

# The first structural characterization of a rare earth ethanesulfonate

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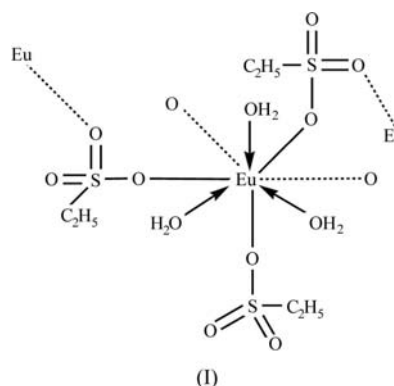
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The crystal structure of *catena*-poly[[triaquabis(ethanesulfonato- $\kappa$ O)europium(III)]- $\mu$ -ethanesulfonato- $\kappa^2$ O':O'], [Eu(C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>3</sub>·(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>, is the first reported determination of a rare earth ethanesulfonate and also of any hydrated binary metal ethanesulfonate. Two of the three ethanesulfonate anions act as bidentate bridging ligands and connect the single [Eu·(C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>3</sub>·(H<sub>2</sub>O)<sub>3</sub>] building blocks into infinite chains along the [010] direction. Hydrogen bonds between the water molecules of one chain and sulfonate anions and water molecules of adjacent chains associate the chains into a two-dimensional supramolecular network. In the third direction, only van der Waals forces between the alkyl groups are observed.

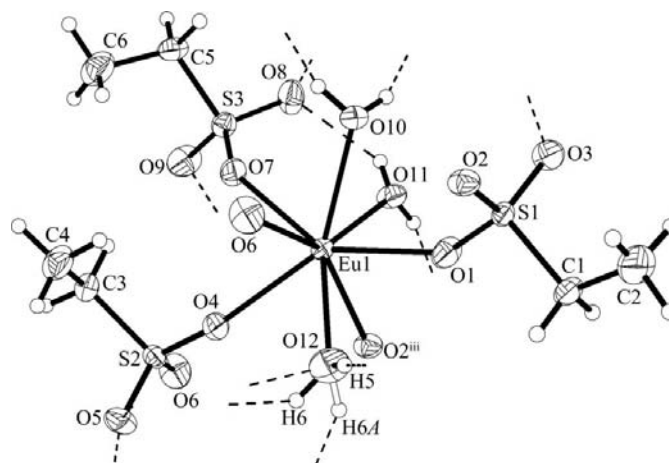
## Comment

Since the beginning of the 20th century, some alkanesulfonates of the rare earth elements, such as samarium and neodymium methane-, ethane-, propane- and isobutane-sulfonate, have been known and characterized by elemental analysis (James *et al.*, 1912). Crystal structure analyses have only, thus far, been performed on methanesulfonates of the lanthanoids and their hydrates (Arico *et al.*, 1997, 2001; Wickleder, 2001, 2002; Wickleder & Müller, 2004). The first crystallographically characterized rare earth ethanesulfonate is presented here. *catena*-Poly[[triaquabis(ethanesulfonato- $\kappa$ O)europium(III)]- $\mu$ -ethanesulfonato- $\kappa^2$ O':O'], (I), was obtained from a solution of europium(III) oxide and ethanesulfonic acid in water after slow evaporation of the solvent at room temperature. After recrystallization of the raw product from a mixture of water and selected alcohols, thin colourless needles suitable for single-crystal diffraction experiments were isolated. The title compound crystallizes in the monoclinic space group *I2/a* and in the chosen asymmetric unit the central Eu atom is surrounded by three sulfonate anions and three water molecules, all in general positions. The primary coordination is completed by two additional O atoms from two further ethanesulfonate anions (Fig. 1). In total, the Eu atom is eightfold coordinated by O atoms. The coordination

polyhedron is a bicapped trigonal prism. The Eu—O distances are in the range 2.354 (2)–2.454 (3) Å. The bond lengths and angles of the sulfonate groups are as expected, with S—O distances of 1.449 (3)–1.479 (2) Å, S—C distances of 1.760 (3)–1.773 (3) Å and C—C distances of 1.513 (5)–1.515 (5) Å.



The ethanesulfonate anions containing atoms S1 and S2 operate as bidentate ligands; they link the metal atoms in a  $\mu$ - $\kappa$ O: $\kappa$ O' mode and thus connect the building blocks into infinite chains along [010] (Fig. 2). In contrast, the anion containing atom S3 only acts as a monodentate ligand. Some  $\mu$ - $\kappa$ O: $\kappa$ O'-bridging ethanesulfonate ligands are also found in dinuclear chloride-sulfonate-antimony(V) complexes (Burchardt *et al.*, 1998; Lang *et al.*, 1998) and in polymeric chains of the dioxouranium(VI) complex [(UO<sub>2</sub>)(H<sub>2</sub>O)(C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>2</sub>] (Alcock *et al.*, 1993) and the ethanesulfonate-hydrogen-methanephosphonate-diorganyltin(IV) compound [(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>-Sn{OP(O)(OH)CH<sub>3</sub>}OS(O)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>] (Shankar *et al.*, 2006). In contrast to this bridging mode, the ethanesulfonate group in the polymeric chain structure of [Cu(CO)C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub>] is  $1\kappa$ O: $2\kappa$ O', $\kappa$ O''-bridging (Doyle *et al.*, 1983).



**Figure 1**  
The coordination environment about the Eu atom in (I); displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn with an arbitrary radius. The disorder of one H atom at O12 is indicated by the use of solid and open bond types. Dashed lines indicate hydrogen bonds. [Symmetry codes: (ii) *x*, *y* + 1, *z*; (iii) *x*, *y* − 1, *z*.]

The structural assembly of (I) in the solid state is determined by a hierarchical system of supramolecular interactions with a pronounced gradation in bond strength with respect to each of the three dimensions. Firstly, strong Eu—O bonds are responsible for the formation of a one-dimensional chain structure. Secondly, hydrogen bonding occurs between water molecules of one chain and sulfonate anions and water molecules of adjacent chains (Table 1), and thus provides an association of the one-dimensional supramolecular system in a second direction, resulting in a layered assembly of chains. Atoms H3 and H4 take part in hydrogen bonding to O atoms of the same chain exclusively. Although the bond strengths can be classified as only weak to medium, proved by the O...O distances of 2.774 (3)–3.302 (4) Å, the contribution of hydrogen bonding to the composition of the solid is essential. In the third direction, van der Waals forces between ethyl

groups are the only interactions of note. Fig. 3 shows the connection of the chains in the solid-state packing.

## Experimental

A sample of  $\text{Eu}_2\text{O}_3$  (0.354 g, 1 mmol) was suspended in water (10 ml), and ethanesulfonic acid (0.5 ml, 6 mmol) was added carefully to avoid uncontrolled local heating. The mixture was heated slowly to ca 343 K and stirred until dissolution of the rare earth oxide after a few minutes. Colourless needles of (I) were obtained by evaporation of the solvent at room temperature. To isolate crystals suitable for X-ray structure and single-crystal attenuated total reflection IR analyses, recrystallization of the raw product from a mixture composed of ca 4 ml of water, 4 ml of methanol, 1 ml of ethanol and a few drops of glycerol proved to be necessary. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3387 (*m, br*), 2980 (*m, sh*), 2943 (*m, sh*), 2884 (*w, sh*), 1716 (*w, br*), 1660 (*w*), 1618 (*w, sh*), 1458 (*w*), 1429 (*w, sh*), 1421 (*w*), 1302 (*w*), 1254 (*m*), 1200 (*m, sh*), 1139 (*vs*), 1073 (*s, sh*), 1052 (*s, sh*), 1038 (*vs*), 983 (*m, sh*), 787 (*w*), 746 (*m*), 575 (*m*). CHN analyses (533.41) found: C 13.60, H 3.95%; calculated: C 13.51, H 3.97%.

## Crystal data

$[\text{Eu}(\text{C}_2\text{H}_5\text{SO}_3)_3(\text{H}_2\text{O})_3]$   
 $M_r = 533.41$   
 Monoclinic,  $I2/a$   
 $a = 24.323$  (2) Å  
 $b = 5.4408$  (4) Å  
 $c = 27.066$  (2) Å  
 $\beta = 111.328$  (9)°

$V = 3336.5$  (5) Å<sup>3</sup>  
 $Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.19$  mm<sup>-1</sup>  
 $T = 233$  (2) K  
 $0.57 \times 0.10 \times 0.10$  mm

## Data collection

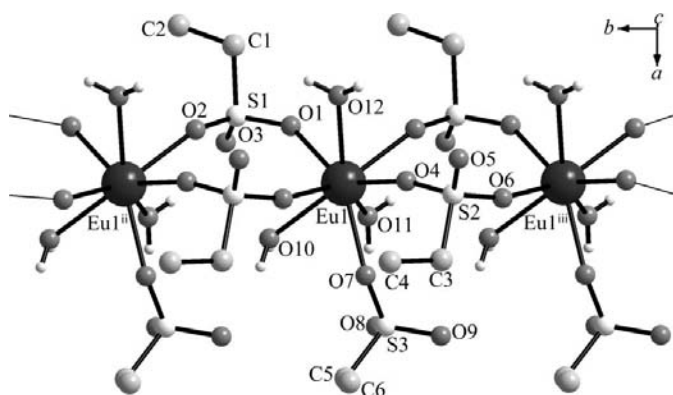
Stoe IPDS diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.578$ ,  $T_{\max} = 0.672$

22872 measured reflections  
 3282 independent reflections  
 2788 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.085$

## Refinement

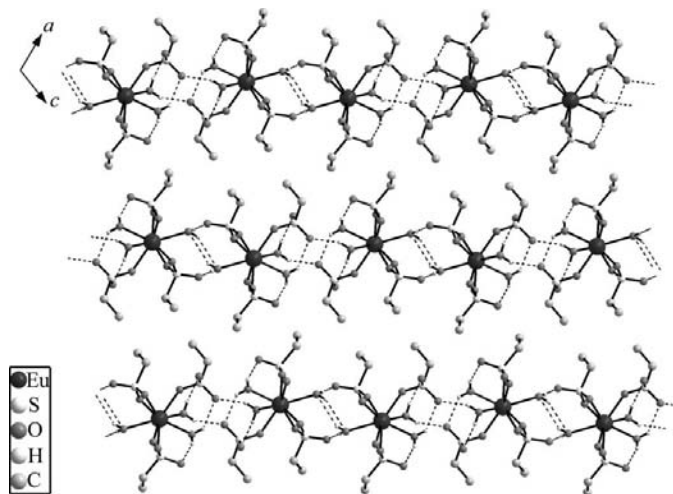
$R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.050$   
 $S = 1.22$   
 3282 reflections  
 216 parameters

3 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.16$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.19$  e Å<sup>-3</sup>



**Figure 2**

Ethanesulfonate anions connect  $[\text{Eu}(\text{C}_2\text{H}_5\text{SO}_3)_3(\text{H}_2\text{O})_3]$  units into chains in the [010] direction. Only one of the disordered H atoms is shown. Thin lines indicate extension bonds. H atoms of the alkyl groups have been omitted for clarity. [Symmetry codes: (ii)  $x, y + 1, z$ ; (iii)  $x, y - 1, z$ .]



**Figure 3**

The packing of (I). Hydrogen bonds and van der Waals interactions associate the chains into a supramolecular network. Dashed lines indicate hydrogen bonds. Only one of the disordered H atoms is shown. H atoms of the alkyl groups have been omitted for clarity.

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O10}-\text{H1}\cdots\text{O8}^{\text{i}}$	0.83	2.00	2.774 (3)	156
$\text{O10}-\text{H2}\cdots\text{O9}^{\text{ii}}$	0.83	2.10	2.894 (3)	159
$\text{O11}-\text{H3}\cdots\text{O8}$	0.83	2.12	2.804 (3)	139
$\text{O11}-\text{H4}\cdots\text{O3}^{\text{iii}}$	0.83	2.04	2.818 (3)	155
$\text{O12}-\text{H5}\cdots\text{O5}^{\text{iv}}$	0.83	1.96	2.787 (4)	178
$\text{O12}-\text{H6}\cdots\text{O12}^{\text{v}}$	0.83	2.53	3.092 (4)	126
$\text{O12}-\text{H6A}\cdots\text{O5}^{\text{v}}$	0.83	2.58	3.302 (4)	146

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

As the difference between the atomic displacement parameters of Eu1 and O11 along the corresponding bond direction was somewhat too high, one 'rigid bond' restraint was applied. All H-atom positions of the water molecules, including the partial occupancy positions H6 and H6A (Fig. 1), could be located in difference Fourier maps. The water molecules were treated as rigid groups with idealized geometry but with freedom of rotation and translation. The  $U_{\text{iso}}(\text{H})$  values were

refined, except for those of H5, H6 and H6A, for which the  $U_{\text{iso}}(\text{H})$  values were fixed at  $1.5U_{\text{eq}}$  of the parent atom O12. As the partial occupancy positions of the disordered atoms H6 and H6A were not stable during refinement, their principal orientation found in the difference map was stabilized by restraining the intermolecular distances between H6 and H6A<sup>v</sup> and between H6A and H6<sup>v</sup> [symmetry code: (v)  $-x + \frac{1}{2}, y, -z$ ] to 2.70 Å, with a standard uncertainty of 0.01 Å. The H atoms of the CH<sub>2</sub> groups were treated as riding on their C atoms with idealized bond lengths and angles. Those of the CH<sub>3</sub> groups were allowed to ride on the C atoms likewise, but were additionally free to rotate about the C–C bond. The  $U_{\text{iso}}(\text{H})$  values of the CH<sub>2</sub> groups were fixed at  $1.2U_{\text{eq}}$  of the respective parent C atom, whereas the  $U_{\text{iso}}(\text{H})$  values of the CH<sub>3</sub> groups were fixed at  $1.5U_{\text{eq}}(\text{C})$ . Three significant electron-density maxima ( $1.16 \text{ e } \text{\AA}^{-3}$  at 0.90 Å,  $1.04 \text{ e } \text{\AA}^{-3}$  at 0.93 Å and  $1.04 \text{ e } \text{\AA}^{-3}$  at 0.90 Å from Eu1) were found in the final difference Fourier map.

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97* and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3175). Services for accessing these data are described at the back of the journal.

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