

Dinuclear 1,4,7-triazacyclononane (tacn) complexes of cobalt(III) with amido and tacn bridges. Synthesis, characterization and reversible acid-accelerated bridge cleavage

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Amido-bridged dinuclear cobalt(III) complexes with 1,4,7-triazacyclononane (tacn) were synthesized from $[\text{Co}(\text{tacn})(\text{O}_3\text{SCF}_3)_3]$ by treatment with potassium amide in liquid ammonia at 100 °C. Two isomeric triply bridged complexes, $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$ and $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\{\mu\text{-tacn}(\text{-H})\}\text{Co}(\text{NH}_3)]^{3+}$, were isolated as perchlorates, and the crystal structure of the perchlorate of the latter complex was determined by X-ray diffraction. In this compound a nitrogen atom (deprotonated) from one of the tacn ligands forms a third bridge together with two amido bridges. In 1.0 M (Na,H)ClO₄ ($[\text{H}^+] = 0.1\text{--}1.0$ M) the two isomers undergo acid-accelerated amido bridge cleavage, as earlier found for chromium(III) analogues, in spite of the fact that such bridges are co-ordinatively saturated. The triamido-bridged isomer is in this acid medium in equilibrium with $[(\text{H}_2\text{O})(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{tacn})(\text{NH}_3)]^{4+}$. An isolated perchlorate of this complex appeared to be the salt of the *trans*-ammineaqua isomer as determined by X-ray diffraction. Equilibration from both sides fits the first-order rate constant dependence $k_{\text{obs}} = 6.2(3) \times 10^{-5}[\text{H}^+] + 2.1(2) \times 10^{-5}(\text{s}^{-1})$ at 40 °C. Prolonged treatment of the two triply bridged isomers in 1.0 M HClO₄ at elevated temperature produces primarily triply bridged dinuclear species where one or two amido bridges have been replaced by hydroxo bridges.

Introduction

Dinuclear cobalt(III) complexes with one or two amido bridges have since Alfred Werner's extensive description of these compounds¹ been the subject of several studies. A thorough review on dinuclear complexes of cobalt by Sykes and Weil² includes a chapter on the interconversion of such complexes with the emphasis on those with one amido bridge and no or one alternative bridge. The complexes may contain one or two additional bridges,¹ other than NH₂, between the two cobalt nuclei, *e.g.* OH, O₂, Cl, Br, NO₂, SO₄, RCOO, RC(NH)₂³ and RC(O)NH.⁴ The non-bridging ligands in these complexes are typically ammonia or amines like H₂NCH₂CH₂NH₂ or N(CH₂CH₂NH₂)₃,^{3,4} and *e.g.* H₂O, OH[−] or Cl[−] may be part of the non-bridging co-ordination sphere. The crystallographic data bases in Karlsruhe⁵ and Cambridge⁶ contain *ca.* 40 examples of structure solutions of such compounds. Less well documented amido-bridged complexes with more than two cobalt(III) nuclei have also been described.⁷

Syntheses of amido-bridged cobalt(III) complexes usually take place in aqueous (concentrated) or liquid ammonia. Of the amminecobalt(III) dimers with amido bridges only, $[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)\text{Co}(\text{NH}_3)_3]^{5+}$ and $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{NH}_3)_4]^{4+}$, go back to Werner,¹ and reproducible methods of synthesis with high yields have been worked out later.^{8,9} In case of the diamido-bridged species this is a result of studies by Ludwig Heck and co-workers in the 1980s and 1990s on the formation of amido bridges for a series of metal amines, first of all those of chromium(III),¹⁰ cobalt(III),^{11,12} rhodium(III)¹² and platinum(IV).¹³

Another result of their work was the synthesis and structural characterization of the first triply amido-bridged metal complex, $[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{NH}_3)_3]^{3+}$ [from $\text{Co}(\text{NH}_3)_6^{3+}$ and KNH₂ in NH₃(l)].¹¹ In water this complex is remarkably robust, and the first bridge cleavage was investigated at $[\text{H}^+] = 0.005\text{--}0.5$ M, where the observed rate constant increases linearly with $[\text{H}^+]$ ($k_{\text{obs}} \approx 0.45[\text{H}^+] \text{ s}^{-1}$ at 35 °C in 1 M (Na,H)NO₃ (extrapolated)).¹² Such a $[\text{H}^+]$ dependency is in contrast to what has been found for the bridge cleavage of $[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{NH}_3)_3]^{5+}$ where the rate constant is independent of $[\text{H}^+]$ over the range 0.02–2.00 M [$1.35 \times 10^{-4} \text{ s}^{-1}$ at 65 °C in 2.00 M (Na,H)ClO₄].¹⁴

Whereas an acid-accelerated path for the cleavage of a hydroxo bridge can be explained by H⁺ binding to the bridging atom,^{15–17} this is not possible for the co-ordinatively saturated amido bridge. Nevertheless, acid-accelerated amido bridge cleavage was observed recently¹⁸ also for the chromium(III) analogue, $[(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{NH}_3)_3]^{3+}$, and for $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{tacn})]^{3+}$ and $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})]^{3+}$ (tacn = 1,4,7-triazacyclononane).

In the following we present a comparative investigation, including synthesis and characterization, of the corresponding (tacn)cobalt(III) complex, $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$, and of an isomer, $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\{\mu\text{-tacn}(\text{-H})\}\text{Co}(\text{NH}_3)]^{3+}$, where a nitrogen atom (deprotonated) from one of the tacn ligands forms one of the three bridges.

Results and discussion

Identification

X-Ray diffraction, ¹³C-{¹H} NMR and electrospray mass spectrometry (ESMS, a very useful technique for the characterization of bridged, multiply charged complexes¹⁹) have been the primary means of identification of the three complexes **1**, **2** and **3** isolated as perchlorates after treatment of $[\text{Co}(\text{tacn})(\text{O}_3\text{SCF}_3)_3]$ with KNH₂ (mol fraction 1 : 1.4) in liquid ammonia at 100 °C for three days. In the following we describe these compounds in more detail including the behaviour of the amido-bridged complexes **2** and **3** in perchloric acid.

$[\text{Co}(\text{tacn})_2]^{3+}$ (**1**)

This yellow complex, first reported by Koyama and Yoshino,²⁰ is the main product (37% based on tacn), leaving compound **2** and **3** to be produced in smaller yields. The ¹³C NMR spectrum shows only one peak with $\delta = 50.3$, and ESMS: $m/z = 105.73$ (calc. 105.73 for **1**) and 515.09 (calc. 515.08 for **1** + 2ClO₄[−], see below). This complex will not be discussed further.

$[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$ (**2**)

The ¹³C NMR spectrum of this red complex shows only one peak with $\delta = 48.5$, and the ¹H NMR spectrum four peaks with $\delta = -1.32$,

2.57, 3.04 and 5.23 with the intensity ratio *ca.* 1:2:2:1, respectively. ESMS: $m/z = 141.39$ (calc. 141.39 for **2**), 261.55 (calc. 261.56 for **2** + ClO₄⁻) and 622.06 (calc. 622.07 for **2** + 2ClO₄⁻) (the isotope pattern is shown in Fig. 1). X-Ray powder diffraction data for the perchlorate of **2** and for the corresponding chromium(III) compound²¹ show that these two compounds are isomorphous.

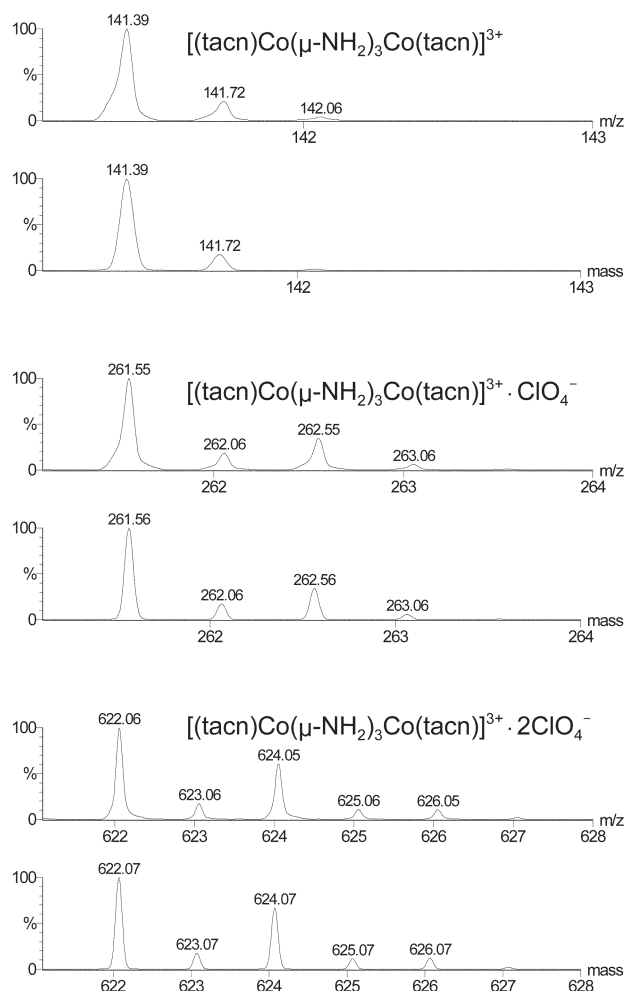


Fig. 1 Electrospray mass spectrum (cone volt.: 5.0 V) of [(tacn)Co(μ-NH₂)₃Co(tacn)](ClO₄)₃·H₂O in water with simulated spectrum (below).

[(tacn)Co(μ-NH₂)₂{μ-tacn(-H)}Co(NH₃)]³⁺ (**3**)

This complex, which has a more muddy red colour than the red colour of its isomer, **2**, shows a ¹³C NMR spectrum with six peaks with approximately the same intensity in contrast to the one peak only found in complex **2** (and **1**). Chemical shifts are $\delta = 48.7, 48.8, 49.0, 49.2, 50.8$ and 56.9 in accordance with six different pairs of carbon atoms, with one pair differing significantly from the carbon atoms of complex **2** (and **1**). The ESMS e/z values are the same as for complex **2**.

Single crystals of the perchlorate of complex **3** for X-ray analysis showed a substantial disorder. In the perrhenate the disorder is less pronounced, and Fig. 2 and Table 1 shows the result of an X-ray structure analysis of the perrhenate of complex **3**.

Description of the crystal structure of the perrhenate of complex 3. The structure of the cation exhibit several similarities to the structure of the only other example of a dinuclear complex (**A**) where one nitrogen atom in tacn participates as a bridge. In **A** two cobalt ions are co-ordinated to one 3-thiapentane-1,5-diamine, S(CH₂CH₂NH₂)₂, giving rise to two amido bridges, to one tacn forming one amido bridge and to one tacn co-ordinated facially non-bridging.²³ In complex **3** the Co–N bond lengths are in the range 1.912(4)–2.002(4) Å [1.910(3)–2.007(4) in **A**]. The shortest and longest co-ordinate bond are from the tacn(-H) bridging nitrogen atom. In this asymmetric bridge the long bond is to the

Table 1 Selected bond lengths (in Å) and bond angles (in °) in [(tacn)Co(μ-NH₂)₂{μ-tacn(-H)}Co(NH₃)](ReO₄)₃·H₂O

Co(11)–N(3)	1.916(4)	Co(21)–N(4)	1.912(4)
Co(11)–N(2)	1.932(4)	Co(21)–N(2)	1.923(4)
Co(11)–N(9)	1.948(4)	Co(21)–N(3)	1.925(4)
Co(11)–N(8)	1.974(4)	Co(21)–N(6)	1.954(4)
Co(11)–N(7)	1.977(4)	Co(21)–N(5)	1.979(4)
Co(11)–N(4)	2.002(4)	Co(21)–N(1)	1.990(4)
Co(11)–Co(21)	2.5945(10)		
Co(11)–N(2)–Co(21)	84.61(16)		
Co(11)–N(3)–Co(21)	84.98(15)		
Co(11)–N(4)–Co(21)	83.01(16)		

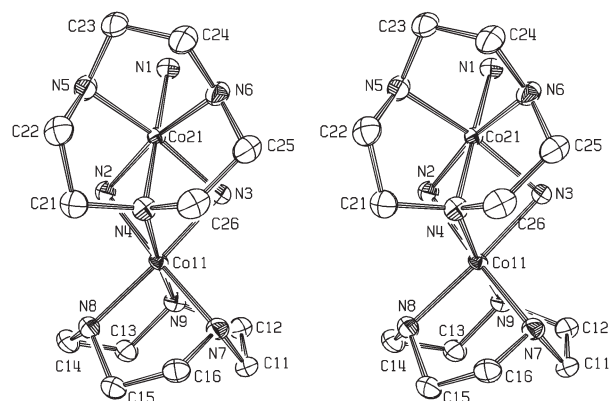
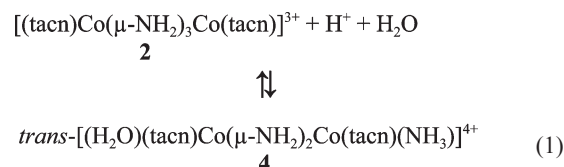


Fig. 2 Stereoscopic ORTEP²² drawing of complex **3**, [(tacn)Co(μ-NH₂)₂{μ-tacn(-H)}Co(NH₃)]³⁺. Ellipsoids are at the 50% probability level, and for clarity the hydrogen atoms are omitted.

adjacent cobalt atom with the non-bridging tacn, and the bridging Co–N–Co angle is 83.01(16)° [82.4(14)° in **A**] against 84.61(16) and 84.98(15)° for the NH₂ bridges which have Co–N bond lengths from 1.916(4) to 1.932(4) Å (84.4° and 1.939 Å in [(NH₃)₃Co(μ-NH₂)₃Co(NH₃)]³⁺ (**B**)).¹¹ Other bond lengths and bond angles are similar to those found in comparable complexes, including the Co–Co distance, 2.5945(10) Å [2.5816(8) in **A** and 2.605 in **B**]. The conformation of the two tacn rings in **3** are different, $\delta\delta\delta$ and $\lambda\lambda\lambda$, while both ring conformations in **A** are either $\delta\delta\delta$ or $\lambda\lambda\lambda$. The bond lengths between the rhenium and oxygen atoms with highest population are in the range 1.710(6) to 1.737(6) Å, the perrhenate ions, the water molecule and the nitrogen atoms being involved in a three-dimensional network of hydrogen bonds.

[(tacn)Co(μ-NH₂)₂Co(tacn)]³⁺ (**2**) in 1.0 M (Na,H)ClO₄

In acid medium, 1.0 M (Na,H)ClO₄ ([H⁺] 0.1–1.0 M), the tri-amido-bridged complex **2** undergoes bridge cleavage to form the diamido-bridged ammineaqua complex [(H₂O)(tacn)Co(μ-NH₂)₂Co(tacn)(NH₃)]⁴⁺ (**4**). This complex was isolated as a perchlorate (83% yield, see Experimental), and a single X-ray structure determination of this salt (see below) showed that the complex has a *trans*-configuration of the water and ammonia ligand with respect to the bridge plane. In the same medium [1.0 M (Na,H)ClO₄] complex **4** undergoes bridge formation to produce complex **2**. The reversible equilibration reaction



was followed from both sides by UV/Vis time drives and in a more qualitative way by FPLC and by ESMS of isolated product mixtures (see Experimental). Fig. 3 shows the result of the UV/Vis measurements in form of observed first order rate constants, k_{obs} , as a function of [H⁺] (40, 50 and 60 °C) approximated with $k_{\text{obs}} = a[\text{H}^+] + b$. Table 2 gives the values of a and b and their activation parameters, together with those of the trihydroxo-bridged analogue.²⁴

Table 2 a and b in $k_{\text{obs}} = a[\text{H}^+] + b$ (cf. Fig. 3) and their activation parameters [1.0 M (Na,H)ClO₄ at 40 °C] compared to those of the trihydroxo-bridged analogue²⁴ [1.0 M (Li,H)ClO₄ at 40 °C (extrapolated)]

$[(\text{tacn})\text{Co}(\text{X})_3\text{Co}(\text{tacn})]^{3+}$	$\text{X} = \mu\text{-NH}_2$	$\text{X} = \mu\text{-OH}$
$a/\text{M}^{-1} \text{s}^{-1}$	$6.2(3) \times 10^{-5}$	0.125
$\Delta H_a^\ddagger/\text{kJ mol}^{-1}$	82(2)	63(2)
$\Delta S_a^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	-62(7)	-63(5)
b/s^{-1}	$2.1(2) \times 10^{-5}$	0.035
$\Delta H_b^\ddagger/\text{kJ mol}^{-1}$	104(8)	100(8)
$\Delta S_b^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	-3(25)	50(25)

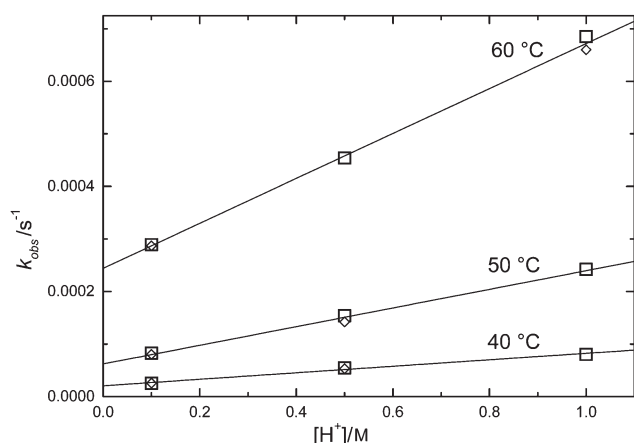


Fig. 3 Experimental pseudo-first order rate constants from UV/Vis measurements (270 nm) of complex **2** (□) and **4** (◇) in 1.0 M (Na,H)-ClO₄ [reaction (1)]. The lines are the result of least squares refinements (unit weights) using $k_{\text{obs}} = a[\text{H}^+] + b$ (cf. Table 2).

Table 3 compares values of a and b for similar reactions of dinuclear cobalt(III) and chromium(III) complexes with amido or hydroxo bridges and with tacn or NH₃ as non-bridging ligands. In the case of hydroxo bridge cleavage, the acid-dependent term, $a[\text{H}^+]$, is generally explained by a path involving protonation of the bridge to form a water bridge, which is a strong acid (references in Table 3). A similar protonation of the co-ordinatively saturated amido bridge is not expected. Nevertheless, such $[\text{H}^+]$ dependency is dominant in all the triamido-bridged examples in Table 3. The values of a span more than eight orders of magnitude from the slowest, complex **2**, to the fastest, $[(\text{NH}_3)_3\text{Cr}(\mu\text{-OH})_3\text{Cr}(\text{NH}_3)_3]^{3+}$. This reflects that the bridge cleavage is slower for cobalt(III) than for chromium(III), slower for $\mu\text{-NH}_2$ than for $\mu\text{-OH}$ and slower with tacn than with NH₃ as non-bridging ligands, in accordance with the general tendencies for cobalt(III) vs. chromium(III) and nitrogen vs. oxygen.

The $[\text{H}^+]$ -independent term, b , can be interpreted as associated with a $[\text{H}^+]$ -independent bridge cleavage path as it e.g. is the case²⁹ for the irreversible cleavage of the first hydroxo bridge in $[(\text{NH}_3)_3\text{Cr}(\mu\text{-OH})_3\text{Cr}(\text{NH}_3)_3]^{3+}$ reacting to $\text{cis}[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]^{3+}$. The term b can also be associated with reversibility as for the reaction analogous to reaction (1) for $[(\text{tacn})\text{Co}(\mu\text{-OH})_3\text{Co}(\text{tacn})]^{3+}$, studied by Wieghardt *et al.*,²⁴ where no significant contribution to b from a $[\text{H}^+]$ -independent path was found.

For the trihydroxo-bridged complexes the first bridge cleavage is succeeded by a *cis-trans* isomerization where the dihydroxo-bridged *trans*-isomer dominates this equilibrium in acid medium^{30,31} (cf. Table 3). In some cases the rate constants for the bridge cleavage/formation as well as for the *cis-trans* isomerization have been determined^{27–30} and the two dihydroxo-bridged isomers isolated.³⁰ In general the equilibrium ratio, $K_{\text{T/D}}$ ($[\text{H}^+] \equiv 1 \text{ M}$), between the triply bridged complexes and their doubly bridged cleavage products is smaller for chromium(III) than for cobalt(III) (cf. Table 3).

The behaviour of the present $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$ in many ways resembles that of $[(\text{tacn})\text{Co}(\mu\text{-OH})_3\text{Co}(\text{tacn})]^{3+}$ except for the factor more than 10^3 on a and b (Table 2). For both systems only one observed rate constant was determined at fixed $[\text{H}^+]$ in acid medium, and after cleavage of the first bridge the *trans*-

isomer of the doubly bridged cleavage product was isolated in high yields. Also the activation parameters on a and b are rather similar (Table 2). For $[(\text{tacn})\text{Co}(\mu\text{-OH})_3\text{Co}(\text{tacn})]^{3+}$ the equilibrium ratio $K_{\text{T/D}}$ is 0.28 M ($K_{\text{T/D}} = b/a$ with the proposed mechanism²⁴) at 40 °C, and the magnitude of $K_{\text{T/D}}$ determined directly from spectral data on equilibrated solutions agrees with b/a . This excludes a significant contribution to b from a $[\text{H}^+]$ -independent path. For the present $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$ $b/a = 0.34(4) \text{ M}$ at 40 °C, and $K_{\text{T/D}} = 0.19(2) \text{ M}$ as determined from spectral data on equilibrated solutions ($[\text{H}^+]$: 0.1, 0.5 and 1.0 M) indicating that in this case there might be a contribution to b from a $[\text{H}^+]$ -independent path. It should also be noted that the equilibrated solutions may contain the doubly bridged *cis*-isomer as well as the *trans*-isomer, a lower solubility of the latter being the reason for its high yield of crystallization.

In spite of the many similarities between $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$ and the trihydroxo-bridged analogue the intimate mechanism for reaction (1) can hardly be the same as described for the trihydroxo-bridged analogue. As mentioned above it is improbable that a proton binds to the bridging amido group. An explanation for the $[\text{H}^+]$ dependency could rather be that a proton binds to an undetected reaction intermediate. A *cis-trans* isomerisation involving an intramolecular bridge shift mechanism has been suggested for dihydroxo-bridged dinuclear complexes with non-bridging hydroxide or water ligands in a *cis*-position to the bridges.³¹ Such a mechanism seems also less probable for the diamido-bridged complex **4**, and it is unknown whether an undetected *cis*-isomer of complex **4** is involved in reaction (1) at all.

In connection with the first amido bridge cleavage, reaction (1), another reaction was observed. This reaction, most marked at higher temperatures, is a loss of ammonia from complex **4** under the formation of $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Co}(\text{tacn})]^{3+}$ (a similar irreversible reaction has been described for the chromium analogue¹⁸). ESMS of an isolated product (perchlorate, see Experimental) showed a mixture of this complex and complex **4** (deprotonated) after 30–60 min in 1.0 M HClO₄ at 70 °C. The rate constant, under these conditions, for this loss of ammonia under the formation of a hydroxo bridge was determined by UV/Vis to $2.0(2) \times 10^{-4} \text{ s}^{-1}$ (FPLC was used as a more qualitative control). As for the chromium(III) analogue this is, as expected, significantly faster than the first acid hydrolysis step for, e.g., the mononuclear hexaammine complex,^{32,33} the bridges being responsible for the increase. The complex $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{NH}_3)_4]^{4+}$ in Table 3 is another example showing an increased rate for water substitution of ammonia.²⁶

By prolonged treatment of $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_3\text{Co}(\text{tacn})]^{3+}$ in 1.0 M HClO₄ (1–4 h at 70 °C) the reaction proceeds, as for the chromium(III) analogue,¹⁸ and $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})_2\text{Co}(\text{tacn})]^{3+}$ is formed (FPLC and ESMS). In addition these reactions are accompanied by bridge cleavage of the triply bridged species to form doubly bridged species, which may exist as *cis*- and *trans*-isomers, making the whole system rather complicated. Further steps to form singly bridged and mononuclear species are slower as seen in other cases¹⁵ (and references in Table 3) and were not investigated.

Description of the crystal structure of the perchlorate of *trans*- $[(\text{H}_2\text{O})(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{tacn})(\text{NH}_3)]^{4+}$ (4**).** The structure of this dinuclear complex **4** has similarities to that of the centrosymmetric dihydroxo-bridged diaqua analogue, which is the product isolated after bridge cleavage of $[(\text{tacn})\text{Co}(\mu\text{-OH})_3\text{Co}(\text{tacn})]^{3+}$ in acid medium.²⁴ Like this cleavage product complex **4** has *trans*-configuration of the monodentate non-bridging ligands with respect to the bridge plane. The bond lengths of the present ammonia and water ligand to the cobalt atom are equal (Table 4 and Fig. 4). This should be seen in the light of a rather short hydrogen bond from the water ligand to the water molecule of crystallization [2.5854(12) Å, O(4)–H(4b)–O(5) = 178(2)°]. O(4) is approximately tetrahedrally surrounded with a hydrogen bond also to a tacn nitrogen atom on the other cobalt atom [O(4)–N(11) is 2.8324(12) Å]. The corresponding distance on the other side of the bridge plane, N(1)–N(21), is 3.5206(13) Å. The hydrogen atoms on the nitrogen and water oxygen atoms are otherwise involved in a network of hydrogen bonds to the oxygen atoms of the well-ordered perchlorate ions, which

Table 3 Rate constants for amido or hydroxo (italicized when ambiguous) bridge cleavage where $k_{\text{obs}} = a[\text{H}^+] + b$ and the equilibrium ratio, $K_{\text{T/D}} ([\text{H}^+] \equiv 1 \text{ M})$, between the triply bridged complexes and their doubly bridged cleavage products (*cis* and *trans*) in 1.0 M (Na,H)ClO₄ at 25 °C, unless otherwise quoted. Values marked with * have been calculated on the basis of experimental activation parameters

Complex	$a/\text{M}^{-1} \text{ s}^{-1}$	b/s^{-1}	$K_{\text{T/D}}/\text{M}$	Ref.
$[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{tacn})]^{3+}$	* 1.2×10^{-5}	* 2.5×10^{-6}	* $b/a = 0.21$	This work
$[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{tacn})]^{3+}$	$2.64(6) \times 10^{-3}$	Insignificant	Unobserved	18
$[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})]^{3+}$	$1.72(10) \times 10^{-3}$	Insignificant	Unobserved	18
$[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})]^{3+}$	$4.3(8) \times 10^{-3}$	$5.1(2) \times 10^{-3}$	1.2(3) (<i>cis</i>)	
$[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{NH}_3)_3]^{3+}$	3×10^{-1}			12
$[(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{NH}_3)_3]^{3+}$	11.9(9)	Insignificant	Unobserved	18
$[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)\text{Co}(\text{NH}_3)_5]^{5+}$		* b 2.4×10^{-7}		14
$[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$	$1.01(2)$	$2.0(4) \times 10^{-2}$	0.018 (<i>trans</i>)	25
$[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Co}(\text{NH}_3)_4]^{4+}$	* d 8.1×10^{-4}			26
$[(\text{tacn})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{tacn})]^{3+}$	$3.7(1) \times 10^{-2}$	$5.2(5) \times 10^{-3}$	0.14 (<i>trans</i>)	24
$[(\text{tacn})\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{tacn})]^{3+}$	fast	$1.22(2) \times 10^{-2}$	Unobserved	27
$[(\text{NH}_3)_3\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$	4.22	1.80	0.43 (<i>cis</i>)	
	2.81×10^{-1}	6.6×10^{-3}	0.0153 (<i>trans</i>)	28
$[(\text{NH}_3)_3\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{NH}_3)_3]^{3+}$	$3.36(9) \times 10^3$	$3.64(5) \times 10^{-2}$	Unobserved	29

^a 1 M (Na,H)NO₃ (extrapolated). ^b 2 M (Na,H)ClO₄. ^c 1 M (Li,H)ClO₄. ^d 2 M (Li,H)ClO₄. ^e H₂O (extrapolated).

Table 4 Selected bond lengths (in Å) and bond angles (in °) in $[(\text{H}_2\text{O})(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{tacn})(\text{NH}_3)](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$

Co(1)–N(1)	1.9855(9)	Co(2)–O(4)	1.9855(7)
Co(1)–N(2)	1.9411(8)	Co(2)–N(2)	1.9327(8)
Co(1)–N(3)	1.9477(8)	Co(2)–N(3)	1.9402(8)
Co(1)–N(11)	1.9528(8)	Co(2)–N(21)	1.9355(8)
Co(1)–N(14)	1.9804(8)	Co(2)–N(24)	1.9701(8)
Co(1)–N(17)	1.9655(9)	Co(2)–N(27)	1.9849(8)
Co(1)–Co(2)	2.9772(5)		
Co(1)–N(2)–Co(2)	100.45(4)		
Co(1)–N(3)–Co(2)	99.95(4)		

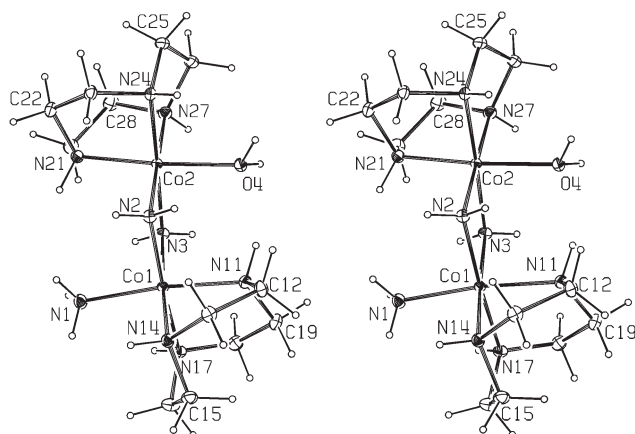


Fig. 4 Stereoscopic ORTEP²² drawing of complex **4**, $\text{trans}-[(\text{H}_2\text{O})(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{tacn})(\text{NH}_3)]^{4+}$. Ellipsoids are at 50% probability level (hydrogen atoms arbitrary). For clarity labels for the hydrogen atoms and half of the carbon atoms are omitted.

have Cl–O bonds in the range 1.4180(12) to 1.4579(10) Å. The conformation of the tacn ligand on Co(2) is $\delta\delta\delta$ (C–N–N–C torsion angles: 40.5, 41.1 and 42.2°) while the tacn ligand on Co(1) is more irregular (torsion angles: –36.2, 18.0 and 43.2°).

$[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2(\mu\text{-tacn}(\text{-H}))\text{Co}(\text{NH}_3)]^{3+}$ (**3**) in 1.0 M HClO₄

Kinetic investigations of complex **3** in perchloric acid met the same complications as mentioned for $[(\text{tacn})\text{Co}(\mu\text{-NH}_2)_2\text{Co}(\text{tacn})]^{3+}$. A further complication for studying the bridge cleavage in complex **3** is a simultaneous loss of the non-bridging ammonia ligand in this complex. No detailed results have been obtained, but a few qualitative observations should be mentioned.

In 1.0 M HClO₄ at 70 °C complex **3** disappears with a rate constant $k_{\text{obs}} = 0.0011(1) \text{ s}^{-1}$ (decreasing with decreasing $[\text{H}^+]$) to form a complex with a UV/Vis spectrum and FPLC behaviour very similar to complex **3** with only traces of a doubly bridged complex. After

60 min, ESMS on an isolated product mixture showed that the main products are triply bridged derivatives (charge 3+) with one and two hydroxo bridges. However, ESMS also pointed to smaller, but significant, amounts of analogous species where the non-bridging ammonia ligand had been replaced by water. After 30 h in 1.0 M HClO₄ at 70 °C FPLC and ESMS showed a major product with $m/z = 213.08$ ($z = 2+$), consistent with a $[(\text{tacn})\text{Co}(\mu\text{-OH})_2(\mu\text{-tacn}(\text{-H}))\text{Co}(\text{OH})]^{2+}$ ion ($m/z = 213.06$). It was possible to isolate an iodide of the protonated form of this complex directly from the perchloric acid solution (see Experimental). The complex shows acid–base properties (UV/Vis spectra), and the acid dissociation constant was determined to $10^{-9.08(2)} \text{ M}$ (1.0 M NaClO₄ at 25 °C). From these observations it is concluded that complex **3** under these conditions (1.0 M HClO₄ at 70 °C) undergoes bridge cleavage primarily of the $\mu\text{-NH}_2$ bridges, and not of the tacn bridge, under simultaneous loss of ammonia.

Experimental

¹H and ¹³C–{¹H} NMR spectra were recorded on a Bruker AM-250 instrument at 250.13 and 62.9 MHz, respectively. The solvent, deuterated DMSO, served as lock and the quoted chemical shifts are relative to TMS. UV/Vis spectral data were collected on a Perkin-Elmer Lambda 40 instrument equipped with a PTP-6 temperature controller. Electrospray mass spectra (ESMS), were recorded on a Micromass Q-ToF instrument using 5–25 V cone voltage; perchlorates of the (tacn)cobalt(III) complexes were dissolved in water and identified as the cations with 1–3 charges associated to 0–2 perchlorate ions. Smaller signals, which could be assigned to solvated (low cone voltage), deprotonated or other forms (high cone voltage), were present, but are not quoted. Ion-exchange liquid chromatography (FPLC) was performed on a Pharmacia instrument using a Mono HR 5/5 column with an elution gradient from water to 1 M NaCl buffered with 0.02 M propane-1,3-diamine/0.002 M HCl. Peak areas (UV detection at 254 nm) were determined using a program developed by Ole Mønsted,³⁴ and further details concerning the FPLC separation (of similar chromium(III) complexes) are described elsewhere.^{18,21} Acid dissociation constants were determined¹⁸ on a Radiometer PHM52 instrument as described by Mønsted and Mønsted.³⁵

Single crystal X-ray diffraction data were collected at 122 K on a Nonius KappaCCD area-detector diffractometer equipped with an Oxford Cryostreams low-temperature device. A STOE Stadi P X-ray powder diffractometer was used to obtain powder diffraction data with Cu–K α 1 radiation selected by a curved germanium monochromator.

The chemicals were of reagent grade or better quality (the liquid ammonia contained less than 20 ppm water). The synthesized compounds were analysed for C, H, N and Cl by our Department for Microanalysis and the purities were further controlled by FPLC.

Syntheses

Caution! In the following syntheses handling of the perchlorates must be done with caution.³⁶ Preparations on a larger scale should be avoided. Avoid scraping and (local) heat, and dilute acid mixtures of organic solvents and perchlorate as soon as possible. We did not experience explosions when these precautions were taken.

Potassium (0.34 g, 8.7 mmol) and an ampoule with [Co(tacn)(O₃SCF₃)₃]^{24,37} (3.8 g, 6.0 mmol) were placed in a steel autoclave under nitrogen, after which *ca.* 75 ml of liquid ammonia (<20 ppm H₂O) were distilled into the autoclave. After one day at room temperature the ampoule was broken in the potassium amide solution by shaking the closed autoclave thoroughly. The autoclave was then kept for four days at 100 °C with occasional swirling. After cooling and evaporation of the ammonia the crude red product was dissolved in 400 ml of water and after filtration (G4) separated by ion-exchange chromatography on Sephadex C-25 using 0.24 M Na₂HPO₄/0.12 M NaH₂PO₄ as eluent. After a small red band and a brown one, three bands followed, a yellow, a red and a violet one, leaving a slowly moving red-brown band on the column. The eluates from the three last bands were, after dilution ×20 with water, reabsorbed on short columns of Sephadex C-25 and eluted with minimum volumes of 0.5 M Na₂SO₄. Each of the three eluates were precipitated with solid NaClO₄, the precipitates were filtered off, washed with ethanol and diethyl ether and dried in air to give, respectively, the following three compounds:

[Co(tacn)₂](ClO₄)₃·5H₂O. Yield: 0.78 g yellow crystals (37% based on tacn). Calc. for C₁₂H₄₀N₆O₁₇Cl₃Co: C, 20.42; H, 5.71; N, 11.91; Cl, 15.07. Found: C, 20.41; H, 3.96; N, 12.14; Cl, 14.50%.

[(tacn)Co(μ-NH₂)₃Co(tacn)](ClO₄)₃·4H₂O. Yield: 0.16 g red crystals (7%). Calc. for C₁₂H₄₄N₉O₁₆Cl₃Co₂: C, 18.14; H, 5.58; N, 15.86; Cl, 13.38. Found: C, 18.32; H, 4.38; N, 15.76; Cl, 12.92%.

[(tacn)Co(μ-NH₂)₂{μ-tacn(-H)}Co(NH₃)](ClO₄)₃·2H₂O. Yield: 0.55 g reddish crystals (24%). Calc. for C₁₂H₄₀N₉O₁₄Cl₃Co₂: C, 19.00; H, 5.31; N, 16.62; Cl, 14.02. Found: C, 19.17; H, 4.42; N, 16.94; Cl, 13.72%.

Crystals of the perrhenate, suitable for single crystal X-ray diffraction, were obtained by saturating a 1 cm column (1 cm Ø) of Sephadex C-25 with 20 ml aqueous solution of *ca.* 20 mg of the perchlorate. After washing with a few ml of a 0.1 M solution of NH₄ReO₄ the column was eluted with a saturated solution of NH₄ReO₄. Suitable crystals precipitated after heating the eluate to 40 °C followed by slow cooling to 0 °C. The crystals were washed with a little cold water and ethanol and air-dried.

trans-[(H₂O)(tacn)Co(μ-NH₂)₂Co(tacn)(NH₃)](ClO₄)₄·H₂O. 20 mg of the perchlorate of [(tacn)Co(μ-NH₂)₃Co(tacn)]³⁺ were dissolved in 600 μl of 4.0 M HClO₄ at 40 °C and kept at this temperature for 110 min. The orange-red crystals formed during the process was washed with 4.0 M HClO₄ (0 °C), then with ethanol and finally air-dried. Yield: 18 mg of the perchlorate of *trans*-[(H₂O)(tacn)Co(μ-NH₂)₂Co(tacn)(NH₃)]⁴⁺ (83%), the composition of which was determined by single crystal X-ray diffraction and ESMS [*m/z* = 147.38 (calc. 147.40 for the deprotonated form of the complex)].

[(tacn)Co(μ-OH)₂{μ-tacn(-H)}Co(H₂O)]I₃·3H₂O. 102 mg of the perchlorate of [(tacn)Co(μ-NH₂)₂{μ-tacn(-H)}Co(NH₃)]³⁺ were treated with 800 μl of 1.0 M HClO₄ at 70 °C for 30 h and then cooled in ice. 1.0 g of NaI was added, and the solution was left for crystallization at 5 °C for two days. The crystals were washed with a little 2 M NaI, then with ethanol and diethyl ether and finally dried in air. Yield: 26 mg of dark violet crystals (23%). Calc. for Co₂C₁₂H₃₉N₆O₆I₃: Co, 13.68; C, 16.72; H, 4.56; N, 9.75; I, 44.17. Found: Co, 13.63; C, 16.96; H, 4.06; N, 9.66; I, 44.66%.

Perchlorates of reaction products for ESMS measurements. Reaction products of complex **2**, **3**, and **4** were obtained as mixtures

Table 5 Crystal data and summary of the data collection and structural refinements results for [(tacn)Co(μ-NH₂)₂{μ-tacn(-H)}Co(tacn)](ReO₄)₃·H₂O and *trans*-[(H₂O)(tacn)Co(μ-NH₂)₂Co(tacn)(NH₃)](ClO₄)₄·H₂O

Formula	Co ₂ C ₁₂ H ₃₈ N ₉ O ₁₃ Re ₃	Co ₂ C ₁₂ H ₄₁ N ₉ O ₁₈ Cl ₄
<i>M</i>	1192.97	859.20
<i>T</i> /K	122(2)	122(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Crystal symmetry	Monoclinic	Orthorhombic
<i>a</i> /Å	11.8951(17)	12.2549(18)
<i>b</i> /Å	11.2445(5)	13.0817(12)
<i>c</i> /Å	20.9616(16)	18.1943(16)
β /°	101.016(10)	
<i>Z</i>	4	4
μ /mm ⁻¹	14.400	1.599
Unique reflections	13023, 11895 with <i>I</i> > 2σ(<i>I</i>)	18088, 16848 with <i>I</i> > 2σ(<i>I</i>)
<i>R</i> _{int}	0.0571	0.0486
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0383	0.0226
<i>wR</i> (<i>F</i> ²)	0.0878	0.0517

of dry perchlorates in the following way. 5–10 mg of a complex (as perchlorate) were treated with 0.2–0.4 ml of 1.0 M (Na,H)ClO₄ at fixed elevated temperature (typically 40–70 °C) for the relevant time after which the solution was cooled to 0 °C. The solution was diluted with 10–20 ml of water (0 °C), concentrated on a 1 cm column (1 cm Ø) of Sephadex C-25, washed with 10 ml of 0.1 M LiClO₄ and then eluted with 1–2 M LiClO₄. The eluate (*ca.* 1 ml) was dried in a vacuum desiccator over P₂O₅, after which the lithium perchlorate in the remaining powder was extracted with a 1 : 10 mixture of ethanol and diethyl ether. The remaining mixture of reaction products as perchlorates was washed with diethyl ether, dried in air and used directly for ESMS measurements.

Crystal structure determinations. The crystal structures of the perrhenate of complex **3** and the perchlorate of complex **4** were solved using SHELXS³⁸ and refined using SHELXL.³⁹ Crystal, data collection and refinement parameters are given in Table 5.

During the refinement of the perrhenate of complex **3** disorder showed up involving two of the three perrhenate ions. The main source of the disorder was resolved by refining each of the two perrhenate ions occupying two sites (occupancy: 84 and 92% for the main sites). The cation also displayed some disorder which was resolved by refining the two cobalt atoms occupying two sites (occupancy: 93% for the main sites). At this point some larger peaks and holes remained in the difference Fourier map lying *ca.* 0.5 Å from the disordered rhenium atoms, and no further attempts were made to model this disorder. Hydrogen atoms were added to the model and included in the refinement at idealized positions, riding on their parent atoms.

For the perchlorate of complex **4** all non-hydrogen atoms were assigned after a few cycles of refinement, and the structure showed no signs of disorder. All hydrogen atoms were found in a difference Fourier map. The hydrogen atoms on carbon atoms were included in the refinement at idealized positions, whereas all the other hydrogen atoms were included in the refinement as independent atoms. The absolute structure was determined as described by Flack⁴⁰ resulting in a Flack parameter of 0.002(4).

CCDC reference numbers 237801 and 237802.

See <http://www.rsc.org/suppdata/dt/b4/b406782g/> for crystallographic data in CIF or other electronic format.

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