Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Triaqua-μ_3-oxo-hexa-μ_2-propionato-$\kappa^{12}O{:}O'$-trichromium(III) nitrate hemihydrate

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(O–N) = 0.007 Å
Disorder in main residue
R factor = 0.043
wR factor = 0.126
Data-to-parameter ratio = 15.8

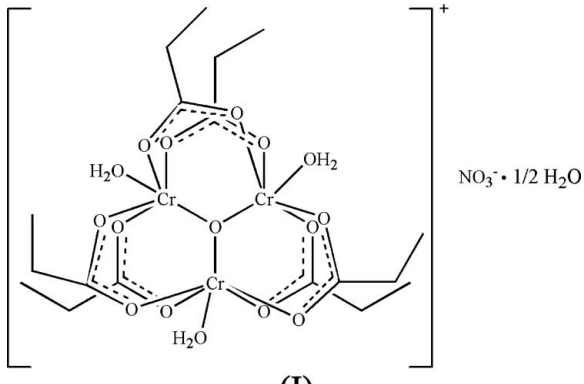
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 22 March 2006
Accepted 28 April 2006

The title compound, $[Cr_3(C_3H_5O_2)_6O(H_2O)_3]NO_3{\cdot}0.5H_2O$, has a trinuclear cluster structure with three Cr atoms in a triangle linked through a μ_3-oxo bridge, each Cr atom having a terminal water molecule as ligand, and pairs of Cr atoms being additionally bridged by two propionate ligands. There are two chemically equivalent but independent triaqua-μ_3-oxo-hexa-μ_2-propionato-$\kappa^{12}O{:}O'$-trichromium cations, two NO_3^- anions and one water solvent molecule in the asymmetric unit. Extensive hydrogen bonds lead to zigzag stacks of cations along the b axis.

Comment

Bioactive organic metal complexes have been considered as effective supplements for essential elements, since the deficiency of certain trace minerals can cause different diseases and disorders (Farrel, 1999). Among these, chromium(III) is one of the most interesting metals since the shortage of chromium(III) might contribute to the development of different diseases such as type II diabetes (Cefalu & Hu, 2004). Chromium carboxylate complexes, in particular the acetate complexes, have been extensively studied and characterized in the past (Chang & Jeffrey, 1970; Anson *et al.*, 1997; Fujihara *et al.*, 1998).



(I)

We report here a chromium(III) propionate complex, (I), synthesized by two different methods. In the first method, the reaction starts with Cr^{VI} with reduction by glycol (Catron, 1998). This complex is currently being marketed as a trace mineral additive (KemTRACETM brand Chromium Propionate). The other method of synthesis starts with Cr^{III}, as reported in the literature (Earnshaw *et al.*, 1966). Both methods result in the same crystal modification, which was confirmed by the X-ray powder diffraction method.

According to the single-crystal X-ray structure determination, there are two chemically equivalent, but structurally non-

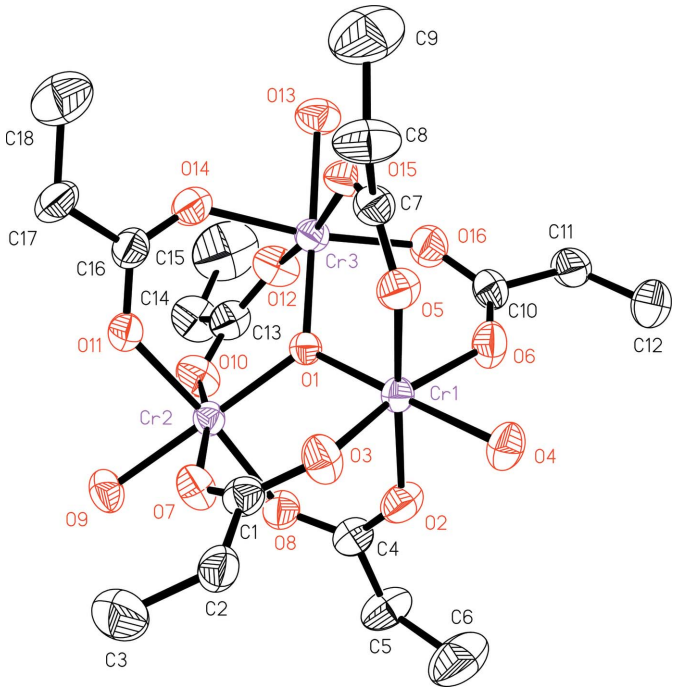


Figure 1
Molecular structure at the 50% probability level and the numbering scheme for one of the crystallographically independent complex cations in (I). Only one set of split positions for Et groups is shown for clarity. H atoms have been omitted.

equivalent, isolated cations of $[Cr_3C_{18}H_{36}O_{16}]^+$, two NO_3^- anions and one water solvent molecule in the asymmetric unit of a *C*-centered monoclinic cell. In the crystal structure of (I), Cr atoms of the cation form a regular triangle (Fig. 1). Three chromium coordination octahedra have a common vertex occupied by a central O atom. All coordinated water ligands are in *trans* positions to that center and the other sites of Cr polyhedra are occupied by O atoms of the bridging μ_2-propionato-*O*,*O*′ ligands. Cr atoms are displaced from the four-propionate oxygen plane (all six O_4 arrangements for the two structurally independent cations are planar to within 0.005–0.086 Å) by about 0.16 Å in the direction of the central O atom. The atoms of the terminal ethyl groups of the bridging ligands have high displacement parameters that are very typical for hydrocarbon terminal groups.

In the structure of (I), the average Cr—OH_2 bond length [2.039 (3) Å] is in the range published for μ_2-acetato-*O*,*O*′ derivatives (2.02–2.07 Å; Karu *et al.*, 1993; Glowiak *et al.*, 1996; Anson *et al.*, 1997). Other bond lengths, such as μ_3-*O* [1.891 (3) Å] and μ_2-*R*CO_2 [1.988 (2) Å], are also in a good accordance with the literature for other trinuclear chromium complexes (Fujihara *et al.*, 1998).

Packing diagrams indicate the existence of stacks along the monoclinic *b* axis, with a zigzag arrangement of cations linked by very extensive hydrogen bonding (Table 2 shows the O···H intermolecular contacts shorter than 2.45 Å). These stacks are also linked by intermolecular interactions. The strongest three types of intermolecular interactions are illustrated in Fig. 2, including (coordinated water molecule)–(μ_2-acetato-*O*,*O*′), (coordinated water molecule)–(O—NO_2)$^-$ and (coordinated water molecule)–(solvent water molecule).

Many derivatives have been synthesized with a $[Cr_3O]$ triangle core with different bridging ligands in the past. However, only one structure of triaqua-μ_3-oxo-hexa-μ_2-propionato-*O*,*O*′-trichromium(III) nitrate dihydrate had been reported up to the end of 2005 (Antsyshkina *et al.*, 1987); it apparently has four times more water molecules per cluster.

The results for this complex were retrieved from the Cambridge Structural Database (CSD, Version of 2006; Allen, 2002). The crystals were reported as monoclinic [a = 18.286 (5) Å, b = 13.006 (3) Å, c = 19.967 (6) Å, β = 134.91 (1)°, V = 3363.11 Å, space group $A2/m$]. However, the comments in the CSD indicate the existence of serious errors and discrepancies in the submitted data, including an unreasonable connectivity table and incorrect values for atomic coordinates. The C atoms in the μ_2-propionato-*O*,*O*′ bridges were found to be disordered. The space group of this complex was reported as $A2/m$, which is not very common for organic and metallo-organic substances. This could be a sign of an incorrect space group assignment and may represent the refinement of a fraction of the real cell. We calculated the packing diagram from the CSD data for this modification and found the packing mode of this complex was very different from that observed for (I).

In a very recent publication, the clathrate structure of the potassium salt of the same chromium propionate cation with a bulky α-(silicatopolyoxotungstate) pseudo-spherical anion was reported (Kawamoto *et al.*, 2005). Hydrophilic and hydrophobic channels were found in the crystal packing mode of this compound with its spherical Keggin-type polyoxometalate. There are three molecules of water per cation and all reside in the hydrophilic channel. The geometry of the cation is very close to that observed for (I); however, the Cr—OH_2 bonds are not so regular [1.993 (3)–2.112 (3) Å].

Experimental

Method I. To a 250 ml double-necked round-bottomed flask equipped with a magnetic stirring bar, a condenser and a thermometer, sodium dichromate (16.66 g, 56 mmol) and propionic acid (49.97 g, 67.5 mmol, 50.4 ml) were added and heated to 363 K. Propylene glycol (3.36 g, 44.2 mmol, 3.24 ml) was then added slowly in three portions. Bubbles were observed to form spontaneously upon the addition of propylene glycol. The resulting solution was refluxed at 393 K for more than 5 h. The resulting liquid was then vacuum-evaporated (approximately 50 mTorr) to dryness at around 373 K in an oil bath. Subsequently, a 1 *M* HNO_3 solution (150 ml) was added to the resulting green solid (25 g). The solution was concentrated to around 50 ml with heating at 343–353 K. After the concentrated solution was cooled, a dark-green crystalline solid (10 g) was collected by filtration and washed with cold water. Method II is the same as that reported previously using $CrCl_3{\cdot}6H_2O$ as a starting material (Earnshaw *et al.*, 1966). Dark-green thin plate-shaped crystals were obtained after the crystalline materials had been dissolved in pure water and the solvent slowly evaporated at room temperature with the cap loosened for one to three weeks.

Crystal data

$[Cr_3(C_3H_5O_2)_6O(H_2O)_3]$-$NO_3{\cdot}0.5H_2O$
M_r = 735.49
Monoclinic, $C2/c$
a = 31.836 (8) Å
b = 12.844 (3) Å
c = 31.837 (7) Å
β = 103.549 (7)°
V = 12656 (5) Å^3
Z = 16
D_x = 1.544 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.09 mm^{-1}
T = 193 (2) K
Thin plate, green
0.40 × 0.20 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.74, T_{max} = 1
(expected range = 0.642–0.868)
52397 measured reflections
12916 independent reflections
9325 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 26.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.126
S = 1.01
12916 reflections
820 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 29.355P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4H···O11^{i}	0.82	1.97	2.785 (3)	173
O4—H4G···O35	0.82	1.91	2.728 (4)	173
O9—H9H···O5^{ii}	0.82	2.08	2.892 (3)	174
O9—H9G···O34^{iii}	0.82	2.08	2.879 (6)	167
O13—H13G···O39^{iv}	0.82	1.84	2.655 (4)	172
O19—H19H···O37^{v}	0.82	1.90	2.699 (6)	165
O26—H26G···O38	0.81	1.94	2.716 (7)	160
O31—H31G···O34	0.82	1.94	2.750 (5)	175
O31—H31H···O8^{v}	0.82	2.17	2.966 (3)	164
O39—H39H···O25	0.82	2.26	2.931 (4)	139
O39—H39G···O36	0.82	2.09	2.878 (7)	160

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

Terminal ethyl groups of the μ_2-propionato-O,O' ligands were found to be disordered, giving unrealistically short C—C distances. The refinement of the model with 'soft' restraints without splitting the positions for the C atoms led to satisfactory results, but the displacement parameters were still far from desired; therefore, a model with splitting the positions of the C atoms, together with tight restraints on bond lengths, 1–3 distances and displacement parameters, was used to prevent a spread of C—C distances. Fixed occupancy factors of 0.5 were applied for each position as it was not possible to obtain reasonable refined values for related pairs. The H atoms of μ_2-propionato-O,O' groups were placed in idealized positions and refined using a riding model, with C—H = 0.98 and 0.99 Å, and U_{iso}(H) = 1.2U_{eq}(C) for CH_2 groups or 1.5U_{eq}(C) for methyl groups. All H atoms belonging to coordinated and solvent water molecules were located in a difference Fourier map and initially refined with restrained geometrical parameters [O—H = 0.82 (1) Å, H···H = 1.30 (1) Å and U_{iso}(H) = 1.5U_{eq}(O)]; they were then fixed in position for the final refinement.

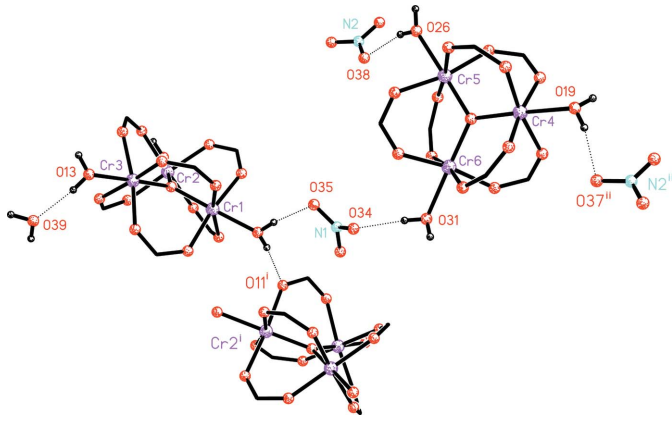


Figure 2
Hydrogen-bonding pattern in the crystal structure of (I), showing O···H contacts shorter than 2 Å. Et groups of μ_2-propionato-O,O' ligands have been omitted for clarity. Only H atoms of water molecules are displayed. Symmetry codes are as in Table 1.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT*.

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