

Poly[hexaquaocta- μ_3 -hydroxido-tetrakis(μ_3 -methylenedisulfonato)- μ_6 -oxido-hexaytterbium(III)]: the first lanthanide sulfonate containing a hexanuclear Ln–hydroxide/oxide cluster synthesized *via* ‘ligand-controlled acidolysis’ of lanthanide oxide

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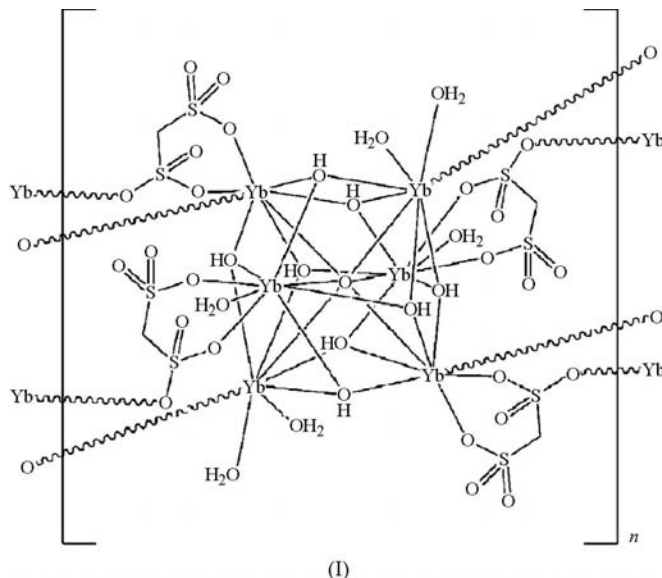
The combination of redox and acid sites in lanthanide sulfonate leads to a potentially multifunctional catalyst for oxidation reactions. The title lanthanide sulfonate compound, $[\text{Yb}_6(\text{CH}_2\text{O}_6\text{S}_2)_4\text{O}(\text{OH})_8(\text{H}_2\text{O})_6]_n$, exhibits a novel one-dimensional columnar structure along the *a* direction. In the building unit of the columnar oligomer, a face-capped lanthanide octahedron, *viz.* $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$, is found with an interstitial μ_6 -oxide group lying on an inversion centre, reports of which are rare in the literature. Adjacent hexameric cations are connected *via* two pairs of O–S–O bridges, thus forming a neutral column. The three-dimensional network is stabilized by an intricate pattern of intercolumnar hydrogen bonds.

Comment

Polynuclear metal–hydroxide/oxide complexes are of interest not only because of their promising application as advanced materials with noteworthy spectroscopic, magnetic and catalytic properties (Zheng, 2004), but also because of their potential biological relevance. It is known that Ln–hydroxide/oxide (Ln = lanthanide) clusters are capable of catalysing the hydrolytic cleavage of phosphate diester bonds (Straeter *et al.*, 1996) and the robust bonds of nucleic acids (Oh *et al.*, 1996).

Simple hydrolysis of lanthanide ions often leads to unpredictable, serendipitous and ill-defined lanthanide hydroxides and oxide/hydroxides as a result of the inherent properties of the lanthanide cations (Cotton, 1991). Because of the high charge and polarizing power of the lanthanide ions,

there is a strong tendency for them to hydrolyse readily in aqueous solutions. Furthermore, trivalent rare earth ions show large and variable coordination numbers and geometries with small energy differences (Bünzli, 1997). Thus, it is generally difficult to control the oligomerization of rare earth centres. Chelating ligands such as amino acids, ketonates, carboxylates and alkoxides are introduced to control the hydrolysis of the lanthanide ions and selectively incorporate them into highly organized cluster architectures (Wang *et al.*, 1999, 2001, 2002; Ma *et al.*, 2000; Plakatouras *et al.*, 1994; Chen *et al.*, 1997; Evans *et al.*, 1998; Anwender *et al.*, 1997).



Due to the weak coordination strength of monosulfonate ions, the coordination chemistry of the sulfonate ion has been less well investigated in comparison with other organic acidate anions such as carbonates and phosphonates (Côté & Shimizu, 2003). However, by employing disulfonates, which can provide multiple potentially chelating coordination sites, stable architectures sustained by sulfonate–metal interactions can be obtained with various dimensionalities (Cai, 2004; Li *et al.*, 2008; Mi *et al.*, 2007; Videnova-Adrabinska, 2007). This integration into complexes of rare earth sulfonates could produce a multifunctional catalyst, especially for oxidation reactions, considering the strong catalytic activity of the rare earth elements and the relatively strong acidic character of sulfonate groups (Snejko *et al.*, 2002; Gándara *et al.*, 2007). Nevertheless, to the best of my knowledge, reports of sulfonate-supported lanthanide cluster architectures are rare in the literature. As an extension of these studies, I herein report the unique synthesis and structure of a hexanuclear Ln–hydroxide/oxide cluster supported by methylenedisulfonate (mds), $[\text{Yb}_6(\text{mds})_4\text{O}(\text{OH})_8(\text{H}_2\text{O})_6]_n$, (I). As relatively strong acids, sulfonates could accordingly react easily with metal oxides. Hence, instead of hydrolysis of the lanthanide ion with assistance of the ligand, hydrothermal reaction of mdsH_2 and Yb_2O_3 at a proper ratio results in acidolysis products, yielding colourless prism-like crystals of compound (I).

X-ray structure analysis reveals that (I) is composed of an unusual hexanuclear $[\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_6]^{8+}$ cation

and mds anions (Fig. 1). The hexameric cation is based on a slightly distorted Yb_6 octahedron, which is sustained by a μ_6 -oxide ligand, O1, lying on an inversion centre. Each Yb_3 triangular face is further capped by a μ_3 -hydroxide ligand. All bond lengths are comparable with those in $\{[(\text{DMF})_{16}\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\mu\text{-CN})\text{Pd}(\mu\text{-CN})(\text{CN})_2]^{6+}\}_n$ (DMF = is dimethylformamide) which is a cyanide-bridged chain polymer, with a similar hexametal core [Yb—O (interstitial O atom): 2.413 (1)–2.450 (1) Å; Yb—O (hydroxide O atom): 2.270 (7)–2.405 (7) Å; Liu *et al.*, 1998]. The Yb^{3+} cations in the asymmetric unit of (I) (Yb1, Yb2 and Yb3 in Fig. 1) are eight-coordinate. In addition to one interstitial and four hydroxide O atoms, Yb1 and Yb2 are each chelated by an mds ligand using two sulfonate O atoms, and the remaining eighth coordination positions are occupied by a water O atom (O18) and a sulfonate O atom [O7ⁱⁱ; symmetry code: (ii) $1 + x, y, z$],

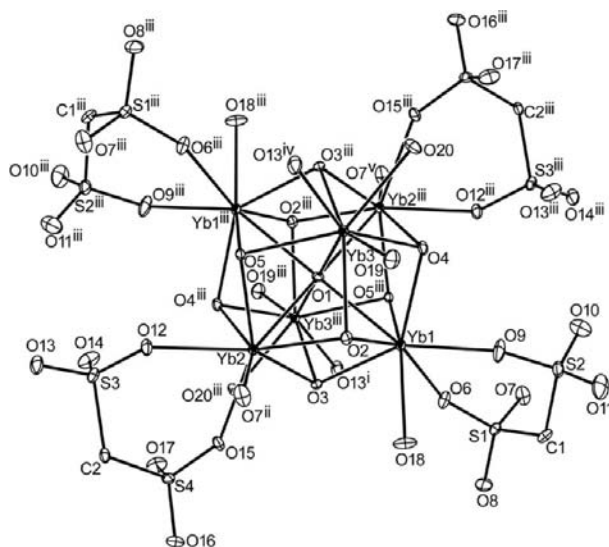


Figure 1
The building unit of compound (I), showing the atomic labelling scheme (30% probability displacement ellipsoids). All H atoms have been omitted for clarity. [Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, 1 - z$; (v) $-x, 1 - y, 1 - z$.]

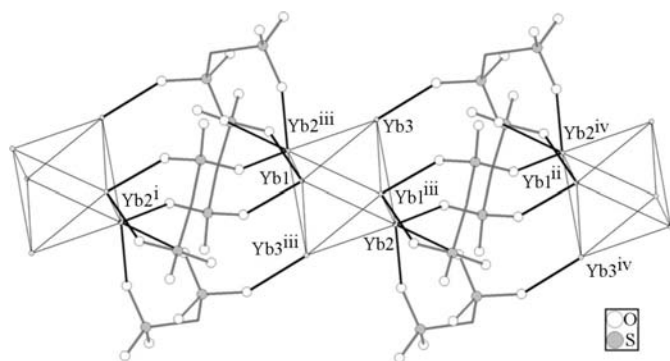


Figure 2
A chain consisting of bridged rare earth clusters in compound (I). The cluster consists of an octahedron, the six vertices of which represent Yb atoms. H atoms and coordinated O atoms, except for sulfonate O atoms, have been omitted for clarity. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $1 + x, y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, 1 - z$.]

respectively. Yb3 is further surrounded by two coordinated water O atoms (O19 and O20) and one sulfonate O atom [O13^{iv}; symmetry code: (iv) $2 - x, 1 - y, 1 - z$].

Adjacent hexameric cations are bridged *via* two pairs of O—S—O bridges (O6—S1—O7 and O12—S3—O13) from chelating mds ligands, thus generating a novel neutral one-dimensional columnar structure along the *a* direction (Fig. 2). Within the column, four intracolumn hydrogen bonds are found: O4(H)···O14ⁱ, O5(H)···O12^{iv}, O19(H)···O10^{vi} and O20(H)···O17ⁱ [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, 1 - z$; (vi) $1 + x, y, z$; Table 2]. Each column has six equivalent neighbours. The three-dimensional network is stabilized by an intricate intercolumn hydrogen-bond network [O2(H)···O16ⁱⁱ, O3(H)···O11ⁱⁱⁱ, O18(H)···O16ⁱⁱ, O8(H)···O14^v, O19(H)···O8^{vii} and O20(H)···O17^{viii}; symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, 1 - y, 1 - z$; (v) $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (viii) $x, -1 + y, z$; see Table 2].

In summary, compound (I) was directly synthesized *via* ‘ligand-controlled acidolysis’ of lanthanide oxide and demonstrates a novel one-dimensional columnar structure. A face-capped octahedron $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8]^{8+}$ with an interstitial μ_6 -oxide group acts as the building block of the column. Thus, compound (I) is the first lanthanide sulfonate containing a hexanuclear Ln–hydroxide/oxide cluster. The chelating multidentate mds ligand is crucial in the synthesis and formation of compound (I). Because methylenedisulfonic acid is a relatively strong acid, it is possible to synthesize the Ln–hydroxide/oxide cluster *via* acidolysis of lanthanide oxide. In addition, the chelation of mds to the Yb cation stabilizes the hexameric cluster. The three-dimensional network is formed by bridged clusters *via* the coordination of unchelating sulfonate O atoms to Yb cations of neighbouring clusters, and then by intercolumnar hydrogen bonds with sulfonate O atoms acting as acceptors. In this way, a high-dimensional architecture constructed from the Ln–hydroxide/oxide cluster unit is rationally synthesized *via* acidolysis of lanthanide oxide with the co-operation of other chelating multidentate sulfonate ligands. By the introduction of suitable guest moieties into the current system, these high-dimensional framework complexes may potentially become competitive catalysts for oxidation reactions.

Experimental

Compound (I) was prepared by the hydrothermal reaction of a mixture of Yb_2O_3 (2 mmol, 0.78 g), mdsH_2 (3 mmol, 0.46 g) and H_2O (8.0 ml) in a Teflon-lined stainless steel autoclave (25 ml), which was heated at 413 K for 48 h. Prism-like colourless crystals were collected (yield: 16%, based on Yb_2O_3). Analysis found: C 2.35, H 1.43%; calculated for $\text{C}_4\text{H}_{28}\text{O}_{39}\text{S}_8\text{Yb}_6$: C 2.41, H 1.41%.

Crystal data

$[\text{Yb}_6(\text{CH}_2\text{O}_6\text{S}_2)_4\text{O}(\text{OH})_8(\text{H}_2\text{O})_6]$	$V = 1759.17 (6) \text{ \AA}^3$
$M_r = 1994.98$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.7633 (2) \text{ \AA}$	$\mu = 16.39 \text{ mm}^{-1}$
$b = 12.4480 (2) \text{ \AA}$	$T = 296 (2) \text{ K}$
$c = 16.2201 (3) \text{ \AA}$	$0.20 \times 0.15 \times 0.15 \text{ mm}$
$\beta = 96.1580 (10)^\circ$	

Data collection

Bruker SMART APEXII diffractometer	14471 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	3100 independent reflections
$T_{\min} = 0.06$, $T_{\max} = 0.09$	2962 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.075$	
$S = 1.06$	
3100 reflections	$\Delta\rho_{\text{max}} = 0.95 \text{ e } \text{\AA}^{-3}$
289 parameters	$\Delta\rho_{\text{min}} = -1.50 \text{ e } \text{\AA}^{-3}$
13 restraints	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—Yb2	2.4001 (3)	O3—Yb2	2.309 (4)
O1—Yb1	2.4357 (3)	O4—Yb3	2.282 (5)
O1—Yb3	2.4736 (3)	O4—Yb2 ⁱ	2.297 (5)
O2—Yb1	2.276 (4)	O4—Yb1	2.324 (4)
O2—Yb3	2.309 (5)	O5—Yb2	2.272 (4)
O2—Yb2	2.313 (4)	O5—Yb3	2.308 (4)
O3—Yb1	2.254 (4)	O5—Yb1 ⁱ	2.334 (5)
O3—Yb3 ⁱ	2.273 (4)		
Yb2 ⁱ —O1—Yb1	90.266 (9)	Yb1—O1—Yb3	90.589 (9)
Yb2—O1—Yb1	89.734 (9)	Yb2—O1—Yb3 ⁱ	89.287 (9)
Yb2—O1—Yb3	90.713 (9)	Yb1—O1—Yb3 ⁱ	89.411 (9)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O16 ⁱⁱ	0.82 (4)	2.23 (5)	2.923 (7)	143 (7)
O3—H3 \cdots O11 ⁱⁱⁱ	0.82 (5)	2.05 (4)	2.789 (7)	149 (7)
O4—H4 \cdots O14 ⁱ	0.82 (6)	2.55 (5)	3.220 (8)	140 (7)
O5—H5 \cdots O12 ^{iv}	0.82 (4)	2.24 (3)	3.029 (6)	162 (7)
O18—H18A \cdots O16 ⁱⁱ	0.82 (7)	2.03 (7)	2.805 (7)	157 (8)
O18—H18B \cdots O14 ^v	0.82 (5)	2.47 (8)	2.880 (7)	112 (7)
O19—H19A \cdots O10 ^{vi}	0.82 (6)	1.88 (5)	2.682 (8)	166 (7)
O19—H19B \cdots O8 ^{vii}	0.82 (5)	1.95 (3)	2.708 (7)	154 (7)
O20—H20A \cdots O17 ⁱ	0.82 (5)	2.09 (3)	2.877 (7)	159 (8)
O20—H20B \cdots O17 ^{viii}	0.82 (5)	2.18 (4)	2.900 (7)	148 (7)

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

H atoms of methylene groups were positioned geometrically and refined using a riding model. H atoms attached to oxygen were located in a difference Fourier map and refined with distance restraints on O—H bond lengths and restraining all H—O—H angles of water molecules to be similar. The isotropic displacement para-

eters of H atoms are related to the non-H atom to which they are bonded, *viz.* $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$. A rigid bond restraint was used for atoms O9 and Yb1.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3004). Services for accessing these data are described at the back of the journal.

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