metal-organic papers

Hexaaquatrioxalatodierbium(III) tetrahydrate: [{Er(H₂O)₃}₂(C₂O₄)₃]·4H₂O

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Key indicators

Single-crystal X-ray study
$T = 173$ K
Mean σ(C–C) = 0.004 Å
H-atom completeness 61%
R factor = 0.028
wR factor = 0.070
Data-to-parameter ratio = 28.5

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

In the layered structure of the title compound, $[Er_2(C_2O_4)_3(H_2O)_6]\cdot 4H_2O$, the Er atoms are bridged by oxalate ligands. Each Er atom coordinates to six O atoms from three oxalate ligands, and three water molecules. The layers are parallel to the ac plane and four disordered water molecules of crystallization are situated between the layers.

Comment

The lanthanoid elements all form hydrated oxalates of composition $M_2(C_2O_4)_3\cdot nH_2O$ (M = lanthanoid). There are two large isomorphous series of lanthanide oxalates, one with $n \sim 10$ (monoclinic) and one with $n = 6$ (triclinic). In the isomorphous series with $n \sim 10$, the n value varies slightly, and it appears to be dependent on the crystallographic radius of the lanthanide ion and the method of preparation. Compounds with M = Y, La–Ho form a series of 'decahydrates', while compounds with M = Sc, Tm–Lu form a series of 'hexahydrates'. Only erbium oxalate can be synthesized both as a decahydrate and a hexahydrate (Hansson, 1973), and this is of special interest.

(I)
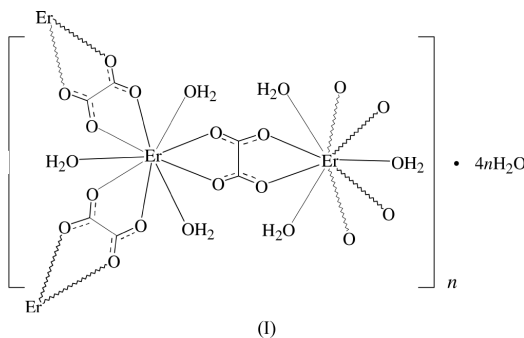
Until the present study, no structurally characterized erbium(III) oxalates have been reported; only powder X-ray diffraction data have been measured and indexed (Hansson, 1973; Ollendorff & Weigel, 1969; Watanabe & Nagashima, 1971). We report here the crystal and molecular structure of erbium(III) oxalate decahydrate, (I).

Two crystallographically equivalent Er atoms, three centrosymmetric oxalate groups, and ten water molecules (six aqua ligands and four water molecules of crystallization) account for one structural unit of (I). Each Er atom coordinates six O atoms from three bidentate oxalates, and three aqua ligands (Fig. 1). The coordination polyhedron ErO₉ is a distorted three-capped trigonal prism. The Er—O distances range from 2.355 (2) to 2.522 (2) Å [average 2.41 (6) Å] in good agreement with the values found in the Cambridge Structural Database (CSD; Version of October 2002; Allen, 2002) of 2.348–2.450 Å, average 2.408 Å (5 hits, $R < 0.1$).
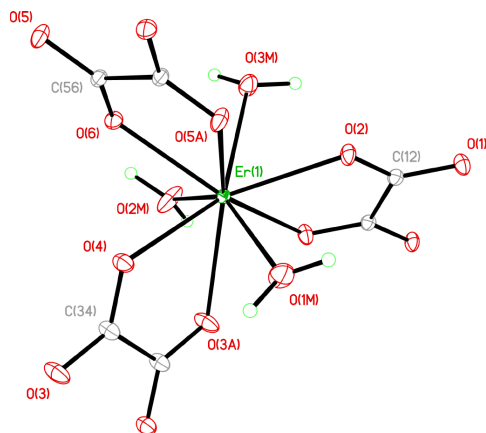
Figure 1
The coordination environment of the Er atom. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.
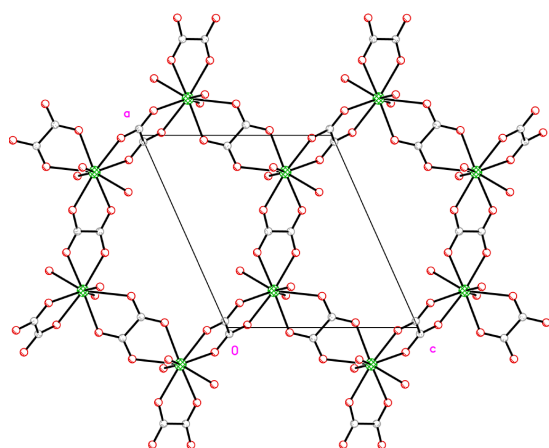

Figure 2
Part of the erbium–oxalate layer around $y = \frac{1}{2}$, projected on to (010).

The oxalate ligands are planar, with C—C distances between 1.530 (6) and 1.549 (6) Å [average 1.538 (10) Å], and C—O distances between 1.246 (3) and 1.262 (4) Å [average 1.253 (6) Å]. All these values are in good agreement with values found in the CSD: 1.426–1.669 Å (average 1.549 Å) and 1.076–1.435 Å (average 1.252 Å) for C—C and C—O distances, respectively (536 hits, $R < 0.05$).

The structure of (I) is composed of infinite erbium oxalate layers perpendicular to the b axis and situated around $y = 0$ and $y = \frac{1}{2}$. The layers are held together by hydrogen bonds *via* the water molecules of crystallization situated between the layers. Fig. 2 shows part of the infinite layer around $y = \frac{1}{2}$, projected along the b axis. Each oxalate ligand is coordinated to two metal atoms, forming two chelates. The four water molecules of crystallization, situated between the layers, are disordered over five positions.

Experimental

Colourless crystals of the title compound were obtained from an aqueous solution containing HCl (0.1 M), $K_4[Nb_2(S_2)_2(C_2O_4)_4]$ (0.01 g) (Sokolov *et al.*, 2001) and $Er(NO_3)_3$ (0.02 g). Yield 70%.

Crystal data

Table 1
Selected geometric parameters (Å, °).

Er1—O1M	2.366 (3)	O1—C12	1.246 (3)
Er1—O2M	2.357 (3)	O2—C12	1.256 (3)
Er1—O3M	2.420 (2)	C12—C12^i	1.536 (6)
Er1—O1^i	2.359 (2)	O3—C34	1.247 (4)
Er1—O2	2.434 (2)	O4—C34	1.262 (4)
Er1—O3^{ii}	2.522 (2)	C34—C34^{ii}	1.530 (6)
Er1—O4	2.404 (2)	O5—C56	1.249 (3)
Er1—O5^{iii}	2.355 (2)	O6—C56	1.257 (3)
Er1—O6	2.440 (2)	C56—C56^{iii}	1.549 (6)

O1M—Er1—O2M	142.85 (10)	O4—Er1—O6	69.46 (8)
O1M—Er1—O3M	137.06 (9)	O5^{iii}—Er1—O1M	75.67 (9)
O1M—Er1—O2	68.67 (9)	O5^{iii}—Er1—O2M	138.12 (8)
O1M—Er1—O3^{ii}	72.97 (10)	O5^{iii}—Er1—O3M	83.67 (9)
O1M—Er1—O4	72.58 (9)	O5^{iii}—Er1—O1^i	138.22 (8)
O1M—Er1—O6	129.89 (8)	O5^{iii}—Er1—O2	71.06 (7)
O2M—Er1—O3M	73.56 (10)	O5^{iii}—Er1—O3^{ii}	139.76 (8)
O2M—Er1—O1^i	72.96 (9)	O5^{iii}—Er1—O4	81.68 (8)
O2M—Er1—O2	128.24 (10)	O5^{iii}—Er1—O6	67.64 (7)
O2M—Er1—O3^{ii}	70.00 (9)	O6—Er1—O3^{ii}	116.76 (8)
O2M—Er1—O4	94.38 (10)	C12—O1—Er1^i	121.21 (18)
O2M—Er1—O6	71.95 (8)	C12—O2—Er1	118.43 (19)
O3M—Er1—O2	69.13 (8)	O1—C12—O2	127.0 (3)
O3M—Er1—O3^{ii}	136.54 (9)	O1—C12—C12^i	116.8 (3)
O3M—Er1—O6	71.69 (8)	O2—C12—C12^i	116.2 (3)
O1^i—Er1—O1M	89.50 (9)	C34—O3—Er1^{ii}	118.4 (2)
O1^i—Er1—O3M	81.39 (8)	C34—O4—Er1	122.56 (19)
O1^i—Er1—O2	67.17 (7)	O3—C34—O4	126.4 (3)
O1^i—Er1—O3^{ii}	66.01 (8)	O3—C34—C34^{ii}	117.2 (3)
O1^i—Er1—O4	131.17 (8)	O4—C34—C34^{ii}	116.4 (3)
O1^i—Er1—O6	140.44 (8)	C56—O5—Er1^{iii}	121.12 (19)
O2—Er1—O3^{ii}	118.24 (8)	C56—O6—Er1	117.83 (18)
O2—Er1—O6	125.00 (7)	O5—C56—O6	126.9 (3)
O4—Er1—O3M	141.15 (8)	O5—C56—C56^{iii}	116.6 (3)
O4—Er1—O2	136.82 (8)	O6—C56—C56^{iii}	116.5 (3)
O4—Er1—O3^{ii}	65.35 (8)		

Symmetry codes: (i) $1-x, 1-y, -1-z$; (ii) $-x, 1-y, -1-z$; (iii) $-x, 1-y, -2-z$.

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The H atoms of the coordinated water molecules were located geometrically and refined with O—H distances restrained to 0.98 (1) Å and H···H distances restrained to 1.60 (3) Å. The isotropic displacement parameters of all the H atoms were fixed at 1.5 times U_{eq} of the parent O atom. The four water molecules of crystallization are disordered over five positions and were refined isotropically, with equivalent displacement parameters. The largest difference peak is 0.99 Å from the disordered water molecule O4W and the deepest hole is 1.07 Å from the water molecule O1M, coordinated to the Er atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1998); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1998); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXL*97.

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