atoms of the methylene group linked to the coordinated sulfur atom have different geometry with respect to the unshared electron pair of the sulfur atom. One of the C–H bonds (H$_a$) is in both conformations nearly parallel to the direction of the unshared electron pair. Hence a pπ–dπ interaction is favoured and will promote dissociation of H$_a$. The other C–H bond (H$_b$) is perpendicular to the unshared electron pair of the coordinated sulfur atom in one of the conformations and skewed in the other conformation. Hence the acceleration of the dissociation of H$_b$ due to a pπ–dπ interaction is expected to be small.

Addition of base to a solution of Co(tacn)(daes)$^{3+}$ results in an immediate deprotonation of one of the coordinated nitrogens forming an aminato species. In one of these aminato species the unshared electron pair is di-

rected towards the sulfur-bonded methylene group. It has previously been suggested[2] that the H/D-exchange reaction in Co(tacn)(aeaps)$^{3+}$ could proceed by an intramolecular proton transfer from CH to N$^-$. The same mechanism might contribute for the H/D exchange reaction in Co(tacn)(daes)$^{3+}$. A model of Co(tacn)(daes)$^{3+}$ shows that the C–H$_a$ bond is directed towards the unshared electron pair of one of the possible aminato species, whereas H$_b$ is directed away from the nitrogen atom (Scheme 1). The effect of an intramolecular proton transfer is a labilization of H$_a$ relative to H$_b$. Thus pπ–dπ interaction and an intramolecular proton transfer mechanism both predict that one of the protons dissociates faster that the other proton, in agreement with the experimental results. We therefore suggest that the fast exchanging proton is H$_a$ and the slowly exchanging proton is H$_b$.

The discussion above is based upon the assumption that there is no significant inversion of the carbanion during the exchange reactions, i.e. the exchange of H$_a$ and H$_b$ is initiated by dissociation of H$_a$ and H$_b$, respectively. From the present data, however, it is not possible to distinguish this mechanism from a mechanism in which the observed exchange of H$_b$ partly or entirely occurs via dissociation of H$_a$ followed by inversion of the carbanion prior to reprotonation.

For Co(tacn)(daes)$^{3+}$ it is found that the sulfur-bonded methylene groups exchange protons much faster than the other methylene groups belonging to either daes or tacn. A similar H/D exchange reaction has been observed earlier under identical conditions for Co(tacn)(aeaps)$^{3+}$ in basic solution,[2] with the second-order rate constant being $k_H = 3.17 \times 10^{-2}$ $M^{-1} s^{-1}$, i.e. about 100 times faster than the fastest exchanging proton in Co(tacn)(daes)$^{3+}$. The exchange rate for the remaining three S–CH$_2$– protons in the coordinated aeaps ligand are smaller than the rate by which Co(tacn)(C-aeaps)$^{2+}$ is formed, and only an upper-limit value for the rate-constant k_H could be determined, $k_H < 10^{-4}$ $M^{-1} s^{-1}$. This upper limit is close to the k_H-values for the S–CH$_2$ protons in Co(tacn)(daes)$^{3+}$ and therefore quite reasonable.

The high stereospecifity of the H/D-exchange reactions in CH$_2$ groups in cobalt(III) coordination compounds are, to our knowledge, unprecedented in the literature. By contrast, in Co(en)$_2$(gly)$^{2+}$ the two protons of CH$_2$ group in the glycinato ligand undergo base-catalysed H/D exchange with a ratio of the rate constants of 1.25 (Table 2).[11] This difference in stereospecificity may be ascribed to the puckering of the five-membered ring in Co(tacn)(daes)$^{3+}$ leading to different geometry of the two C–H bonds relative to the sulfur lone pair, contrary to what is observed in the nearly planar glycinato chelate.

Conclusions

The base-catalysed CH/CD exchange of CH$_2$–S protons in 3-thiahexane-1,5-diamine are enhanced several orders

of magnitude by coordination to a cobalt(III) ion. The exchange rates of the two protons differ by one order of magnitude. The different reactivity may be explained by different degrees of $p\pi$–$d\pi$ interaction in the two carbanions and by an intramolecular hydrogen bond that assists dissociation of the most labile proton.

References

1. Kofod, P., Larsen, E., Larsen, S., Pedersen, C. H., Springborg, J. and Wang, D.-N. *Acta Chem. Scand. 46* (1992) 841.
2. Kofod, P., Larsen, E., Petersen, C. H. and Springborg, J. *Acta Chem. Scand. 46* (1992) 1149.
3. Larsen, E., Larsen, S., Poulsen, G., Springborg, J. and Wang, D.-N. *Acta Chem. Scand. 48* (1994) 107.
4. Kofod, P., Larsen, E., Larsen, S., Poulsen, G., Springborg, J. and Wang, D.-N. *Acta Chem. Scand. 48* (1994) 283.
5. Wieghardt, K., Schmidt, W., Nuber, B. and Weiss, J. *Chem. Ber. 112* (1979) 2220.
6. Okamoto, M. S. and Barefield, E. K. *Inorg. Chim. Acta 17* (1976) 91.
7. Bjerrum, M. J., Kaas, K., Larsen, E., Nielsen, B. and Springborg, J. *Inorg. Chem. 28* (1989) 532.
8. Doddrell, D. M., Pegg, D. T. and Bendall, M. R. *J. Magn. Reson. 48* (1982) 323.
9. Sørensen, O. W., Eich, G. W., Levitt, M. H., Bodenhausen, G. and Ernst, R. R. *Progr. NMR Spectrosc. 16* (1983) 163.
10. Pyper, N. C. *Molec. Phys. 19* (1970) 161.
11. Buckingham, D. A., Stewart, I. and Sutton, P. A. *J. Am. Chem. Soc. 112* (1990) 845.
12. March, J. *Advanced Organic Chemistry*, 3rd. ed., Wiley, New York 1985, Chap. 5.
13. Wolfe, S., LaJohn, L. A., Bernardi, F., Mangini, A. and Tonachini, C. *Tetrahedron Lett. 24* (1983) 3789.
14. Borden, W. T., Davidson, E. R., Andersen, N. H., Denniston, A. D. and Epiotis, N. D. *J. Am. Chem. Soc. 100* (1978) 1604.
15. Laier, T. and Larsen, E. *Acta Chem. Scand., Ser. A 33* (1979) 257.