

Formation of Dinuclear (1,4,7-Triazacyclononane)chromium(III) Complexes with Three Hydroxo or One Acetamidato and Two Hydroxo Bridges from the Aquahydroxo Monomers in Acetonitrile

Peter Andersen,[†] Hayato Matsui, Karen M. Nielsen and Anne S. Nygaard

Department of Chemistry, H.C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Andersen, P., Matsui, H., Nielsen, K. M. and Nygaard, A. S., 1994. Formation of Dinuclear (1,4,7-Triazacyclononane)chromium(III) Complexes with Three Hydroxo or One Acetamidato and Two Hydroxo Bridges from the Aquahydroxo Monomers in Acetonitrile. – Acta Chem. Scand. 48: 542–547 © Acta Chemica Scandinavica 1994.

$[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_2(\text{OH})][\text{Cr}(\text{tacn})(\text{H}_2\text{O})(\text{OH})_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ (**2**), where tacn is 1,4,7-triazacyclononane, can be isolated by the addition of base to $[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$. In acetonitrile **2** condenses nearly quantitatively to give the trihydroxo-bridged dimer, $[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$, in solution provided $C_{\text{Cr}} < 5\text{--}10$ mM. At higher chromium concentrations other reactions compete, and from such solutions $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]\text{I}_3 \cdot 3\text{H}_2\text{O}$ (**3**) was isolated in relatively high yields.

The cleavage of one of the bridges in the trihydroxo-bridged dimer was studied in acetonitrile–water mixtures, and the rate constant was determined to be $0.0122(2) \text{ s}^{-1}$ in water at 25.0°C .

The acetamidato-bridged complex is very robust in aqueous solution over a wide pH range, and it was possible to determine the acid dissociation constant for the deprotonation of one of the hydroxo bridges: $-\log(K_a/M) = 12.8$ in 1.0 M Na(Br,OH). For comparison the analogous acetato-bridged dimer was isolated, and it showed many similarities to **3**.

A single crystal X-ray structure determination of **3** confirms the constitution. It crystallizes in the space group $P2_12_12_1$ with $a = 9.972(2)$, $b = 13.731(4)$ and $c = 21.577(6)$ Å (at 122 K) and $Z = 4$. Using 4618 independent reflections the structure was refined to $R(F_{\text{obs}}) = 0.04$ and $R_w(F^2, \text{all}) = 0.14$.

In a recent paper¹ we reported that the trihydroxo-bridged dimer $[\text{L}_3\text{Cr}(\text{OH})_3\text{CrL}_3]^{3+}$, where L_3 is *N,N',N''*-trimethyl-1,1,1-tris(aminomethyl)ethane ($\text{Me}_3\text{-tame}$), can be obtained by heating the salt $[\text{L}_3\text{Cr}(\text{H}_3\text{O}_2)_3\text{CrL}_3](\text{CF}_3\text{SO}_3)_3$ (**1**), in which the monomers are connected through three short $\text{HO} \cdots \text{H} \cdots \text{OH}$ intermolecular hydrogen bonds.

The present work takes this observation as its starting point. The trihydroxo-bridged chromium(III) dimer with 1,4,7-triazacyclononane (tacn) has until now not been observed. One of the probable reasons is its low stability in aqueous solution compared to that of the 3+ charged dihydroxo-bridged dimer,² as is the case when L_3 is facially coordinated $(\text{NH}_3)_3$.³ It seemed obvious to try the same condensation procedure with the tacn complex. It is possible, with L_3 being tacn, to synthesize a salt,

$[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_2(\text{OH})][\text{Cr}(\text{tacn})(\text{H}_2\text{O})(\text{OH})_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ (**2**), with the same stoichiometry as **1**, except for an additional molecule of water of crystallization. The salt **2**, however, on heating forms other oligomers and not the trihydroxo-bridged dimer.

If, instead, **2** is heated in acetonitrile solutions two principal products are formed, depending on the chromium concentration. At low concentration (5–10 mM) a nearly pure solution of the trihydroxo-bridged dimer is formed. At higher concentrations increasing amounts of other species are produced, and from such solutions salts of the dimer with one acetamidato and two hydroxo bridges can be isolated. In this paper we present some investigations of these species, including the crystal structure of $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]\text{I}_3 \cdot 3\text{H}_2\text{O}$ and kinetic measurements of the relatively fast cleavage of one of the bridges in the trihydroxo-bridged dimer after addition of water.

[†] To whom correspondence should be addressed.

Results and discussion

$[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_2(\text{OH})][\text{Cr}(\text{tacn})(\text{H}_2\text{O})(\text{OH})_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ (**2**). The composition of this compound was determined by elemental analysis, the UV/VIS spectrum in 0.1 M $\text{CF}_3\text{SO}_3\text{H}$ [identical to that of $[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$] and from acid–base titrations giving the same acid dissociation constants as those determined for the triaqua compound.⁴ The values of $\text{p}K_a = -\log(K_a/M)$ in 1.0 M NaClO_4 at 25°C are $\text{p}K_1 = 4.57(2)$, $\text{p}K_2 = 6.74(1)$ and $\text{p}K_3 = 8.85(1)$. The titration of **2** also confirmed the degree of deprotonation in this compound.

$[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$. Figure 1 shows the UV/VIS spectrum of $[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$, as it is formed in acetonitrile from the condensation of **2**. Owing to the water of crystallization in **2** and the water released by the condensation, the final water concentration in acetonitrile will be twice the chromium concentration. When $C_{\text{Cr}} < 0.01$ M the spectrum is constant at room temperature for several hours and independent of C_{Cr} . This fact, combined with the similarity to the characteristic spectra of other trihydroxo-bridged chromium(III) dimers,¹ provide strong evidence that we are dealing with $[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$, and that only minor amounts of other chromium(III) species may be present.

On addition of water to such solutions one of the bridges is cleaved to give the *cis*-isomer of $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\text{OH})_2\text{Cr}(\text{tacn})(\text{OH})]^{3+}$ as judged from comparison with the UV/VIS spectrum of this ion² in acetonitrile. The rate of this process increases with increasing water concentration and is catalyzed by acid and base, as is the case with other trihydroxo-bridged dimers.³ The temperature dependence of the first-order rate constant was determined in neutral solution with $[\text{H}_2\text{O}] = 5.6$ M. Under these conditions no trihydroxo-bridged dimer remains, and the measurements gave the rate constant,

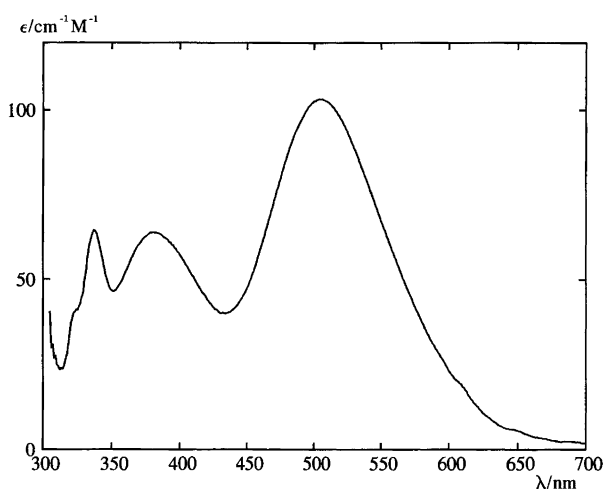
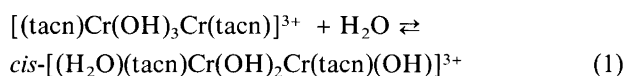


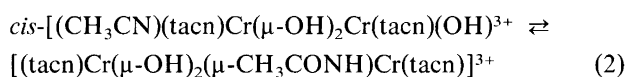
Fig. 1. UV/VIS spectrum of $[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$ in acetonitrile (compound **2** after 20 min at 50°C in acetonitrile with $C_{\text{Cr}} = 5$ mM). The ϵ -values are per two Cr.

$k(25.0^\circ\text{C}) = 0.0109(1) \text{ s}^{-1}$, and the activation parameters $\Delta H^\ddagger = 74(1) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -33(5) \text{ J mol}^{-1} \text{ K}^{-1}$ (10.0, 15.0 and 25.0°C). Addition of increasing amounts of water showed, by extrapolation, that $k = 0.0122(2) \text{ s}^{-1}$ in water at 25.0°C. The corresponding values for $[(\text{NH}_3)_3\text{Cr}(\text{OH})_3\text{Cr}(\text{NH}_3)_3]^{3+}$ at 25.0°C in 1.0 M NaClO_4 are $k = 0.0364(5) \text{ s}^{-1}$, $\Delta H^\ddagger = 83(6) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 5(19) \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

$[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]^{3+}$. Attempts to produce more concentrated acetonitrile solutions of $[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$ have so far been futile. The reason is probably a combination of different factors. Concentration without removal of the water (from the water of crystallization and the condensation process) will shift the equilibrium of eqn. (1) to the right:



Concentration by distilling the water/acetonitrile/benzene azeotrope results in disappearance of the trihydroxo-bridged dimer, and other red oligomers are formed. From such concentrated solutions, as well as from solutions obtained by decocing without benzene, $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]_3 \cdot 3\text{H}_2\text{O}$ can be isolated in 40–50% yields by addition of NaI. Like other examples with cobalt(III),⁵ palladium(II)⁶ and iron(III)⁷ the last steps in the reaction are probably an intramolecular attack by hydroxide coordinated to one metal ion on acetonitrile coordinated to the other metal ion and a shift of a proton position from the oxygen to the nitrogen [eqn. (2)].



In order to clarify the constitution of the complex the analogous acetato-bridged dimer was synthesized by adding sodium acetate to an aqueous solution of *trans*- $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\text{OH})_2\text{Cr}(\text{tacn})(\text{H}_2\text{O})]^{4+}$ until pH ca. 5.5. At this pH the dimer isomerizes to the 3+ charged *cis*-isomer,² and the acetato-bridged analogue could be crystallized in good yields. The anhydrous perchlorates of the two compounds have nearly identical IR spectra (no CN triple bonds), ESR frozen glass spectra and Guinier X-ray powder diffraction diagrams. The UV/VIS spectra (Fig. 2) of the two compounds in aqueous solution are also rather similar and constant in time over a wide pH range. In 0.1 M $\text{CF}_3\text{SO}_3\text{H}$ the acetato-bridged dimer is robust while the acetamidato-bridged dimer slowly (hours) turns violet. On addition of base the acetamidato-bridged compound reversibly loses a proton to give a dimer in which one of the bridges is an oxo bridge as judged from the spectra in 1.0 M $\text{Na}(\text{Br},\text{OH})$ (Fig. 2). The $[(\text{tacn})\text{Cr}(\mu\text{-OH})(\mu\text{-O})(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]^{2+}$ ion is robust even in 1 M NaOH, and the acid dissociation constant of the conjugate acid was determined from the spectra: $\text{p}K_a = -\log(K_a/M) = 12.83(5)$ at 25°C. The analogous acetato-bridged complex behaves

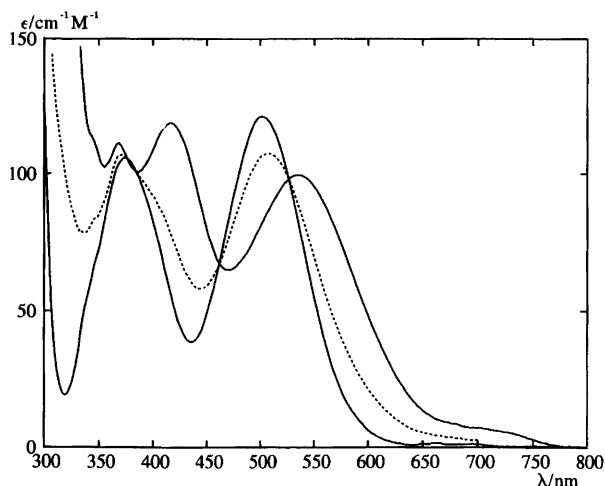


Fig. 2. UV/VIS spectra of $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]I_3 \cdot 3\text{H}_2\text{O}$ in 1.00 M Na(Br,OH) ($C_{\text{Cr}} = 6.5$ mM). The full line represents the acid form (1.00 M NaBr with $\lambda_{\text{max}} = 501$ nm) and the conjugate base (0.80 M NaOH/0.20 M NaBr with $\lambda_{\text{max}} = 535$ nm). The dotted line represents one (0.05 M NaOH/0.95 M NaBr) of some intermediate spectra used for the determination of the acid dissociation constant. The ϵ -values are per two Cr.

similarly, but is less robust in the basic medium. As expected, these complexes in many respects resemble the $\text{Cr}(\mu\text{-OH})_2(\mu\text{-CO}_3)\text{Cr}$ and $\text{Cr}(\mu\text{-OH})(\mu\text{-CH}_3\text{COO})_2\text{Cr}$ dimers with tacn or the trimethylated tacn, which have been thoroughly investigated by Wieghardt *et al.*^{8,9}

Crystal structure of $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]I_3 \cdot 3\text{H}_2\text{O}$. The result of the structure determination from single-crystal X-ray diffraction data confirms the conclusions above concerning the constitution of the dinuclear complex ion.

The cation in the salt is shown in Fig. 3 and selected bond lengths and angles in Table 1. The acetamidato bridge causes the $\text{Cr}(\mu\text{-OH})_2\text{Cr}$ part to deviate markedly from planarity, the angle between the O1-Cr1-O2 and the O1-Cr2-O2 planes being $28.3(4)^\circ$. For comparison the corresponding angle in $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-H}_3\text{O}_2)\text{Cr}(\text{tacn})]I_3 \cdot 3\text{H}_2\text{O}$ is 21° and the Cr-O-Cr angles $4\text{--}5^\circ$ larger.¹⁰ In the latter salt the two tacn ligands adopt the same conformation, whereas in the present μ -acetamidato complex the Cr1-tacn moiety has $\delta\delta\delta$ conformation and the Cr2-tacn moiety $\lambda\lambda\lambda$ conformation. Bond distances and angles in the $(\text{tacn})\text{Cr}(\text{OH})_2\text{Cr}(\text{tacn})$ fragment otherwise resemble those in similar compounds.⁸⁻¹⁰

In the CH_3CONH^- bridge the bond distances indicate a similar degree of double-bond character in the C-N and in the C-O bond.¹¹ The C2-O3 and Cr2-O3 bond lengths are nearly the same as in acetato-bridged chromium(III) dimers.⁹ Cr1-N2 is slightly longer than the Cr2-O3 bond, although not as long as in chromium(III) amine complexes (typically 2.06–2.10 Å). In this context it should be pointed out that there seems to be no disordering of N2 and O3 in the present structure: The ther-

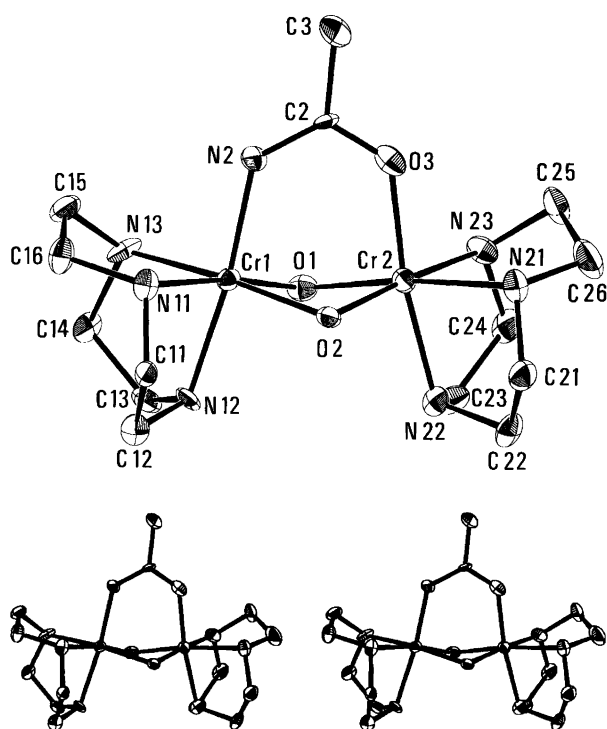


Fig. 3. ORTEP drawings of the cation in $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]I_3 \cdot 3\text{H}_2\text{O}$ showing the labelling and a stereo view. The thermal ellipsoids enclose 50% probability.

mal parameters for O3 and N2 are normal and almost of the same magnitude, the distances C2-N2 and C2-O3 differ significantly, and this model is significantly better than the one in which N2 and O3 were interchanged.

The crystal packing is characterized by a three-dimensional network of hydrogen bonds involving all iodine

Table 1. Bond distances (in Å) and angles (in $^\circ$) in $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]I_3 \cdot 3\text{H}_2\text{O}$, illustrating the coordination around chromium (e.s.d.s in parentheses).

Cr1-O1	1.967(7)	Cr2-O1	1.957(8)
Cr1-O2	1.981(7)	Cr2-O2	1.975(6)
Cr1-N11	2.062(8)	Cr2-N21	2.100(9)
Cr1-N12	2.061(8)	Cr2-N22	2.070(9)
Cr1-N13	2.067(8)	Cr2-N23	2.059(8)
Cr1-N2	2.003(9)	Cr2-O3	1.972(8)
C2-O3	1.270(12)	C2-N2	1.331(13)
C2-C3	1.488(14)		
O1-Cr1-O2	80.9(3)	O1-Cr2-O2	81.3(3)
O1-Cr1-N11	172.8(4)	O2-Cr2-N23	176.0(4)
O1-Cr1-N12	90.6(3)	O2-Cr2-N22	92.6(3)
O1-Cr1-N13	96.0(3)	O2-Cr2-N21	97.6(3)
O2-Cr1-N11	99.6(3)	O1-Cr2-N23	97.2(3)
O2-Cr1-N12	92.7(3)	O1-Cr2-N22	91.4(3)
O2-Cr1-N13	174.2(3)	O1-Cr2-N21	174.0(3)
N11-Cr1-N12	82.2(4)	N21-Cr2-N22	82.8(4)
N12-Cr1-N13	82.4(3)	N22-Cr2-N23	83.7(3)
N13-Cr1-N11	82.9(3)	N23-Cr2-N21	83.4(4)
Cr1-O1-Cr2	95.4(3)	Cr1-O2-Cr2	94.4(3)
O1-Cr1-N2	94.1(3)	O2-Cr2-O3	94.9(3)
O2-Cr1-N2	92.7(3)	O1-Cr2-O3	93.6(3)

Table 2. Short intermolecular contact distances (in Å) in $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]_3 \cdot 3\text{H}_2\text{O}$.

O1–I3A ^b	3.366(7)	N12–I1 ^a	3.590(8)
O1–I3B ^b	3.53(1)	N22–I1 ^a	3.59(1)
O2–I3A ^a	3.413(7)	N21–I3A ^a	3.647(9)
O2–I3B ^a	3.469(9)	N23–O4 ^{Wa}	2.96(1)
O4 ^W –I3B ^b	3.37(3)	N11–O4 ^{We}	2.88(1)
O5 ^W –I2 ^a	3.48(1)	O4 ^W –O5 ^{Wf}	2.97(1)
O5 ^W –I3A ^c	3.455(9)	O4 ^W –O6 ^{Wd}	2.75(2)
O5 ^W –I3B ^c	2.80(3)	O5 ^W –O6 ^{Wa}	2.75(2)
O6 ^W –I2 ^d	3.58(1)		

Symmetry codes: ^a(x, y, z), ^b($1-x, 1/2+y, 3/2-z$), ^c($2-x, 1/2+y, 3/2-z$), ^d($1/2+x, 5/2-y, 1-z$), ^e($1-x, -1/2+y, 3/2-z$), ^f($-1+x, y, z$).

and most of the nitrogen and oxygen atoms. Table 2 shows the contact distances.

Experimental

Chemicals and chemical analysis. The chemicals were of reagent grade or of a better quality. The synthesized compounds were analyzed for Cr, C, H, N, S and I, and were within 1–2% in accordance with the given formulae.

Apparatus. UV/VIS absorption spectra were recorded on a Perkin-Elmer Lambda 2 or Lambda 17 spectrophotometer with automatic disk data collection. The latter instrument was also used for the determination of the rate constants as described earlier.³ $[\text{H}^+]$ measurements and determination of acid dissociation constants were performed as described elsewhere.² The X-ray equipment is described in the X-ray section.

Syntheses. Caution! In the following procedures handling of the perchlorates must be done with care.¹² Syntheses on a larger scale should be avoided or done with the utmost caution. Avoid scraping and (local) heat, and dilute mixtures of organic solvents and HClO_4 at once. We did not experience explosions when these precautions were taken.

$[\text{Cr}(\text{tacn})(\text{CF}_3\text{SO}_3)_3]$ and $[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$. A mixture of 40 ml of 4 M $\text{CF}_3\text{SO}_3\text{H}$ and 1.02 g of $[\text{Cr}(\text{tacn})\text{Cl}_3]_2$ (3.55 mmol) was kept at 80°C for a few hours to give a red–violet solution, which was then evaporated at 90°C on a rotary evaporator until the solution over the formed precipitate was almost colourless. After being cooled in ice, the pink precipitate was filtered off, washed with water, ethanol and diethyl ether in turn, and dried in air. Yield: 2.03 g of $[\text{Cr}(\text{tacn})(\text{CF}_3\text{SO}_3)_3]$ (91%).

1.00 g of this product (1.59 mmol) was added to a mixture of 50 ml of acetone and 0.2 ml 2 M $\text{CF}_3\text{SO}_3\text{H}$, and the suspension was stirred for 2 d at room temperature. After this a clear red solution formed, which was then evaporated almost to dryness on a rotary evaporator. The orange–red crystal powder was washed several

times with diethyl ether and dried in air. Yield: 0.90 g of $[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$ (83%). With a higher water concentration at a lower temperature larger needles of a trihydrate could be isolated.

The product was used directly for the next synthesis, but it could be reprecipitated from a concentrated, filtered aqueous solution by slow addition of 100% $\text{CF}_3\text{SO}_3\text{H}$ at 0°C. After being washed with diethyl ether as above and dried in air, the product should be stored in a freezer.

$[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_2(\text{OH})][\text{Cr}(\text{tacn})(\text{H}_2\text{O})(\text{OH})_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ (**2**). This synthesis should be carried out rapidly at 0°C to prevent the formation of hydroxo-bridged complexes. 3.5 g of $[\text{Cr}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$ (5.1 mmol) were dissolved in 1.8 ml of water. After filtration 0.7 ml of 12 M NH_3 was added followed by ca. 1 g of $\text{Na}(\text{CF}_3\text{SO}_3)$, and the mixture was allowed to precipitate for 5 min. Then the violet crystals were filtered off, washed with diethyl ether several times and dried in air. Yield: 1.8 g of **2** (75%). The product should be stored in a freezer.

$[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]_3 \cdot 3\text{H}_2\text{O}$ (**3**). 0.5 g of compound **2** (0.5 mmol) was dissolved in 2 ml of acetonitrile, and the solution was refluxed for 2 h at 80°C. After cooling to room temperature ca. 0.3 g of NaI was added, and the solution was left uncovered overnight to allow slow evaporation and crystallization. The orange–red crystals were separated from the mother liquor, washed with ethanol and diethyl ether and dried in air. Yield: 0.22 g of **3** (45%).

The anhydrous perchlorate of this complex could be obtained from a saturated solution of the iodide by addition of solid LiClO_4 and slow cooling to 0°C. The precipitated crystals were washed once with a little ethanol, then with diethyl ether and dried in air. Precipitation at 5–10°C resulted in a tetrahydrate.

$[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{COO})\text{Cr}(\text{tacn})](\text{ClO}_4)_3$ (**4**). 0.50 g of *trans*- $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\text{OH})_2\text{Cr}(\text{tacn})(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_4$ (0.48 mol) (synthesized in the same manner as the perchlorate)² was dissolved in 1.0 ml of water, and 0.33 g of $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ (2.4 mmol) was added. After 1 h at 50°C solid LiClO_4 was added to the red solution, which was then left for crystallization at 0°C. The orange–red crystals were filtered off, washed with ethanol and diethyl ether and dried in air. Yield: 0.30 g of **4** (80%).

The iodide (dihydrate) was synthesized in the same manner in similar yields using solid NaI instead of LiClO_4 .

$[(\text{tacn})\text{Cr}(\text{OH})_3\text{Cr}(\text{tacn})]^{3+}$ in acetonitrile solution. 70 mg of **2** (0.075 mmol) were dissolved in 30 ml of dry acetonitrile and heated for 15–30 min at 50°C and then cooled to room temperature. Such solutions were used for the spectral and kinetic investigations discussed above. As mentioned above, different attempts to increase the concentration of the trihydroxo-bridged dimer resulted in a lower

content of this species compared to other chromium(III) species.

Crystal structure determination. Powder diffraction diagrams were taken at room temperature with a Guinier-Hägg camera using $\text{CuK}\alpha$ radiation and silicon as an internal standard. For the selected single crystal the data collection was performed with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated $\text{MoK}\alpha$ ra-

Table 3. Crystal data and a summary of data collection and refinement results for $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]_3 \cdot 3\text{H}_2\text{O}$.

Formula	$\text{Cr}_2\text{C}_{14}\text{H}_{42}\text{N}_7\text{O}_6\text{I}_3$	
FW/g mol ⁻¹	889.25	
Space group	$P2_12_12_1$	
Cell parameters, single crystal (122 K) and powder (295 K), respectively:		
Radiation	$\text{MoK}\alpha$	$\text{CuK}\alpha$
$a/\text{Å}$	9.972(2)	10.044(4)
$b/\text{Å}$	13.731(4)	13.728(6)
$c/\text{Å}$	21.577(6)	21.708(13)
$V/\text{Å}^3$	2954.7(13)	2993(2)
Calculated density (122 K)/g cm ⁻³	1.999	
Molecules per cell, Z	4	
Data collection and SHELXL-93 refinement:		
Crystal size/mm ³	0.14 × 0.12 × 0.33	
Faces	{001} {110} {010}	
Radiation ($\text{MoK}\alpha$) $\lambda/\text{Å}$	0.71073	
Linear absorption coefficient μ/cm^{-1}	39.08	
Range of absorption correction factor	0.168–0.235	
Scan type	$\omega/2\theta$	
Scan range, $\Delta\omega/^\circ$	1.0+0.35tan θ	
Maximum scan time/s	60	
θ limits/ $^\circ$	1–27.5	
Octants collected	$hk\pm l$	
Max. – min. hkl	0–17, 0–24, ± 38	
No. of measurements	9346	
No. of unique data	5211	
No. of observed with $I \geq 2\sigma(I)$	4618	
R_{int}	0.030	
No. of parameters	305	
Weights, w^{-1}	$\sigma^2(F_o ^2) + (0.0343P)^2 + 22.35P$, where $P = (F_o ^2 + 2 F_c ^2)/3$	
Flack parameter	0.02(5)	
$R(F_{\text{obs}})^a$	0.04	
$R_w(F^2, \text{all})^b$	0.14	
Goodness of fit, $S(\text{obs})$	1.135	
(Shift/error) _{max}	0.005	
$\Delta\rho_{\text{max}}/e \text{ Å}^{-3}$	1.96	
$\Delta\rho_{\text{min}}/e \text{ Å}^{-3}$	–1.73	

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ calculated for reflections with $I \geq 2\sigma(I)$. ^b $R_w = (\sum w||F_o|^2 - |F_c|^2| / \sum |F_o|^2)^{1/2}$.

diation. The crystal was cooled to 122 K by a Nonius gas flow low-temperature device. The variations of the temperature were within 1 K. Unit-cell dimensions were determined from a least-squares refinement on the setting angles of 22 reflections with θ in the range 18.04–20.85°. The intensities of three standard reflections were measured every 10000 s of X-ray exposure time. The orientation of the crystal was checked after every 300 reflections by measuring setting angles for seven reflections. These measurements showed that no misalignment or deterioration occurred during data collection. The crystal data are presented in Table 3. Absorption correction was performed using the Gaussian integration procedure.¹³ The DREADD¹⁴ programs used for data reduction included corrections for Lorentz, polarization, background and absorption. The space group was uniquely determined from the systematically absent reflections, $h00$: for $h = 2n + 1$, $0k0$: for $k = 2n + 1$ and $00l$: for $l = 2n + 1$.

The structure was solved by direct methods using SHELXS-86.¹⁵ A standard run provided the positions for three iodine atoms, in agreement with a calculated Patterson function. Subsequent difference electron den-

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[(\text{tacn})\text{Cr}(\mu\text{-OH})_2(\mu\text{-CH}_3\text{CONH})\text{Cr}(\text{tacn})]_3 \cdot 3\text{H}_2\text{O}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
I1	71(1)	6817(1)	6148(1)	28(1)
I2	9635(1)	10526(1)	4946(1)	34(1)
I3A ^a	7048(1)	6607(1)	7692(1)	23(1)
I3B ^b	6899(11)	6757(7)	8027(13)	37(5)
Cr1	2946(2)	8470(1)	7824(1)	16(1)
Cr2	4483(2)	8553(1)	6683(1)	17(1)
O1	2906(8)	9193(5)	7037(3)	22(2)
O2	3999(7)	7558(4)	7305(3)	16(1)
O3	5748(7)	9248(5)	7229(3)	24(2)
O4 ^w	5118(9)	11666(5)	5720(4)	37(3)
O5 ^w	12143(11)	11721(8)	5753(4)	50(3)
O6 ^w	11366(13)	13559(9)	5405(5)	62(4)
N11	2759(9)	7640(6)	8616(4)	20(2)
N12	1158(8)	7801(5)	7606(4)	18(2)
N13	1694(9)	9405(6)	8301(4)	21(2)
N21	6035(10)	7777(6)	6249(4)	23(2)
N22	3328(10)	7899(6)	6003(3)	21(2)
N23	4868(10)	9565(6)	6002(4)	26(2)
N2	4595(9)	9145(6)	8135(4)	21(2)
C11	2038(12)	6746(7)	8415(4)	23(2)
C12	812(12)	7004(7)	8051(5)	22(2)
C13	120(11)	8591(7)	7565(5)	25(2)
C14	259(11)	9211(7)	8143(5)	25(2)
C15	1944(13)	9260(8)	8974(5)	30(2)
C16	2023(12)	8176(7)	9119(4)	25(2)
C21	5371(13)	6874(7)	6004(5)	28(2)
C22	4125(13)	7157(7)	5652(5)	25(2)
C23	2832(14)	8712(8)	5610(5)	30(2)
C24	3989(14)	9399(8)	5457(5)	31(3)
C25	6362(12)	9451(8)	5858(6)	33(3)
C26	6655(14)	8371(9)	5745(6)	38(3)
C2	5665(10)	9409(6)	7807(4)	18(2)
C3	6804(12)	9939(10)	8100(6)	34(3)

^a S.o.f.: 0.92(1). ^b S.o.f.: 0.08(1).

sity ($\Delta\rho$) maps yielded the locations of the remaining non-hydrogen atoms in the structure, but did not provide definitive information about the positions of the hydrogen atoms. The structure was refined by the method of least squares, minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$ using SHELXL-93.¹⁶ At an early stage of the refinements the large thermal parameters in two of the iodine atoms indicated disorder of these ions. A refinement with two positions for I2 and I3 showed that both iodine positions can be divided into two positions. The two sites for I2 are separated by 0.333(9) Å, with site occupation factors of 0.72(2) and 0.28(2). The two sites for I3 are separated by 0.76(3) Å and site occupation factors are 0.929(8) and 0.081(8). The $R(\text{Free})$ ¹⁷ test showed that the model with I2 and I3 each resolved into two positions, refined isotropically for I2 and anisotropically for I3, does not give a better description of the structure than a model with only one position for I2 refined anisotropically. The $R(\text{Free})$ value for the first model is 13.68%, compared with 13.60% for the second model. The same conclusion was obtained from an R -value test. The positions of the hydrogen atoms binding to carbon were introduced in idealized positions.

The maximum peak of 1.960 e Å⁻³ is found close to I2 in the difference Fourier map. Further details from the solution and refinements are listed in Table 3, and the final positional parameters for the non-hydrogen atoms are listed in Table 4. Lists of observed and calculated squares of structure amplitudes, anisotropic displacement parameters and positional parameters for the hydrogen atoms are available from the authors.

Acknowledgments. We thank Dr. Sine Larsen for valuable discussions and Karen Jørgensen and Flemming Hansen

for their contribution to the analytical work and the X-ray data collection, respectively. The Danish Natural Science Research Council is thanked for its support.

References

1. Andersen, P., Larsen, S. and Pretzmann, U. *Acta Chem. Scand.* 47 (1993) 1147.
2. Andersen, P., Døssing, A. and Nielsen, K. M. *Acta Chem. Scand.* A40 (1986) 142.
3. Andersen, P. and Døssing, A. *Acta Chem. Scand.* 47 (1993) 24.
4. Døssing, A. *Ph.D. Thesis*, University of Copenhagen 1990.
5. Curtis, N. J., Hagen, K. S. and Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* (1984) 1571.
6. McKenzie, C. J. and Robson, R. J. *Chem. Soc., Chem. Commun.* (1988) 112.
7. Hazell, A., Jensen, K. B., McKenzie, C. J. and Toftlund, H. *Inorg. Chem.* 33 (1994). *In press.*
8. Wieghardt, K., Schmidt, W., van Eldik, R., Nuber, B. and Weiss, J. *Inorg. Chem.* 19 (1980) 2922.
9. Martin, L. L., Wieghardt, K., Blondin, G., Girerd, J.-J., Nuber, B. and Weiss, J. *J. Chem. Soc., Chem. Commun.* (1990) 1767 and references therein.
10. Andersen, P., Døssing, A. and Larsen, S. *Acta Chem. Scand.* 44 (1990) 455.
11. Sigel, H. and Martin, R. B. *Chem. Rev.* 82 (1982) 385.
12. Springborg, J. and Schäffer, C. E. *Inorg. Synth.* 18 (1978) 75.
13. DeTitta, G. T. *J. Appl. Crystallogr.* 18 (1985) 75.
14. Blessing, R. H. *Crystallogr. Rev.* 1 (1987) 3.
15. Sheldrick, G. M. *Acta Crystallogr., Sect. A46* (1990) 467.
16. Sheldrick, G. M. SHELXL-93. *J. Appl. Crystallogr.* (1993) *To be submitted.*
17. Brunger, A. T. *Nature (London)* 335 (1992) 472.

Received December 12, 1993.