

Tetramethylammonium tetraaquadichloro-chromium(III) trichloride dihydrate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{Cr}-\text{O}) = 0.003 \text{ \AA}$
Disorder in main residue
R factor = 0.053
wR factor = 0.149
Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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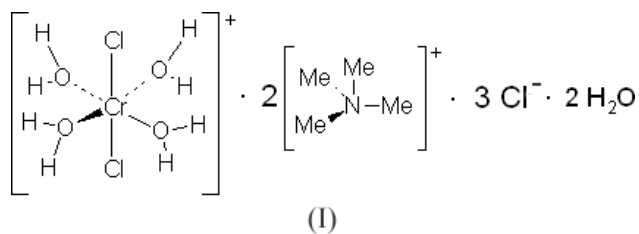
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The title metal-organic octahedral chromium compound, $(\text{C}_4\text{H}_{12}\text{N})_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, was synthesized according to the Palmer method. The chromium complex ion possesses mirror symmetry and has two axial Cl^- ions and four equatorial water molecules. The octahedral complex cation and tetramethyl ammonium tetrahedra pack in a 'parquet'-style pattern, with Cl^- ions and water molecules in between the 'bricks'. The structure is compared with aquapentachlorochromate(III) complexes in the literature.

Comment

In the last decade, octahedral complexes of chromium(III) have attracted increasing interest after the discovery of their catalytic properties (Ogura & Yoshida, 1987). Ligand-substitution reactions are slow in chromium(III) complexes, due to their considerable kinetic stability.

The title compound, (I), was synthesized according to the method of Palmer (1954). The chromium(III) ion was expected to be coordinated by five Cl^- anions and a water molecule, as observed in the structures described for the Rb and Cs aquapentachlorochromates(III) (Eriksson *et al.*, 2004). However, the product was not stable enough to produce a similar compound, as it was found to be amorphous and hygroscopic under ambient conditions. We believe that, due to the hygroscopic effect, the red-violet aquapentachlorochromate complex slowly turned, by ligand substitution, into the green complex tetraaquadichlorochromium(III), which seems to be more prone to crystallize as the title double salt.



The tetraaquadichlorochromium(III) complex was first described by Dance & Freeman (1965), and then by Morosin (1966), as the chromium(III) chloride complex $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}(\text{H}_2\text{O})_2$. Another chromium(III) compound, $\text{Cs}_2[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_3$, was described by Nyburg *et al.* (1997) and is more similar to (I).

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The cation possesses mirror symmetry, with two axial Cl^- ions and four equatorial water molecules. The three Cl^- ions each lie

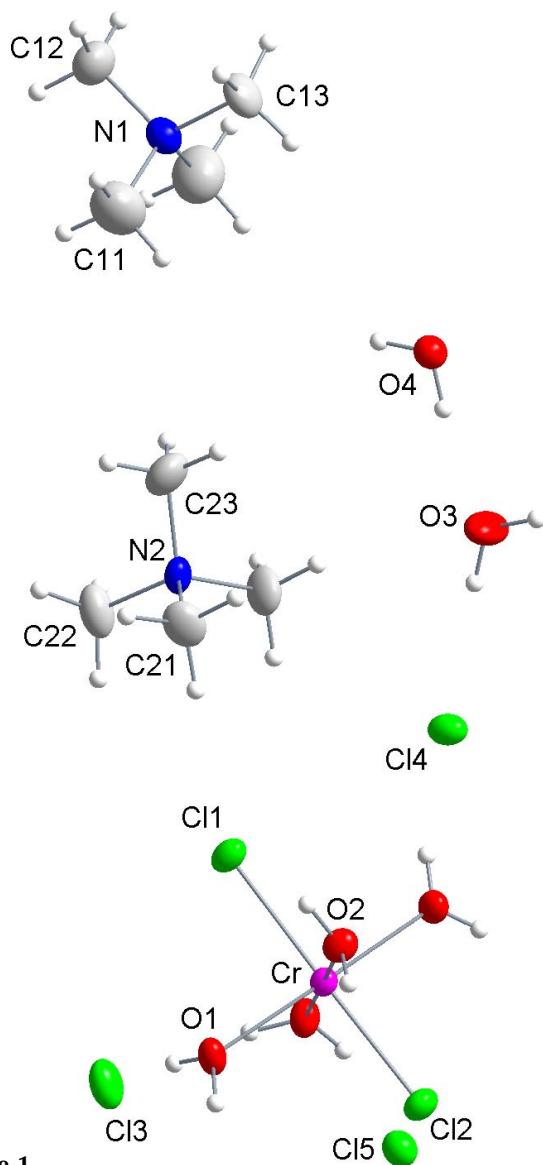


Figure 1
The molecular structure and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

on mirror planes. In each ammonium cation the N and two C atoms lie on mirror planes. The axial Cl^- ion Cl1 is linked to one Me *via* $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds. The equatorial water molecules are surrounded by three different Cl^- ions (Cl3, Cl4 and Cl5) and are linked by $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds. The hydrogen-bonding network is rather complex and is summarized in Table 2.

The octahedral complex cation and tetramethylammonium tetrahedra pack in a parquet-style pattern, with Cl^- ions and water molecules in between (Fig. 2).

In complex (I), the $\text{Cr}-\text{Cl}$ and $\text{Cr}-\text{OH}_2$ bond distances are *ca.* 0.04 Å shorter than the equivalent distances in the aquapentachlorochromate(III) complexes (Eriksson *et al.*, 2004). This can be explained by the lower electronegative contribution from the smaller number of Cl^- ions, which results in tighter covalent bonding of the Cr^{III} ion, and by fewer electronic steric effects of the Cl^- ions (Fig. 3).

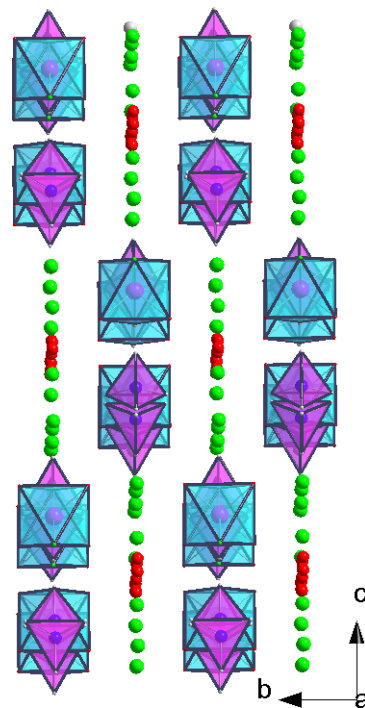


Figure 2
The octahedral complex cations and tetramethylammonium tetrahedra packed in a parquet-style pattern, with Cl^- ions and water molecules in between.

Experimental

Tetramethylammonium chloride and chromium(VI) oxide were dissolved in deionized water, according to the method of Palmer (1954). The product became amorphous and hygroscopic under ambient conditions and formed no crystals. In an environment with low relative humidity, single crystals of (I) were formed.

Crystal data

$(\text{C}_4\text{H}_{12}\text{N})_2[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3\cdot 2\text{H}_2\text{O}$
 $M_r = 485.64$
 Orthorhombic, $Pnma$
 $a = 18.4374(2)$ Å
 $b = 6.8192(1)$ Å
 $c = 18.4330(2)$ Å
 $V = 2317.55(5)$ Å³
 $Z = 4$
 $D_x = 1.392$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 8192 reflections
 $\theta = 2.2\text{--}27.3^\circ$
 $\mu = 1.09$ mm⁻¹
 $T = 173(2)$ K
 Fragment of plate, green
 $0.20 \times 0.08 \times 0.04$ mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{\text{min}} = 0.811$, $T_{\text{max}} = 0.958$
 27 823 measured reflections

2822 independent reflections
 2139 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$
 $\theta_{\text{max}} = 27.3^\circ$
 $h = -23 \rightarrow 23$
 $k = -8 \rightarrow 8$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.149$
 $S = 1.00$
 2822 reflections
 156 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 2.33P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.73$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cr1—O2	1.992 (2)	Cr1—Cl2	2.2889 (14)
Cr1—O1	2.008 (3)	Cr1—Cl1	2.3133 (14)
O2 ⁱ —Cr1—O2	91.17 (15)	O1 ⁱ —Cr1—Cl2	91.98 (8)
O2 ⁱ —Cr1—O1 ⁱ	89.52 (11)	O1—Cr1—Cl2	91.97 (8)
O2—Cr1—O1 ⁱ	178.97 (11)	O2 ⁱ —Cr1—Cl1	90.13 (8)
O2 ⁱ —Cr1—O1	178.97 (11)	O2—Cr1—Cl1	90.13 (8)
O2—Cr1—O1	89.53 (11)	O1 ⁱ —Cr1—Cl1	89.10 (8)
O1 ⁱ —Cr1—O1	89.77 (15)	O1—Cr1—Cl1	89.10 (8)
O2 ⁱ —Cr1—Cl2	88.81 (8)	Cl2—Cr1—Cl1	178.48 (6)
O2—Cr1—Cl2	88.81 (8)		

 Symmetry code: (i) $x, \frac{1}{2} - y, z$.

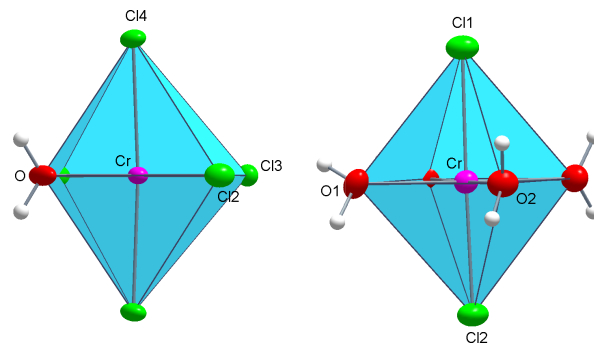
Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...Cl5 ⁱⁱ	0.85 (2)	2.27 (3)	3.073 (3)	159 (5)
O1—H1B...Cl3	0.84 (2)	2.20 (2)	3.027 (3)	166 (5)
O2—H2A...O4 ⁱⁱⁱ	0.83 (2)	1.88 (2)	2.709 (3)	175 (5)
O2—H2B...Cl4 ⁱⁱ	0.84 (2)	2.23 (2)	3.036 (3)	163 (4)
O3—H3A...Cl5 ^{iv}	0.86 (2)	2.27 (2)	3.123 (5)	178 (7)
O3—H3B...Cl4	0.85 (2)	2.26 (2)	3.115 (4)	177 (6)
O4—H4A...O3	0.85 (2)	1.84 (2)	2.679 (6)	172 (7)
O4—H4B...Cl3 ^v	0.85 (2)	2.27 (2)	3.112 (4)	178 (6)
C12—H12C...Cl5 ^{vi}	0.98	2.82	3.803 (3)	177
C22—H22A...Cl1 ^v	0.98	2.74	3.715 (2)	172

 Symmetry codes: (ii) $x, y - 1, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} - z$; (v) $1 - x, \frac{1}{2} + y, -z$; (vi) $x - 1, y, z$.

The water H atoms were located in a difference Fourier map and were refined isotropically without any constraints. For the methyl groups, the C—H distances (0.98 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine, with the starting position based on a threefold averaged circular Fourier synthesis. Some of the methyl groups (C12, C13, C22 and C23) are positioned on a mirror plane and, as a result, the methyl H atoms are disordered. A common isotropic displacement parameter was refined for the methyl H atoms.


Figure 3

A comparison of the aquapentachlorochromate(III) and tetraaquachlorochromium(III) complexes. Displacement ellipsoids are drawn at the 50% probability level.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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