

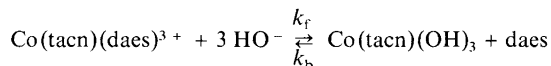
Base Hydrolysis of (1,4,7-Triazacyclononane)(3-thiapentane-1,5-diamine)cobalt(III) and the Crystal and Molecular Structure of Sodium Tri- μ -hydroxobis{1,4,7-triazacyclononanecobalt(III)} Dichloride Diperchlorate Dihydrate Isolated from the Reaction

Erik Larsen,^{*,a} Sine Larsen,^b Gudrun B. Paulsen,^a Johan Springborg^a and Dong-Ni Wang^a

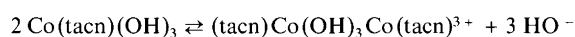
^aChemistry Department, The Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg, Denmark and ^bChemistry Department, The H.C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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The reaction between the cation (1,4,7-triazacyclononane)(3-thiapentane-1,5-diamine)cobalt(III), $\text{Co}(\text{tacn})(\text{daes})^{3+}$, and hydroxide at 59°C has been studied spectrophotometrically and with ion-exchange high-performance liquid chromatography. A study of the hydrolysis of 0.002–0.06 M solutions of $\text{Co}(\text{tacn})(\text{daes})^{3+}$ in 1 M NaOH shows that the system has two dominant equilibria:



with equilibrium constant K_h , and



with equilibrium constant K_d .

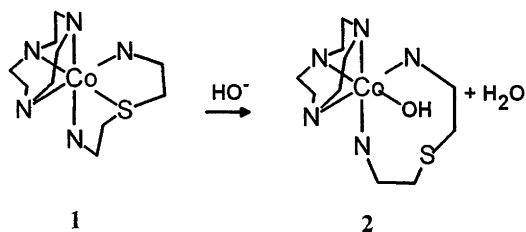
The following equilibrium and rate constants were determined: $K_h = 0.08(2) \text{ M}^{-2}$, $K_d = 17(3) \text{ M}^2$ and $k_f^{\text{obs}} = 1.02(2) \times 10^{-3} \text{ s}^{-1}$ in 1 M NaOH at 59°C.

From the reaction mixture $\text{Na}[(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was isolated. The structure was determined from low-temperature (122 K) X-ray diffraction data: $a = 7.235(5) \text{ \AA}$, $b = 17.662(2) \text{ \AA}$, $c = 20.870(6) \text{ \AA}$, $\beta = 93.41(3)^\circ$, $Z = 4$, space group $P2_1/c$. $R_w = 0.092$. The double salt composition seems important for crystal stability. The dinuclear cation has the expected triol structure.

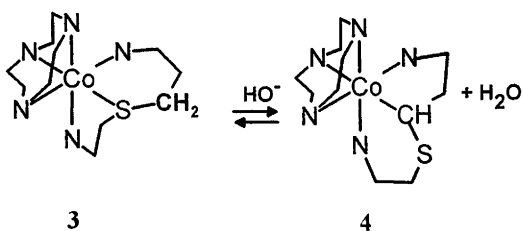
Previously we have reported a study of the base hydrolysis of $\text{Co}(\text{aeaps})^{3+}_2$ (aeaps = 2-aminoethyl-3-aminopropyl sulfide = 3-thiahexane-1,6-diamine).¹ The initial purpose of this study was to demonstrate the anticipated labile character of a Co–S bond as exemplified in Scheme 1 for the corresponding complex $\text{Co}(\text{tacn})(\text{daes})^{3+}$ (tacn = 1,4,7-triazacyclononane, daes = 3-thiapentane-1,5-diamine = di(2-aminoethyl)sulfide). However, the reaction of $\text{Co}(\text{aeaps})^{3+}_2$ with base gave a very complex equilibrium mixture of cobalt(III) species and, rather sur-

prisingly, it was found that one of the dominant species formed was a novel cobalt–alkyl complex.¹ Presumably the reaction mixture also contained hydroxo species analogous to **2**, but the existence of such a species was never established with certainty. Recently it was shown^{2,3} that the corresponding $\text{Co}(\text{tacn})(\text{aeaps})^{3+}$ species reacts in a more simple way and that the only observed reaction is a reversible formation of the alkyl species as shown in Scheme 2. In this case the tacn ligand functions as a symmetric blocking group for its coordination face. The alkyl species is formed quantitatively at large hydroxide concentration, and it was shown that other reactions,

* To whom correspondence should be addressed.



Scheme 1.



Scheme 2.

such as formation of hydroxo species, do not occur to any stoichiometrically important extent. In connection with these results it is worth mentioning that a thioether coordinates weakly to cobalt(III).^{4,5}

In this paper we describe a kinetic and thermodynamic study of the reaction between **1** and hydroxide ions (Scheme 1) and also report on the crystal structure of one of the isolated reaction products, $\text{Na}[\text{tacnCo}(\text{OH})_3\text{-Co}(\text{tacn})]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. The syntheses of the dinuclear tri- μ -hydroxo-bis{1,4,7-triazacyclononane cobalt(III)} cation was first reported by Wiegardt *et al.*⁶ and the crystal structure of a salt of the corresponding di- μ -hydroxodi-aquabis{1,4,7-triazacyclononane cobalt(III)} cation was presented. The crystal structure of a salt of $(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})^{3+}$ has not formerly been reported.

Experimental

Materials and instrumentation. $[\text{Co}(\text{tacn})(\text{daes})]\text{Cl}_3 \cdot \text{H}_2\text{O}$, $[(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$, *trans*- $[(\text{H}_2\text{O})-(\text{tacn})\text{Co}(\text{OH})_2\text{Co}(\text{tacn})(\text{OH})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{tacn})\text{Cl}_3$ were prepared as described previously.^{2,6,7} All other chemicals were of analytical grade. UV-VIS absorption spectra were obtained using a Perkin-Elmer Lambda Diode Array 3840 spectrophotometer or a Cary 3 spectrophotometer.

Ion-exchange high-performance liquid chromatography (IE-HPLC) was performed using a Waters system with 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. The given retention volumes (V_R) refer to a flow of 1.0 ml min^{-1} .² 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 by addition of an excess of cold 1 M NH_4Cl prior to the IE-HPLC analysis.

Solutions of pure $\text{Co}(\text{tacn})(\text{OH})_3$ were made by dissolving $\text{Co}(\text{tacn})\text{Cl}_3$ in 1 M NaOH. The hydrolysis was complete within minutes at room temperature. The purity was controlled by IE-HPLC analyses.

Spectral measurements and calculations of rate constants. Pseudo-first-order rate constants, k_{obs} , and spectra of the pure species were calculated from the absorbance, A , as a function of time, t , by means of regression analysis using eqn. (1).

$$A = A_1 + A_2 \exp(-k_{\text{obs}} t) \quad (1)$$

The calculations of k_{obs} were based on the method of successive integration,⁸ modified to include in each calculation absorbances versus time for many wavelengths. Absorbances were measured at 200–300 different wavelengths. The values of k_{obs} given in the following are in each case the average of at least two independent determinations.

IE-HPLC measurements. The concentrations of the cobalt(III) species in the product solutions were determined from elution curves measured at 246 nm. At this wavelength the species $\text{Co}(\text{tacn})(\text{daes})^{3+}$, $\text{Co}(\text{tacn})(\text{OH})_3$ and $(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})^{3+}$ have similar and high molar absorption coefficients, 10300, 9062 and 7825 $\text{M}^{-1} \text{cm}^{-1}$, respectively [molarity with respect to Co(III)]. The concentrations of the individual species were then calculated using these values and the integrated elution curves as described previously.⁹

Crystals of $\text{Na}[(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. A solution of 0.6 M $[(\text{tacn})\text{Co}(\text{daes})]\text{Cl}_3 \cdot \text{H}_2\text{O}$ in 1 M NaOH was kept for 90 min at 59°C, then cooled in ice, and to this solution was added an equal volume of a saturated solution of NaClO_4 . The addition was performed with a Pasteur pipette placing the dense solution of NaClO_4 at the bottom and giving a minimum of mixing of the two solvents. The mixture was kept at 5°C for 24 h. A mixture of red and yellow crystals separated (sometimes minor amounts of purple-brown crystals also were found). The red and yellow crystals were qualitatively identified by IE-HPLC as salts of $\text{Co}(\text{tacn})(\text{daes})^{3+}$ and $(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})^{3+}$, respectively. The red crystals were also characterized by a crystal structure analysis as described in the following.

X-Ray crystallography of $\text{Na}[(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. The red brick-like crystals were characterized by Weissenberg photographs. They belong to the monoclinic system. The space group was unambiguously determined to be $P2_1/c$ from the systematically absent reflections. The diffraction data were collected with a CAD4 diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation. The crystal was cooled to 122 K with

Table 1. A summary of crystal data, data reduction and structure refinement.

| | |
|---|--|
| Compound | Na[(tacn)Co(OH) ₃ Co(tacn)]- Cl ₂ (ClO ₄) ₂ ·2H ₂ O |
| Formula | Co ₂ NaC ₁₂ H ₃₇ N ₆ O ₁₃ Cl ₄ |
| Formula mass/g mol ⁻¹ | 756.13 |
| Space group | P2 ₁ /c |
| Wavelength (MoKα)/Å | 0.71073 |
| Unit-cell dimensions at 122 K: | |
| <i>a</i> /Å | 7.235(5) |
| <i>b</i> /Å | 17.662(2) |
| <i>c</i> /Å | 20.870(6) |
| β/° | 93.41(3) |
| <i>V</i> /Å ³ | 2662(3) |
| <i>Z</i> | 4 |
| <i>F</i> (000) | 1552 |
| <i>D_c</i> /g cm ⁻³ | 1.886 |
| <i>D_{ex}</i> /g cm ⁻³ | 1.879 |
| μ(MoKα)/cm ⁻¹ | 17.34 |
| Crystal dimensions/mm ³ | 0.22 × 0.20 × 0.045 |
| Scan mode | ω-2θ |
| Scan range, Δω | 1.2 + 0.35 tan θ |
| θ range/° | 1-30 |
| Weights, <i>w</i> ⁻¹ | σ ² (<i>F</i>) + 0.0012 <i>F</i> ² |
| <i>S</i> = {Σ <i>w</i> Δ <i>F</i> ² /(<i>n</i> - <i>m</i>)} ^{1/2} | 2.0 |
| No. of independent reflections | 9982 |
| No. of observed reflections | 4938 |
| No. of variables, <i>m</i> | 343 |
| <i>R</i> | 0.064 |
| <i>R_w</i> | 0.092 |

an Enraf-Nonius gas-flow low-temperature device. The temperature monitored with a thermocouple in the exhaust pipe was constant within 1 K.

Data reduction included corrections for Lorentz polarization and absorption effects. The latter correction was performed by the Gaussian integration procedure.

A standard run with the SHELXS-86 program¹⁰ gave starting positions for most heavy atoms in the structure. The remaining atoms were found through successive Fourier syntheses. The structure was refined by least-squares minimization of Σ*w*(|*F_o*| - |*F_c*|)². The long axis of Na[(tacn)Co(OH)₃Co(tacn)]Cl₂(ClO₄)₂·2H₂O caused some of the reflections to overlap. These reflections were excluded from the data set.

The hydrogen atoms of the tacn ligands were introduced in idealized positions. The positions of the remaining hydrogen atoms in the structure were taken from the difference Fourier. The positional parameters for the hydrogen atoms were fixed and were given a common displacement parameter of 2.5 Å². The maximum shift after the final cycle was 0.06σ. The residual density had values between 1.66 and -1.72 e Å⁻³. The final heavy atom parameters are given in Table 2.

Anisotropic displacement parameters, positional parameters for the hydrogen atoms and lists of observed and calculated structure amplitudes can be obtained from the authors. The SDP System¹¹ was used for the crystallographic computations. The atomic scattering factors were from Ref. 12 and were used as contained in the program.

Table 2. Fractional coordinates and equivalent isotropic parameters, *B*_{iso}, for the atoms in Na[(tacn)Co(OH)₃Co(tacn)]Cl₂(ClO₄)₂·2H₂O.

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> _{iso} ^a /Å ³ |
|------|------------|------------|------------|--|
| Co1 | 0.4548(1) | 0.37627(4) | 0.31141(4) | 0.75(1) |
| Co2 | 0.4155(1) | 0.37431(4) | 0.18922(4) | 0.74(1) |
| N11 | 0.6803(6) | 0.3596(3) | 0.3627(2) | 1.07(8) |
| N12 | 0.4058(6) | 0.4596(3) | 0.3680(2) | 0.95(8) |
| N13 | 0.3335(6) | 0.3112(3) | 0.3710(2) | 1.02(8) |
| C11 | 0.7151(8) | 0.4218(4) | 0.4109(3) | 1.5(1) |
| C12 | 0.5928(8) | 0.4892(4) | 0.3911(3) | 1.3(1) |
| C13 | 0.6667(8) | 0.2830(4) | 0.3913(3) | 1.4(1) |
| C14 | 0.4752(8) | 0.2769(4) | 0.4174(3) | 1.5(1) |
| C15 | 0.2909(8) | 0.4338(3) | 0.4210(3) | 1.2(1) |
| C16 | 0.1964(8) | 0.3594(3) | 0.4010(3) | 1.2(1) |
| N21 | 0.6069(6) | 0.3621(3) | 0.1302(2) | 0.98(8) |
| N22 | 0.3155(7) | 0.4539(3) | 0.1336(2) | 1.06(8) |
| N23 | 0.2694(7) | 0.3028(3) | 0.1371(2) | 1.07(8) |
| C21 | 0.6327(7) | 0.4379(3) | 0.1015(3) | 1.2(1) |
| C22 | 0.4456(8) | 0.4703(3) | 0.0820(3) | 1.3(1) |
| C23 | 0.5536(8) | 0.3009(3) | 0.0815(3) | 1.2(1) |
| C24 | 0.4064(8) | 0.2515(3) | 0.1084(3) | 1.2(1) |
| C25 | 0.1311(7) | 0.4261(3) | 0.1087(3) | 1.04(9) |
| C26 | 0.1502(7) | 0.3448(3) | 0.0875(3) | 1.07(9) |
| Oa | 0.5668(5) | 0.4363(2) | 0.2474(2) | 0.96(7) |
| Ob | 0.4939(5) | 0.2978(2) | 0.2498(2) | 0.92(7) |
| Oc | 0.2431(5) | 0.3936(2) | 0.2538(2) | 0.88(7) |
| Cl3 | -0.0864(2) | 0.28860(8) | 0.23837(8) | 1.28(2) |
| Cl4 | 1.3602(2) | 0.58473(8) | 0.24862(9) | 1.73(3) |
| Cl1 | 0.9485(2) | 0.62055(9) | 0.08473(7) | 1.85(3) |
| O11 | 0.9420(7) | 0.7002(3) | 0.0947(3) | 2.7(1) |
| O12 | 0.7684(8) | 0.5966(4) | 0.0578(3) | 3.4(1) |
| O13 | 0.9859(9) | 0.5813(3) | 0.1445(3) | 3.8(1) |
| O14 | 1.0873(8) | 0.6028(3) | 0.0414(3) | 3.2(1) |
| Cl2 | 1.0543(2) | 0.63373(8) | 0.42653(7) | 1.29(2) |
| O21 | 0.9600(8) | 0.6546(3) | 0.3665(2) | 2.7(1) |
| O22 | 1.2437(7) | 0.6136(3) | 0.4165(3) | 2.4(1) |
| O23 | 0.9625(6) | 0.5709(3) | 0.4540(3) | 1.93(9) |
| O24 | 1.0498(7) | 0.6973(3) | 0.4697(2) | 2.03(9) |
| Na | 1.0027(4) | 0.6278(1) | 0.2545(1) | 1.37(4) |
| Ow1 | 0.9373(6) | 0.4955(3) | 0.2783(3) | 1.87(9) |
| Ow2 | 0.7127(6) | 0.6749(3) | 0.2232(3) | 1.87(9) |

$$^a B_{\text{iso}} = 8/3 \pi^2 \sum_i \sum_j U_{ij} a_i a_j a_j$$

Results and discussion

Base-induced hydrolysis of Co(tacn)(daes)³⁺. The reaction of 0.002–0.05 M solutions of [Co(tacn)(daes)]Cl₃·H₂O in 1 M NaOH at 59°C was followed by IE-HPLC. For a given cobalt(III) concentration the elution curves for 60 and 90 min reaction were identical, indicating that equilibrium had been attained. The elution curves varied with the cobalt(III) concentration as shown in Fig. 1. For [Co] = 0.05 M (Fig. 1A) the equilibrium solution contains three major components identified as Co(tacn)(OH)₃, (tacn)Co(OH)₃Co(tacn)³⁺ and Co(tacn)(daes)³⁺ by comparison with the chromatography of authentic species. A minor tail following the elution curve of the trihydroxo-bridged species was identified as being due to a small content of *trans*-(H₂O)(tacn)Co(OH)₂Co(tacn)-(H₂O)⁴⁺. This species elutes as a broad band (*V_R* = 4–10 ml) at 25°C, but at 0°C it elutes as a well defined

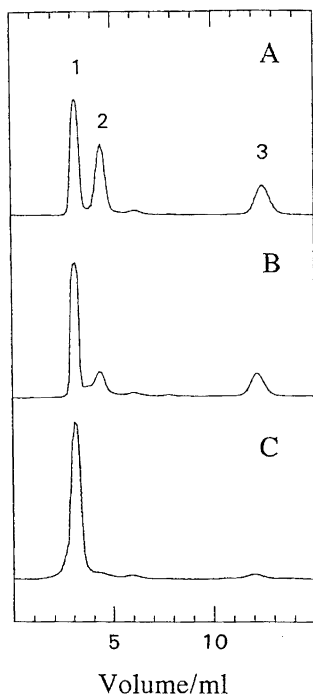
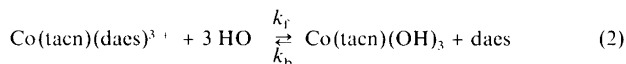


Fig. 1. IE-HPLC elution curves for the equilibrium solutions obtained from the reaction of $\text{Co}(\text{tacn})(\text{daes})^{3+}$ in 1 M NaOH at 59°C (monitored at 246 nm and eluted at 25°C). Curves A, B and C are for cobalt(III) concentrations of 0.0578, 0.0115 and 0.0023 M, respectively. The eluted peaks 1, 2 and 3 were identified as due to $\text{Co}(\text{tacn})(\text{OH})_3$, $(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})^{3+}$ and $\text{Co}(\text{tacn})(\text{daes})^{3+}$ ($V_R = 3.2$, 4.5 and 12.4 ml, respectively). The minor peaks with $V_R = 6$ and 7 ml were not identified. A minor tail following the peak for $(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})^{3+}$ was identified as $\text{trans}(\text{H}_2\text{O})(\text{tacn})\text{Co}(\text{OH})_2\text{Co}(\text{tacn})(\text{H}_2\text{O})^{4+}$.

band with $V_R = 20$ ml. This difference in elution behaviour is assumed to be caused by an equilibration reaction between this species and the less stable *cis* isomer. At room temperature this isomerization reaction probably occurs fast compared to the elution rate.⁶ The stoichio-

metry of the reaction was further established by the isolation of a perchlorate salt of the trihydroxo bridged species from the reaction mixture (see experimental) and the X-ray structure determination of this salt as described in the following section.

The relative content of both $(\text{tacn})\text{Co}(\text{OH})_3\text{Co}(\text{tacn})^{3+}$ and $\text{Co}(\text{tacn})(\text{daes})^{3+}$ decreases when the cobalt(III) concentration decreases, and at very low cobalt(III) concentration (Fig. 1C) the reaction gives a nearly quantitative formation of $\text{Co}(\text{tacn})(\text{OH})_3$. The latter observation was confirmed by a spectrophotometric study using cobalt(III) concentrations in the region 2×10^{-3} – 5×10^{-5} M. Finally, it was also shown that addition of free ligand to the reaction mixture resulted in an increase of the final concentration of $\text{Co}(\text{tacn})(\text{daes})^{3+}$. It is therefore concluded that the equilibrium reactions can be described in terms of eqn. (2), with the hydrolysis equilibrium constant K_h , and eqn. (3), with the dinuclearization equilibrium constant K_d .



In strong base the $\text{Co}(\text{tacn})(\text{daes})^{3+}$ species deprotonates with $\text{p}K_a = 13.3$ at 25°C , presumably at one of the coordinated, secondary amine groups of the tacn ligand.¹ It is possible that a coordinated, primary amine deprotonates to the corresponding amido complex. For the sake of simplicity these equilibria are ignored in the following discussion. Likewise, a possible partial deprotonation of the hydroxo bridge to form oxohydroxo bridged species is ignored.^{13,14}

From the IE-HPLC experiments with cobalt concentrations in the range 0.002–0.06 M the equilibrium concentrations of the three dominant species and the concentration of the free daes ligand were calculated (the small amount of the dihydroxo-bridged species was ignored, see the experimental section). The concentration equilibrium constants were estimated to be

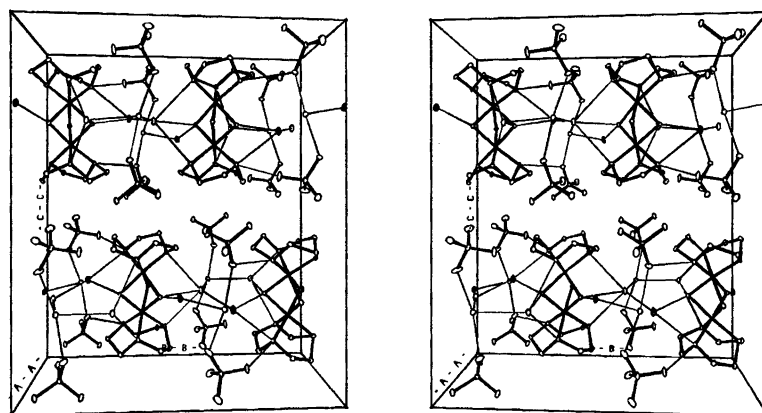


Fig. 2. ORTEP stereoscopic drawing of the unit cell for $\text{Na}[\text{tacnCo}(\text{OH})_3\text{Cotacn}]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. The hydrogen bonds are shown as thin lines. The open spheres are Cl^- .

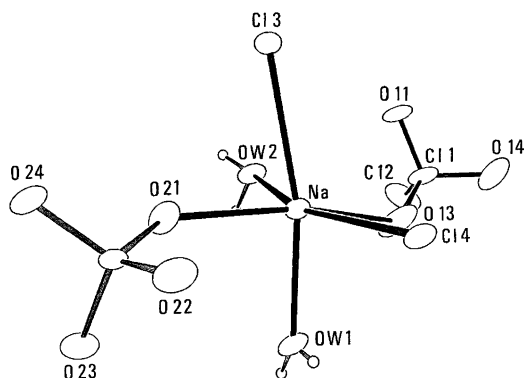


Fig. 3. ORTEP drawing of the surroundings of the sodium ion in $\text{Na}[\text{tacnCo}(\text{OH})_3\text{Cotacn}]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

$K_h = 0.08(2) \text{ M}^{-2}$ and $K_d = 17(3) \text{ M}^2$ (59°C and 1 M NaOH).

The kinetics of the reaction at low cobalt(III) concentration was studied spectrophotometrically in the UV region using $C_{\text{Co}} = 5 \times 10^{-5} \text{ M}$ and in the visible region using $C_{\text{Co}} = 2 \times 10^{-3} \text{ M}$. In both sets of experiments the changes of the absorbance with time followed strictly the expression for first-order kinetics and gave identical pseudo-first-order rate constants. It follows from above that the equilibrium under these conditions is completely shifted to the right [eqn. (2)]. The observed rate constant, k_f^{obs} , was calculated to be $1.02(2) \times 10^{-3} \text{ s}^{-1}$ (59°C and 1 M NaOH). This result was confirmed by IE-HPLC experiments using $C_{\text{Co}} = 0.01 \text{ M}$. The kinetics of the reaction in 1 M NaOH was followed by a quantitative IE-HPLC analysis of the reaction mixture at different times, which directly gave the variation of $[\text{Co}(\text{tacn})(\text{daes})^{3+}]$ with time, and the pseudo-first-order rate constant, $k_f^{\text{obs}} = 1.0 \times 10^{-3} \text{ s}^{-1}$, was calculated from such data.

Eqn. (2) involves at least three steps, of which one could be the reaction shown in Scheme 2. It seems likely, therefore, that k_f and k_b are composite terms. However, the analyses of the product solutions during the equilibration did not provide evidence for the presence of significant amounts of intermediates. Further attempts to interpret k_f would therefore be highly speculative at present.

Table 3. Bond distances (in Å) and bond angles (in $^\circ$) for the sodium ion in $\text{Na}[\text{tacnCo}(\text{OH})_3\text{Cotacn}]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

| | | | |
|------------|-----------|------------|-----------|
| Na—O13 | 2.434(4) | Na—Ow2 | 2.313(4) |
| Na—O21 | 2.421(4) | Na—Cl3 | 2.906(2) |
| Na—Ow1 | 2.440(4) | Na—Cl4 | 2.707(2) |
| O13—Na—O21 | 166.9(2) | O21—Na—Cl4 | 106.0(12) |
| O13—Na—Ow1 | 82.6(15) | Cl3—Na—Ow1 | 165.3(12) |
| O13—Na—Ow2 | 82.1(2) | Cl3—Na—Ow2 | 81.1(10) |
| O13—Na—Cl3 | 112.1(13) | Cl3—Na—Cl4 | 94.59(6) |
| O13—Na—Cl4 | 81.3(13) | Cl4—Na—Ow1 | 86.4(10) |
| O21—Na—Ow1 | 87.3(15) | Cl4—Na—Ow2 | 160.2(13) |
| O21—Na—Ow2 | 92.1(2) | Ow1—Na—Ow2 | 102.6(13) |
| O21—Na—Cl3 | 78.4(11) | | |

Table 4. Hydrogen-bond distances and angles for $\text{Na}[\text{tacnCo}(\text{OH})_3\text{Cotacn}]\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

| Atoms D—H...A | Distance D—A/Å | Angle D—H—A/ $^\circ$ | Distance H—A/Å |
|---------------------------|-------------------|--------------------------|-------------------|
| N11—H11N—Cl3 ^a | 3.418(4) | 139(2) | 2.649(11) |
| N12—H12N—Cl4 ^c | 3.332(4) | 138(2) | 2.559(12) |
| N13—H13N—O11 ^b | 2.914(5) | 121(2) | 2.311(4) |
| N13—H13N—Ow2 ^b | 3.114(5) | 146(2) | 2.279(4) |
| N21—H21N—Cl3 ^a | 3.334(4) | 154(2) | 2.447(11) |
| H22—H22N—Cl4 ^c | 3.334(4) | 152(2) | 2.466(12) |
| N23—H23N—O21 ^b | 3.098(5) | 129(2) | 2.416(4) |
| N23—H23N—Cl3 | 3.436(4) | 142(2) | 2.639(10) |
| Ow1—Hw1a—Oa | 2.914(4) | 153(2) | 1.941(3) |
| Ow1—Hw1b—Oc ^a | 2.920(4) | 174(4) | 2.404(3) |
| Ow2—Hw2a—Cl4 ^c | 3.080(3) | 166(2) | 2.049(11) |
| Ow2—Hw2b—Ob ^d | 2.715(4) | 166(3) | 1.945(3) |
| Oa—Hoa—Ow1 ^e | 2.917(4) | 146(2) | 2.282(3) |
| Ob—Hob—Cl3 ^a | 3.065(3) | 171(2) | 2.2759(9) |
| Oc—Hoe—Cl3 | 3.022(3) | 160(3) | 2.4042(9) |

Symmetry relations: ^a($x+1, y, z$); ^b($-x+1, y-1/2, -z+1/2$); ^c($x-1, y, z$); ^d($-x+1, y+1/2, -z+1/2$); ^e($-x+1, -y+1, -z+1$).

Equilibrium data for the formation of trihydroxo-bridged cobalt(III) species are few. One well documented example is the formation of the corresponding *cis,cis*-1,3,6-cyclohexanetriamine (tach) system with $K_d = 10^{-5.2} \text{ M}^2$.¹⁵ The pronounced increase in the stability of the dinuclear tacn complex is very surprising, even when considering that the two equilibria have been determined under different conditions, 1 M NaOH at 59°C (tacn) and 0.1 M NaOH at 20°C (tach). Finally it is noted that preliminary experiments with cobalt(III) and hydroxide concentrations as used above show that the equilibration reaction between the monomeric and dimeric species, eqn. (3), occurs somewhat faster than the hydrolysis reaction, eqn. (2).

Structural results. The crystal structure determination demonstrated that the dinuclear $(\text{tacn})\text{Co}(\text{OH})_3\text{-Co}(\text{tacn})^{3+}$ ion was formed during the reaction of $\text{Co}(\text{tacn})(\text{daes})^{3+}$ with base. The crystal packing is influ-

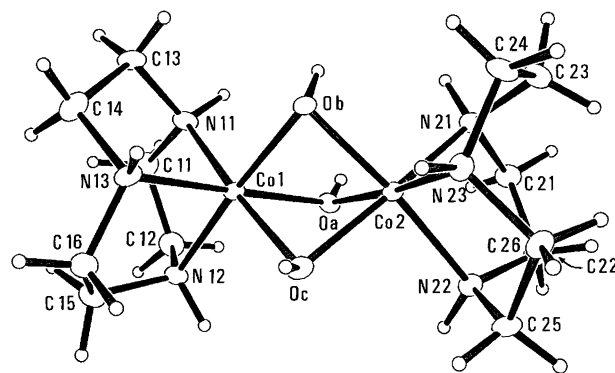


Fig. 4. Drawing of the dinuclear cation $(\text{tacn})\text{Co}(\text{OH})_3\text{-Co}(\text{tacn})^{3+}$.

Table 5. Bond distances (in Å) and bond angles (in °) in (tacn) Co(OH)₃Co(tacn)³⁺.

| | <i>i</i> =1 | <i>i</i> =2 |
|----------------------|-------------|-------------|
| Co <i>i</i> -Oa | 1.925(3) | 1.922(3) |
| Co <i>i</i> -Ob | 1.924(3) | 1.912(3) |
| Co <i>i</i> -Oc | 1.915(3) | 1.921(3) |
| Co <i>i</i> -Ni1 | 1.921(3) | 1.919(4) |
| Co <i>i</i> -Ni2 | 1.932(4) | 1.937(4) |
| Co <i>i</i> -Ni3 | 1.941(4) | 1.939(4) |
| Ni1-Ci1 | 1.503(6) | 1.483(5) |
| Ni1-Ci3 | 1.484(6) | 1.517(5) |
| Ni2-Ci2 | 1.506(5) | 1.500(6) |
| Ni2-Ci5 | 1.495(5) | 1.484(5) |
| Ni3-Ci4 | 1.498(5) | 1.495(5) |
| Ni3-Ci6 | 1.475(5) | 1.505(5) |
| Ci1-Ci2 | 1.524(6) | 1.506(6) |
| Ci3-Ci4 | 1.523(6) | 1.511(6) |
| Ci5-Ci6 | 1.527(6) | 1.511(6) |
| | | |
| Oa-Co <i>i</i> -Ob | 81.0(13) | 81.4(13) |
| Oa-Co <i>i</i> -Oc | 80.2(12) | 80.1(12) |
| Ob-Co <i>i</i> -Oc | 80.7(12) | 80.9(12) |
| Oa-Co <i>i</i> -Ni1 | 95.4(14) | 93.5(13) |
| Oa-Co <i>i</i> -Ni2 | 96.2(14) | 98.3(14) |
| Oa-Co <i>i</i> -Ni3 | 175.6(14) | 173.7(14) |
| Ob-Co <i>i</i> -Ni1 | 96.2(14) | 98.5(14) |
| Ob-Co <i>i</i> -Ni2 | 175.5(14) | 174.0(14) |
| Ob-Co <i>i</i> -Ni3 | 95.3(14) | 92.3(14) |
| Oc-Co <i>i</i> -Ni1 | 174.9(14) | 173.6(14) |
| Oc-Co <i>i</i> -Ni2 | 95.3(13) | 93.2(14) |
| Oc-Co <i>i</i> -Ni3 | 97.0(13) | 98.8(14) |
| Co <i>i</i> -Ni1-Ci1 | 111.3(3) | 105.7(3) |
| Co <i>i</i> -Ni1-Ci3 | 106.8(3) | 110.3(2) |
| Co <i>i</i> -Ni2-Ci2 | 105.4(2) | 110.0(3) |
| Co <i>i</i> -Ni2-Ci5 | 110.5(3) | 105.4(3) |
| Co <i>i</i> -Ni3-Ci4 | 109.6(3) | 105.4(3) |
| Co <i>i</i> -Ni3-Ci6 | 105.8(3) | 109.6(3) |
| Ni1-Ci1-Ci2 | 108.6(4) | 108.6(3) |
| Ni1-Ci3-Ci4 | 107.0(3) | 108.5(3) |
| Ni2-Ci2-Ci1 | 108.2(4) | 109.0(4) |
| Ni2-Ci5-Ci6 | 108.6(4) | 108.8(3) |
| Ni3-Ci4-Ci3 | 110.0(4) | 107.4(3) |
| Ni3-Ci6-Ci5 | 108.1(3) | 108.9(3) |
| Co1-Oa-Co2 | 83.0(11) | |
| Co1-Ob-Co2 | 83.3(11) | |
| Co1-Oc-Co2 | 83.3(11) | |

enced by direct coordination involving the sodium ion as well as extensive hydrogen bonding with all possible donor atoms forming hydrogen bonds. The stereo drawing of the unit cell, Fig. 2, illustrates these points. The coordination sphere of the sodium ion, shown in Fig. 3, forms a distorted octahedron and is not similar to the [Na(H₂O)₃]⁺ ion recently found in a polynuclear molybdenum salt.¹⁶ It is coordinated to two perchlorate ions, two water molecules and two chloride ions with a geometry demonstrated in Table 3. As mentioned above, the atoms coordinated to the sodium ion also participate in extensive hydrogen bonding involving the nitrogen-

bound hydrogen atoms and the bridging hydroxo groups of the cobalt species, as seen from Table 4. Thus, the presence of the 'extra NaCl' in the structure is probably important for the crystal stability allowing for crystal size and a quality suitable for single-crystal diffraction.

The bonding within the cobalt(III) coordination ion (Fig. 4) is shown by bond distances and bond angles given in Table 5. The bond distances of the dinuclear species seem to reflect the structure of an ion with *D*_{3h} symmetry distorted slightly in the field of its unsymmetric surroundings. All bond distances and bond angles in Table 5 are in accordance with expected values. The cobalt-cobalt distance is 2.5491(8) Å, and this is similar to the distance 2.565(1) Å found for (NH₃)₃Co(OH)₃-Co(NH₃)₃³⁺.¹⁷

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References

- Bjerrum, M. J., Gajhede, M., Larsen, E. and Springborg, J. *Inorg. Chem.* 27 (1988) 3960.
- Kofod, P., Larsen, E., Larsen, S., Petersen, C. H., Springborg, J. and Wang, D.-N., *Acta Chem. Scand.* 42 (1992) 841.
- Kofod, P., Larsen, E., Petersen, C. H. and Springborg, J., *Acta Chem. Scand.* 42 (1992) 1149.
- Bjerrum, M. J., Lair, T. and Larsen, E., *Inorg. Chem.* 25 (1986) 816.
- Hammershøi, A. and Larsen, E., *Acta Chem. Scand., Ser. A32* (1978) 485.
- Wiegardt, K., Schmidt, W., Nuber, B., Weiss, J., *Chem. Ber.* 112 (1979) 2220.
- Okamoto, M. S. and Barefield, E. K. *Inorg. Chim. Acta* 17 (1976) 91.
- Matheson, I. B. C. *Anal. Instrum.* 16 (1987) 345 and references therein.
- Bjerrum, M. J., Kaas, K., Larsen, E., Nielsen, B. and Springborg, J. *Inorg. Chem.* 28 (1989) 532.
- Sheldrick, G. M. *Acta Crystallogr., Sect. A* 46 (1990) 467.
- Enraf-Nonius *Structure Determination Package*, Delft, The Netherlands 1985.
- International Table for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
- Springborg, J. In: Sykes, A. G., Ed., *Advances in Inorganic Chemistry*, Academic Press, San Diego, CA 1988, Vol. 32, p. 55.
- Kähler, H. C., Geier, G. and Schwarzenbach, G. *Helv. Chim. Acta* 57 (1974) 802.
- Schwarzenbach, G., Boesch, J. and Egli, H. J. *Inorg. Nucl. Chem.* 33 (1971) 2141.
- Khan, M. I. and Zubieta, J. *J. Am. Chem. Soc.* 114 (1992) 10058.
- Andersen, P. *Acta Chem. Scand.* 21 (1967) 243.

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