

Synthesis and Characterization of a Dinuclear Chromium(III) Complex with Two Amido Bridges and One Hydroxo Bridge. Crystal Structure of $\text{Na}[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ ($\text{tacn} = 1,4,7\text{-Triazacyclononane}$)

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Triply bridged dinuclear chromium(III) complexes with 1,4,7-triazacyclononane (tacn) with three amido bridges, or two amido bridges and one hydroxo bridge, were obtained in 15–20% yield in liquid ammonia at 100 °C from $[\text{Cr}(\text{tacn})\text{Cl}_3]$ or $[\text{Cr}(\text{tacn})(\text{CF}_3\text{SO}_3)_3]$ after addition of stoichiometric amounts of potassium amide.

The chemical properties of these dinuclear complexes in an aqueous medium are described in terms of bridge cleavage and formation, substitution of coordinated ammonia and acid–base properties.

The structural properties of the dinuclear chromium(III) complex with one hydroxo and two amido bridges were investigated by X-ray diffraction methods. $\text{Na}[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ forms monoclinic crystals belonging to the space group $P2_1/a$ with $a = 14.417(2)$, $b = 18.045(2)$, $c = 23.480(3)$ Å and $\beta = 90.244(11)^\circ$ (122 K) and $Z = 8$. The two independent complex ions have identical geometry with the very short Cr–Cr distances 2.587(2) and 2.594(2) Å. The crystals undergo small structural changes with time, that involve the interactions of the perchlorate ions.

During the last decade several new amido-bridged metal complexes have been synthesized and characterized. Ludwig Heck and co-workers have synthesized in this period, among other amido-bridged complexes, the tri- μ -amido-bis(triamminemetal) complexes of chromium(III),¹ cobalt(III),² rhodium(III)³ and platinum(IV),⁴ and investigated some of their chemical properties. The reaction medium in the syntheses has typically been anhydrous liquid ammonia, with stoichiometric amounts of potassium amide or concentrated aqueous ammonia (in the case of cobalt) at 30–150 °C. $[(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{NH}_3)_3]^{3+}$ was synthesized from the hexaamminechromium(III) in liquid ammonia under such moderate conditions shortly after it was made for the first time in supercritical ammonia at 6000 bar and 500 °C from chromium(II) iodide.⁵

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Reactivity studies of $[(\text{NH}_3)_3\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{NH}_3)_3]^{3+}$ showed that in aqueous solution cleavage of the first amido bridge is acid-catalyzed.⁶ Further reactivity studies of this system were difficult to interpret because of loss of ammonia from different positions in the complex. In our efforts to compare these amido-bridged complexes with corresponding hydroxo-bridged analogues⁷ we therefore decided to block one face in the chromium(III) octahedron with the facially coordinating ligand $\text{tacn} = 1,4,7\text{-triazacyclononane}$.

The reactivity and other properties of the system derived from $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_3\text{Cr}(\text{tacn})]^{3+}$ (1) are under investigation. Meanwhile we here present the synthesis of $[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})]^{3+}$ (2), some of its chemical properties explaining the synthesis and handling of the compound, and the crystal structure, determined by X-ray diffraction, of its perchlorate obtained as a double salt with sodium.

Experimental

Chemicals and apparatus. The chemicals were of reagent grade or better quality (the liquid ammonia contained less than 20 ppm H₂O). The synthesized compounds were analysed for Cr, C, H and N at our Department for Microanalysis, and the analyses were within 1–2% in accordance with the given formulae (see the comment below in the paragraph on FPLC). UV/VIS spectral data were collected on a Perkin-Elmer Lambda 40 instrument. The liquid chromatography (FPLC) was performed on a Pharmacia instrument.

Syntheses. Caution! In the following syntheses handling of the perchlorates must be done with caution.⁸ 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.

1,4,7-Triazaacyclononane trihydrochloride (tacn · 3HCl). The compound was synthesized as described elsewhere.⁹

[Cr(tacn)Cl₃]. The synthesis published by Wiegardt *et al.*¹⁰ was modified slightly: A slurry of tacn · 3HCl and LiOH (three equivalents) in methanol was used instead of a methanolic solution of the free amine. The crude product was washed with water. Yield: 82%.

[Cr(tacn)(CF₃SO₃)₃]. A slurry of 7.1 g of Cr(tacn)Cl₃ in 30 ml of CF₃SO₃H was stirred for 3 h at 25 °C under nitrogen, after which the mixture was slowly added to 500 ml of cold diethyl ether. The pink precipitate was filtered off, washed with 1000 ml of diethyl ether and dried in air. Yield: 12.65 g of [Cr(tacn)(CF₃SO₃)₃] (82%).

[(tacn)Cr(μ-NH₂)₃Cr(tacn)](ClO₄)₃ (1). In a 250 ml steel autoclave equipped with a stirrer 8 g of [Cr(tacn)Cl₃] (28 mmol) were transferred to a solution of potassium amide. This solution had been made in advance in the autoclave by reaction of 1.1 g of potassium (28 mmol) with 70 ml of liquid ammonia (<20 ppm H₂O) at room temperature. The autoclave was now heated for 3 d at 100 °C. After evaporation of the ammonia, a brownish solid reaction mixture was obtained (8 g). Two-gram portions of this crude product were dissolved in water, filtered and separated by ion-exchange chromatography on Sephadex C-25 using 0.12 M/0.06 M Na₂HPO₄/NaH₂PO₄ as eluent. After a large red band, a yellow band appeared, which was identified as [Cr(tacn)(NH₃)₃]³⁺. Then a yellow–green band appeared, which contained the cation of **1**. This band was, after dilution with water, reabsorbed on Sephadex C-25 and eluted with 1 M NaClO₄. Compound **1** crystallized spontaneously in the eluate within 1 h at 0 °C. The yellow–green precipitate was filtered off, washed with ethanol and diethyl ether and air-dried. Yield: 400 mg of **1** per 2 g portion of crude product (16%).

Na[(tacn)Cr(μ-NH₂)₂(μ-OH)Cr(tacn)](ClO₄)₄ (2).

(a) The synthesis was made as described above for **1**, except that 8 g of [Cr(tacn)(CF₃SO₃)₃] (0.5 g of potassium) were used instead of [Cr(tacn)Cl₃]. During the ion exchange separation an additional, brown band appeared in front of the yellow [Cr(tacn)(NH₃)₃]³⁺ band. The brown band was, after dilution with water, reabsorbed on Sephadex C-25 and eluted with 1 M NaClO₄. Compound **2** crystallized at 0 °C after addition of solid NaClO₄. The brown precipitate was filtered off, washed with a 1:1 mixture of ethanol and diethyl ether, then with diethyl ether and finally air-dried. Yield: 210 mg of **2** per 2 g portion of crude product (16%).

(b) A solution of 175 mg (0.23 mmol) of **4** (*vide infra*) and 11 mg of NH₄Br (0.11 mmol) in 1 ml of water were heated for 1 h at 50 °C. Then 0.9 g of NaClO₄ · H₂O were added and the solution was cooled to 0 °C. After 30 min at 0 °C the brown precipitate was filtered off, washed with a 1:1 mixture of ethanol and diethyl ether, then with diethyl ether and finally air-dried. Yield: 175 mg of **2** (76%).

[(NH₃)(tacn)Cr(μ-NH₂)₂Cr(tacn)(OH)](ClO₄)₃ · 2H₂O (4).

A slurry of 300 mg of **1** and 4 ml of 1 M HClO₄ was stirred for 50 min at room temperature. The reaction mixture was then filtered (whereby 55 mg of **1** were recovered), and the filtrate was allowed to stand for 30 min at room temperature. After addition of excess 10 M NaOH and 0.5 g of NaClO₄ (cooling to 0 °C) an orange precipitate was formed, which was filtered off after 30 min, washed with a 1:1 mixture of ethanol and diethyl ether, then with diethyl ether and finally air-dried. Yield: 176 mg of **4** (55%).

FPLC separations. Separation of the reaction mixtures using liquid chromatography in form of FPLC has been a very powerful tool in these investigations. With this method, combined with UV/VIS spectral data, it has been possible to distinguish between the many products involved and to design optimum procedures for the isolation of most of the compounds described in this paper.

A Mono HR 5/5 column with 2 ml injection and UV detection at 254 nm was used. Additionally the different bands could be collected and their chromium content (AAS) and UV/VIS spectrum measured. Typically ca. 0.5 mg of the dinuclear chromium(III) compound has been enough for an informative FPLC separation.

The reaction mixtures were quenched by diluting 10–500 times with 0 °C water. With an elution gradient from water to 1 M NaCl buffered with 0.02 M propane-1,3-diamine/0.002 M HCl the doubly bridged dinuclear species with charge 2+ showed up after 8–10 ml (two non-bridging OH[−] ligands), the 3+ charged doubly bridged after ca. 12 ml (one non-bridging OH[−]) and the triply bridged species after 13–14 ml, with half-widths corresponding to 0.2–0.4 ml. The separations were highly reproducible. The assignment of the bands was based on

standards of the respective pure compounds as was the content, which could also be determined by AAS.

While elemental analysis and UV/VIS spectra of the synthesized compounds tell little about impurities of the related complexes, often involved in the syntheses, FPLC showed easily 1% or less of other dinuclear species in the main products.

X-Ray crystallography. A single crystal of **2** was selected from the batch prepared as described above. The data collection was performed with a CAD4 diffractometer using graphite monochromatized Cu K α radiation ($\lambda = 1.54184$ Å). An Oxford Cryosystems low-temperature device was used to cool the crystal to 122.5(5) K. The cell parameters were obtained from a refinement of 25 reflections with θ in the range 36.51–42.12°, $a = 14.381(3)$ Å, $b = 18.048(2)$ Å, $c = 23.483(2)$ Å, $\beta = 90.05(1)^\circ$, $V = 6095(2)$ Å³. The data collection was performed under the assumption that the crystal belongs to the orthorhombic system, and $-hkl$ and ca. 40% of the hkl reflections were measured. After the data collection was completed analysis of the data showed that the crystal is monoclinic with β accidentally close to 90°. The space group was assigned to be $P2_1/a$ from the systematically absent reflections. The data reduction performed with the DREADD¹¹ system included corrections for background, Lorentz, polarization, and absorption effects. The intensities of the five standard reflections measured every 10^4 s decreased by less than 4%. Using this partial data set consisting of 8715 contributing reflections the structure was solved to $R_1 = 0.066$ and $R_{2w} = 0.151$. However, as a complete set was required for the refinement, another data collection was undertaken three months later using the original crystal on the same instrument employing the same experimental parameters as previously, but including all the reflections in the octants hkl and $hk-l$ and ca. 30% of the $-hkl$ and $-hk-l$ reflections.

The refinement of the cell parameters showed significant deviations for a and β from the values obtained earlier. The standard reflections decreased up to 15% in intensity and corrections for this decrease were applied using a polynomial up to third order. Correction for absorption was also performed using a Gaussian integration procedure. The transmission factors were in the range 0.273–0.628. Symmetry related reflections were averaged giving $R_{int} = 0.0295$ and $R_w = 0.0856$. An analysis of the systematically absent reflections showed that the space group had not changed since the first data collection. SHELXL97¹² was used for the structure determination by direct methods and the full matrix least squares refinement minimizing $\sum w(F_o^2 - F_c^2)^2$. Anisotropic displacement parameters were used for all non-hydrogen atoms. The large anisotropic displacement parameters observed for some of the oxygen atoms in three of the perchlorate ions indicated disorder of these ions. In two of the perchlorate ions one oxygen atom was split into two with the populations free to refine

with the constraint that the sum of the occupancies equals one, and in another perchlorate ion two oxygen atoms were split to account for the disorder. The identity of the atoms forming the bridges between the chromium atoms was established unambiguously from their displacement parameters. The hydrogen atoms were fixed in their idealized positions with the isotropic displacement parameters $U_i = 1.2 \times U_{eq}$ of the adjacent atom, except for the hydrogen atoms bonded to the bridging hydroxo groups and in the water molecules. As they were not shown clearly in the difference electron density, they could not be included in the refinement. The highest peak in the difference Fourier map after the final refinements is located 1.03 Å from Cl5. Table 1 contains additional information of the experimental conditions and a summary of data reduction and refinement of the second data set. It is apparent from the refinement results based on the second data set that the final model apparently is of lower accuracy than the one obtained previously from the partial data set. The parameters from the refinement of the second data set, the atomic coordinates, isotropic displacement parameters and occupancies, are listed in Table 2, as they are unbiased from lacking parts of the data set. Anisotropic displacement parameters, positional

Table 1. Crystal data and summary of the data collection and structure refinement results.

M_r	850.27
Radiation	Cu K α ($\lambda = 1.54184$ Å)
Temperature/K	122.5(5)
Space group	$P2_1/a$
$a/\text{Å}$	14.417(2)
$b/\text{Å}$	18.045(2)
$c/\text{Å}$	23.480(3)
$\beta/^\circ$	90.244(11)
$V/\text{Å}^3$	6108.4(13)
Z	8
$D_x/\text{g cm}^{-3}$	1.836
Scan type	ω -2 θ
$\mu(\text{Cu K}\alpha)/\text{mm}^{-1}$	10.039
$F(000)$	3440
Crystal size/ mm^3	$0.15 \times 0.14 \times 0.05$
Determination of cell parameters	
No. of reflections	25
θ -Range/ $^\circ$	36.51–42.12
No. of reflections	
Measured	17610
Independent	12176
Observed [$I > 2\sigma(I)$]	6367
h -Range	–18 → 18
k -Range	0 → 22
l -Range	–29 → 29
$\theta_{min}/^\circ$	3.09
$\theta_{max}/^\circ$	74.94
No. of parameters	811
R_1	0.0894
wR_2	0.1649
$w [P = (F_o^2 + 2F_c^2)/3]$	$[\sigma^2(F_o^2) + (0.0477P)^2]^{-1}$
S	1.229
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}/\text{e Å}^{-3}$	1.052
$\Delta\rho_{min}/\text{e Å}^{-3}$	–0.737

Table 2. Positional parameters and equivalent isotropic displacement parameters, U_{eq} .

Atom	x	y	z	U_{eq}	Occupancy
Cr1A	0.82699(10)	0.41685(8)	0.34994(5)	0.0207(3)	1
Cr2A	0.80321(10)	0.54606(8)	0.39529(5)	0.0226(3)	1
O1A	0.8563(4)	0.4535(3)	0.4269(2)	0.0285(14)	1
N1A	0.8815(5)	0.5153(4)	0.3280(2)	0.025(2)	1
N2A	0.7100(5)	0.4772(4)	0.3587(3)	0.031(2)	1
N11A	0.8032(5)	0.3740(4)	0.2679(3)	0.032(2)	1
N12A	0.7728(5)	0.3142(4)	0.3736(3)	0.030(2)	1
N13A	0.9478(5)	0.3539(4)	0.3427(3)	0.026(2)	1
N21A	0.7539(5)	0.6453(4)	0.3634(3)	0.033(2)	1
N22A	0.7233(5)	0.5767(4)	0.4653(3)	0.029(2)	1
N23A	0.8974(5)	0.6159(4)	0.4339(3)	0.028(2)	1
C11A	0.7502(7)	0.3037(5)	0.2700(4)	0.034(2)	1
C12A	0.7043(7)	0.2960(6)	0.3282(4)	0.039(2)	1
C13A	0.8471(7)	0.2577(5)	0.3823(4)	0.038(2)	1
C14A	0.9399(7)	0.2950(5)	0.3869(4)	0.034(2)	1
C15A	0.9570(7)	0.3227(5)	0.2839(3)	0.035(2)	1
C16A	0.8970(7)	0.3649(5)	0.2430(3)	0.033(2)	1
C21A	0.6810(7)	0.6774(6)	0.4010(4)	0.038(2)	1
C22A	0.6446(6)	0.6200(5)	0.4402(4)	0.037(2)	1
C23A	0.7778(7)	0.6195(6)	0.5069(3)	0.038(2)	1
C24A	0.8809(7)	0.6113(5)	0.4966(3)	0.036(2)	1
C25A	0.8911(7)	0.6927(5)	0.4110(4)	0.035(2)	1
C26A	0.8369(7)	0.6935(5)	0.3564(4)	0.032(2)	1
Cr1B	0.18066(11)	0.44360(8)	0.10490(6)	0.0288(4)	1
Cr2B	0.14734(10)	0.57331(8)	0.14786(5)	0.0254(3)	1
O1B	0.1384(5)	0.5364(4)	0.0695(2)	0.038(2)	1
N1B	0.0824(5)	0.4763(4)	0.1604(3)	0.034(2)	1
N2B	0.2605(5)	0.5098(4)	0.1543(3)	0.030(2)	1
N11B	0.2156(6)	0.3440(4)	0.1421(3)	0.040(2)	1
N12B	0.2849(6)	0.4136(5)	0.0481(3)	0.041(2)	1
N13B	0.1022(6)	0.3737(4)	0.0531(3)	0.036(2)	1
N21B	0.1498(5)	0.6151(4)	0.2306(3)	0.030(2)	1
N22B	0.2146(6)	0.6725(4)	0.1298(3)	0.038(2)	1
N23B	0.0306(5)	0.6412(4)	0.1425(3)	0.036(2)	1
C11B	0.3013(9)	0.3137(6)	0.1167(5)	0.056(3)	1
C12B	0.3509(7)	0.3705(7)	0.0819(4)	0.048(3)	1
C13B	0.2464(9)	0.3731(6)	-0.0020(4)	0.050(3)	1
C14B	0.1427(8)	0.3802(6)	-0.0048(4)	0.053(3)	1
C15B	0.0991(8)	0.2958(6)	0.0746(4)	0.053(3)	1
C16B	0.1332(8)	0.2949(6)	0.1355(4)	0.052(3)	1
C21B	0.2075(7)	0.6826(6)	0.2349(4)	0.039(2)	1
C22B	0.2690(7)	0.6889(6)	0.1827(4)	0.042(3)	1
C23B	0.1462(8)	0.7317(6)	0.1128(4)	0.050(3)	1
C24B	0.0547(8)	0.6977(6)	0.0985(4)	0.051(3)	1
C25B	0.0070(7)	0.6741(6)	0.1985(4)	0.041(2)	1
C26B	0.0505(7)	0.6299(5)	0.2452(4)	0.038(2)	1
Cl1	0.1846(2)	0.42796(12)	0.30681(8)	0.0349(5)	1
O11	0.2121(5)	0.3737(4)	0.2660(3)	0.047(2)	1
O12	0.0943(5)	0.4575(4)	0.2889(3)	0.046(2)	1
O13	0.2492(5)	0.4884(4)	0.3079(3)	0.047(2)	1
O14	0.1725(6)	0.3942(4)	0.3607(3)	0.060(2)	1
Cl2	0.8264(2)	0.3900(2)	0.07046(10)	0.0460(6)	1
O21	0.7668(6)	0.3678(4)	0.1163(3)	0.069(3)	1
O22	0.8408(8)	0.3303(5)	0.0316(4)	0.091(3)	1
O23	0.7788(6)	0.4482(5)	0.0396(3)	0.076(3)	1
O24	0.9118(12)	0.436(2)	0.0855(8)	0.067(7)	0.52(4)
O24'	0.9111(12)	0.396(2)	0.0963(8)	0.050(7)	0.48(4)
Cl3	0.4406(2)	0.6117(2)	0.05361(10)	0.0456(6)	1
O31	0.3755(6)	0.6713(5)	0.0477(4)	0.081(3)	1
O32	0.5290(9)	0.6321(6)	0.0369(5)	0.060(5)	0.72(3)
O32'	0.475(3)	0.632(2)	0.001(2)	0.11(2)	0.28(3)
O33	0.4110(8)	0.5464(5)	0.0243(4)	0.100(4)	1
O34	0.4460(8)	0.5922(6)	0.1122(3)	0.103(4)	1
Cl4	0.4936(2)	0.63619(13)	0.28480(9)	0.0351(5)	1
O41	0.5169(6)	0.7096(4)	0.3028(3)	0.059(2)	1
O42	0.5035(6)	0.6306(4)	0.2247(3)	0.066(3)	1

Table 2. (Continued.)

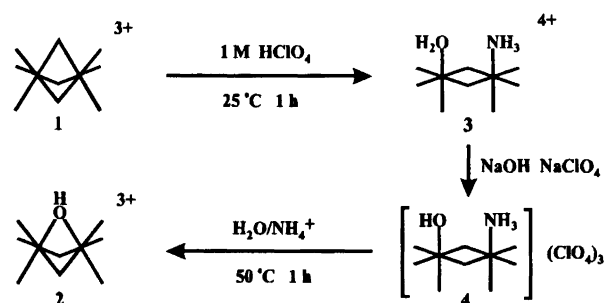
Atom	x	y	z	U_{eq}	Occupancy
O43	0.3998(5)	0.6228(5)	0.2995(3)	0.061(2)	1
O44	0.5530(6)	0.5829(4)	0.3121(3)	0.065(2)	1
Cl5	0.4032(2)	0.63808(14)	0.50546(9)	0.0358(5)	1
O51	0.4168(5)	0.6308(4)	0.4449(2)	0.040(2)	1
O52	0.4014(5)	0.5651(4)	0.5307(3)	0.055(2)	1
O53	0.4753(6)	0.6788(5)	0.5299(3)	0.069(3)	1
O54	0.3146(6)	0.6750(5)	0.5151(3)	0.071(3)	1
Cl6	0.1537(2)	0.60147(13)	0.41958(9)	0.0344(5)	1
O61	0.1180(5)	0.6527(4)	0.4610(3)	0.048(2)	1
O62	0.2109(5)	0.5469(4)	0.4466(3)	0.040(2)	1
O63	0.2074(5)	0.6389(4)	0.3776(3)	0.050(2)	1
O64	0.0766(5)	0.5643(5)	0.3926(3)	0.061(2)	1
Cl7	0.4891(2)	0.38555(14)	0.24116(10)	0.0483(7)	1
O71	0.4335(5)	0.4426(5)	0.2182(3)	0.067(3)	1
O72	0.4687(7)	0.3712(5)	0.2999(3)	0.080(3)	1
O73	0.4880(8)	0.3197(5)	0.2082(3)	0.097(4)	1
O74	0.5837(7)	0.4131(6)	0.2391(4)	0.090(3)	1
Cl8	0.7701(2)	0.5778(2)	0.18834(10)	0.0425(6)	1
O81	0.7754(6)	0.6317(4)	0.2330(3)	0.058(2)	1
O82	0.806(2)	0.620(2)	0.1382(10)	0.046(8)	0.29(2)
O82'	0.7052(8)	0.5991(7)	0.1480(5)	0.065(4)	0.72(2)
O83	0.8580(10)	0.5397(9)	0.1905(8)	0.070(6)	0.63(3)
O83'	0.848(2)	0.563(2)	0.1538(13)	0.067(10)	0.37(3)
O84	0.7207(8)	0.5148(5)	0.2116(5)	0.113(4)	1
O(W1)	0.4182(6)	0.4481(4)	0.4008(3)	0.064(2)	1
O(W2)	0.5846(6)	0.4433(5)	0.1013(3)	0.062(2)	1
Na1	0.3438(3)	0.5535(2)	0.3766(2)	0.0414(9)	1
Na2	0.5517(3)	0.5269(2)	0.1725(2)	0.0428(10)	1

parameters for the hydrogen atoms and the results from the refinement of the first data set are provided as supplementary material.

Results and discussion

Synthesis and some chemical properties of $[(tacn)Cr(\mu-NH_2)_2(\mu-OH)Cr(tacn)]^{3+}$ (**2**). This complex, **2**, was first obtained directly by reacting $[Cr(tacn)(CF_3SO_3)_3]$ in liquid ammonia with stoichiometric amounts of potassium amide in an autoclave at 100 °C for 3 d. After ion exchange separation of the reaction mixture, **2** was obtained in 16% yield as a sodium double salt with perchlorate. The reaction mixture gives a ca. 8% yield of $[(tacn)Cr(\mu-NH_2)_3Cr(tacn)]^{3+}$ (**1**) precipitated as the perchlorate. A similar procedure using $[Cr(tacn)Cl_3]$ instead of the tris(triflate) complex gives **1** in 16% yield, but nothing of compound **2**. In both cases efforts were made to obtain as water-free conditions in the autoclave as possible.

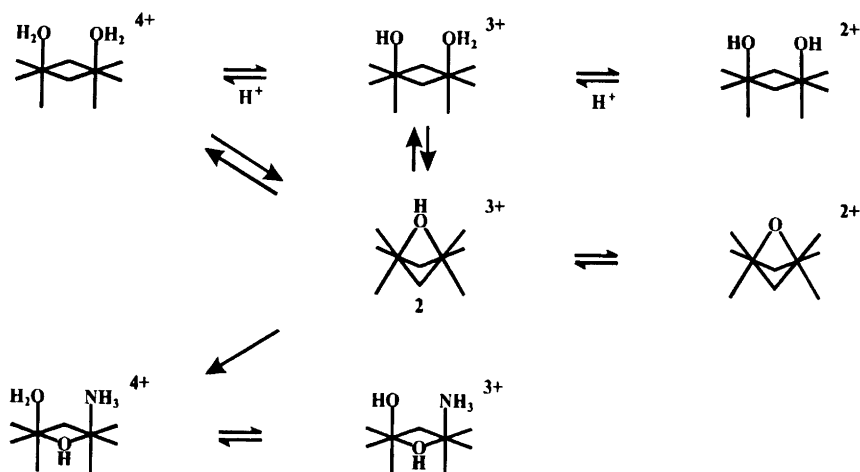
Compound **2** can be obtained from compound **1** according to Scheme 1 (where tacn and the $\mu-NH_2$ groups are omitted). The conditions used in this synthesis are based on the reactivity of the involved species in aqueous solution [determined in 1.0 M (Na,H)(ClO₄,OH) at 25 °C]. The first irreversible bridge cleavage of **1** to form **3** is, as in the case of the ammine analogue, acid-catalyzed. In aqueous solution **4** loses the non-bridging ammonia to form **2**. Heating is here applied, since this reaction is slow at room temperature. A maximum yield



Scheme 1.

of **2** is obtained at ca. pH 9 (*vide infra*), and therefore an equivalent amount of NH_4^+ is added to buffer the liberated NH_3 .

When handling **2** the following properties are of importance, cf. Scheme 2 (where tacn and $\mu-NH_2$ groups are omitted). Irreversible cleavage of an amido bridge in **2** is acid-catalyzed, and is only significant in acid solution, where the product is $[(H_2O)(tacn)Cr(\mu-NH_2)(\mu-OH)-Cr(tacn)(NH_3)]^{4+}$. Alternatively **2** undergoes reversible cleavage of the hydroxo bridge over the entire pH interval 0–13, with the rate constant falling with increasing pH in an irregular manner, connected to the acid–base properties of the diamido-bridged product. This complex with two non-bridging H_2O/OH^- will, for equilibrium reasons, be present (more than 1%) only at pH < 2 or pH > 9 as the 4+, respectively the 2+ charged species, $[(HO)(tacn)Cr(\mu-NH_2)_2Cr(tacn)(OH)]^{2+}$.



Scheme 2.

However, owing to the irreversibility of the amido bridge cleavage the final bridge cleavage product of **2** in acid medium is $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu\text{-NH}_2)(\mu\text{-OH})\text{Cr}(\text{tacn})(\text{NH}_3)]^{4+}$ (which can be isolated as a perchlorate).⁶ In aqueous solution this product slowly exchanges the non-bridging ammonia with water. In neutral solution **2** can be kept for weeks in equilibrium with ca. 1% of $[(\text{H}_2\text{O})(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{tacn})(\text{OH})]^{3+}$. With increasing pH, **2** or its deprotonated form is in slow equilibrium with increasing amounts of $[(\text{OH})(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2\text{Cr}(\text{tacn})(\text{OH})]^{2+}$ (which can be isolated as a perchlorate).⁶ At pH 11 their ratio is ca. 1.

Description of the crystal structure of $\text{Na}[(\text{tacn})\text{Cr}(\mu\text{-NH}_2)_2(\mu\text{-OH})\text{Cr}(\text{tacn})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$. Though there are small differences between the structural models obtained from the two data collections (*vide infra*) these do not affect the geometry of the complex cations. The unit cell contains two chemically but not crystallographically equivalent dinuclear chromium(III) complexes. They have been labelled identically and are distinguished by the letters A and B as shown in Fig. 1. The two cations are almost related by non-crystallographic inversion symmetry: $(x_B, y_B, z_B) \approx (1 - x_A, 1 - y_A, 0.5 - z_A)$. Two amido groups and one hydroxo group bridge the two chromium atoms in the complex cation. The exact identities of the bridging atoms were established without any ambiguity from the refinement of the structure. To our knowledge this is the first example of a dinuclear chromium(III) complex with one hydroxo bridge and two amido bridges. The drawings in Fig. 1 as well as the equivalent isotropic displacement parameters listed in Table 2 show that the B cation in general has larger displacement parameters than the other cation. This indicates some small disorder of cation B, since the crystallographic packing of the two cations is not significantly different.

Inspection of Table 3 shows that the tacn ligands have virtually identical geometry and conformation in cation A and B, which is in agreement with the results from

other structures containing this ligand. The small deviations can be attributed to the slight disorder of the B cation. It is apparent from Fig. 1 and the torsion angles in Table 3 that the two halves of the cation A and B are related by non-crystallographic mirror planes through the bridging ligands. The two Cr–Cr distances are almost identical: 2.587(2) Å in A and 2.594(2) Å in B [2.589(2) and 2.590(2) Å, respectively, from the first data set]. These distances are significantly shorter than the Cr–Cr distance observed in the dinuclear chromium(III) complex bridged by three amido groups, tri- μ -amidobis[tri-amminchromium(III)] iodide, where Cr–Cr is 2.65 Å.⁵ In the analogous tri- μ -hydroxo complexes the Cr–Cr distances are found in the range 2.607–2.642 Å.¹³ The present structure represents the dinuclear chromium(III) complex with the shortest Cr–Cr distance. The Cr–O1 distances in the range 1.961(6)–1.980(6) Å are significantly shorter than the Cr–NH₂ distances and identical to the distances in the analogous trihydroxo-bridged ions. The Cr–N(tacn) bond distances show fairly large variations in the range 2.059–2.101 Å. The average Cr–N(tacn) value is 2.081(7) and 2.080(7) Å in cations A and B, respectively.

The crystal also contains eight independent perchlorate ions, two sodium ions and two water molecules. Five of the perchlorate ions are well ordered and conform well with the geometry of other ordered perchlorate ions. The remaining three (Cl2, Cl3 and Cl8) display different degrees of disorder which makes their calculated geometry deviate from the accepted values. The sodium ions and water molecules appear to play an important role for the crystal packing. The Na1 ion is surrounded by six and Na2 by six or seven (*vide infra*) oxygen atoms. The six ligands around Na1 are one of the water molecules (OW1) and five oxygen atoms from four different perchlorate ions (O43, O51, O13, O63 and O62). The Na–O distances are in the range 2.256(9) to 2.532(7) Å, with the shortest to the water molecule and the longest to the oxygen atoms belonging to the same perchlorate ion. The coordination geometry around Na1 can be

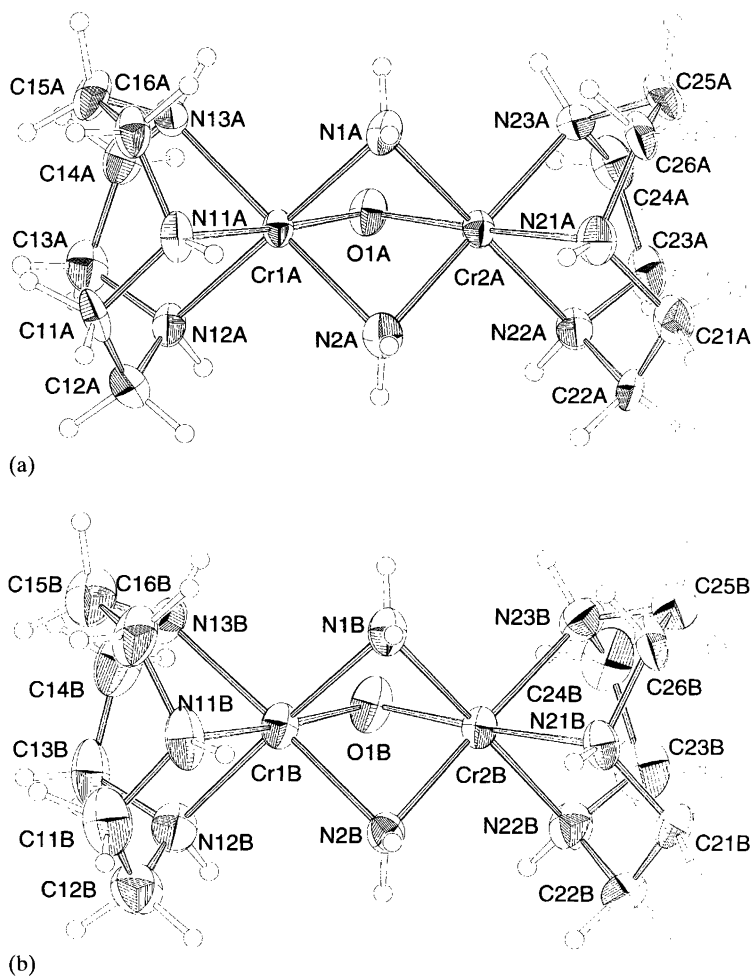


Fig. 1. Ortep11¹⁴ drawings showing the molecular geometry of the two independent dinuclear complexes A and B. The thermal ellipsoids are scaled to include 50% probability.

described as an irregular octahedron. Na2 displays an even more irregular coordination geometry. One of its potential ligands is a partially (0.71) occupied oxygen atom, O82', from a disordered perchlorate ion. The corresponding Na–O distance, 2.634 Å, is also the longest. O84 from the same anion is also in contact with Na2, which is surrounded by a water molecule and six oxygen atoms from four different perchlorate ions with Na–O distances in the range 2.302–2.634 Å. The stereo pair in Fig. 2 shows how the sodium atoms connect the different perchlorate ions. Besides these interactions an extensive system of fairly long hydrogen bonds stabilizes the crystal packing. From the intermolecular contact distances listed in Table 4 we note that all possible hydrogen-bond donors have hydrogen-bond acceptors at the expected distances. Each of the dinuclear cations are interacting with five different perchlorate ions through hydrogen bonds from the three bridging groups. The interactions with these anions are further stabilized by hydrogen bonds from the donor atoms in the tacn ligands. It can be seen from Table 4 that cation A is interacting with six different perchlorate ions (Cl1, Cl4,

Cl5, 2 × Cl6 and Cl8), and cation B has also equivalent distances to six different perchlorate ions, Cl1, 2 × Cl2, Cl3, Cl7 and Cl8. The two water molecules form links from the sodium atoms to two different perchlorate ions. OW1 has hydrogen-bond distances to two perchlorate ions which interact with both cation A and B, whereas OW2 forms hydrogen bonds to perchlorate ions Cl2 and Cl3 which only are in contact with cation B. The above discussion demonstrates well the complex set of interactions that keep the entities in the crystal together. However, it is noteworthy that most of the N–O distances are larger than 3 Å, which indicate that they correspond to weak hydrogen bonds. The only distance that corresponds to a hydrogen bond of medium strength is from the bridging hydroxo group in cation B to O23. The remaining interactions appear to be significantly weaker.

A possible solid-state transformation. Two data sets were collected on the same crystal three months apart. During the latter data collection it became obvious that the crystal had and were still undergoing some changes, as the variation of the intensities of the standard reflections

Table 3. Bond distances (in Å), bond, and torsion angles (in °) in the two complex cations.

	A	B
Cr(1)–Cr(2)	2.587(2)	2.594(2)
Cr(1)–O(1)	1.968(5)	1.964(6)
Cr(1)–N(1)	2.010(7)	2.017(7)
Cr(1)–N(2)	2.019(7)	2.021(7)
Cr(1)–N(11)	2.101(7)	2.059(8)
Cr(1)–N(12)	2.087(7)	2.086(7)
Cr(1)–N(13)	2.087(7)	2.083(7)
Cr(2)–O(1)	1.980(6)	1.961(6)
Cr(2)–N(1)	2.024(6)	2.007(8)
Cr(2)–N(2)	2.019(7)	1.999(7)
Cr(2)–N(21)	2.066(8)	2.085(7)
Cr(2)–N(22)	2.085(7)	2.080(8)
Cr(2)–N(23)	2.060(7)	2.086(8)
N(11)–C(11)	1.482(11)	1.478(13)
N(11)–C(16)	1.486(11)	1.491(13)
N(12)–C(12)	1.487(11)	1.461(13)
N(12)–C(13)	1.491(11)	1.491(12)
N(13)–C(14)	1.490(10)	1.487(11)
N(13)–C(15)	1.496(10)	1.495(12)
N(21)–C(21)	1.492(11)	1.479(11)
N(21)–C(26)	1.488(11)	1.497(11)
N(22)–C(22)	1.496(11)	1.495(12)
N(22)–C(23)	1.470(11)	1.506(12)
N(23)–C(24)	1.494(10)	1.493(12)
N(23)–C(25)	1.490(11)	1.484(11)
C(11)–C(12)	1.527(12)	1.493(14)
C(13)–C(14)	1.501(13)	1.501(15)
C(15)–C(16)	1.500(12)	1.511(14)
C(22)–C(21)	1.484(13)	1.519(12)
C(24)–C(23)	1.515(13)	1.492(14)
C(26)–C(25)	1.499(12)	1.492(12)
O(1)–Cr(1)–N(1)	81.7(2)	78.8(3)
O(1)–Cr(1)–N(2)	84.3(3)	85.1(3)
O(1)–Cr(1)–N(11)	176.6(3)	176.1(3)
O(1)–Cr(1)–N(12)	97.6(3)	100.0(3)
O(1)–Cr(1)–N(13)	94.7(3)	95.9(3)
O(1)–Cr(2)–N(1)	81.1(2)	79.2(3)
O(1)–Cr(2)–N(2)	84.0(3)	85.8(3)
O(1)–Cr(2)–N(21)	177.1(3)	176.9(3)
O(1)–Cr(2)–N(22)	98.2(3)	97.5(3)
O(1)–Cr(2)–N(23)	95.6(3)	95.4(3)
Cr(1)–O(1)–Cr(2)	81.9(2)	82.7(2)
Cr(1)–N(1)–Cr(2)	79.8(2)	80.3(3)
Cr(2)–N(2)–Cr(1)	79.7(3)	80.4(3)
N(11)–C(11)–C(12)–N(12)	–46.1(10)	–41.6(12)
C(11)–C(12)–N(12)–C(13)	–71.7(9)	–74.8(10)
C(12)–N(12)–C(13)–C(14)	134.3(8)	131.9(9)
N(12)–C(13)–C(14)–N(13)	–43.3(9)	–40.9(12)
C(13)–C(14)–N(13)–C(15)	–71.1(9)	–76.4(11)
C(14)–N(13)–C(15)–C(16)	136.7(8)	134.8(9)
N(13)–C(15)–C(16)–N(11)	–47.0(10)	–42.0(12)
C(15)–C(16)–N(11)–C(11)	–70.8(9)	–73.0(11)
C(16)–N(11)–C(11)–C(12)	134.8(8)	133.5(9)
N(21)–C(21)–C(22)–N(22)	45.1(10)	44.5(11)
C(21)–C(22)–N(22)–C(23)	71.5(9)	71.8(10)
C(22)–N(22)–C(23)–C(24)	–133.5(8)	–133.2(9)
N(22)–C(23)–C(24)–N(23)	42.5(10)	44.9(11)
C(23)–C(24)–N(23)–C(25)	75.6(9)	70.4(11)
C(24)–N(23)–C(25)–C(26)	–136.1(8)	–137.8(9)
N(23)–C(25)–C(26)–N(21)	43.3(10)	46.7(11)
C(25)–C(26)–N(21)–C(21)	72.2(9)	71.5(9)
C(26)–N(21)–C(21)–C(22)	–136.6(8)	–134.0(8)

Table 4. Intermolecular contact distances (in Å).

D···A	d (D···A)	D···A	d (D···A)
O1A···O62 ¹	3.130(8)	N(21B)···O(12)	3.257(10)
N(1A)···O(83)	3.28(2)	N(21B)···O(13)	3.249(10)
N(1A)···O(64) ³	3.311(10)	N(22B)···O(31)	3.022(11)
N(2A)···O(52) ¹	3.153(10)	N(23B)···O83 ²	3.00(2)
N(2A)···O(44)	3.153(10)	OW1···O72	2.844(11)
N(11A)···O(84)	3.099(13)	OW1···O52 ¹	3.061(11)
N(12A)···O(54) ¹	2.913(9)	OW2···O21	2.979(12)
N(13A)···O(14) ³	3.346(11)	OW2···O33 ⁴	2.954(12)
N(13A)···O(12) ³	3.094(10)	Na1···OW1	2.560(9)
N(21A)···O(81)	3.090(9)	Na1···O43	2.347(8)
N(22A)···O(52) ¹	3.130(10)	Na1···O5 ¹	2.370(7)
N(22A)···O(62) ¹	3.186(9)	Na1···O13	2.411(8)
N(23A)···O(64) ³	2.917(10)	Na1···O63	2.499(8)
O1B···O23 ⁴	2.845(10)	Na1···O62	2.532(7)
N(1B)···O(24) ²	3.11(2)	Na2···OW2	2.302(8)
N(1B)···O(12)	3.040(10)	Na2···O42	2.344(8)
N(2B)···O(71)	3.149(11)	Na2···O34	2.388(10)
N(2B)···O(34)	3.219(13)	Na2···O71	2.528(9)
N(11B)···O(11)	2.959(9)	Na2···O84	2.609(12)
N(12B)···O(33)	3.061(12)	Na2···O74	2.620(10)
N(13B)···O(24) ²	3.06(2)	Na2···O82 ¹	2.634(12)

Symmetry codes: ¹–x+1, –y+1, –z+1; ²x–1, y, z; ³x+1, y, z; ⁴1–x, 1–y, –z.

was most significant under the second data collection. Though the initial data set is not complete it was still possible to refine the structure to satisfactory *R*-values. A comparison of the structural models obtained from the two data sets could give some indications of the structural changes, that had taken place. Though the two data collections were performed with the crystal cooled to the same temperature (122 K), the atomic displacement parameters obtained from the second data set are significantly larger, by a factor ca. 1.8 for cation A and ca. 2.0 for cation B. Both data sets give larger displacement parameters for cation B compared to cation A. The displacement parameters for the water molecules, perchlorate and sodium ions from the second data set are also ca. twice those from the first data set.

The most distinct difference between the two structural models is found with respect to the perchlorate ions. Refinement of the initial data set shows only disorder of two of the ions (Cl2 and Cl8), whereas it was necessary to employ a model that also included disorder of perchlorate ion Cl3 and more disorder of perchlorate ion Cl8 in the refinement of the second data set. These differences are reflected in the small differences in the intermolecular interactions in the crystal. The interactions between the cations and anions are maintained as are the coordination of the sodium atoms. The additional disorder observed for perchlorate ion Cl3 in the second data set involves the oxygen atom O32 that is not within contact distance of any other atom.

The compound contains 38 potential hydrogen bond donors and, besides the two water molecules, 32 oxygen atoms from the perchlorate ions. In neither of the two structural models are all oxygen atoms involved in hydro-

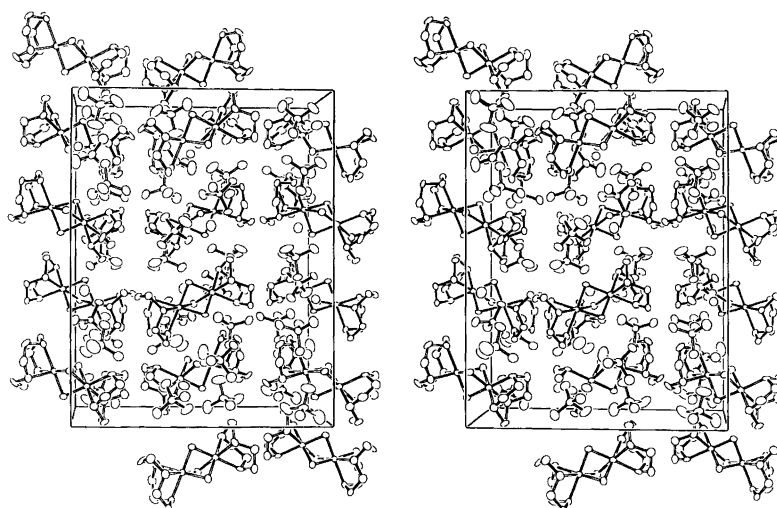


Fig. 2. Stereo pair¹⁴ illustrating the packing in the title compound as seen along the *c*-axis.

gen bonds. Considering that almost all the hydrogen bond interactions in this structure are weak it is not surprising that several arrangements are possible with very similar interactions that differ only slightly with respect to the orientation of the perchlorate ions. According to the 'law of successive reactions' by Ostwald, a metastable form is often obtained by rapid precipitation.¹⁵ This metastable form is subsequently changing to a thermodynamically stable form through a normally very slow solid state reaction. Following this interpretation we believe that the first data set, with its low displacement parameters, represents an ordered metastable modification and the second data set a structure on its way to the thermodynamically stable form. Fortunately the transformation is so slow that it has not led to significant changes of the overall structural picture.

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