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Poly[[tetraaquatri-μ-oxolato-dithulium] dihydrate]

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Key indicators

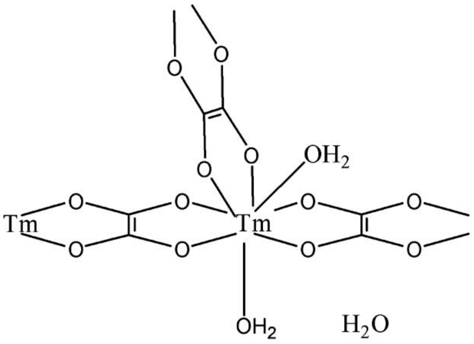
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.019
wR factor = 0.046
Data-to-parameter ratio = 11.4

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

The structure of the oxalate-bridged title complex, $[Tm_2(C_2O_4)_3(H_2O)_4]\cdot 2H_2O$, consists of layers built from $Tm_2(C_2O_4)_3$ units. The coordination polyhedron of Tm can be described as a distorted dicapped trigonal prism. Each oxalate is located on an inversion centre.

Comment

The structures and properties of lanthanide oxalates attract attention for their ability to act as precursors of lanthanide oxides. A few single crystals of lanthanide oxalates, such as $[Ln_2(C_2O_4)_3(H_2O)_4]\cdot 2H_2O$ (Ln = Sc or Yb), $[Ln_2(C_2O_4)_3(H_2O)_6]\cdot 4H_2O$ (Ln = La, Ce, Pr or Nd) and $[Nd_2(C_2O_4)_3(H_2O)_6]$ have been obtained either in silica gel (Ollendorff & Weigel, 1969), by hydrothermal reaction (Michaelides *et al.*, 1988) or by other methods (Hansson, 1970, 1972, 1973*a*,*b*; Ünaleroglu *et al.*, 1997; Tröllet *et al.*, 1998; Trombe, 2003). Crystals of $[Ln(C_2O_4)(HC_2O_4)]\cdot 4H_2O$ (Ln = Er or Tm) were prepared by saturating a boiling solution of oxalic acid in 3 *M* H_2SO_4 with the lanthanide oxide and then slowly cooling to 273 K (Steinfink & Brunton, 1970). However, as an X-ray structural analysis of a thulium oxalate complex has not been reported to date, we carried out the structural analysis of the title complex, (I), and present the results here.



(I)

A view of the structure of (I) is shown in Fig. 1. The mid-point of the C—C bond for each oxalate is located on an inversion centre. Each oxalate ligand chelates two Tm atoms to form stable five-membered rings with a Tm···Tm separation of 6.107 (4) Å. Each oxalate thus bridges two Tm atoms. Two of the oxalate ligands build up an infinite chain, whereas the third oxalate ligand links these chains to form a two-dimensional network parallel to the *ab* plane. A three-dimensional network is constructed by hydrogen bonds between water molecules (Table 1 and Fig. 2).

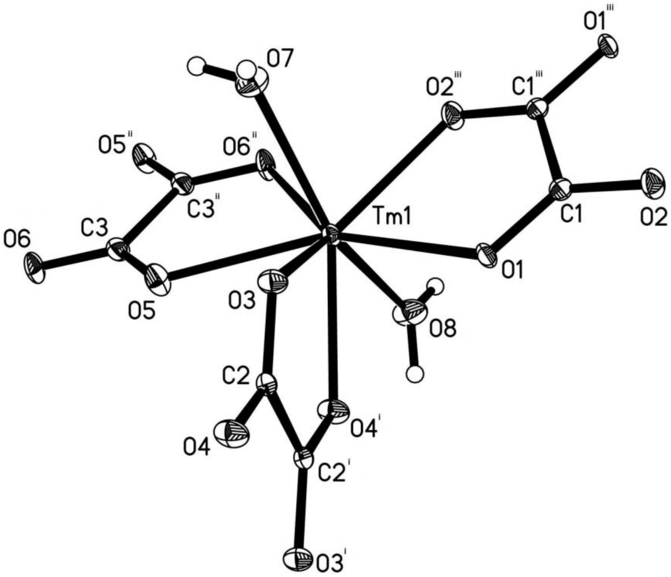


Figure 1
A drawing of the title complex, with 35% probability displacement ellipsoids, showing the atomic numbering scheme. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$; (iii) $-x, -y, -z+1$.]

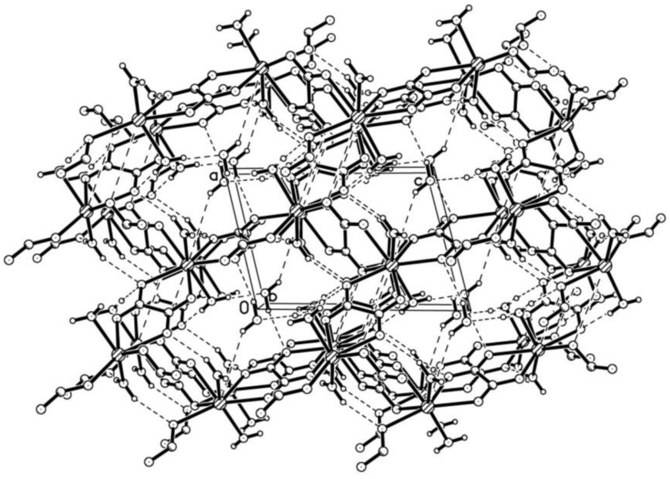


Figure 2
A packing view of (I), down the *b* axis, showing the three-dimensional hydrogen-bonding network (dashed lines).

Besides the six O atoms from the three oxalates, the Tm atom is also connected to two O atoms belonging to two water molecules. Thus, the Tm atom has an eight-coordinate environment forming a 4,4′-bicapped trigonal prism in which the sets of atoms O3, O5 and $O4^{i}$, and O8, $O2^{iii}$ and $O6^{ii}$ [symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$; (iii) $-x, -y, -z+1$] form two triangles, with the capping atoms being O1 and O7, respectively (Fig. 3). The Tm—O bond distances range from 2.316 (3) to 2.623 (3) Å (mean distance 2.435 Å). Comparison of these bond lengths with those of related lanthanide complexes (Michaelides *et al.*, 1988; Ollendorff *et al.*, 1969), shows that the mean Ln^{III}—O bond distance decreases when the atomic number increases (see Table 2). This phenomenon agrees with the theory of lanthanide contraction.

Experimental

The title complex was prepared by a simple approach. Aqueous NaOH (6 ml, 1 mol l^{-1}) was added to an aqueous solution of oxalic acid (0.25 g, 3.0 mmol) and benzoic acid (0.50 g, 4.0 mmol) to adjust the pH value of the mixture to approximately 5.5, and then an aqueous solution (3 ml) of $Tm(ClO_4)_3\cdot 6H_2O$ (0.84 g, 1.5 mmol) was added. The resulting mixture was placed in a Parr Teflon-lined autoclave. The autoclave was then sealed and heated at 413 K for one week. Colourless crystals of (I) suitable for X-ray crystallography were obtained. Elemental analysis, calculated for $C_6H_{12}O_{18}Tm_2$: C 10.15, H 1.70%; found: C 10.34, H 1.72%. All chemicals used in this experiment were purchased commercially and used without further purification.

Crystal data

$[Tm_2(C_2O_4)_3(H_2O)_4]\cdot 2H_2O$
$M_r = 710.02$
Triclinic, $P\bar{1}$
$a = 6.289$ (3) Å
$b = 6.660$ (3) Å
$c = 9.628$ (4) Å
$\alpha = 75.043$ (6)°
$\beta = 80.778$ (6)°
$\gamma = 81.575$ (6)°
$V = 382.2$ (3) Å^3
$Z = 1$

$D_x = 3.085$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 926 reflections
$\theta = 3.2$–25.1°
$\mu = 11.63$ mm^{-1}
$T = 295$ (2) K
Block, colourless
0.18 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.153$, $T_{max} = 0.248$
2179 measured reflections

1345 independent reflections
1284 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.1°$
$h = -7 \rightarrow 5$
$k = -8 \rightarrow 7$
$l = -12 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.046$
$S = 1.08$
1345 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 0.1731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.06$ e Å^{-3}
$\Delta\rho_{min} = -0.97$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O1^{i}	0.85	2.07	2.906 (5)	166
O7—H7A···O3^{i}	0.85	2.57	3.059 (5)	118
O7—H7B···O9	0.85	1.88	2.724 (6)	177
O8—H8A···O1^{ii}	0.85	2.17	2.963 (5)	155
O8—H8B···O5^{iii}	0.85	2.05	2.888 (5)	167
O9—H9A···O2^{iv}	0.85	2.57	3.184 (6)	130
O9—H9B···O8^{v}	0.85	2.60	3.347 (7)	148

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x-1, y, z$; (iv) $x+1, y, z-1$; (v) $-x+1, -y+1, -z$.

Table 2
Ln—O bond distances (Å) for some lanathanide oxalates.

Complex	Minimum Ln—O	Maximum Ln—O	Mean Ln—O
$[La_2(C_2O_4)_3]\cdot10H_2O^a$	2.505	2.606	2.548
$[Nd_2(C_2O_4)_3]\cdot10H_2O^a$	2.46	2.57	2.50
$[Tm_2(C_2O_4)_3]\cdot6H_2O^b$	2.316	2.623	2.435
$[Yb_2(C_2O_4)_3]\cdot6H_2O^c$	2.281	2.368	2.343

References: (*a*) Ollendorf & Weigel (1969). (*b*) This study. (*c*) Michaelides *et al.* (1988).

All H atoms were positioned geometrically with O—H = 0.85 Å and they were treated as riding on their parent O atoms, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(O).

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

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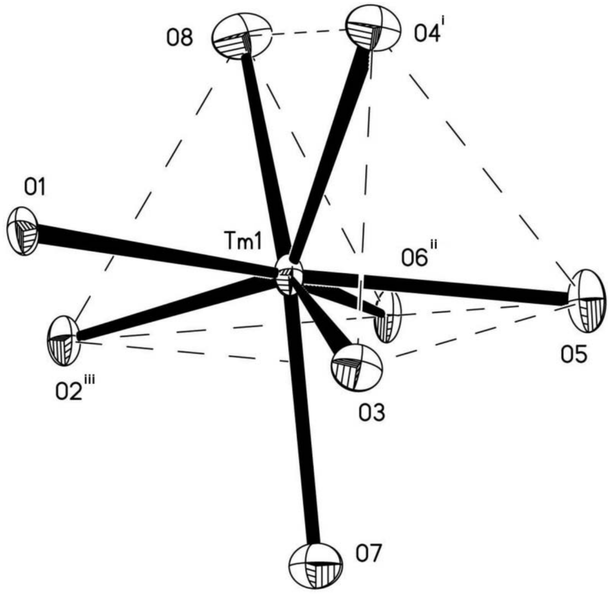

Figure 3
A view of the coordination environment around the Tm atom in (I). [Symmetry codes: (i) $-x+1, -y+1, -z+1$, (ii) $-x+1, -y+1, -z$; (iii) $-x, -y, -z+1$.]

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