(Acetato-κ^2O,O')dihydroxido-ytterbium(III) hemihydrate

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The title compound, $[Yb(C_2H_3O_2)(OH)_2]\cdot0.5H_2O$, was obtained *via* hydrothermal reaction of $Yb(CH_3COO)_3\cdot H_2O$ with NaOH at 443 K. The compound forms two-dimensional layers with six crystallographically independent Yb^{III} atoms. Four of these form YbO_8 coordination polyhedra, while the coordination number of the remaining two Yb^{III} atoms is 7. Five of these coordination polyhedra are interconnected mainly *via* hydroxide groups, as they build a narrow inner layer that extends infinitely within the *ab* plane. The sixth Yb^{III} atom resides outside this inner layer and builds a terminal YbO_8 coordination polyhedron on the layer surface. Its coordination environment comprises four carboxylate O atoms belonging to three different acetate entities, three hydroxide groups and one water molecule. Adjacent layers experience weak interactions *via* hydrogen bonds. The Yb—O distances lie in the range 2.232 (4)–2.613 (5) Å.

Comment

The creation of open frameworks has increased considerably over the last decade due to their widespread potential applications in areas such as electronics (Férey *et al.*, 2007), drug delivery (Horcajada *et al.*, 2008; Vallet-Regi *et al.*, 2007) and catalytic systems (Gándara *et al.*, 2008; Mueller *et al.*, 2008). We recently discussed the structural trends within an extended series of lanthanide bis(hydroxychlorides) [Ln(OH)₂Cl; Zehnder *et al.*, 2010], which represent purely inorganic three-dimensional open frameworks, as they may have potential implications for the long-term isolation and storage of radioactive waste materials. Other purely inorganic three-dimensional networks, assembling to various forms of zeolite structures, have become very useful as molecular sieves (Meier *et al.*, 1996). In more recent years, these purely inorganic three-dimensional extended lattices have evolved into frameworks incorporating organic building units (Li *et al.*, 2007). The replacement of inorganic entities with larger

organic spacer entities has led to a large number of new materials with significantly larger pore sizes and unique properties. These new materials, mainly integrating organic ligand systems into three-dimensional coordination polymers, are known as metal–organic frameworks (MOFs) (Bradshaw *et al.*, 2005; Kawano *et al.*, 2007).

We are currently extending our work from exclusively inorganic lanthanide mixed-ligand compounds to MOF materials, and we therefore consider the acetate ligand as one of the possible organic entities. We were curious to see if we could construct the acetate analogues of the Ln(OH)₂Cl compounds that we investigated recently. We were able to obtain single crystals of (acetato-κ^2O,O')dihydroxidoytterbium(III) hemihydrate, (I), of sufficiently high quality for a single-crystal X-ray structural analysis. Compound (I) is an excellent candidate for demonstrating the feasibility of replacing inorganic ligand systems with organic entities in order to obtain hybrid frameworks. In such frameworks, inorganic ligands and organic entities are part of the resulting coordination environment. Moreover, (I) shows that organic entities with one major coordination site will rather lead to the creation of frameworks with limited dimensionality. As we illustrate here, (I) assembles as a two-dimensional layered framework, in which individual layers interact through hydrogen bonds.

(I)
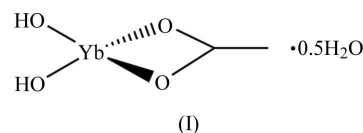
To our knowledge, the single-crystal X-ray structural characterization of a lanthanide bis(hydroxide) acetate is unprecedented. However, a small number of related lanthanide compounds have been under investigation. Sakagami and co-workers discussed the structure of a heteronuclear Cr^{III}–Nd^{III} complex, which incorporates hydroxide and acetate groups in the coordination environment. These researchers point out that compounds such as $[Cr_2Nd_3(\mu\text{-OOCCH}_3)_6(\mu\text{-OH})_6(H_2O)_9]Br_3(NaBr)\cdot8H_2O$ may have unusual electronic and magnetic properties (Sakagami *et al.*, 1997). Another research team reported the synthesis and structural characterization of $CsLu(CH_3COO)_4$ and $Cs_2[Lu_3(CH_3COO)_{10}(OH)(H_2O)]$, and the changes these compounds undergo during thermal decomposition. $Cs_2[Lu_3(CH_3COO)_{10}(OH)(H_2O)]$ assembles to form trimers of Lu centers that are linked by Cs⁺ cations (Lossin & Meyer, 1993). More recently, a group of investigators assessed the structural and magnetic properties of Tb₄ spin clusters incorporating acetate anions and various organic ligands with hydroxide groups that possess chelating as well as linking capacities. The coordination of the acetate entities in these Tb compounds seems to prevent the formation of a three-dimensional linked crystal structure. Therefore, the trimers integrating carboxylate O atoms and OH groups into the coordination environment remain as isolated individual clusters (Bircher *et al.*, 2007).
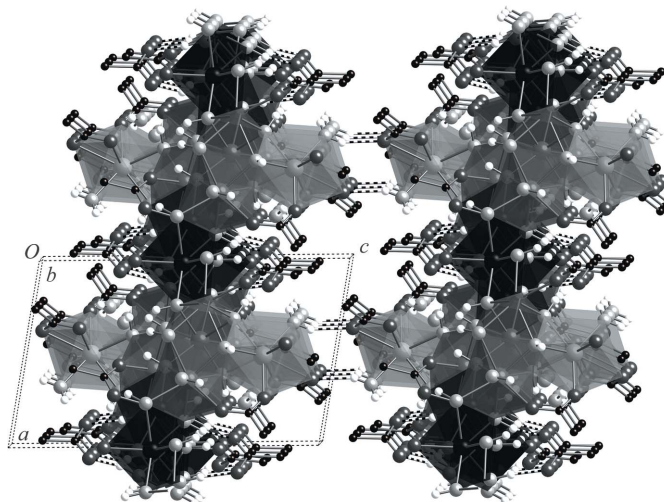
In various other experiments, we extended the organic part of the ligand by exchanging acetate with phenylacetate. We

metal-organic compounds
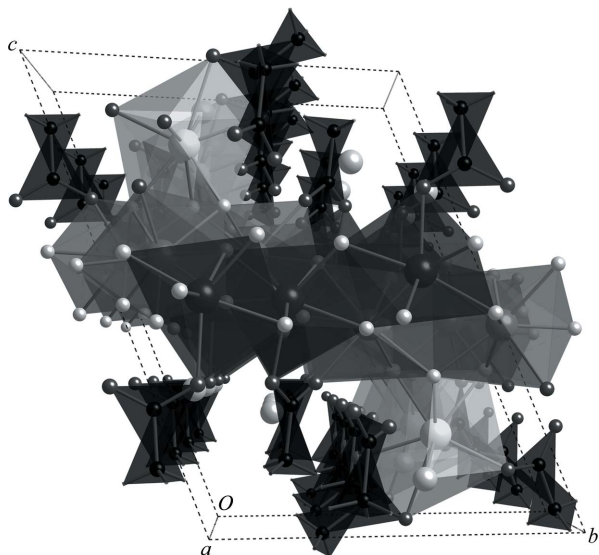
Figure 1
The packing of the YbO_8 and YbO_7 polyhedra in (I), viewed along the a axis, showing interstitial water molecules. Large light-grey spheres denote water molecules, small light-grey spheres hydroxide groups, small dark-grey spheres carboxylate O atoms, grey and light-grey polyhedra $[YbO_8]$ units, dark-grey polyhedra $[YbO_7]$ units, and interlaced black triangles acetate groups.

Figure 2
The highly interlinked two-dimensional layers in (I) that experience weak interactions *via* hydrogen bonds originating from coordinating water molecules. Light-grey spheres denote water and hydroxy O atoms, dark-grey spheres carboxylate O atoms, black spheres C atoms, white spheres H atoms, grey and light-grey polyhedra $[YbO_8]$ units, and dark-grey polyhedra $[YbO_7]$ units. The H atoms bonded to C atoms have been omitted for clarity.

obtained a small number of lanthanide phenylacetates that have been discussed previously (Hasegawa, Ikeuchi *et al.*, 1989; Hasegawa, Morita *et al.*, 1989; Hasegawa *et al.*, 1990). These compounds assemble in one-dimensional channels of lanthanide metal centers that are linked by carboxylate groups and stretch infinitely along the a axis. The bulky hydrophobic parts of the phenylacetate entities are oriented in all directions surrounding the metal–carboxylate channels. In order to obtain an extended structure that is linked *via* strong coordination bonds in three dimensions, it is essential to employ spacer units that contain two or more major coordination sites. This has been established by a number of researchers who have made use of organic entities, *e.g.* terephthalic acid (Daiguebonne *et al.*, 2006, 2008; Haquin *et al.*, 2009; Kerbellec *et al.*, 2009; Long *et al.*, 2001), phthalic acid (Li *et al.*, 2009) and glutaric acid (Serpaggi & Férey, 1998). We recently obtained various MOF materials incorporating these types of organic ligands, which will be discussed elsewhere.

We present here the synthesis and characterization of (I), a lanthanide mixed-ligand complex comprised of inorganic and organic components. Compound (I) crystallizes in the triclinic crystal system (space group $P\bar{1}$) and assembles as a two-dimensional layered framework. Individual layers are composed of highly linked Yb^{III} centers, hydroxide groups and acetate entities that stretch infinitely along the a and b axes. Each layer is segmented into an inner layer that accommodates a dense network of Yb^{III} cations and hydroxide groups, while the outer layer also includes carboxylate groups and water molecules. The layers exhibit six crystallographically independent Yb^{III} atoms as the centers of four eight-coordinate and two seven-coordinate Yb–O polyhedra. Three of the four YbO_8 and the two YbO_7 polyhedra contain Yb^{III} centers that are narrowly interlinked within the inner

layer of the ab plane. The other YbO_8 polyhedra feature the terminal Yb^{III} cations, which stick out from the surface of the outer layer on both sides, pointing towards adjacent layers in the c direction. The Yb^{III} centers of the five coordination polyhedra in the inner layer comprise only hydroxide groups and one carboxylate O atom. The Yb—O bond distances within these five polyhedra vary between 2.232 (4) and 2.418 (4) Å. The corresponding bond distances in the YbO_8 polyhedra of the terminal Yb^{III} cations are somewhat longer and range between 2.257 (4) and 2.613 (5) Å. The coordination polyhedra are interlinked *via* edge-sharing, utilizing two hydroxide groups. Hydroxide groups bind in both μ_3- and μ_2-fashion, connecting to three and two Yb^{III} cations, respectively.

The carboxylate O atoms bind in an exclusively bidentate fashion to the Yb^{III} atoms. Fig. 1 emphasizes the arrangement of the six different coordination polyhedra, in a view along the a axis utilizing different shaded patterns. The acetate anions are arranged with their carboxylate groups oriented towards the Yb^{III} atoms, while their CH_3 groups point towards the adjacent layer in the c direction. Fig. 2 illustrates the layered system of (I) in a view along the b axis, demonstrating that the individual layers interact *via* hydrogen bonding between coordinated water molecules and carboxylate O atoms (Table 1). One can also recognize two different kinds of interstitial water molecules.

Two groups of acetate anions coordinate in a monodentate fashion to two Yb^{III} atoms of the inner layer, with bond distances of Yb4—O8($-x + 2$, $-y + 2$, $-z + 1$) = 2.261 (5) Å and Yb2—O7 = 2.279 (4) Å for one, and Yb3—O9 = 2.265 (5) Å and Yb5—O10 = 2.271 (5) Å for the other. One group of acetate units does not coordinate to any metal center whatsoever. In these cases, both carboxylate O atoms are held
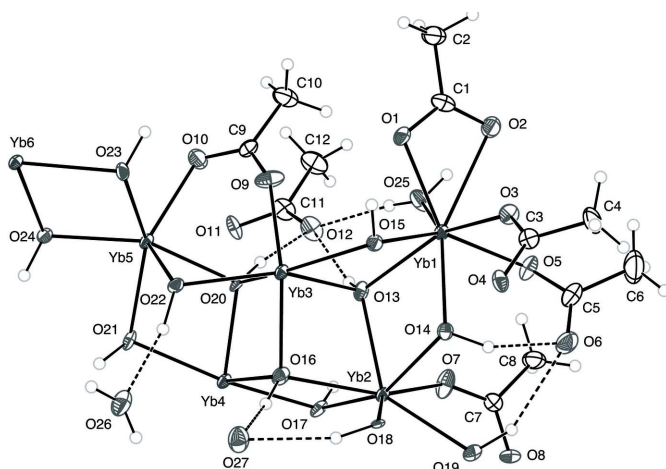
Figure 3
The asymmetric unit in (I), showing the atom-numbering scheme and with displacement ellipsoids drawn at the 80% probability level. H atoms are drawn as circles of arbitrary radius and dashed lines represent hydrogen bonds.

in place *via* hydrogen bonds originating from the hydroxide groups, with hydrogen-bond H···O distances of 1.77 and 1.78 Å. The terminal Yb^{III} atom is linked to one bidentate carboxylate group [Yb1—O1 = 2.333 (4) Å and Yb1—O2 = 2.613 (5) Å] and two different carboxylate groups, of which only one O atom coordinates to the terminal Yb^{III} atom. One of these two carboxylate units possesses an O atom that remains uncoordinated which is the receiver of a hydrogen bond (H···O = 2.29 Å) from one hydroxide group. The Yb1—O5 distance of the coordinated O atom is 2.257 (4) Å. The second O atom of the other carboxylate group coordinates to one of the Yb^{III} atoms within the inner layer, with Yb6—O4(−x + 1, −y + 1, −z + 1) = 2.308 (4) Å. The coordination bond to the external Yb^{III} atom is Yb1—O3 = 2.276 (4) Å.

Thus, the terminal Yb^{III} atoms exhibit the most diverse coordination environments, as their YbO$_8$ polyhedra also accommodate one water molecule. These are the only coordinating water O atoms, with Yb1—O25 = 2.333 (4) Å. One of the water H atoms connects *via* a hydrogen bond (2.00 Å) to one of the carboxylate groups within the adjacent layer that coordinates in a bidentate fashion to a terminal Yb^{III} atom of that layer.

Experimental

Ytterbium acetate hydrate (Acros Organics, 99.90%; 1.0 g, 2.9 mmol) was mixed with 0.19 *M* sodium acetate solution (15.6 ml, 3.0 mmol). The mixture was placed in a Teflon liner inside a Parr acid-digestion vessel (Model 4744; 45 ml). The vessel was sealed and heated to a temperature of 443 K inside a conventional laboratory oven. After two weeks, the vessel was removed from the hot oven and allowed to cool to room temperature on the laboratory bench before opening. A colorless solid material was obtained, submerged in the mother liquor. The mother liquor was decanted and the solid product rinsed four times with deionized water in order to remove any water-soluble starting materials and by-products. Most of the product had formed crystals in the form of long needles. A small amount of the product

was stored in a scintillation vial with a small quantity of deionized water until a single crystal was chosen for X-ray structural analysis.

Crystal data

[Yb(C$_2$H$_3$O$_2$)(OH)$_2$]·0.5H$_2$O	$\gamma = 108.745$ (5)°
$M_r = 275.11$	$V = 1548.9$ (3) Å^3
Triclinic, $P\bar{1}$	$Z = 12$
$a = 9.3235$ (10) Å	Mo $K\alpha$ radiation
$b = 12.1765$ (14) Å	$\mu = 18.03$ mm^{-1}
$c = 15.5502$ (15) Å	$T = 90$ K
$\alpha = 109.796$ (5)°	$0.15 \times 0.10 \times 0.07$ mm
$\beta = 92.666$ (6)°	

Data collection

Nonius KappaCCD area-detector diffractometer with an Oxford Cryosystems Cryostream cooler	Otwinowski & Minor, 1997)
	$T_{min} = 0.173$, $T_{max} = 0.365$
	56149 measured reflections
Absorption correction: multi-scan (*SCALEPACK*;	14105 independent reflections
	11613 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	413 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 5.71$ e Å^{-3}
14105 reflections	$\Delta\rho_{min} = -5.73$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O13—H13···O12	1.00	2.06	2.989 (6)	153
O14—H14···O6	1.00	1.79	2.718 (6)	154
O15—H15···O11^i	1.00	2.20	3.115 (6)	152
O16—H16···O27	1.00	1.89	2.873 (6)	166
O17—H17···O4^{ii}	1.00	1.91	2.820 (6)	150
O18—H18···O27	1.00	2.16	3.124 (6)	163
O19—H19···O6	1.00	2.29	3.194 (7)	151
O20—H20···O12	1.00	1.77	2.762 (6)	170
O21—H21···O11^{iii}	1.00	2.00	2.829 (6)	138
O22—H22···O26	1.00	1.94	2.906 (7)	161
O23—H23···O27^{iv}	1.00	1.89	2.864 (7)	164
O24—H24···O11^{iii}	1.00	1.78	2.722 (6)	155
O25—H25A···O2^v	0.84	2.00	2.779 (7)	154
O25—H25A···O2	0.84	2.36	2.802 (6)	113
O25—H25B···O12	0.84	1.88	2.691 (6)	163
O26—H26A···O1^{iv}	0.84	1.97	2.810 (6)	173
O26—H26B···O27	0.84	2.30	2.781 (6)	116

Symmetry codes: (i) $x − 1, y, z$; (ii) $x + 1, y, z$; (iii) $−x + 2, −y + 1, −z + 1$; (iv) $−x + 1, −y + 1, −z + 1$; (v) $−x + 1, −y + 1, −z$.

The H atoms on water molecule O27 could not be located. All other H atoms were visible in difference maps. Hydroxide H atoms were idealized to yield three equal Yb—O—H angles and O—H distances of 1.00 Å, and were treated as riding. The H atoms of the acetate methyl groups were idealized with C—H distances of 0.98 Å based on electron density in the expected circles, and a torsional parameter was refined for each methyl group. Water H atoms were placed based on difference maps and treated as riding in the refinement, after adjusting the O—H distances to 0.84 Å. U_{iso}(H) values were assigned as $1.2U_{eq}$ of the attached atom for OH groups and as $1.5U_{eq}$ of the attached atom for methyl groups and water molecules.

The largest difference peak is 0.72 Å from atom Yb6, and the top 30 peaks are within 1.08 Å of Yb positions. The deepest hole is 0.65 Å from atom Yb2. The deepest hole which is not near a Yb position is 1.18 Å from atom O4, with a depth of −2.96 e Å^{-3}. This is about 10% of the magnitude of the electron density at the O4 site, 28.8 e Å^{-3}.

metal-organic compounds

The r.m.s. deviation from the mean in the final difference map is 0.59 e Å^{-3}.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Version 8.3.1 for Mac; Palmer, 2010); software used to prepare material for publication: *SHELXL97*.

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