

Short Communication

Crystal Structure of Tri- μ -hydroxobis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] Dithionate Tetrahydrate

Nicoline Kalsbeek^a and Sine Larsen^{b,*}

^aThe Royal Academy of Fine Arts, School of Conservation, Esplanaden 34, DK-1263 Copenhagen K and ^bCentre for Crystallographic Studies, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Kalsbeek, N. and Larsen, S., 1999. Crystal Structure of Tri- μ -hydroxobis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] Dithionate Tetrahydrate. – Acta Chem. Scand. 53: 149–154. © Acta Chemica Scandinavica 1999.

Binuclear chromium(III) complexes with three bridging hydroxo groups, chromium(III) triols, have been the subject of investigations since they were first described by Werner.¹ Of particular interest are the interactions between the two antiferromagnetically coupled chromium ions. Apart from the ammonia complex the other chromium(III) triols investigated structurally have been those with ligands having bulky groups adjacent to the bridging triol unit.^{2–4} The chromium(III) triol with the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane as ligand has been studied earlier by Wieghardt *et al.*² In the iodide salt these authors found the complex cation on a crystallographic threefold axis with a mirror plane through the bridging hydroxo groups. In the binuclear chromium(III) diols it has been observed that the nature of the counterion influences the electronic interaction between the two chromium ions: this can be attributed to variations in the geometry and the hydrogen bond interactions of the bridging hydroxo group.⁵ Well diffracting crystals could also be obtained of the dithionate salt of the chromium(III) triol with 1,4,7-trimethyl-1,4,7-triazacyclononane, and a structure determination for this compound was undertaken to investigate the possible effects of the counterion on a chromium(III) triol with a ligand having bulky groups adjacent to the hydroxo groups.

Experimental

Crystals suitable for the diffraction study were kindly provided by Jørgen Glerup. The compound crystallizes as red rods elongated in the *a*-direction. On the basis of Weissenberg and precession photographs showing the

systematically absent reflections $h0l$ for $h+l=2n+1$ and $0k0$ for $k=2n+1$, the space group was uniquely determined to be $P2_1/n$. Diffraction data were obtained from a single crystal with dimensions $0.10 \times 0.24 \times 0.40$ mm mounted with the long direction parallel to the glass needle. The data were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The crystal was cooled to ca. 105 K with an Enraf-Nonius gas flow low-temperature device during the data collection. The temperature variations, as measured with a thermocouple, were within 1 K. The cell parameters at 105 K were determined from a least-squares refinement of 18 reflections with θ in the range 14.5 – 17.0° . The choice of the ω – 2θ scan type and the scan width $0.70+0.35 \tan \theta$ was based on the profile analysis of a number of reflections. The intensity of three standard reflections was measured every 10^4 s during data collection and showed no systematic variations. The orientation of the crystal was checked after every 300 reflections. The data reduction performed with the DREADD⁶ programs included corrections for Lorentz-polarization and background effects. The symmetry-related reflections were averaged; $R_{\text{int}}=0.026$. Crystal data and details from data collection and structure refinement are listed in Table 1. The structure was solved by Patterson and Fourier methods. The structure was refined using the full-matrix least-squares method minimizing $\Sigma w(F_o^2 - F_c^2)^2$. Isotropic refinement of the 45 non-hydrogen atoms converged at an *R*-value of 0.0593; refining these atoms with anisotropic displacement parameters reduced *R* to 0.0479. All hydrogen atoms were shown clearly in a difference Fourier calculation performed at this stage of the refinement. The final model included refinement of the scale factor, positional and anisotropic displacement parameters for the non-hydro-

* To whom correspondence should be addressed.

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

Molecular formula	Cr ₂ C ₁₈ H ₅₃ N ₆ O ₁₆ S ₃
Formula weight/g mol ⁻¹	809.84
Space group	<i>P</i> 2 ₁ / <i>n</i> , monoclinic
Temperature/K	105
Cell constants at 105 K:	
<i>a</i> /Å	8.420(2)
<i>b</i> /Å	20.526(5)
<i>c</i> /Å	18.877(3)
β/°	91.1(2)
<i>V</i> /Å ³	3262(2)
Molecules/cell, <i>Z</i>	4
Calculated density/g cm ⁻³	1.649
Radiation, λ/Å	Mo Kα, 0.71073
Linear absorption coefficient/cm ⁻¹	9.36
Scan type	ω-2θ
Scan width/°	0.70 + 0.35 tan θ
Background	25% of full scan on both sides
Max. scan time/s	180
θ range/°	1–30
Range of <i>h, k, l</i>	0–11, –19–28, –26–26
Number of measured reflections including standard reflections	14 470
Number of unique reflections	9493
Refinement method	Full-matrix least-squares on <i>F</i> ²
Number of reflections used in the refinement	9493
Number of variables	618
Weights, <i>w</i> ⁻¹	$w^{-1} = \sigma^2(F_o^2) + (0.0397P)^2 + 3.93P, P = (F_o^2 + 2F_c^2)/3$
Final <i>R</i> based on ($ F > 4\sigma F $)	0.0313
Final <i>R_w</i> based on all reflections	0.0911
<i>S</i>	1.008
Mean shift/error	0.01
Max. and min. in Δρ/e Å ⁻³	0.740, –0.621

gen atoms, and positional and isotropic displacement parameters for the hydrogen atoms. The SDP program⁷ was used for the structure solution and the initial refinements. The SHELXL93 program⁸ was employed for locating the hydrogen atoms and also for the final refinements and crystallographic computations.

Examination of the *U*_{eq}-values for the oxygen atoms of the four water molecules revealed a significantly larger value of *U*_{eq} for O(W4), 0.0386(5) Å² compared to values 0.0230(4)–0.0247(4) Å² for the three other water molecules. As this could indicate a slight disorder of O(W4), a site occupancy factor (s.o.f.) for O(W4) was included in the refinement, which resulted in an s.o.f. of 0.89 for O(W4) and reduced *U*_{eq} for O(W4) to 0.0310(8) Å². This *U*_{eq}-value had twice as large a standard deviation and was still larger than the *U*_{eq}-values for the other water molecules. The *R*- and *R_w*-values for the two models, O(W4) fully populated and partially populated, did not provide any guidance for the selection of the more suited model: they are virtually identical (0.0313, 0.0911 and 0.0310, 0.0904, respectively). To discriminate between the two models we also employed the *R*_{free}-test⁹ excluding 10% of the reflections. However, it did not help us in the discrimination between the two

models: the corresponding *R*_{free}-values are almost identical, 0.0831 and 0.0829. The final refinements are based on the model with a fully populated O(W4). Details from the refinement are listed in Table 1. Scattering factor values for all atoms were taken from Ref. 10 and used as contained in the program systems. The final positional and equivalent isotropic displacement parameters are listed in Table 2. The anisotropic displacement parameters for the non-hydrogen atoms, parameters for the hydrogen atoms as well as a list of observed and

Table 2. Final fractional coordinates and equivalent isotropic displacement parameters *U*_{eq}/Å².

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Cation				
Cr(1)	0.56845(4)	0.211033(15)	0.36680(2)	0.00580(7)
Cr(2)	0.55310(4)	0.115055(15)	0.27652(2)	0.00620(7)
O(1)	0.6020(2)	0.20758(7)	0.26451(8)	0.0081(3)
O(2)	0.7016(2)	0.13234(7)	0.35667(8)	0.0086(3)
O(3)	0.3942(2)	0.15138(7)	0.34030(8)	0.0083(3)
N(11)	0.4234(2)	0.29311(8)	0.37219(9)	0.0077(3)
N(12)	0.7531(2)	0.27671(8)	0.38614(9)	0.0082(3)
N(13)	0.5505(2)	0.21167(8)	0.47688(9)	0.0082(3)
C(11)	0.3127(2)	0.30025(11)	0.31029(11)	0.0118(4)
C(12)	0.9038(2)	0.25755(11)	0.35202(12)	0.0133(4)
C(13)	0.4967(3)	0.14772(10)	0.50513(11)	0.0114(4)
C(14)	0.5272(2)	0.35309(10)	0.37852(11)	0.0101(4)
C(15)	0.6922(2)	0.33798(10)	0.35254(11)	0.0104(4)
C(16)	0.7814(2)	0.28423(10)	0.46472(11)	0.0110(4)
C(17)	0.7163(2)	0.22524(10)	0.50270(11)	0.0108(4)
C(18)	0.4375(2)	0.26438(10)	0.49937(11)	0.0106(4)
C(19)	0.3286(2)	0.28257(10)	0.43725(11)	0.0106(4)
N(21)	0.3890(2)	0.10115(8)	0.19331(9)	0.0089(3)
N(22)	0.7191(2)	0.08562(8)	0.20240(9)	0.0086(3)
N(23)	0.5236(2)	0.01518(8)	0.29227(9)	0.0093(3)
C(21)	0.2830(3)	0.15803(10)	0.18049(11)	0.0119(4)
C(22)	0.8766(2)	0.11701(11)	0.21273(12)	0.0137(4)
C(23)	0.4815(3)	–0.00225(11)	0.36631(11)	0.0135(4)
C(24)	0.4764(3)	0.08519(11)	0.12646(11)	0.0116(4)
C(25)	0.6482(2)	0.10751(10)	0.13289(10)	0.0108(4)
C(26)	0.7385(3)	0.01273(10)	0.20538(11)	0.0120(4)
C(27)	0.6832(3)	–0.01254(10)	0.27622(11)	0.0121(4)
C(28)	0.3969(3)	–0.01047(10)	0.24221(11)	0.0109(4)
C(29)	0.2906(2)	0.04505(10)	0.21800(11)	0.0111(4)
Anions				
S(1)	0.44324(6)	0.40876(2)	0.14326(3)	0.01116(10)
S(2)	0.59689(6)	0.33226(2)	0.10944(3)	0.00904(9)
S(3)	0.11082(6)	0.02008(2)	0.01924(2)	0.00810(9)
O(11)	0.4823(2)	0.42003(8)	0.21679(8)	0.0149(3)
O(12)	0.4792(2)	0.46371(8)	0.09724(9)	0.0241(4)
O(13)	0.2841(2)	0.38306(9)	0.13003(10)	0.0252(4)
O(21)	0.5807(2)	0.33105(8)	0.03258(8)	0.0150(3)
O(22)	0.7534(2)	0.34989(9)	0.13647(9)	0.0193(3)
O(23)	0.5308(2)	0.27449(8)	0.14254(8)	0.0170(3)
O(31)	0.2075(2)	0.02818(8)	–0.04335(8)	0.0130(3)
O(32)	0.0665(2)	0.08124(7)	0.05233(8)	0.0138(3)
O(33)	0.1744(2)	–0.02845(7)	0.06859(8)	0.0134(3)
Water molecules				
O(W1)	0.7923(2)	0.04370(10)	0.46493(10)	0.0238(4)
O(W2)	0.5193(2)	0.08783(9)	0.93295(11)	0.0230(4)
O(W3)	0.1418(2)	0.09788(10)	0.40809(11)	0.0247(4)
O(W4)	0.5495(3)	0.21076(12)	0.68556(12)	0.0386(5)

^a *U*_{eq} is defined as $\frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$.

calculated structure factor amplitudes may be obtained from the authors.

Results and discussion

The tri- μ -hydroxobis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] cations, dithionate anions and

water molecules interact through a complex system of hydrogen bonds in the crystal structure. To match the stoichiometry one of the dithionate anions is on a crystallographic inversion centre. The overall geometry of the binuclear cation is illustrated by the two drawings in Fig. 1. It is apparent that the bridging hydroxo groups deviate significantly from threefold symmetry, but both

Table 3. Bond lengths (in Å) and bond angles (in °) for the cation.

	$j = 1$	$j = 2$	
Cr(1)–Cr(2)			2.6065(7)
Cr(j)–O(1)	1.958(2)	1.958(2)	
Cr(j)–O(2)	1.978(2)	1.976(4)	
Cr(j)–O(3)	1.968(2)	1.965(3)	
Cr(j)–N(j1)	2.085(2)	2.091(4)	
Cr(j)–N(j2)	2.085(2)	2.086(4)	
Cr(j)–N(j3)	2.086(2)	2.087(2)	
N(j1)–C(j1)	1.487(4)	1.487(3)	
N(j1)–C(j4)	1.513(3)	1.509(3)	
N(j1)–C(j9)	1.494(3)	1.498(3)	
N(j2)–C(j2)	1.487(3)	1.484(3)	
N(j2)–C(j5)	1.495(3)	1.499(3)	
N(j2)–C(j6)	1.506(3)	1.506(3)	
N(j3)–C(j3)	1.490(3)	1.492(3)	
N(j3)–C(j7)	1.496(3)	1.496(3)	
N(j3)–C(j8)	1.507(3)	1.506(3)	
C(j4)–C(j5)	1.515(3)	1.521(3)	
C(j6)–C(j7)	1.515(3)	1.516(3)	
C(j8)–C(j9)	1.521(4)	1.514(3)	
Cr(1)–O(1)–Cr(2)			83.46(7)
Cr(1)–O(2)–Cr(2)			82.49(9)
Cr(1)–O(3)–Cr(2)			83.02(8)
O(1)–Cr(j)–O(2)	77.40(13)	77.47(6)	
O(1)–Cr(j)–O(3)	81.3(2)	81.39(8)	
O(2)–Cr(j)–O(3)	83.60(7)	83.74(7)	
N(j1)–Cr(j)–O(1)	99.99(13)	100.54(6)	
N(j1)–Cr(j)–O(2)	177.03(6)	176.93(7)	
N(j1)–Cr(j)–O(3)	94.63(7)	93.68(7)	
N(j2)–Cr(j)–O(1)	94.3(2)	93.32(8)	
N(j2)–Cr(j)–O(2)	97.05(7)	98.24(7)	
N(j2)–Cr(j)–O(3)	175.25(6)	173.85(7)	
N(j3)–Cr(j)–O(1)	175.51(7)	174.52(7)	
N(j3)–Cr(j)–O(2)	98.85(13)	98.19(7)	
N(j3)–Cr(j)–O(3)	100.9(2)	101.60(8)	
Cr(j)–N(j1)–C(j1)	113.58(13)	113.63(14)	
Cr(j)–N(j1)–C(j4)	108.87(12)	109.38(13)	
Cr(j)–N(j1)–C(j9)	104.26(14)	103.45(12)	
C(j1)–N(j1)–C(j4)	109.5(2)	109.6(2)	
C(j1)–N(j1)–C(j9)	108.9(2)	108.7(2)	
C(j4)–N(j1)–C(j9)	111.7(2)	112.0(2)	
Cr(j)–N(j2)–C(j2)	113.14(13)	113.27(15)	
Cr(j)–N(j2)–C(j5)	102.78(15)	103.88(13)	
Cr(j)–N(j2)–C(j6)	110.0(2)	109.66(13)	
C(j2)–N(j2)–C(j5)	109.1(2)	108.9(2)	
C(j2)–N(j2)–C(j6)	109.5(2)	109.3(2)	
C(j5)–N(j2)–C(j6)	112.2(2)	111.8(2)	
Cr(j)–N(j3)–C(j3)	112.29(14)	113.59(13)	
Cr(j)–N(j3)–C(j7)	103.9(2)	103.59(13)	
Cr(j)–N(j3)–C(j8)	110.1(2)	109.79(12)	
C(j3)–N(j3)–C(j7)	109.6(2)	109.3(2)	
C(j3)–N(j3)–C(j8)	109.5(2)	109.0(2)	
C(j7)–N(j3)–C(j8)	111.4(2)	111.6(2)	
N(j1)–C(j4)–C(j5)	109.9(2)	110.3(2)	
C(j4)–C(j5)–N(j2)	110.1(2)	109.9(2)	
N(j2)–C(j6)–C(j7)	109.4(2)	109.7(2)	
C(j6)–C(j7)–N(j3)	109.8(2)	110.0(2)	
N(j3)–C(j8)–C(j9)	109.5(2)	109.5(2)	
C(j8)–C(j9)–N(j1)	110.2(2)	110.2(2)	

Table 4. Bond lengths (in Å) and bond angles (in °) for the anions.

	$j=1$	$j=2$	
S(1)–S(2)	2.140(2)	S(2)–O(22)	1.450(2)
S(3)–S(3) ^a	2.153(2)	S(2)–O(23)	1.456(2)
S(1)–O(11)	1.439(2)	S(3)–O(31)	1.458(3)
S(1)–O(12)	1.459(2)	S(3)–O(32)	1.454(2)
S(1)–O(13)	1.457(2)	S(3)–O(33)	1.458(2)
S(2)–S(1)–O(11)	106.14(13)	O(21)–S(2)–O(22)	114.9(2)
S(2)–S(1)–O(12)	104.81(13)	O(21)–S(2)–O(23)	112.64(12)
S(2)–S(1)–O(13)	104.04(8)	O(22)–S(2)–O(23)	113.89(12)
O(11)–S(1)–O(12)	113.83(11)	S(3)–S(3)–O(31)	105.33(12)
O(11)–S(1)–O(13)	114.5(2)	S(3) ^a –S(3)–O(32)	104.31(9)
O(12)–S(1)–O(13)	112.3(2)	S(3) ^a –S(3)–O(33)	105.00(13)
S(1)–S(2)–O(21)	105.37(13)	O(31)–S(3)–O(32)	113.71(11)
S(1)–S(2)–O(22)	105.23(8)	O(31)–S(3)–O(33)	113.06(9)
S(1)–S(2)–O(23)	103.36(12)	O(32)–S(3)–O(33)	114.17(9)

^a($-x, -y, -z$).

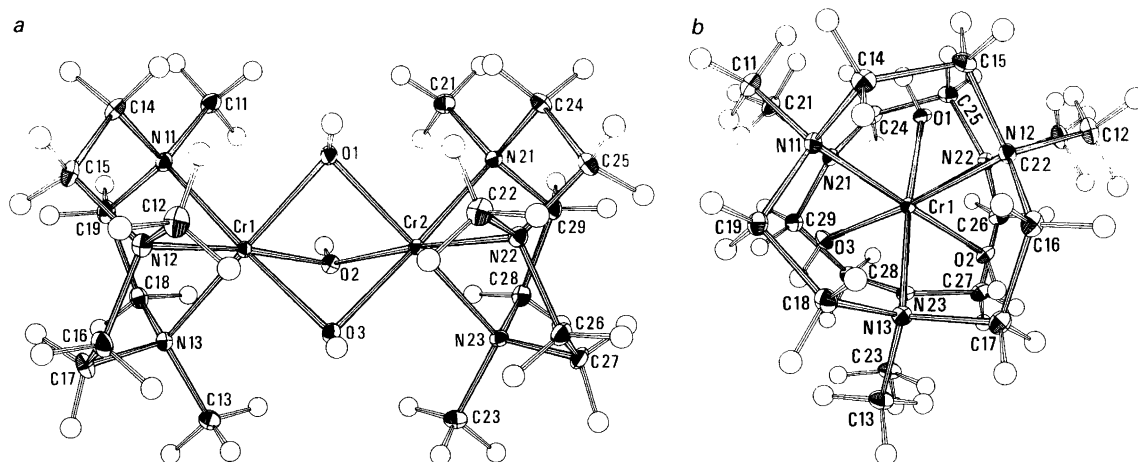


Fig. 1. Two ORTEP¹¹ drawings of the tri- μ -hydroxobis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] cation. The thermal ellipsoids are scaled to include 50% probability and the hydrogen atoms are drawn as spheres with a fixed radius. Fig 1a illustrates the mirror plane symmetry relating the two halves of the cation and Fig. 1b the pseudo threefold axis.

Fig. 1 and the bond lengths and angles listed in Tables 3 and 4 show that the two halves of the molecule are related by a non-crystallographic mirror plane through the bridging hydroxy groups. This symmetry is employed in the atomic labelling. In the equivalent iodide salt this cation possesses also the symmetry of a threefold axis and the distance between the two symmetry-related Cr ions is significantly longer, 2.642(2) Å, than the one found in the present structure, 2.6065(7) Å. The six Cr–O distances display some significant variations in the dithionate salt. The Cr(j)–O(1) ($j=1, 2$) distances are the shorter [1.958(2) Å] and the Cr(j)–O(2) ($j=1, 2$) distances the longer [1.977(3) Å]. All three hydroxy groups are involved in normal linear hydrogen bonds as shown in Table 5. The hydrogen bonds that involve O(1) and O(3) as donors have similar donor–acceptor distances, but the one from O(1) is to a negatively charged oxygen atom O(23), whereas O(3) is hydrogen-bonded to a water molecule. O(2), which has the two longest Cr–O bonds, is also involved in the longest hydrogen bond with length 2.830(3) Å. The variations in hydrogen

bond interactions of the hydroxy groups do not provide an obvious answer to the differences in the Cr–O distances. In the iodide salt of tri- μ -hydroxobis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] the crystallographic symmetry makes the six Cr–O distances identical, 1.972(6) Å, and the hydroxy groups are hydrogen bonded to three water molecules with O–O distances 2.787(4) Å, comparable to what is observed for O(2) and O(3). In accordance with this the Cr–O(2) and Cr–O(3) distances do compare well with the Cr–O bonds in the iodide salt. The coordination geometry of the two chromium atoms can be characterized as a distorted octahedron similar to the geometry found in the related bis- μ -hydroxo compounds.⁵

The packing in the unit cell is illustrated in Fig. 2, which also indicates the hydrogen bonds listed in Table 5. All possible donor atoms are involved in hydrogen bonds. Analysis of the hydrogen bonding shows that the larger displacement parameter for O(W4) can be explained in terms of differences in the hydrogen bonding system. O(W4) is involved in two long hydrogen bonds, while

Table 5. Hydrogen bond geometry (A, donor atom; B, acceptor atom).

A–H···B	A···B/Å	A–H/Å	H···B/Å	A–H···B/°
O(1)–H(11)···O(23)	2.737(3)	0.72(3)	2.04(3)	165(3)
O(2)–H(21)···O(W1)	2.830(3)	0.64(3)	2.19(3)	172(4)
O(3)–H(31)···O(W3)	2.733(4)	0.78(4)	1.98(4)	161(4)
O(W1)–H(W11)···O(12) ^a	2.929(5)	0.88(5)	2.12(5)	152(5)
O(W1)–H(W12)···O(12) ^b	2.804(4)	0.88(4)	1.98(4)	156(4)
O(W2)–H(W21)···O(31) ^c	2.939(3)	0.75(4)	2.24(4)	154(3)
O(W2)–H(W22)···O(33) ^d	2.853(2)	0.82(4)	2.06(4)	162(3)
O(W3)–H(W31)···O(12) ^e	2.937(3)	0.80(4)	2.17(4)	160(4)
O(W3)–H(W32)···O(21) ^f	2.822(3)	0.82(4)	2.02(4)	166(4)
O(W4)–H(W41)···O(22) ^f	2.921(4)	1.05(6)	1.89(6)	166(5)
O(W4)–H(W42)···O(13) ^a	2.965(4)	1.02(5)	1.95(5)	173(4)

^a $(x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2})$. ^b $(-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2})$. ^c $(x, y, z+1)$. ^d $(-x+1, -y, -z+1)$. ^e $(-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2})$. ^f $(x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2})$.

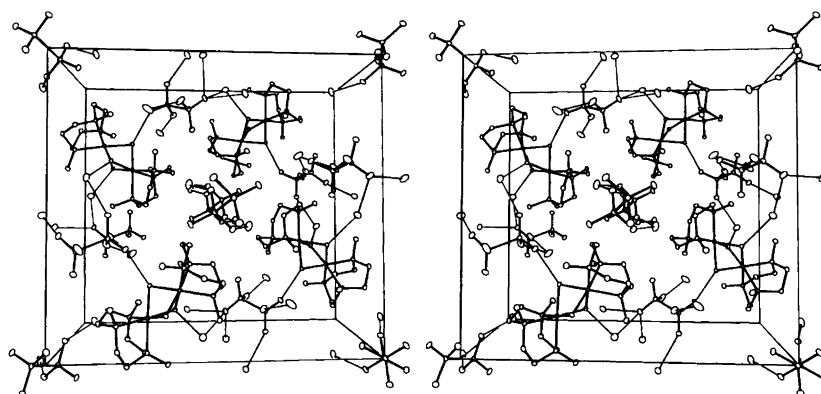


Fig. 2. ORTEP stereo diagram showing the packing viewed along the crystallographic *a*-axis. The hydrogen bonds are drawn as thin lines.

Table 6. A list of Cr^{III} and Co^{III} compounds with bridging tri- μ -hydroxo arrangements.^a

Compound	Point group symmetry of cation	M–M/Å	M–O ^b /Å	O–M–O ^b /°	M–O–M ^b /°	Ref.
<i>Cr^{III} compounds</i>						
LCr(OH) ₃ CrL(S ₂ O ₆) _{1.5} ·4H ₂ O	1	2.6065(7)	1.967	80.82	82.99	This work
LCr(OH) ₃ CrL ₃ ·3H ₂ O	3	2.642(2)	1.972(6)	—	84.1(3)	2
(NH ₃) ₃ Cr(OH) ₃ Cr(NH ₃) ₃ (ClO ₄) _{3-x}	<i>m</i>	2.6307(11)	1.977	80.53	83.41	3
(Me ₃ -tame)Cr(OH) ₃ Cr(Me ₃ -tame)Cl ₃ ·4H ₂ O	1	2.6359(3)	1.9695	80.12	84.01	4
<i>Co^{III} compounds</i>						
Na[tacn]Co(OH) ₃ Co(tacn)Cl ₂ (ClO ₄) ₂ ·2H ₂ O	1	2.5491(8)	1.920	80.7	83.2	12
(dtp)Co(OH) ₃ Co(dtp)(ClO ₄) ₃	1	2.579(1)	1.913	79.4	84.8	13
(NH ₃) ₃ Co(OH) ₃ Co(NH ₃) ₃ Br ₃	1	2.55	1.96	82	—	14
(NH ₃) ₃ Co(OH) ₃ Co(NH ₃) ₃ I ₃	<i>m</i>	2.57	—	—	—	14
[(NH ₃) ₃ Co(OH) ₃ Co(NH ₃) ₃] ₂ (S ₂ O ₆) ₃	1	2.565	1.930(11)	80.7(3)	83.3(6)	15
(NH ₄)[(NH ₃) ₃ Co(OH) ₃ Co(NH ₃) ₃]Cl ₄	<i>m</i>	2.565(1)	1.930(8)	80.6(3)	83.3(3)	16

^aL = 1,4,7-trimethyl-1,4,7-triazacyclononane; Me₃-tame = *N,N',N''*-trimethyl-1,1,1-tris(aminomethyl)ethane; tacn = 1,4,7-triazacyclononane; dtp = di(3-aminopropyl)amine. ^bValues without standard deviations are average values.

O(W1), O(W2) and O(W3) are involved in one long and one shorter hydrogen bond. This could imply that O(W4) is less tightly bound than the other three water molecules, and thus capable of performing larger thermal motion.

A survey of the geometry of dinuclear tri- μ -hydroxo complexes of Cr^{III} and Co^{III} that have been isolated and

structurally characterized is presented in Table 6. The Cr–Cr distances are in the range 2.6065(7)–2.642(2) Å, with the Cr–Cr distance of 2.6065(7) Å found in the present structure as representing the lower limit. The Co–Co distances are shorter, in the range 2.5491(8)–2.579(1) Å due to the smaller radius of the Co ion. The shorter Co–Co distances are also reflected

in the shorter Co–O distances compared to the Cr–O distances. The M–O–M (M=Cr, Co) angles in Table 6 are in the range 83.0–84.8°. These values are significantly smaller than the values found for dimers bridged by two hydroxo groups, where the angles are in the range 97.6–103.4°.⁵

Acknowledgements. Flemming Hansen is gratefully acknowledged for assisting in the experimental crystallographic work. The Centre for Crystallographic Studies was established through funds from the Danish National Research Foundation.

References

1. Werner, A. *Ber. Dtsch. Chem. Ges.* 40 (1907) 4834.
2. Wieghardt, K., Chaudhuri, P., Nuber, B. and Weiss, J. *Inorg. Chem.* 21 (1982) 3086.
3. Andersen, P., Døssing, A., Larsen, S. and Pedersen, E. *Acta Chem. Scand.* 41 (1987) 381.
4. Glerup, J., Larsen, S. and Weihe, H. *Acta Chem. Scand.* 47 (1993) 1154.
5. Cline, S. J., Hodgson, D. J., Kallesøe, S., Larsen, S. and Pedersen, E. *Inorg. Chem.* 22 (1983) 637.
6. Blessing, B. *Crystallogr. Rev.* 1 (1987) 3.
7. Enraf-Nonius *Structure Determination Package*, VAX version, Enraf-Nonius, Delft, The Netherlands 1985.
8. Sheldrick, G. M. *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany 1993. In preparation for *J. Appl. Crystallogr.*
9. Brünger, A. T. *Nature (London)* 355 (1992) 472.
10. Wilson, A. C. T., Ed., *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht 1992.
11. Johnson, C. K. *ORTEP. A Fortran Ellipsoid Plot Program for Crystal Structure Illustrations*, Report ORNL-3794, Second Rev., Oak Ridge National Laboratory, Oak Ridge 1965.
12. Larsen, E., Larsen, S., Paulsen, G. B., Springborg, J. and Wang, D.-N. *Acta Chem. Scand.* 48 (1994) 107.
13. Searle, G. H. and Hambley, T. W. *Aust. J. Chem.* 35 (1982) 1297.
14. Andersen, P. *Acta Chem. Scand.* 21 (1967) 243.
15. Thewalt, U. Z. *Anorg. Allg. Chem.* 412 (1975) 29.
16. Mandel, G. S., Mandel, N. S., Marsh, R. E., and Schaeffer, W. P. *Acta Crystallogr., Sect. B* 33 (1977) 700.

Received April 27, 1998.