

## Thorium(IV) chromate(VI) monohydrate

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## Key indicators

Single-crystal X-ray study  
 $T = 193$  K  
Mean  $\sigma(\text{Cr}-\text{O}) = 0.004$  Å  
 $R$  factor = 0.023  
 $wR$  factor = 0.054  
Data-to-parameter ratio = 16.5

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

A new hydrated thorium chromate,  $\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})$ , has been synthesized under mild hydrothermal conditions. The structure consists of  $\text{ThO}_8$  dodecahedra and  $\text{ThO}_9$  tricapped trigonal prisms that are interconnected by chromate anions into a three-dimensional framework.

## Comment

The only previously reported thorium chromate is  $\text{Th}(\text{OH})_2(\text{CrO}_4)(\text{H}_2\text{O})$  (Lundgren & Sillén, 1949). The structure of the title compound,  $\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})$ , is far more complicated and interesting than the simple thorium chromate name or formula suggests.

In the title compound, the two crystallographically unique Th centers have distinct differences in their coordination environments. Th1 exists as a  $\text{ThO}_8$  dodecahedron with one coordinating water molecule within its inner sphere. The Th—O bond distances range from 2.294 (4) to 2.548 (4) Å, with the longest bond distance being that to the water molecule. All other O atoms are bridging to the four independent Cr atoms that exist within the structure. In contrast, Th2 exists as the more frequently observed  $\text{ThO}_9$  tricapped trigonal prism. A second coordinating water molecule forms one of the bases for the trigonal prism. Again, all remaining O atoms are bridging to Cr atoms, with no chelation involved. The Th—O bond distances range from 2.385 (4) to 2.530 (4) Å. All chromate ( $\text{CrO}_4^{2-}$ ) anions exist as tetrahedra with no significant distortions.

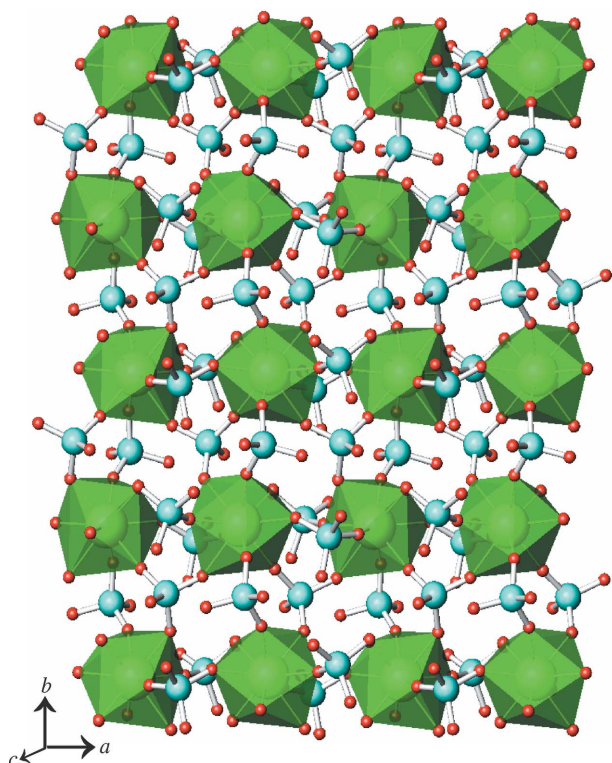
Each  $\text{Th1O}_8$  unit is bound to five adjacent  $\text{Th1O}_8$  polyhedra through five  $\text{CrO}_4$  units. Of these units, three bridge to two other  $\text{Th1O}_8$  units, while the remaining two only bridge to one, forming a  $[\text{Th}(\text{CrO}_4)_3(\text{H}_2\text{O})]$  sheet parallel to the  $ab$  plane (Fig. 1). The coordinating O17 water molecule then fills a small channel that extends down the  $a$  axis within the layer. A second sheet, also parallel to the  $ab$  plane, is composed of the  $\text{Th2O}_9$  polyhedra (Fig. 2). Seven  $\text{CrO}_4$  units bind one  $\text{Th2O}_9$  unit to six others, with four bridging to one unit and three bridging two units, as well as one seemingly terminal chromate. This  $[\text{Th}(\text{CrO}_4)_4(\text{H}_2\text{O})_2]$  unit is not isolated from the previously described sheet containing Th1. These two sheets are joined through utilizing all  $\text{CrO}_4$  units and alternate to form the  $[\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})]$  structure. These two layers are joined through atoms O6, O9 and O16, and the entirety of  $\text{Cr1O}_4$  (Fig. 3).

## Experimental

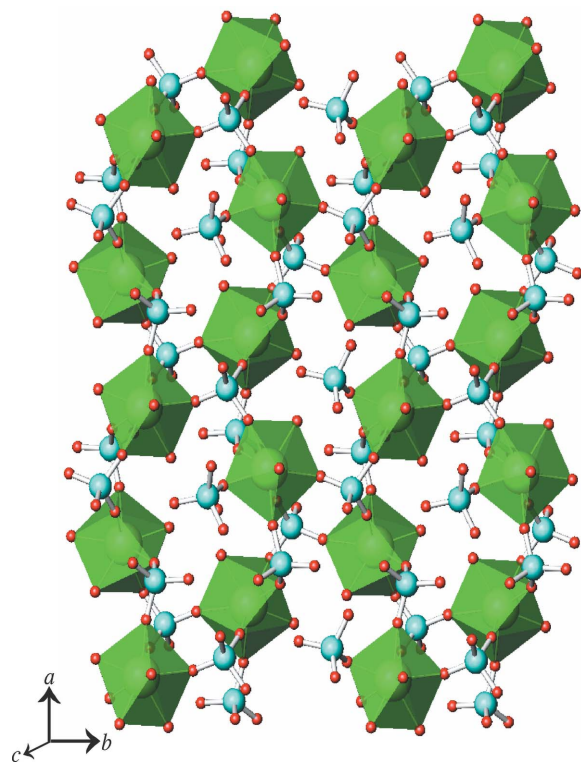
The starting materials  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Fisher, 99%) and  $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$  (Alfa Aesar, 99%) were used as received. Distilled and Millipore-filtered water was used.  $\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})$  was synthesized under mild hydrothermal reaction conditions.  $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$

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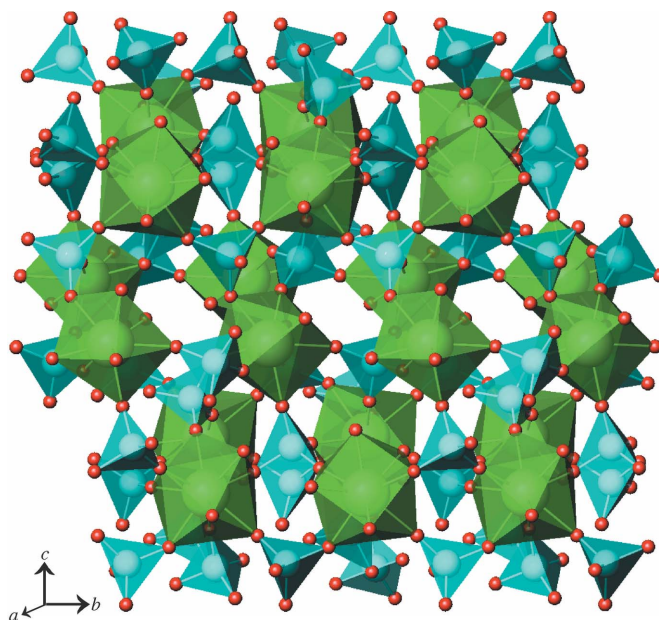
Accepted 8 November 2006



**Figure 1**  
A view of the  $[\text{Th}(\text{CrO}_4)_3(\text{H}_2\text{O})]$  sheet substructure that extends in the  $ab$  plane.



**Figure 2**  
A view of the  $[\text{Th}(\text{CrO}_4)_4(\text{H}_2\text{O})_2]$  sheet substructure that extends in the  $ab$  plane.



**Figure 3**  
A view of the overall structure of  $\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})$ .

(0.2727 g, 0.548 mmol) and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.2273 g, 0.568 mmol) were loaded into a 23 ml PTFE-lined autoclave with  $\text{H}_2\text{O}$  (1.0 ml). The autoclave was sealed and placed in a box furnace preheated at 473 K to react under autogeneous pressure. The autoclave was heated for 3 d and then cooled to room temperature at a rate of  $9 \text{ K h}^{-1}$ . The brown mother liquor was decanted, and the products were rinsed with distilled water and methanol and allowed to dry. Dark-red distorted octahedral crystals of  $\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})$  were interspersed throughout metallic chromium and an unresolved yellow powder. The yield of this reaction was extremely low, with only a few crystals synthesized in each reaction. Energy-dispersive X-ray analysis gives a Th:Cr ratio of approximately 1:2.

#### Crystal data

$\text{Th}(\text{CrO}_4)_2(\text{H}_2\text{O})$   
 $M_r = 480.04$   
 Orthorhombic,  $Pbca$   
 $a = 10.9824$  (6) Å  
 $b = 11.6668$  (6) Å  
 $c = 22.4586$  (12) Å  
 $V = 2877.6$  (3) Å<sup>3</sup>

$Z = 16$   
 $D_x = 4.432 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 23.60 \text{ mm}^{-1}$   
 $T = 193$  (2) K  
 Distorted octahedron, dark red  
 $0.10 \times 0.09 \times 0.09 \text{ mm}$

#### Data collection

Bruker APEX diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 (SHELXL97; Sheldrick, 1997)  
 $T_{\min} = 0.116$ ,  $T_{\max} = 0.124$

27721 measured reflections  
 3581 independent reflections  
 3378 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$   
 $\theta_{\text{max}} = 28.3^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.054$   
 $S = 1.11$   
 3581 reflections  
 217 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 22.6366P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 2.28 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.09 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

Th1—O9	2.294 (4)	Cr1—O2	1.638 (4)
Th1—O16 <sup>i</sup>	2.332 (4)	Cr1—O4	1.646 (4)
Th1—O7 <sup>ii</sup>	2.354 (4)	Cr1—O1	1.647 (4)
Th1—O3 <sup>iii</sup>	2.390 (4)	Cr1—O3	1.664 (4)
Th1—O1	2.400 (4)	Cr2—O6	1.632 (4)
Th1—O8 <sup>iv</sup>	2.416 (4)	Cr2—O5	1.644 (4)
Th1—O5	2.427 (4)	Cr2—O7	1.645 (4)
Th1—O17	2.548 (5)	Cr2—O8	1.652 (4)
Th2—O15 <sup>v</sup>	2.385 (4)	Cr3—O11	1.588 (4)
Th2—O4 <sup>v</sup>	2.398 (4)	Cr3—O10	1.655 (4)
Th2—O10 <sup>vi</sup>	2.413 (4)	Cr3—O12	1.655 (4)
Th2—O12	2.432 (4)	Cr3—O9	1.720 (4)
Th2—O13	2.438 (4)	Cr4—O14	1.631 (4)
Th2—O2	2.442 (4)	Cr4—O15	1.632 (4)
Th2—O18	2.450 (4)	Cr4—O13	1.661 (4)
Th2—O6 <sup>v</sup>	2.462 (4)	Cr4—O16	1.668 (4)
Th2—O14 <sup>vii</sup>	2.530 (4)		
O2—Cr1—O4	110.9 (2)	O11—Cr3—O10	109.6 (2)
O2—Cr1—O1	109.2 (2)	O11—Cr3—O12	110.0 (2)
O4—Cr1—O1	109.0 (2)	O10—Cr3—O12	109.0 (2)
O2—Cr1—O3	110.5 (2)	O11—Cr3—O9	108.0 (2)
O4—Cr1—O3	109.6 (2)	O10—Cr3—O9	110.4 (2)
O1—Cr1—O3	107.6 (2)	O12—Cr3—O9	110.0 (2)
O6—Cr2—O5	110.2 (2)	O14—Cr4—O15	111.8 (2)
O6—Cr2—O7	109.6 (2)	O14—Cr4—O13	107.9 (2)
O5—Cr2—O7	109.6 (2)	O15—Cr4—O13	109.2 (2)
O6—Cr2—O8	108.2 (2)	O14—Cr4—O16	111.1 (2)
O5—Cr2—O8	109.9 (2)	O15—Cr4—O16	108.0 (2)
O7—Cr2—O8	109.3 (2)	O13—Cr4—O16	108.8 (2)

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

The maximum electron-density peak lies 1.77 Å from atom O18 and the minimum electron-density peak lies 1.29 Å from atom Th2.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

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## References

- Bruker (1999). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Bruker (2000). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Dowty, E. (2004). *ATOMS*. Version 6.1. Shape Software, Kingsport, Tennessee, USA. <http://www.shapesoftware.com>  
 Lundgren, G. & Sillén, L. G. (1949). *Ark. Kemi*, **1**, 277–292.  
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.