The Crystal Structure of cis-Aquahydroxo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] Iodide

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The structure of cis-$[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(OH)]I_3\cdot 3H_2O$ (1) was determined using low-temperature X-ray diffraction data. In the dihydroxo-bridged complex ion of 1 tacn = 1,4,7-triazacyclononane and cis refers to the position of H_2O and non-bridging OH^- relative to the $Cr(OH)_2Cr$ plane.

Compound 1 crystallizes in the monoclinic space group $C2/c$ with a = 28.936(11), b = 8.349(7), c = 23.408(9) Å, β = 101.29(3)° and Z = 8. Using the 4234 most significant reflections the structure was refined to R = 0.052 and R_w = 0.068.

The cation of 1 adopts virtually C_2 symmetry, with a short intramolecular hydrogen bond between H_2O and the non-bridging OH^-: This O–O distance is 2.455(7) Å, while Cr–Cr is 2.999(2) Å. The salt is a racemate with the tacn ligands of the cation having either δδδ or λλλ conformation.

The structure refinements revealed disorder for some of the iodine atoms and water of crystallization and a slight disorder of one of the carbon atoms of the tacn ligand.

In a recent paper[1] we presented some investigations of cis-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)]^{3+}$ (2) and cis-$[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(OH)]^{3+}$ (3) (tacn = 1,4,7-triazacyclononane), where cis refers to the position of H_2O and the non-bridging OH^- relative to the $Cr(OH)_2Cr$ plane. It was herein shown that reversible isomerization reactions between the cis and trans isomers, including the protonated and deprotonated forms, take place in aqueous solution, and the formation of an intramolcular hydrogen bond between H_2O and the non-bridging OH^- was proposed in order to explain the observed high stability of the 3+ charged cis-diol.

In order to verify the presence of this intramolecular hydrogen bond, salts of 2 and 3 were synthesized for single-crystal X-ray structure analyses. The attempts to crystallize 2 as the perchlorate resulted[2] in isolation of the fully condensed dimer, $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$. However, the structure analysis of the iodide of 3, presented here, shows that 3 does have the proposed structure with a short intramolecular hydrogen bond.

Experimental

Synthesis. Crystals suitable for single-crystal structure determination were synthesized as follows: 50 mg of cis-$[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(OH)]I_3\cdot 3H_2O$[1] were dissolved in 0.5 ml water, and solid NaI was added until saturation. The solution was kept at room temperature, and after ca. 2 weeks sufficiently large crystals of the reprecitated salt were obtained. The compound was analysed for C, H, N, I and Cr on a microscale, and the analyses

Table 1. Crystal data for $[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(OH)]I_3\cdot 3H_2O$.

Formula	$Cr_2O_7H_6C_{12}I_3H_{41}$
FW/g mol^{-1}	866.20
Space group	$C2/c$

Cell parameters (110 K, single crystal)

a/Å	28.936(11)
b/Å	8.349(7)
c/Å	23.408(9)
β/°	101.29(3)
V/Å^3	5545(10)

Calculated density (110 K)/g cm^{-3}	2.075
Molecules per cell	8

Crystal size/mm^3	0.06×0.33×0.03
Developed forms	{001}, {110}
Radiation (MoKα) λ/Å	0.71073
Linear absorption coefficient μ/cm^{-1}	41.01
Range of transmission factors	0.0126–0.0162
Scan type	ω-2θ
Scan width Δ θ/°	1.20 + 0.350 tan θ
Maximum scan time/s	180
Maximum requested $\sigma(I)/I$	0.01
θ limits/°	1–30
Octants collected	$hk\pm l$
No. of unique data	8049
No. of data with $I/\sigma(I) \geq 3.0$	4234
No. of variables	246

Weights	$w^{-1} = \sigma_{cs}^2(F)+0.0013|F|^2$
$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$	0.052
$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$	0.068

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were all, within 1–2% relative, in accordance with the formula given above. Some deviation with respect to the content of iodide and water of crystallization was found in the crystal used for X-ray diffraction (see later).

Crystal structure determination. Weissenberg photographs showed that the crystals belong to the monoclinic system. The systematically absent reflections $h0l : l = 2n + 1$ and $hkl : h + k = 2n + 1$ are consistent with the space groups $C2/c$ and Cc. Diffraction data were measured at low temperature (ca. 110 K) using a CAD4 diffractometer and MoKα radiation from a graphite monochromator. The crystal was cooled by a Nonius gas flow low-temperature device, and the variations of the temperature, recorded with a thermocouple, were within 1 K. 22 reflections with θ values in the range 15.95–20.99° were used to determine the unit-cell parameters. The intensities of three standard reflections measured every 10 000 s showed no systematic variations. The orientation of the crystal was checked after

every 300 reflections. The crystal data are presented in Table 1.

The data were corrected for background, Lorentz and polarization effects, and correction for absorption was performed by a Gaussian numerical integration procedure.[3] The linear absorption coefficient employed was based on the results from the chemical analyses. Assuming the space group to be $C2/c$, a standard MULTAN run gave the positions of two iodine and the two chromium atoms, in agreement with a calculated Patterson function. Subsequent difference electron density ($\Delta\varrho$) maps provided the parameters for the remaining non-hydrogen atoms in the structure. The structure was refined by a least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$. At an early stage in the refinement it became apparent that this structure displays disorder of the anions as well as of one of the carbon atoms in each of the two tacn ligands. A refinement with isotropic temperature factors ($R = 0.13$) resulted in a physically unrealistic geometry around these carbon atoms, which had

Table 2. Population parameters (P.P.), positional parameters and isotropic thermal parameters (Å^2).

Atom	P.P.	x	y	z	B_{iso}^a
Cr1		0.40426(5)	0.0082(2)	−0.01040(5)	1.34(2)
Cr2		0.37158(5)	−0.1434(2)	−0.12747(6)	1.47(2)
O1		0.4119(2)	0.0342(7)	−0.0916(3)	1.8(1)
O2		0.3512(2)	−0.1204(7)	−0.0532(2)	1.4(1)
O11		0.4502(2)	−0.1706(7)	−0.0005(3)	1.9(1)
O21		0.4175(2)	−0.3097(8)	−0.0919(3)	2.4(1)
N11		0.3609(3)	0.2086(9)	−0.0115(3)	2.2(1)
N12		0.3907(3)	−0.0161(9)	0.0726(3)	1.9(1)
N13		0.4551(3)	0.1667(8)	0.0296(3)	1.9(1)
N21		0.3204(3)	0.010(1)	−0.1692(3)	2.4(2)
N22		0.3242(3)	−0.3157(9)	−0.1649(3)	2.1(1)
N23		0.3904(3)	−0.148(1)	−0.2079(3)	2.6(2)
C11		0.3376(4)	0.213(1)	0.0403(5)	3.0(2)
C12		0.3425(4)	0.052(1)	0.0708(5)	3.1(2)
C131	0.40(2)	0.4223(8)	0.091(3)	0.1129(9)	1.8(3)
C132	0.60(2)	0.4307(5)	0.052(2)	0.1187(6)	2.0(2)
C14		0.4699(4)	0.112(1)	0.0906(5)	2.7(2)
C15		0.4359(4)	0.340(1)	0.0282(5)	2.8(2)
C16		0.3919(3)	0.353(1)	−0.0147(4)	2.6(2)
C21		0.2741(4)	−0.077(1)	−0.1741(5)	3.1(2)
C22		0.2780(4)	−0.249(1)	−0.1929(5)	3.2(2)
C23		0.3475(4)	−0.403(2)	−0.2090(5)	3.7(2)
C241	0.70(2)	0.3653(5)	−0.271(2)	−0.2466(6)	2.4(2)
C242	0.30(2)	0.374(1)	−0.314(4)	−0.237(1)	2.1(5)
C25		0.3768(5)	0.011(2)	−0.2357(5)	4.2(3)
C26		0.3299(4)	0.057(2)	−0.2277(5)	4.5(3)
I1		0.23322(2)	0.84715(8)	0.62367(4)	3.22(1)
I2	0.880(2)	0.02315(2)	−0.14748(8)	0.62932(3)	2.19(1)
I31	0.513(2)	0.13096(4)	0.1274(1)	0.35003(5)	2.37(2)
I32	0.471(2)	0.14744(5)	0.1284(2)	0.36471(6)	2.59(2)
I4		0.50000	0.2421(1)	0.25000	2.48(2)
I5	0.086(2)	0.0296(3)	0.098(1)	0.2705(4)	3.0(2)
I6	0.094(2)	0.4176(2)	0.3658(7)	0.8393(3)	2.2(1)
OW1		0.2953(3)	−0.326(1)	−0.0017(4)	4.4(2)

[a] For the atoms refined with ansisotropic thermal parameters $B_{iso} = \dfrac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

large displacement parameters. A $\Delta\varrho$ map revealed peaks close (0.4 Å) to C13 and C24 indicating a slight disorder of the tacn ligands. In the following refinements two partly populated positions were therefore introduced for C13 (C131 and C132) and C24 (C241 and C242), and the population parameters were included in the refinements. Residual electron density was also found in the $\Delta\varrho$ map, which could be attributed to either partly populated iodide ions or water molecules. Numerous models have been investigated in order to obtain a good description of the disorder of the anions and water of crystallization, including a lowering of the space group symmetry to Cc. The results presented are based on a model in $C2/c$ which has two fully occupied (one in a special position) and five partly populated iodine atoms. Anisotropic thermal parameters were also used for the iodine atoms with small occupancy, as they improved the model significantly. Isotropic thermal parameters were used for the carbon atoms. The final positional parameters and population parameters are listed in Table 2. This model was chosen because it implies a limited number of atomic sites and has reasonable interatomic distances. None of the other models tried had a significantly better goodness of fit. The interatomic distances which are shorter than the sum of the van der Waals radii are listed later in Table 4. This final model, which corresponds to an iodine content of 3.54 per complex cation, is not in complete accordance with the chemical analysis, but in this context it should be emphasized that it can not be excluded that water molecules can be found on the iodide sites and vice versa, and that the crystal may contain small amounts of disordered polyiodide. The maximum parameter shift in the final cycle was 0.01σ. The final $\Delta\varrho$ map did not provide any basis for postulating the positions of the hydrogen atoms; the maximum peak of 2.2 e Å^{-3} was found close to one of the iodine atoms.
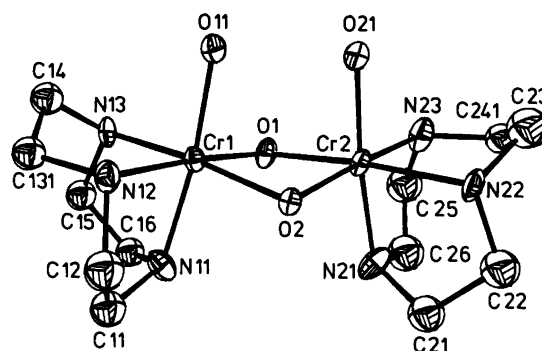

Fig. 1. Perspective ORTEP drawing of the $[(H_2O)(tacn)Cr(OH)_2Cr(tacn)(OH)]^{3+}$ ion showing the atomic labelling. The thermal ellipsoids enclose 50 % probability.

The crystallographic computations were performed with the Enraf Nonius structure determination package, and the atomic scattering factors and anomalous dispersion corrections by Cromer and Waber[4] were used as contained in the program. Lists of observed and calculated structure amplitudes and the anisotropic thermal parameters can be obtained from the authors.

Results and discussion

The cation, which possesses virtually C_2 symmetry, is shown in Fig. 1. Bond lengths and angles illustrating the coordination geometry around chromium are given in Table 3 and are in good agreement with those of related chromium(III) diols.[5] However, the angle between the Cr1–O1–O2 plane and the Cr2–O1–O2 plane is 21° as a consequence of the short hydrogen bond between O11 and O21, 2.455(7)Å [Cr1–Cr2 is 2.999(2)Å]. An analogous short intramolecular hydrogen bond has been observed in the mono-ol $[(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)]^{4+}$ [2.429(9) Å].[6] It is characteristic that in these two compounds the bond lengths between the metal atoms and the non-bridging oxygen donor atoms are equal within experimental error. This is also the case in $trans$-$[(H_2O)(NH_3)_3Cr(OH)_2$ $Cr(NH_3)_3(OH)]Br_3 \cdot 2H_2O^7$ where Cr–O (non-bridging) is 1.979(4) Å. However, in this compound the 2.450(5) Å (H)O–(H)–O(H) hydrogen bonds are intermolecular. In other aquahydroxochromium(III) complexes without such a short hydrogen bond, a significant difference (0.07 Å) is observed between the Cr–OH$_2$ and the Cr–OH bond lengths.[8]

Within experimental error the geometry of the 1,4,7-triazacyclononane ligands compares well with other tacn complexes.[9] Bond lengths and angles of the ligands are part of the supplementary material. The disorder of the tacn ligands corresponds to slightly different conformations illustrated by the dihedral angles N12–C131–C14–N13 and N12–C132–C14–N13, which are 54.1(15) and 27.9(14)°, respectively. Similar discrepancies are observed in the other tacn ligand with dihedral angles of 47.3(12) and 17(3)°. The four other analogous dihedral angles are 39–41°. The two

Table 3. Bond lengths (Å) and bond angles (°) illustrating the coordination around chromium.

Cr1–O1	1.968(5)	Cr2–O2	1.951(5)
Cr1–O2	1.978(5)	Cr2–O1	1.971(5)
Cr1–O11	1.982(5)	Cr2–O21	1.987(6)
Cr1–N11	2.088(7)	Cr2–N21	2.053(7)
Cr1–N12	2.066(6)	Cr2–N23	2.062(7)
Cr1–N13	2.062(6)	Cr2–N22	2.061(6)
O1–Cr1–O2	78.1(2)	O1–Cr2–O2	78.6(2)
O1–Cr1–O11	89.8(2)	O2–Cr2–O21	89.4(2)
O1–Cr1–N11	94.6(3)	O2–Cr2–N21	92.7(3)
O1–Cr1–N12	175.5(3)	O2–Cr2–N23	174.9(3)
O1–Cr1–N13	99.4(2)	O2–Cr2–N22	99.0(2)
O2–Cr1–O11	94.9(2)	O1–Cr2–O21	93.2(2)
O2–Cr1–N11	91.4(2)	O1–Cr2–N21	92.6(3)
O2–Cr1–N12	98.7(2)	O1–Cr2–N23	99.4(2)
O2–Cr1–N13	173.0(2)	O1–Cr2–N22	174.8(3)
N11–Cr1–N12	82.3(3)	N21–Cr2–N23	82.6(3)
N12–Cr1–N13	83.5(3)	N23–Cr2–N22	82.6(3)
N13–Cr1–N11	82.3(3)	N22–Cr2–N21	82.8(3)
Cr1–O1–Cr2	99.2(2)	Cr1–O2–Cr2	99.5(2)

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Table 4. Short intermolecular contacts (Å).

O1–I2[a]	3.467(5)	C25–I6[h]	3.528(12)
O1–I6[b]	3.226(7)	I2–I5[i]	3.067(7)
N11–I1[c]	3.585(7)	I2–I5[j]	3.298(8)
N12–I31[c]	3.602(7)	I2–I6[k]	1.732(5)
N12–I32[c]	3.579(7)	I31–I32	0.531(2)
O2–OW	2.790(8)	I31–I5	3.16(2)
O21–I2[c]	3.502(6)	I32–OW[a]	3.33(2)
O21–I6[d]	3.152(7)	I32–I5	3.69(2)
N21–I1[c]	3.483(8)	I4–I5[a]	3.105(8)
N22–I1[e]	3.499(6)	OW–OW[l]	2.93(2)
C23–I6[f]	2.869(12)	I5–I5[m]	1.79(2)
N23–I4[g]	3.586(7)	I5–I6[n]	3.251(9)
		I5–I6[o]	3.904(9)

Symmetry code:

[a] $(1/2-x, 1/2+y, 1/2-z)$ [h] $(x, y, z-1)$
[b] $(x, y, z-1)$ [i] $(-x, -y, 1-z)$
[c] $(1/2-x, y-1/2, 1/2-z)$ [j] $(x, -y, z-1/2)$
[d] $(x, y-1, z-1)$ [k] $(1/2-x, y-1/2, 3/2-z)$
[e] $(1/2-x, y-3/2, 1/2-z)$ [l] $(1/2-x, -1/2-y, -z)$
[f] $(x, y-1, z-1)$ [m] $(-x, y, 1/2-z)$
[g] $(1-x, -y, -z)$ [n] $(1/2-x, 1/2-y, 1-z)$
[o] $(x-1/2, 1/2-y, z-1/2)$

tacn ligands in the cation of the present salt adopt identical conformations, either δδδ or λλλ, i.e. the salt is a racemate.

The crystal packing appears to be influenced by interactions between the complex cation, iodine and water of crystallization as shown in Table 4.

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