metal-organic papers

Poly[dimethylammonium aquadi-*μ*-oxalato-europate(III) trihydrate]

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In the crystal structure of the polymeric title compound, $(C_2H_8N)[Eu(C_2O_4)_2(H_2O)]\cdot 3H_2O$, the independent oxalate that lies on a general position chelates to two Eu atoms, as do the other two oxalates that lie on different centres of inversion, the bridging mode of the oxalates giving rise to a three-dimensional anionic network. The water-coordinated Eu atom exists in a tricapped trigonal–prismatic geometry. The cations and solvent water molecules occupy the cavities of the network and are involved in hydrogen bonding with each other and with the network.

Comment

Some rare earth/monovalent-cation oxalates contain water, and compounds formulated as $[M][(C_2O_4)_2Ln]\cdot nH_2O$ have been studied in order to understand the nature of the water molecules, as water is crucial to their applications. Such double oxalates have been structurally authenticated by both single-crystal and powder-diffraction methods; the ammonium derivative is a monohydrate, and the water molecule is involved in coordination to the Y atom in $[NH_4][(C_2O_4)_2(H_2O)Y]$ (McDonald & Spink, 1967). The nine-coordinate metal atom displays capped trigonal–prismatic coordination. The caesium analogue also has the rare earth atom in such a geometry (Bataille *et al.*, 2000), as does the trihydrated sodium salt (Bataille & Louër, 1999). Another aquadioxalatoyttrate, a propyl-1,2-diammonium salt, has two solvent water molecules that interact with the cation (Vaidhyanathan *et al.*, 2001). Double salts with other nine-coordinate water-coordinated rare earths include the erbium (Steinfink & Brunton, 1970), lanthanum (Fourcade-Cavillou & Trombe, 2002), neodymium (Fourcade-Cavillou & Trombe, 2002; Kahwa *et al.*, 1984), samarium, europium, gadolinium and terbium (Kahwa *et al.*, 1984) complexes.

(I)
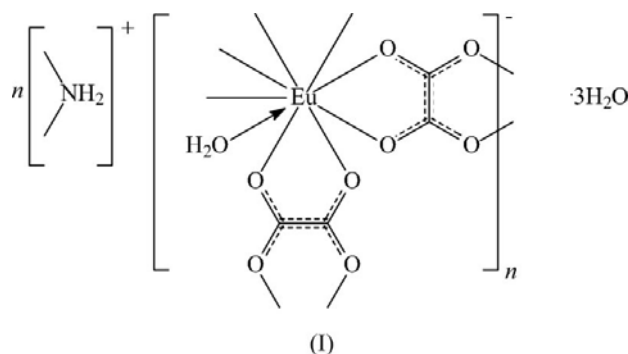
The title dimethylammonium aquadioxalatoeuropate(III) exists as the trihydrate, (I) (Fig. 1). The Eu atom is surrounded
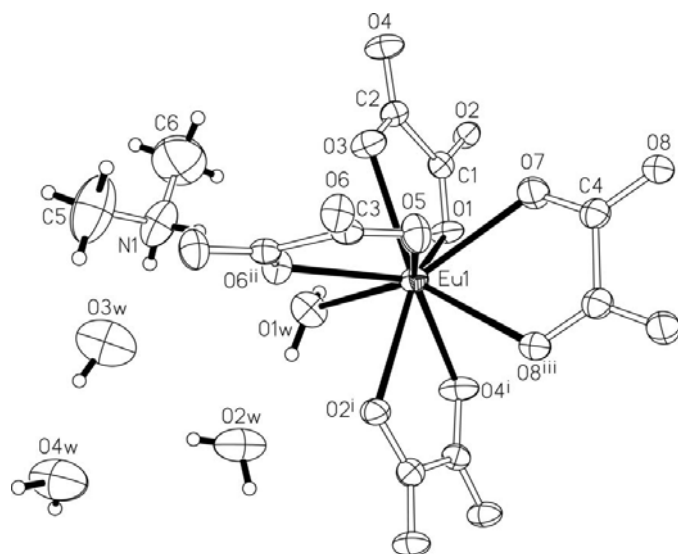
Figure 1
A view of a portion of the three-dimensional structure, showing the geometry of the Eu atom in polymeric (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{3}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $2 - x$, $1 - y$, $1 - z$.]

by the eight atoms of four oxalates and the water molecule in a capped trigonal–prismatic environment (Fig. 2). The cations and solvent water molecules interact with each other along the channels of the polymeric anion (Fig. 3); extensive hydrogen bonds (Table 2) give rise to a tightly held network structure that has no solvent-accessible cavities.

Experimental

A mixture of dieuropium trioxalate x-hydrate (0.012 g, 0.02 mmol), 1,3,5-benzenetricarboxylic acid (0.011 g, 0.05 mmol) and water (4 ml) was heated to 333 K, and to this mixture was added di-n-propyl-ethylamine (0.04 g, 0.05 mmol). The solution was placed in a Teflon-lined Parr bomb, which was heated to 453 K for 48 h. It was cooled at a rate of 5 K h^{-1} to 333 K to yield colourless crystals of (I). As benzenetricarboxylic acid was not incorporated in the product, the reaction is essentially one between dieuropium trioxalate and dipropylethylamine; the dimethylammonium cation in the product probably results from the decomposition of dipropylethylamine.

Crystal data

(C₂H₈N)[Eu(C₂O₄)₂(H₂O)]·3H₂O
$M_r = 446.16$
Monoclinic, $P2_1/n$
$a = 9.674 (1)$ Å
$b = 11.761 (1)$ Å
$c = 12.315 (2)$ Å
$\beta = 99.285 (2)°$
$V = 1382.8 (3)$ Å³
$Z = 4$

$D_x = 2.143$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 885 reflections
$\theta = 2.4–27.2°$
$\mu = 4.60$ mm^{-1}
$T = 295 (2)$ K
Block, colourless
$0.06 \times 0.05 \times 0.05$ mm

Data collection

Bruker SMART 1000 area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.702$, $T_{max} = 0.803$
8455 measured reflections

3113 independent reflections
2578 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 7$
$k = -15 \rightarrow 14$
$l = -15 \rightarrow 15$
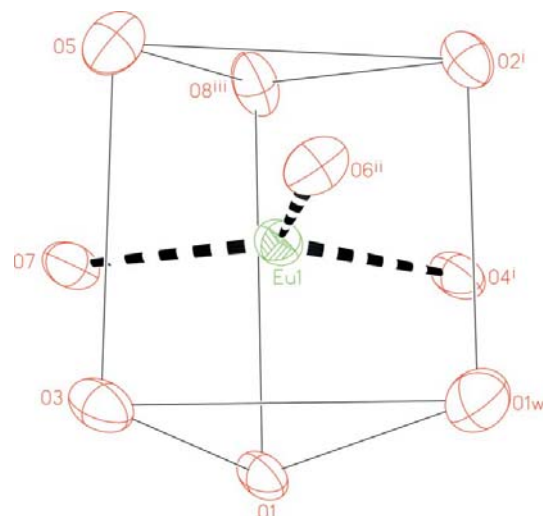
Figure 2
The trigonal–prismatic geometry of the Eu atom in (I). (Symmetry codes as in Fig. 1.)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 0.99$
3113 reflections
212 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Eu1—O1	2.412 (2)	Eu1—O6^{ii}	2.465 (3)
Eu1—O2^{i}	2.430 (2)	Eu1—O7	2.471 (3)
Eu1—O3	2.476 (2)	Eu1—O8^{iii}	2.492 (3)
Eu1—O4^{i}	2.469 (2)	Eu1—O1w	2.505 (3)
Eu1—O5	2.430 (3)		
O1—Eu1—O2^{i}	136.0 (1)	O3—Eu1—O7	73.5 (1)
O1—Eu1—O3	66.4 (1)	O3—Eu1—O8^{iii}	136.0 (1)
O1—Eu1—O4^{i}	72.7 (1)	O3—Eu1—O1w	82.2 (1)
O1—Eu1—O5	138.9 (1)	O4^{i}—Eu1—O5	138.7 (1)
O1—Eu1—O6^{ii}	123.9 (1)	O4^{i}—Eu1—O6^{ii}	125.4 (1)
O1—Eu1—O7	71.5 (1)	O4^{i}—Eu1—O7	104.7 (1)
O1—Eu1—O8^{iii}	111.5 (1)	O4^{i}—Eu1—O8^{iii}	70.3 (1)
O1—Eu1—O1w	71.2 (1)	O4^{i}—Eu1—O1w	73.9 (1)
O2^{i}—Eu1—O3	144.2 (1)	O5—Eu1—O6^{ii}	65.9 (1)
O2^{i}—Eu1—O4^{i}	66.5 (1)	O5—Eu1—O7	74.1 (1)
O2^{i}—Eu1—O5	84.7 (1)	O5—Eu1—O8^{iii}	72.3 (1)
O2^{i}—Eu1—O6^{ii}	71.7 (1)	O5—Eu1—O1w	132.7 (1)
O2^{i}—Eu1—O7	134.1 (1)	O6^{ii}—Eu1—O7	129.7 (1)
O2^{i}—Eu1—O8^{iii}	69.7 (1)	O6^{ii}—Eu1—O8^{iii}	124.5 (1)
O2^{i}—Eu1—O1w	82.0 (1)	O6^{ii}—Eu1—O1w	66.8 (1)
O3—Eu1—O4^{i}	137.5 (1)	O7—Eu1—O8^{iii}	65.2 (1)
O3—Eu1—O5	82.7 (1)	O7—Eu1—O1w	141.2 (1)
O3—Eu1—O6^{ii}	72.5 (1)	O8^{iii}—Eu1—O1w	140.9 (1)

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

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1w-H1w1\cdots O2w$	0.85 (1)	1.92 (1)	2.759 (5)	169 (4)
$O1w-H1w2\cdots O2w^{iv}$	0.85 (1)	2.05 (2)	2.862 (5)	162 (4)
$O2w-H2w2\cdots O7^{i}$	0.85 (1)	2.30 (2)	3.071 (5)	151 (4)
$O2w-H2w2\cdots O8^{i}$	0.85 (1)	2.37 (4)	3.011 (4)	133 (5)
$O3w-H3w1\cdots O4^{v}$	0.85 (1)	2.02 (2)	2.838 (5)	162 (7)
$O3w-H3w2\cdots O4w$	0.84 (1)	2.00 (3)	2.770 (6)	151 (5)
$O4w-H4w1\cdots O2^{iv}$	0.85 (1)	2.08 (2)	2.893 (4)	159 (5)
$O4w-H4w2\cdots O3^{vi}$	0.85 (1)	2.12 (1)	2.962 (5)	173 (5)
$N1-H1n1\cdots O3w$	0.85 (1)	1.96 (1)	2.792 (6)	167 (4)
$N1-H1n2\cdots O6^{ii}$	0.85 (1)	2.05 (2)	2.879 (5)	165 (5)

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

The C-bound H atoms were placed in calculated positions, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, and were included in the refinement in the riding-model approximation. Water and ammonium H atoms were located in difference Fourier maps, and were refined with distance restraints of O—H = N—H = 0.85 (1) Å and H···H = 1.39 (1) Å and with $U_{iso}(H) = 1.2U_{eq}(O,N)$. The short H1w2···H2w1 distance of 2.08 Å is probably a consequence of some disorder in atom O2w, but the disorder could not be resolved. The largest peak in the final difference Fourier map of 1.08 e Å^{-3} was about 1 Å from Eu1.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.
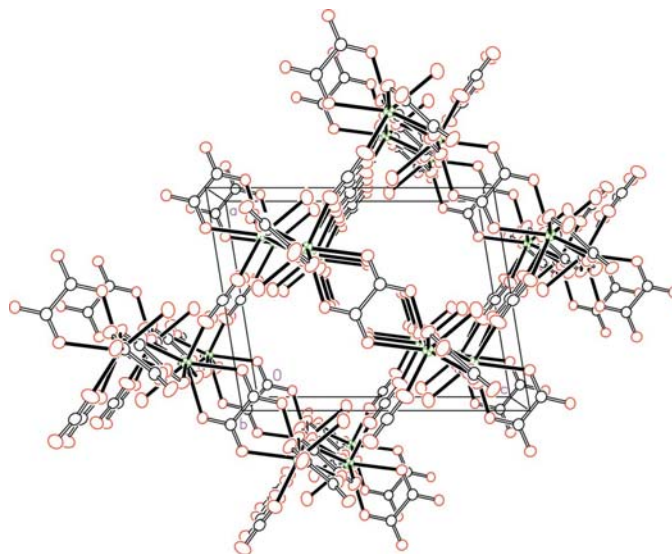
Figure 3
A view of the polymeric $[(C_2O_4)_2(H_2O)Eu]$ network in (I). H atoms have been omitted.

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