# Syntheses in Aqueous Solution and Crystal Structure of a Triamido-Bridged Dicobalt(III) Complex with the Ligands 1,4,7-Triazacyclononane and 3-Thiapentane-1,5-diamine

Pauli Kofod,[a] Erik Larsen,[a] Sine Larsen,[b], Dong-Ni Wang,[a] Johan Springborg,*[a] and Gudrun B. Paulsen[a]

[a] Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40 DK-1871 Frederiksberg C, Denmark and [b] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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The reaction of $Co(tacn)(daes)^{3+}$ [tacn = 1,4,7-triazacyclonane; daes = (3-thiapentane-1,5-diamine = di(2-aminoethyl)sulfide)] in 4 M NaOH yields nearly quantitatively the triamido-bridged dicobalt(III) complex: μ-1,4-diaza-7-azanidocyclononane-$1\kappa^2N^1,N^4,1:2\kappa^2N^7$-$\mu_2$-4-thiapentane-1,5-amido-$1\kappa S,1:2\kappa^4N,N'$-1,4,7--triazacyclononane-$2\kappa^3N^1,N^4,N^7$dicobalt(III) ion, in the following abbreviated as

$Co(tacn$-μ-$N)(daes$-μ_2-$N^1,N^2)Co(tacn)^{3+}$:
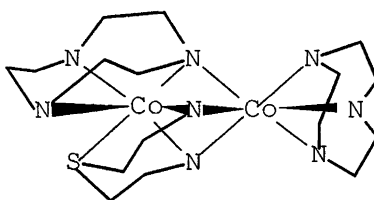
The new dinuclear cation was isolated from the reaction mixture as a perchlorate salt in high yield (63%). The crystal and molecular structure of [Co(tacn-μ-$N)(daes$-μ_2-$N^1,N^2)Co(tacn)](ClO_4)_3 \cdot H_2O$ has been established by X-ray diffraction techniques at 122 K: $a = 15.289(2)$, $b = 21.392(2)$ and $c = 17.834(4)$ Å, $V = 5228(5)$ Å^3, $F(000) = 3344$, $Z = 8$, space group $Pbca$, $R_w = 0.038$ for 3124 unique reflections.

Amido-bridged transition metal complexes are well known and among the first examples are the dicobalt(III) species reported by Werner at the beginning of this century.[1] They are analogues to the much more studied hydroxo-bridged species, and for many of the known amido-bridged species the corresponding hydroxo-bridged analogues have been reported and studied in detail.[2] The kinetics and thermodynamics of the hydroxo-bridged species and the interconversion reactions between these have been studied for, in particular, the trivalent complexes of cobalt, chromium, rhodium and iridium and has recently been reviewed in two articles.[2,3] The formation of a hydroxo-bridged species is initiated by

deprotonation of an aqua complex followed by the condensation of M–OH and M–OH$_2$ species. In the same way amido-bridged ammine complexes probably occur by deprotonation of a coordinated ammonia followed by condensation of M–NH$_2$ and M–NH$_3$ species. It is now well established that the thermodynamic and kinetic properties of hydroxo-bridged complexes are strongly influenced by intramolecular hydrogen bonds between coordinated hydroxide and coordinated water.[2–6] Likewise, recent studies have shown that intermolecular bonds between coordinated NH$^-_2$ and coordinated NH$_3$ play a prominent role in determining the stability of the corresponding amido-bridged ammine complexes.[7]

Following these analogies it is not surprising that, while the hydroxo-bridged complexes often are formed by

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* To whom correspondence should be addressed.

reactions in aqueous solvents, the amide species can be made in liquid ammonia. However, many of the classical amido-bridged compounds are obtained by reactions in aqueous solvent, but in all cases the precursor is then another bridged species. One example is the reaction of the peroxo-bridged complex $(NH_3)_5Co(O_2)Co(NH_3)_5^{4+}$ in aqueous ammonia which gives $(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4^{+}$.[1] Condensation of two monomeric cobalt(III) species to form an amido-bridged species has to our knowledge only been reported for reactions in liquid ammonia. One recent example of the latter type of reaction is the preparation of the first known triamido-bridged complex $(NH_3)_3Co(NH_2)_3Co(NH_3)_3^{3+}$ made by reaction of hexamminecobalt(III) in liquid ammonia at high pressure (24 h at 100°C).[8] The present work reports the synthesis and single-crystal structure of a new and unexpected triamido-bridged complex, which is obtained by a reaction $Co(tacn)(daes)^{3+}$ in aqueous sodium hydroxide [daes = 3-thiapentane-1,5-diamine = di(2-aminoethyl)sulfide)]. To our knowledge this is the first example of formation of a substituted amido-bridged cobalt(III) species by dimerization in aqueous solution of the parent mononuclear species.

Experimental

Materials. $[Co(tacn)(daes)]Cl_3 \cdot H_2O$, $[(tacn)Co(OH)_3Co(tacn)](ClO_4)_3 \cdot 4H_2O$, *trans*-$[(H_2O)(tacn)Co(OH)_2Co(tacn)(OH_2)](ClO_4)_4 \cdot 4H_2O$ and $Co(tacn)Cl_3$ were prepared as described previously.[9-12] All other chemicals were of analytical grade.

UV–VIS absorption spectra. UV–VIS absorption were obtained using a Perkin-Elmer Lambda diode array spectrophotometer or a Cary 3 spectrophotometer.

NMR Spectra. NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer equipped with a 5 mm probe for ^{13}C NMR measurement or a 10 mm broad-band tunable probe for ^{59}Co NMR measurements. ^{13}C chemical shift values (δ) are reported in ppm relative to 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; $\delta = 0$, 17.66, 21.74 and 57.02 ppm). ^{59}Co chemical-shift values (δ) are reported in ppm relative to an external aqueous solution of $K_3[Co(CN)]_6$ ($\delta = 0$ ppm), using replacement of the sample.

Synthesis

[Co(tacn-μ-N)(daes-μ_2-N¹,N²)Co(tacn)](ClO_4)_3·H_2O. A solution of $[Co(tacn)(daes)]Cl_3 \cdot H_2O$ (3.93 g, 9.08 mmol) in 4 M NaOH (4.9 ml, 19.6 mmol) was heated in a closed Teflon tube to 60°C for 1 h and then cooled in ice. To the cold solution was then added, with stirring and cooling in ice, ice-cold water (37 ml) and thereafter ice-cold 1 M NH_4ClO_4 (37 ml). Purple–brown crystals separated.

After 20 min the precipitate was filtered off, washed with one 5 ml portion of ice-cold water, three 20 ml portions of 96% ethanol and finally with diethyl ether and then dried in air. Yield 2.33 g (63%). IE-HPLC analysis showed that the product was pure. (Found: C 23.5; H 5.08; N 13.91; Cl 13.35; S 3.90. Calc. for $Co_2C_{16}H_{41}N_8SCl_3O_{13}$: C 23.7; H 5.10; N 13.84; Cl 13.13; S 3.96.). Data for the UV–VIS absorption spectrum in water are: $\{\varepsilon/[(M \ cobalt(III))^{-1} \ cm^{-1}], \lambda/nm\}_{max} = (19600,212)$; (153,550) and $\{\varepsilon/[(M \ cobalt(III))^{-1} \ cm^{-1}], \lambda/nm\}_{sh} = (389,400);(15800,239)$ (see also Fig. 1). The ^1H decoupled ^{13}C NMR spectrum of a solution of the perchlorate salt in D_2O (300 K) showed the following eight singlets: δ 42.6, 51.1, 51.9, 52.2, 52.3, 53.9, 55.2, 61.5.

Crystals of the triamido-bridged complex, suitable for X-ray structure analysis, were obtained from the reaction of $Co(tacn)(daes)^{3+}$ and base. A 0.6 M solution of $[Co(tacn)(daes)]Cl_3 \cdot H_2O$ in 2 M NaOH was kept 90 min at 59°C, cooled in ice and then added one volume of a saturated solution of $NaClO_4$ with a minimum of mixing of the two solvents. The mixture was kept at 5°C for 24 h. A mixture of red and yellow and purple–brown crystals separated. The red and yellow crystals were identified by IE-HPLC as salts of $Co(tacn)(daes)^{3+}$ and $(tacn)CO(OH)_3Co(tacn)^{3+}$, respectively. The purple–brown crystals were shown by IE-HPLC to be identical with the perchlorate salt described above and were identified as the triamido-bridged species by a crystal structure analysis as described below.

IE-HPLC measurements. Ion-exchange high-performance liquid chromatography (IE-HPLC) was performed using waters IE-HPLC system connected to a diode array detector. A Waters Protein Pak SP-5PW cation-exchanger was used and 0.23 M Na_2SO_4 was used as eluent in all experiments and the volumes of retention (V_r) given all refer to a flow of 1.0 ml min^{-1}. The IE-HPLC experiments were made at 0 and 25°C. All basic solutions were cooled in ice, diluted with cold water and then neutralized
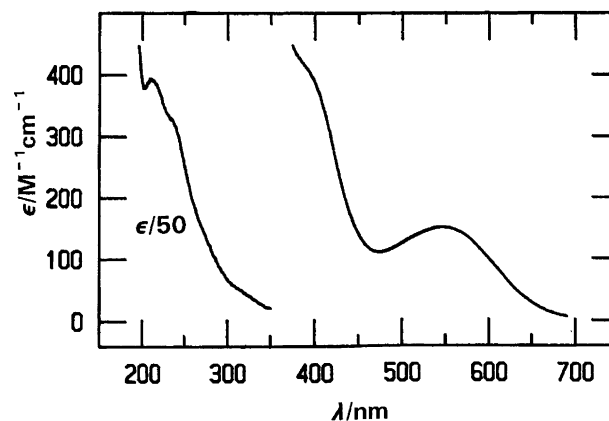

Fig. 1. Absorption spectrum of $[Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)](ClO_4)_3 \cdot H_2O$ in water at 25°C.

by addition of excess cold 1 M ammonium chloride prior to the IE-HPLC analysis. Solutions of pure Co(tacn)(OH)$_3$ were made by dissolving Co(tacn)Cl$_3$ in 1 M NaOH. The hydrolysis is complete within minutes at room temperature. The purity was controlled by IE-HPLC analyses. The concentrations of the cobalt(III) species in the product solutions (Fig. 2) were determined from chromatograms measured at 246 nm. At this wavelength the species Co(tacn)(daes)$^{3+}$, Co(tacn)(OH)$_3$, (tacn)Co(OH)$_3$Co(tacn)$^{3+}$ and Co(tacn-μ-N)(daes-μ$_2$-N^1,N^2)Co(tacn)$^{3+}$ have similar and high molar absorption coefficients: 10300, 9062, 7825 and 14400 M^{-1} cm^{-1}, respectively [molarity with respect to Co(III)]. The concentrations of the individual species were then calculated using these values and the integrated chromatograms as described previously.[13]
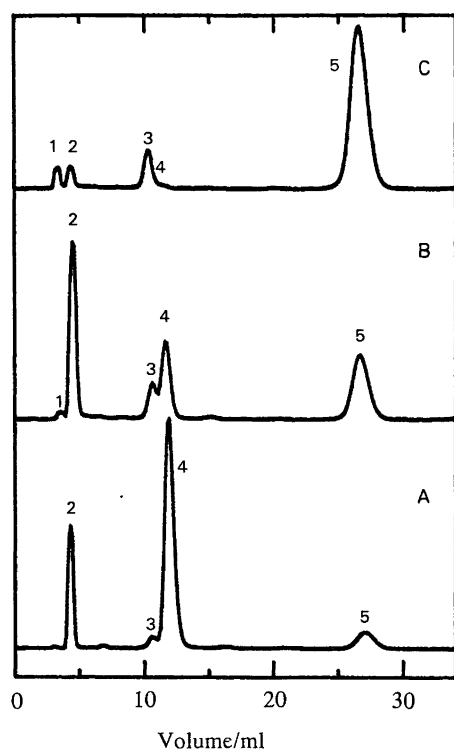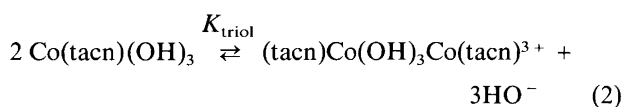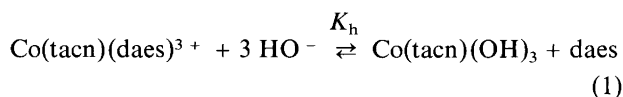

Fig. 2. IE-HPLC chromatograms for the equilibrium solutions obtained from the reaction of 1.6 M Co(tacn)(daes)$^{3+}$ in 1–4 M NaOH at 59°C (monitored using λ=246 nm at 25°C). Curves A, B and C, respectively, are for [NaOH]= 1.0, 2.0 and 4.0 M NaOH; the concentrations of hydroxide in the equilibrium solutions can be calculated from the stoichiometry and are 0.23, 0.29 and 1.8 M, respectively. The peaks 1, 2, 4 and 5, respectively, were identified as Co(tacn)(OH)$_3$, (tacn)Co(OH)$_3$Co(tacn)$^{3+}$, Co(tacn)(daes)$^{3+}$ and Co(tacn-μ-N)(daes-μ$_2$-N^1,N^2)Co(tacn)$^{3+}$ (V_r=3.2, 4.5, 12.4 and 27 ml, respectively). The peak 3 (V_r= 10.2 ml) was not identified. A minor tail following the peak for (tacn)Co(OH)$_3$Co(tacn)$^{3+}$ was identified as trans-(H$_2$O)(tacn)Co(OH)$_2$Co(tacn)(H$_2$O)$^{4+}$.

Crystal structure. A CAD4 diffractometer equipped with an Enraf-Nonius gas-flow temperature device was used for the data collection. The temperature was monitored with a thermocouple placed a few centimeters above the crystal in the exhaust pipe. Graphite monochromatized MoKα radiation was employed. Data reduction included corrections for Lorentz polarization and absorption effects. Transmission factors were in the range 0.653–0.900. The crystal data and a summary of data collection parameters and refinement results are listed in Table 1. The crystallographic computations were performed with the SDP system.[14] The space group was determined using Weissenberg photographs. [Co(tacn-μ-N)(daes-μ$_2$-N^1,N^2)Co(tacn)](ClO$_4$)$_3$·H$_2$O belongs to the orthorhombic system, and the systematically absent reflections determine the space group as *Pbca*.

The structure was solved by a combination of Patterson and direct methods (SHELXS-86).[15] The refinement was made by full-matrix least-squares minimizing of $\Sigma w(|F_o| - |F_c|)^2$. The positions of the hydrogen atoms were revealed in the difference Fourier calculated after an anisotropic refinement. Calculated positions and a fixed thermal parameter of 2.5 Å^2 were used for the final refinement. The final heavy-atom positional parameters are given in Table 2.

Results and discussion

Synthesis and properties of the triamido-bridged dicobalt(III) species. Recently we reported[12] a kinetic study of the base hydrolysis of Co(tacn)(daes)$^{3+}$. It was shown that in 1 M NaOH the dominant reactions for [Co]$_{total}$ = 0.002–0.05 M are formation of Co(tacn)(OH)$_3$ [dominant at lower cobalt(III) concentrations] and of (tacn)Co(OH)$_3$Co(tacn)$^{3+}$ [dominant at higher cobalt(III) concentrations] as shown in eqns. (1) and (2).

$$Co(tacn)(daes)^{3+} + 3\,HO^- \overset{K_h}{\rightleftharpoons} Co(tacn)(OH)_3 + daes$$

$$(1)$$

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

$$(2)$$

In strong base the Co(tacn)(daes)$^{3+}$ species deprotonates, pK_a = 13.44, probably at one of the coordinated amine groups of the tacn ligand.[9] It is also possible that the other species in eqns. (1) and (2) deprotonate to corresponding amido complexes. For the sake of simplicity these equilibria were ignored in Ref. 12, and are also ignored in the discussion here. Likewise, possible[2] deprotonations of the hydroxo-bridges to form hydroxo-oxo-bridged species were ignored. The following equilibrium constants were reported: K_h = 0.78(20) M^{-2} and K_{triol} = 17(3) M^2.

In the present work we have studied the reactions for solutions with very large cobalt(III) concentrations

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Table 1. Crystal data and a summary of data reduction and structure refinement.

Compound	[Co(tacn-μ-N)(daes-μ$_2$-N^1,N^2)Co(tacn)](ClO$_4$·H$_2$O
Formula	Co$_2$Cl$_3$SO$_{13}$N$_8$C$_{16}$H$_{41}$
Formula mass	809.84 g mol^{-1}
Space group	Pbca
Wavelength (Mo$K\alpha$)/Å	0.71073
Unit cell dimensions at 122 K:	
a/Å	15.289(3)
b/Å	21.392(4)
c/Å	17.834(3)
V/Å^3	5833(3)
Z	8
$F(000)$	3344
D_c/g cm^{-3}	1.844
D_{exp}/g cm^{-3}	1.820
μ(Mo$K\alpha$)/cm^{-1}	15.55
Crystal size/mm	0.06×0.20×0.40
Scan mode	ω-2θ
Scan range, $\Delta\omega$/°	0.8+0.35 tan θ
θ-Range/°	1-25
Weights, w^{-1}	$\sigma^2(F)+0.0012|F|^2$
$S=[\Sigma w\Delta F^2/(n-m]^{1/2}$	0.90
No. of independent reflections	5117
No. of observed reflections	3124
No. of variables m	511
R	0.028
R_w	0.038

(1.6 M) and with high base concentrations: 1–4 M NaOH. The reactions were performed at 59°C, and the product distribution was determined by IE-HPLC analysis. For each base concentration it was shown that heating for 1 and 2 h, respectively, gave the same result, and it is therefore assumed that equilibrium has been attained. The chromatograms in Fig. 2 illustrate how the equilibrium concentrations of the different species vary with the base concentration. First it is noted that up to five dominant species are present: the three species already known: [Co(tacn)(OH)$_3$ (V_r = 3.2 ml), (tacn)Co(OH)$_3$Co(tacn)$^{3+}$ (V_r = 4.5 ml) and Co(tacn)(daes)$^{3+}$ (V_r = 12.4 ml)] and two new species with V_r = 10.2 and 27 ml. The known species were identified by comparison of their volumes of retention (V_r) and their UV–VIS spectra with those of the

authentic species. The species which has V_r = 10.2 ml was not identified. The other new cation has a volume of retention (V_r = 27 ml), which indicates that it is an oligomer. In Fig. 2 it is shown how the concentration of this new cation increases when the concentration of base increases and that it is formed nearly quantitatively in 4 M NaOH ([OH$^-$] = 1.8 M at equilibrium). The new species was isolated from the reaction of 1.9 M [Co(tacn)(daes)]Cl$_3$·H$_2$O in 4 M NaOH as a purple-brown perchlorate salt in 63% yield. A single-crystal X-ray structure analysis has shown (see below) that the product is a dinuclear triamido-bridged cation formed by the condensation of Co(tacn)(OH)$_3$ with Co(tacn)(daes)$^{3+}$ as shown in eqn. (3) (see also Figs. 3 and 4).
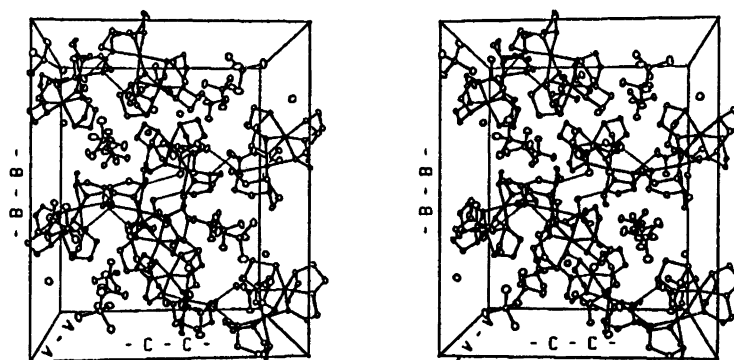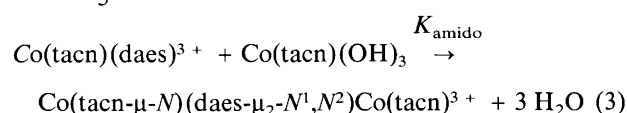

Fig. 3. Stereoscopic picture of the unit cell along the a-axis.

Table 2. Fractional coordinates and the equivalent isotropic temperature factors for atoms in [Co(tacn-μ-N)(daes-μ$_2$-N^1,N^2)Co(tacn)](ClO$_4$)$_3$·H$_2$O. [a]

Atom	x/a	y/b	z/c	$B_{iso}/Å^3$ [b]
Co1	0.75079(3)	0.33071(2)	0.03459(3)	1.249(9)
Co2	0.78070(3)	0.42919(2)	0.11424(3)	1.152(9)
N11	0.6829(2)	0.3377(2)	-0.0596(2)	1.77(6)
N12	0.8374(2)	0.2852(2)	-0.0261(2)	1.81(7)
N13	0.8085(2)	0.4066(1)	0.0076(2)	1.48(6)
C11	0.7247(3)	0.2997(2)	-0.1205(2)	2.64(9)
C12	0.7879(3)	0.2543(2)	-0.0875(2)	2.54(9)
C13	0.6798(3)	0.4058(2)	-0.0777(2)	1.91(8)
C14	0.7683(3)	0.4346(2)	-0.0604(2)	1.79(8)
C15	0.9015(3)	0.3896(2)	-0.0100(2)	1.83(8)
C16	0.9047(3)	0.3302(2)	-0.0550(2)	2.10(8)
S	0.68532(7)	0.24636(5)	0.08395(6)	1.85(2)
N11d	0.8196(2)	0.3413(1)	0.1252(2)	1.29(6)
N12d	0.6737(2)	0.3849(1)	0.0900(2)	1.31(6)
C11d	0.7602(3)	0.2364(2)	0.1627(2)	2.02(8)
C12d	0.5909(3)	0.2874(2)	0.1224(3)	2.45(9)
C13d	0.7993(3)	0.2988(2)	0.1895(2)	1.87(8)
C14d	0.6154(3)	0.3541(2)	0.1472(2)	2.13(8)
N21	0.7335(2)	0.5133(1)	0.0955(2)	1.44(6)
N22	0.8919(2)	0.4728(2)	0.1352(2)	1.61(6)
N23	0.7544(2)	0.4464(1)	0.2201(2)	1.42(6)
C21	0.8038(3)	0.5613(2)	0.057(2)	2.09(8)
C22	0.8917(3)	0.5305(2)	0.0888(2)	2.11(8)
C23	0.6652(3)	0.5240(2)	0.1541(2)	2.20(8)
C24	0.7031(3)	0.5055(2)	0.2283(2)	1.99(8)
C25	0.8397(3)	0.4465(2)	0.2603(2)	2.12(8)
C26	0.9020(3)	0.4864(2)	0.2174(2)	2.10(8)
Cl1	1.10259(6)	0.38055(4)	0.11929(5)	1.75(2)
O11	1.0890(2)	0.4469(1)	0.1155(2)	3.04(7)
O12	1.1103(2)	0.3556(2)	0.0457(2)	2.71(6)
O13	1.0273(2)	0.3530(2)	1.554(2)	2.90(7)
O14	1.1793(2)	0.3665(2)	0.1620(2)	2.78(6)
Cl2	0.59149(6)	0.60564(5)	-0.03183(6)	1.96(2)
O21	0.5920(2)	0.6375(1)	-0.1028(2)	2.63(6)
O22	0.6409(2)	0.6413(1)	0.0226(2)	2.47(6)
O23	0.5037(2)	0.5986(2)	-0.0060(2)	2.96(7)
O24	0.6215(2)	0.5453(1)	-0.0407(2)	3.16(7)
Cl3	1.00391(7)	0.64572(4)	0.25399(6)	1.99(2)
O31	1.0525(2)	0.5996(2)	0.2131(2)	2.98(7)
O32	0.9174(2)	0.6489(1)	0.2244(2)	2.58(8)
O33	0.9989(2)	0.6274(2)	0.3306(2)	3.70(8)
O34	1.0445(2)	0.7053(2)	0.24682)	4.15(8)
Ow	0.5006(2)	0.2335(1)	0.4361(2)	3.32(7)

[a] The cobalt atoms are numbered 1 and 2. To Co1 is bound the tacn ligand 1, where N11 and N12 coordinate in a usual fashion while the deprotonated N13 forms a bridge to Co2. The daes ligand coordinates to Co1 with the thioether sulfur atom, while the deprotonated N11d and N12d form bridges between Co1 and Co2. The second tacn ligand occupies the remaining face of Co2.

[b] $B_{iso} = \dfrac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i a_j a^*_i a^*_j$.

$$Co(tacn)(daes)^{3+} + Co(tacn)(OH)_3 \xrightarrow{K_{amido}}$$

$$Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)^{3+} + 3\,H_2O \quad (3)$$

The new triamido-bridged species is stable for several hours in aqueous basic, neutral or acidic solution (25 °C, pH 2–12) as shown spectrophotometrically. Likewise it was shown that it does not exhibit any acid–base prop-

erties in the pH region 2–12. The UV–VIS absorption spectrum is shown in Fig. 1.

It is not easy to rationalize the observation that the concentration of the new triamido-bridged species increases with increasing base concentration. In terms of eqns. (1)–(3) it was anticipated that the monomeric Co-(tacn)(OH)$_3$ would be dominant at very large hydroxide concentration, which clearly is not the case. The reasons are probably a radical change in the concentration equilibrium constants with the ionic strength combined with a decrease in the water activity with the increasing salt concentration. It is noted that a low water activity will stabilize the triamido-bridged species relative to Co-(tacn)(OH)$_3$ as well as to (tacn)Co(OH)$_3$Co(tacn)$^{3+}$. The effect of ionic strength may be illustrated by the value of the concentration equilibrium constant K_{triol}, which previously was determined[12] as $K_d = 17\,M^{-2}$ in 1 M NaOH ([Co] = 0.05 M), whereas in this work it is estimated that $K_{triol} = 70\,M^{-2}$ in 4 M NaOH ([Co] = 1.6 M). A similar, but more pronounced, change is observed for the concentration equilibrium constant K_{amido}, which has the values $K_{amido} < 10\,M^{-1}$ in 1 M NaOH ([Co] = 0.05 M) and $K_{amido} \approx 10^3\,M^{-1}$ in 4 M NaOH ([Co] = 1.6 M). The former value for K_{amido} is based upon data from Ref. 12 (all values for 59 °C).

Preliminary experiments indicate that a mixture Co-(tacn)(OH)$_3$ and Co(en)$^{3+}_3$ in 4 M NaOH does not form an amido-bridged species. This difference in behaviour of Co(tacn)(daes)$^{3+}$ and Co(en)$^{3+}_3$ is probably due to the different acid strength of the coordinated amine groups of the ligands 1,4,7-triazacyclononane (pK_a = 13.44)[9] and 1,2-ethanediamine (pK_a > 14).[16] Following these lines we propose that the first step in the formation of the present amido complex is deprotonation of an coordinated amine group of tacn in Co(tacn)(daes)$^{3+}$ followed by a nucleophilic attack at the cobalt(III) center of Co(tacn)(OH)$_3$. The subsequent steps involve deprotonation of the amine
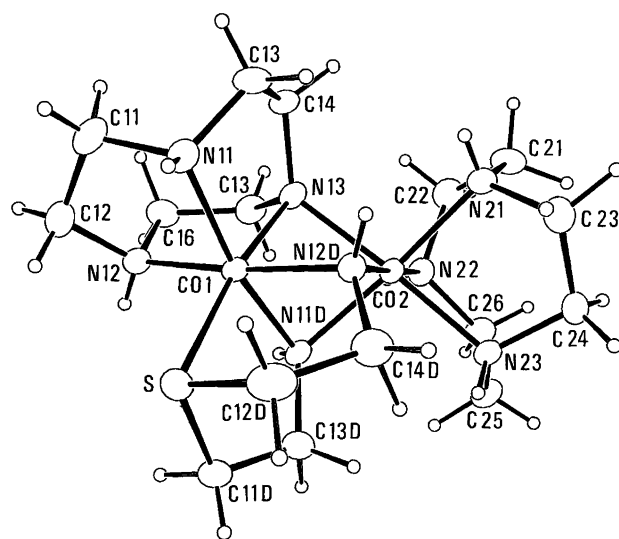

Fig. 4. ORTEP drawing of the dinuclear cation.

groups of the daes ligand; these amine groups are probably much less acidic than those of tacn, but proximity effects are likely to promote the subsequent intramolecular amido-bridge formation reactions.

^{13}C NMR Spectra. The ^{13}C NMR spectrum of a solution of $[Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)](ClO_4)_3 \cdot H_2O$ in D_2O has eight signals (see Experimental), which shows that the cation, as expected, contains a plane of

Table 3. Selected bond lengths, d, and angles, α, for $[Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)](ClO_4)_3 \cdot H_2O$. For labelling of the atoms consult Table 2.

Atoms		$d/\text{Å}$		Atoms		$d/\text{Å}$
Co1	N11	1.980(4)		Co2	N21	1.968(4)
Co1	N12	1.967(4)		Co2	N22	1.975(4)
Co1	N13	1.910(3)		Co2	N23	1.965(4)
Co1	N11d	1.942(3)		Co2	N13	2.007(4)
Co1	N12d	1.926(4)		Co2	N11d	1.981(4)
Co1	S	2.243(1)		Co2	N12d	1.939(3)

		$d/\text{Å}$ for $i=1$	$d/\text{Å}$ for $i=2$
N*i*1	C*i*2	1.500(6)	1.488(6)
		1.491(6)	1.494(6)
N*i*2	C*i*2	1.488(6)	1.485(7)
N*i*2	C*i*6	1.500(6)	1.504(6)
N*i*3	C*i*4	1.487(6)	1.495(6)
N*i*3	C*i*5	1.501(6)	1.487(6)
C*i*1	C*i*2	1.490(7)	1.503(7)
C*i*2	C*i*4	1.518(7)	1.497(7)

		$d/\text{Å}$
S	C11d	1.825(5)
S	C12d	1.824(5)
N11d	C13d	1.497(6)
N12d	C14d	1.505(6)
C11d	C13d	1.537(7)
C12d	C14d	1.540(7)

			$\alpha/1°$
Co1	N13	Co2	82.4(14)
Co1	N11d	Co2	82.3(14)
Co1	N12d	Co2	83.8(14)

			$\alpha/1°$ for $i=1$	$\alpha/1°$ for $i=2$
N13	Co*i*	N11d	81.9(2)	78.6(14)
N13	Co*i*	N12d	84.3(15)	81.4(15)
N13	Co*i*	N*i*1	87.9(2)	97.8(2)
N13	Co*i*	N*i*2	88.3(2)	96.3(2)
N11d	Co*i*	N12d	80.4(2)	79.1(2)
N11d	Co*i*	N*i*1	168.8(2)	174.1(2)
N12d	Co*i*	N*i*1	94.0(2)	95.8(2)
N12d	Co*i*	N*i*2	172.7(2)	177.6(2)
N*i*1	Co*i*	N*i*2	85.6(2)	85.3(2)
S	Co*i*	N*i*1	99.2(12)	
S	Co*i*	N*i*2	96.8(12)	
S	Co*i*	N*i*3	171.5(11)	
S	Co*i*	N11d	90.5(11)	
S	Co*i*	N12d	90.5(11)	
N*i*1	C*i*1	C*i*2	110.1(4)	110.0(4)
N*i*1	C*i*3	C*i*4	108.9(4)	107.9(4)
N*i*2	C*i*2	C*i*1	109.3(4)	108.7(4)
N*i*2	C*i*6	C*i*5	109.7(4)	108.9(4)
N*i*3	C*i*4	C*i*3	111.7(4)	109.9(4)
N*i*3	C*i*5	C*i*6	110.3(4)	108.3(4)
N11d	C13d	C11d	111.7(4)	
N12d	C14d	C12d	110.8(4)	
S	C12d	C14d	111.2(3)	
S	C11d	C13d	112.5(3)	

symmetry. It has not been possible to make any firm assignments of the signals, as all carbon atoms are bonded to amino groups, except C11d and C12d, which are bonded to the thioether sulfur atom and presumably have the lowest resonance frequency. No exchange of deuterium for hydrogen at C11d and C12d was observed after two weeks in 1 M NaOD at 25°C. This is in marked contrast to the rapid deuterium exchange in $Co(tacn)(aeaps)^{3+}$ at similar conditions ($t_{1/2}$ = 2 min).[17] The difference is probably mainly due to the lower charge per cobalt atom in the $Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)^{3+}$ species.

A solution of $[Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)]$ $(ClO_4)_3 \cdot H_2O$ in D_2O gives two ^{59}Co NMR signals at 300 K. One is found at $\delta = 5270$ ppm ($\Delta v_{1/2} = 730$ Hz), the other is found at $\delta = 7870$ ppm ($\Delta v_{1/2} = 3140$ Hz). For comparison $Co(tacn)(daes)^{2+}$ gives a signal at $\delta = 5980$ ppm ($\Delta v_{1/2} = 810$ Hz), while cobalt(III) compounds with six amine ligands typically resonate in the range 7200–8200 ppm.[18] Hence the signal at 5270 ppm in $Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)^{3+}$ is assigned to Co1 and that at 7870 ppm is assigned to Co2. (Co1 and Co2 are defined as shown in Fig. 4.)

Description of the crystal structure. The bond distances and bond angles for the dinuclear cation $[Co(tacn-\mu-N)(daes-\mu_2-N^1,N^2)Co(tacn)](ClO_4)_3 \cdot H_2O$ are given in Table 3. The crystal is held together by hydrogen bonding and electrostatic attractions, as may be seen from Fig. 3. The cation shown in Fig. 4 has Co–N bond lengths varying between 1.910(3) and 2.007(4) Å. The two bridging NH^- groups from daes have relatively short bond distances of 1.942(3) and 1.926(4) Å to Co1, while Co2 has two rather different bond distances of 1.981(4) and 1.939(3) Å to the two bridging NH^- groups. This unsymmetrical binding is unexpected, since the trans ligands all are tacn amino groups. The bridging N^- group of tacn is also unsymmetrically binding, with a short Co–N distance of 1.910(3) Å to Co1 and a long distance of 2.007(4) Å to Co2. In this case the trans ligands are N and S, respectively, but a coordinating thioether has been found to have little effect on the bond distance of a trans coordinating ligand,[9,19] and therefore does not explain the unsymmetrical binding. The unsymmetrical structure of the cation is therefore attributed to crystal packing forces. This is in keeping with the ^{13}C NMR data, which show that the dinuclear cation in solution possesses the

expected plane of symmetry. The Co–Co distance is 2.5816(8) Å, and this is surprisingly similar to the distance 2.565(1) Å found for $(NH_3)_3Co(OH)_3$ $Co(NH_3)_3^{3+}$ and 2.549(8) found for $(tacn)Co(OH)_3$ $Co(tacn)^{3+}$.[9,20]

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