

# Poly[dimethylammonium aquadi- $\mu$ -oxalatoeuropate(III) trihydrate]

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### Key indicators

Single-crystal X-ray study  
 T = 295 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
 R factor = 0.026  
 wR factor = 0.062  
 Data-to-parameter ratio = 14.7

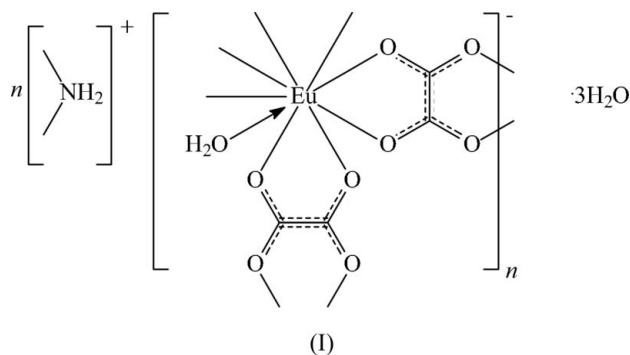
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the polymeric title compound,  $(\text{C}_2\text{H}_8\text{N})[\text{Eu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ , 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.

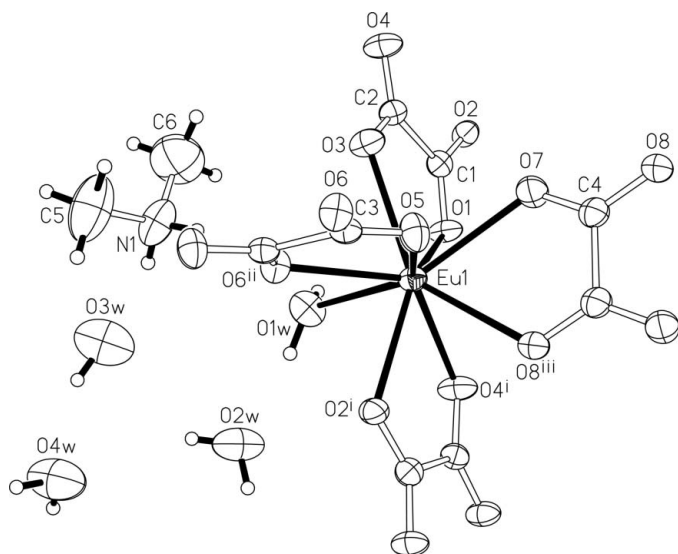
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### Comment

Some rare earth/monovalent-cation oxalates contain water, and compounds formulated as  $[M][(\text{C}_2\text{O}_4)_2\text{Ln}]\cdot n\text{H}_2\text{O}$  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  $[\text{NH}_4][(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})\text{Y}]$  (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.



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*-propylethylamine (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<sup>-1</sup> 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

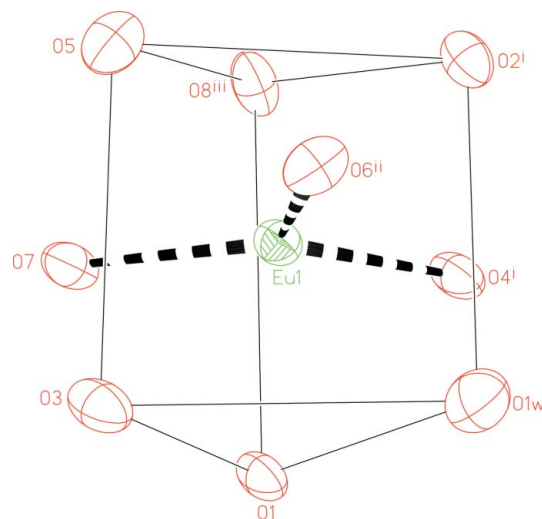
(C<sub>2</sub>H<sub>8</sub>N)[Eu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)]·3H<sub>2</sub>O  
*M<sub>r</sub>* = 446.16  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 9.674 (1) Å  
*b* = 11.761 (1) Å  
*c* = 12.315 (2) Å  
 $\beta$  = 99.285 (2)°  
*V* = 1382.8 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.143 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 885 reflections  
 $\theta$  = 2.4–27.2°  
 $\mu$  = 4.60 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Block, colourless  
 0.06 × 0.05 × 0.05 mm

### Data collection

Bruker SMART 1000 area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.702, *T<sub>max</sub>* = 0.803  
 8455 measured reflections

3113 independent reflections  
 2578 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.026  
 $\theta_{\max}$  = 27.5°  
*h* = -12 → 7  
*k* = -15 → 14  
*l* = -15 → 15

**Figure 2**

The trigonal-prismatic geometry of the Eu atom in (I). (Symmetry codes as in Fig. 1.)

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.026  
*wR* (*F*<sup>2</sup>) = 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.07 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

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

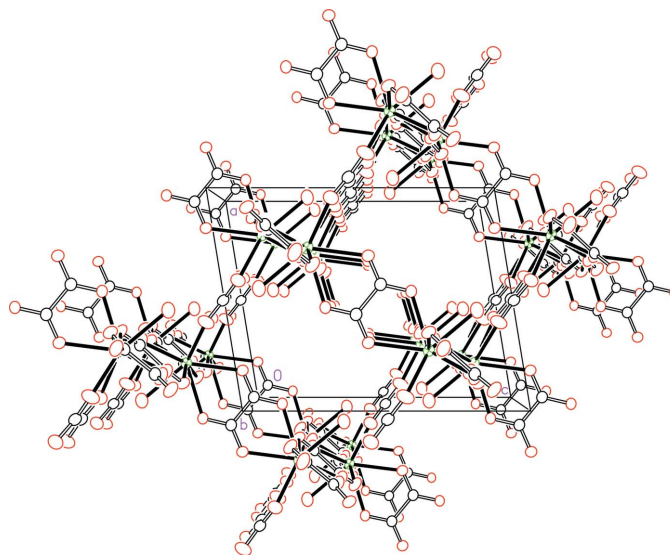
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1 <sub>w</sub> —H1 <sub>w</sub> 1···O2 <sub>w</sub>	0.85 (1)	1.92 (1)	2.759 (5)	169 (4)
O1 <sub>w</sub> —H1 <sub>w</sub> 2···O2 <sub>w</sub> <sup>iv</sup>	0.85 (1)	2.05 (2)	2.862 (5)	162 (4)
O2 <sub>w</sub> —H2 <sub>w</sub> 2···O7 <sup>i</sup>	0.85 (1)	2.30 (2)	3.071 (5)	151 (4)
O2 <sub>w</sub> —H2 <sub>w</sub> 2···O8 <sup>i</sup>	0.85 (1)	2.37 (4)	3.011 (4)	133 (5)
O3 <sub>w</sub> —H3 <sub>w</sub> 1···O4 <sup>v</sup>	0.85 (1)	2.02 (2)	2.838 (5)	162 (7)
O3 <sub>w</sub> —H3 <sub>w</sub> 2···O4 <sub>w</sub>	0.84 (1)	2.00 (3)	2.770 (6)	151 (5)
O4 <sub>w</sub> —H4 <sub>w</sub> 1···O2 <sup>iv</sup>	0.85 (1)	2.08 (2)	2.893 (4)	159 (5)
O4 <sub>w</sub> —H4 <sub>w</sub> 2···O3 <sup>vi</sup>	0.85 (1)	2.12 (1)	2.962 (5)	173 (5)
N1—H1 <sub>n</sub> 1···O3 <sub>w</sub>	0.85 (1)	1.96 (1)	2.792 (6)	167 (4)
N1—H1 <sub>n</sub> 2···O6 <sup>ii</sup>	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  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , 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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O,N})$ . The short H1<sub>w</sub>2···H2<sub>w</sub>1 distance of 2.08 Å is probably a consequence of some disorder in atom O2<sub>w</sub>, but the disorder could not be resolved. The largest peak in the final difference Fourier map of 1.08 e Å<sup>-3</sup> was about 1 Å from Eu1.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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*.

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**Figure 3**  
A view of the polymeric [(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)Eu] network in (I). H atoms have been omitted.

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