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Poly[[bis[aqua(1,10-phenanthroline)-lanthanum(III)]-*μ*-aqua-di-*μ*-5-sulfonatoisophthalato] monohydrate] and poly[[[triaqualanthanum(III)]-*μ*-5-sulfonatoisophthalato] monohydrate]

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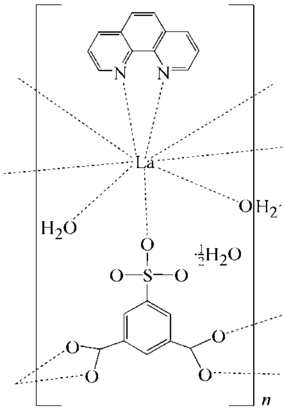
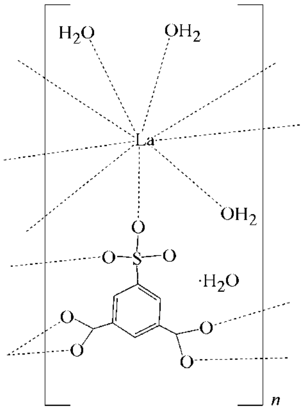
In the two related polymeric title compounds, $\{[La_2(sip)_2(phen)_2(H_2O)_3]\cdot H_2O\}_n$ [sip is the 5-sulfonatoisophthalate trianion ($C_8H_3O_7S^{3-}$) and phen is 1,10-phenanthroline ($C_{12}H_8N_2$)], (I), and $\{[La(sip)(H_2O)_3]\cdot H_2O\}_n$, (II), the lanthanum(III) ions are nine-coordinate, with similar distorted monocapped square-antiprism coordination geometry. The two crystal structures are very different. In (I), the sip anion acts as a pentadentate ligand, one of the coordinated water molecules lies on a twofold axis and further inversion, *n*-glide and translation operations generate a two-dimensional framework. In (II), the sip anion functions as a hexadentate ligand and a three-dimensional network with trinuclear 24-membered rings is developed *via* inversion, *n*-glide, twofold-screw and translation operations. Both structures also have extensive O—H···O hydrogen-bonded networks and *π*–*π* interactions.

Comment

A number of coordination polymers assembled from lanthanide ions and aromatic polycarboxylate ligands have been extensively studied in recent years due to their intriguing structural diversity and potential application as functional materials (Hu, Zhu *et al.*, 2004; Wan *et al.*, 2003; Zhang *et al.*, 2003). However, lanthanide coordination polymers utilizing organic species with two or more different functional groups, both coordinated to the metal ions, are very rare (Hu, Yuan *et al.*, 2004). It is of interest to us that the polytypic sip anion, which is nearly rigid and which has both carboxylate and sulfonate as potential coordinating groups, can form not only short bridges *via* one carboxylate or one sulfonate end, but also long bridges *via* the central aromatic ring between metal ions. In principle, the novelty of coordination polymers depends on the deliberate selection of central metal ions and multifunctional ligands. Lanthanide ions are well known for their large radii and variable coordination number in the range 3–12, which make these ions excellent spacers in assembling fascinating metal–organic frameworks (Wan *et al.*, 2002). Thus, we have selected the La–sip–phen system and the La–sip system to extend this research and present here the crystal structures of the two title compounds, $\{[La_2(sip)_2(phen)_2(H_2O)_3]\cdot H_2O\}_n$, (I), and $\{[La(sip)(H_2O)_3]\cdot H_2O\}_n$, (II), where sip is the 5-sulfonatoisophthalate trianion and phen is 1,10-phenanthroline.



(I)



(II)

In (I), each La^{III} ion coordinates to four O atoms from three carboxylate groups of three sip anions, with a typical La—O(carboxylate) distance range [2.442 (4)–2.617 (4) Å; Kim & Jung, 2002], one bridging water molecule (O8) with a longer La—O distance [2.9231 (9) Å] due to its weak coordination role between two La^{III} ions (Liu *et al.*, 2001), one water molecule (O9) with a normal La—O distance [2.538 (4) Å], one sulfonate O1 atom from another sip anion with an La—O distance of 2.474 (4) Å, and atoms N1 and N10 of the phen ligand in a chelating fashion, with typical La—N distances of 2.730 (5) and 2.712 (5) Å (Shi *et al.*, 2001), resulting in a

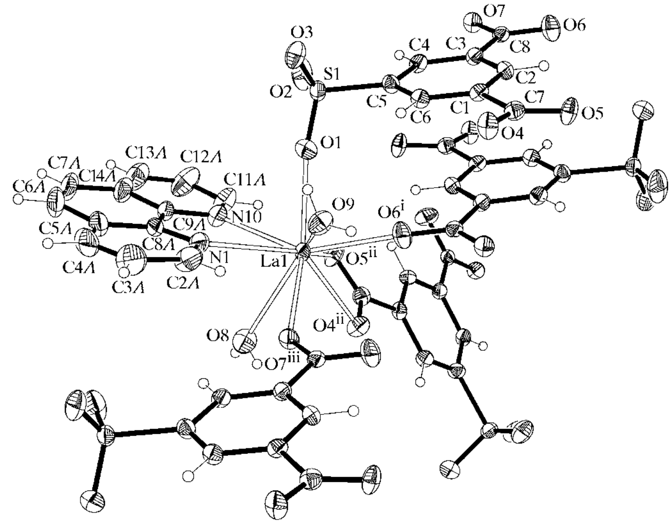


Figure 1
The coordination environment of the La^{III} ion in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{2}+x, -y, \frac{1}{2}+z$; (iii) $1+x, y, z$.]

distorted monocapped square antiprism (Fig. 1). The square plane of atoms N1, N2, O7^{iii} and O8 [symmetry code: (iii) $1 + x$, y, z], with a mean deviation of 0.42 Å, is seriously distorted, but the mean deviation of the other square plane composed of atoms O1, O4^{ii}, O5^{ii} and O9 is only 0.05 Å [symmetry code: (ii) $\frac{1}{2} + x$, $-y$, $\frac{1}{2} + z$]. To complete the coordination environment of the La centre, atom O6^{i} is located as the cap [symmetry code: (i) $-x$, $-y$, $-z$].

Each sip anion acts as a pentadentate ligand connecting four La^{III} ions through one bridging carboxylate group, one chelating carboxylate group and one monodentate sulfonate group. This coordination mode is slightly different from that in the lanthanide coordination polymer $[Eu(sip)(H_2O)_4]_n$ (Wang *et al.*, 2002), in which the two carboxylate groups of each sip anion show bidentate chelation. As shown in Fig. 2, each pair of La^{III} ions is bridged by a pair of carboxylate groups, forming an eight-membered ring with an La1···La1^{v} separation of 5.1426 (6) Å [symmetry code: (v) $1 - x$, $-y$, $-z$], and each pair of such rings is interconnected by two carboxylate–carboxylate bridges of two sip anions *via* benzene rings to form an intersecting double chain along the [10$\overline{1}$] direction. Within this double chain, there are also 16-membered rings, each of which is formed by two La^{III} ions and two carboxylate–carboxylate bridges of two sip anions *via* benzene rings, with an La1···La1^{iv} separation of 7.8646 (6) Å [symmetry code: (iv) $\frac{1}{2} - x$, y, $\frac{1}{2} - z$]. This double chain is similar to that found in [Zn(sip)(H-4,4′-bipyridine)(H_2O)]·$2H_2O$ (Sun *et al.*, 2004).

Moreover, as shown in Fig. 3, each pair of La^{III} ions is linked by a carboxylate–sulfonate bridge of a sip anion *via* a benzene ring, with an La1···La1^{vi} separation of 8.5572 (6) Å [symmetry code: (vi) $x - \frac{1}{2}$, $-y$, $z - \frac{1}{2}$], extending in a wave-like chain, and two adjacent chains are connected by bridging water molecules to produce a ribbon-like double chain containing 20-membered rings, each of which comprises two carboxylate–sulfonate bridges of two sip anions, two bridging water molecules and four La^{III} ions, along the [101] direction. The two different kinds of double chains are staggered relative to each other, generating a two-dimensional network with

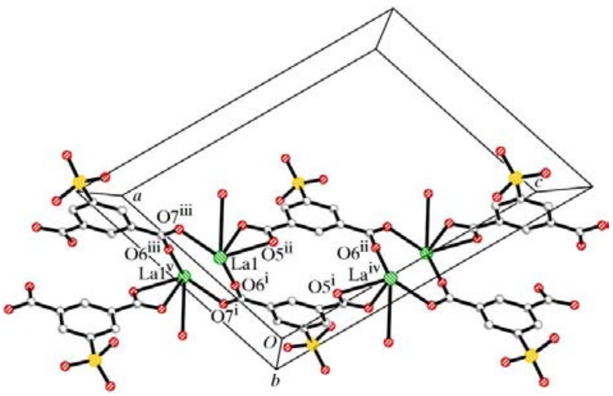


Figure 2
The intersecting double chain of (I) along the [10$\overline{1}$] direction. H atoms, non-bridging water molecules and 1,10-phenanthroline molecules have been omitted for clarity. [Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{2} + x, -y, \frac{1}{2} + z$; (iii) $1 + x, y, z$; (iv) $\frac{1}{2} - x, y, \frac{1}{2} - z$; (v) $1 - x, -y, -z$.]

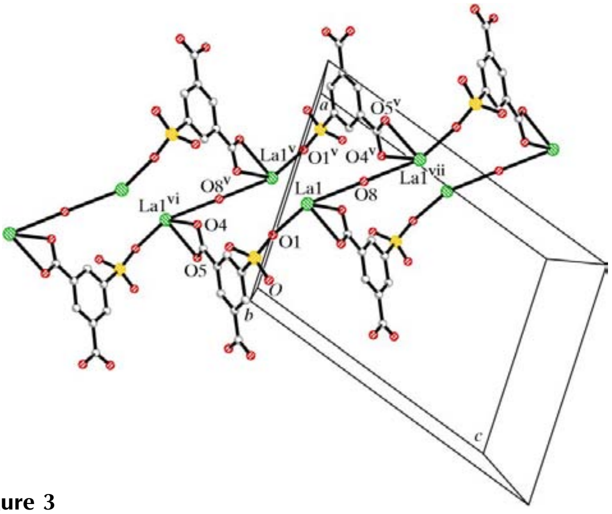


Figure 3
The ribbon-like double chain of (I) along the [101] direction. H atoms, non-bridging water molecules and 1,10-phenanthroline molecules have been omitted for clarity. [Symmetry codes: (v) $1 - x, -y, -z$; (vi) $x - \frac{1}{2}, -y, z - \frac{1}{2}$; (vii) $\frac{3}{2} - x, y, \frac{1}{2} - z$.]

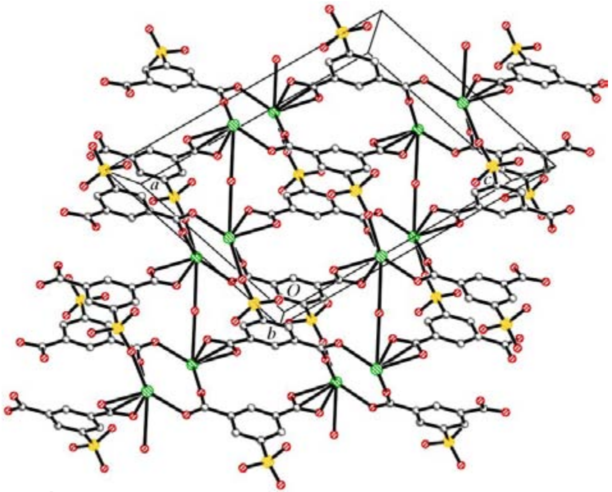


Figure 4
Perspective view of the two-dimensional network in (I) viewed along the *b* axis. H atoms, non-bridging water molecules and 1,10-phenanthroline molecules have been omitted for clarity.

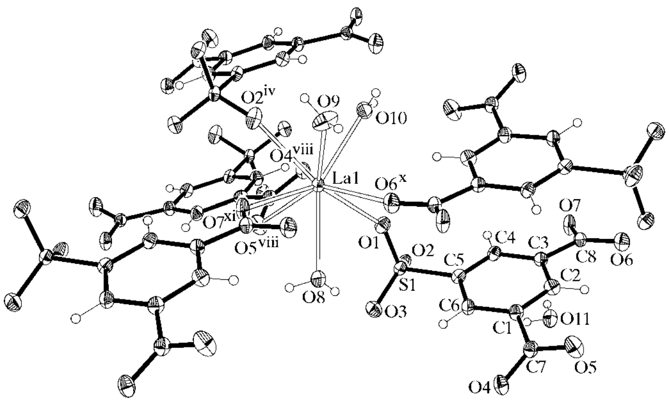


Figure 5
The coordination environment of the La^{III} ion in (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (viii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ix) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (x) $-x, 1 - y, 1 - z$; (xi) $x, y, 1 + z$.]

octanuclear units, each of which comprises four sip anions, eight La^{III} ions and two bridging water molecules (Fig. 4).

In the crystal structure of (I), the non-complexed water molecule (O10) lies on a twofold axis and all water O—H groups participate in O—H$\cdots$O hydrogen bonds with sip anions (details in Table 2). There are also π–π interactions between inversion-related sip aromatic rings [at (x, y, z) and ($-x$, $-y$, $-z$)], with the ring centroids separated by 3.523 Å (3.214 Å between planes), and also between inversion-related rings of the phen moieties [at (x, y, z) and ($1 - x$, $1 - y$, $-z$)], with the ring centroids separated by 3.478 Å and with a 3.214 Å separation between the planes.

In (II), the coordination geometry of the unique La^{III} ion is a distorted monocapped square antiprism similar to that of (I) (Fig. 5). The square plane of atoms O1, O4^{viii}, O5^{viii} and O8, with a mean deviation of 0.20 Å, is seriously distorted, but the mean deviation of the other square plane composed of atoms O2^{ix}, O6^{x}, O7^{xi} and O10 is only 0.10 Å [symmetry codes: (viii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ix) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (x) $-x, 1 - y, 1 - z$; (xi) $x, y, 1 + z$]. Atom O9 as the cap completes the coordination at La.

Each sip anion of (II) acts as a hexadentate ligand connecting five La^{III} ions through one bridging carboxylate group, one chelating carboxylate group and one bidentate sulfonate group. This coordination mode is quite different from the pentadentate mode of (I) and that in $[Cu_4(OH)_2(sip)_2(bipy)_2]\cdot 2H_2O$ (bipy is 4,4′-bipyridine; Sun *et al.*, 2003), in which the two carboxylate groups of each sip anion are bidentate chelating and the sulfonate group uses one O atom to make significant contact with two Cu atoms.

As shown in Fig. 6, three La^{III} ions in (II) are bridged by three sip anions, forming a trinuclear 24-membered ring with three different La1$^{viii}\cdots$La1^{xi}, La1$^{viii}\cdots$La1 and La1$^{xi}\cdots$La1 separations of 10.5645 (3), 9.8022 (3) and 10.5753 (3) Å, respectively. Each trinuclear ring links six adjacent rings, extending to form a two-dimensional layer in the crystallographic *bc* plane. This is comparable with what was found in an Eu–sip–H$_2$O analogue (Wang *et al.*, 2002).

Each pair of La^{III} ions in (II) is connected by three different kinds of bridges, namely carboxylate short-bridge, carboxylate–carboxylate and carboxylate–sulfonate long-bridge, generating three different kinds of binuclear rings, with La1$^{xiii}\cdots$La1^{xiv}, La1$^{xiii}\cdots$La1^{xv} and La1$^{xiii}\cdots$La1 separations of 5.0235 (3), 7.0487 (3) and 10.5235 (3) Å, respectively [symmetry codes: (xiii) $1 - x, 1 - y, 1 - z$; (xiv) $x, y - 1, z$; (xv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$]. Each binuclear eight-membered ring links six binuclear 16-membered rings to produce another two-dimensional layer in the *ab* plane (Fig. 7), which is different from the double chain found in (I) and $[Zn(sip)(H\text{-}bipy)(H_2O)]\cdot 2H_2O$ (Sun *et al.*, 2004). Thus, each sip anion in (II) acts as a hexadentate bridge, interconnecting the two different kinds of layers to yield a three-dimensional framework.

As in (I), the water O—H groups in (II) participate in O—H$\cdots$O hydrogen bonds (with sip anions or uncoordinated water molecules; details in Table 4). There are also π–π interactions between inversion-related sip anions [at (x, y, z) and ($1 - x$, $2 - y$, $2 - z$)], with the ring centroids separated by 3.697 Å and a 3.566 Å separation between the planes.

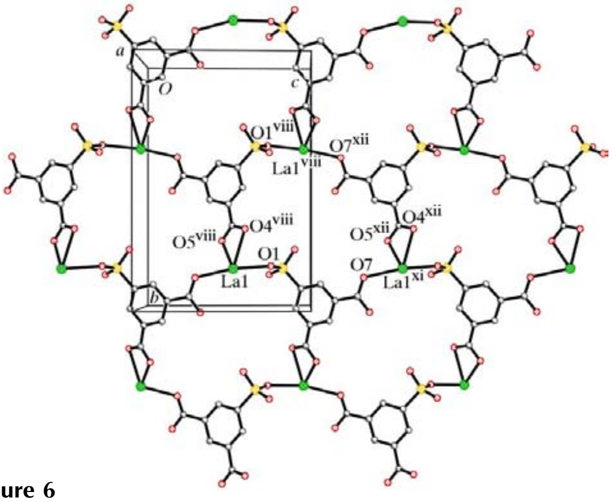


Figure 6
The two-dimensional layer of (II) in the crystallographic *bc* plane. H atoms and water molecules have been omitted for clarity. [Symmetry codes: (viii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (xi) $x, y, 1 + z$; (xii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{5}{2} - z$.]

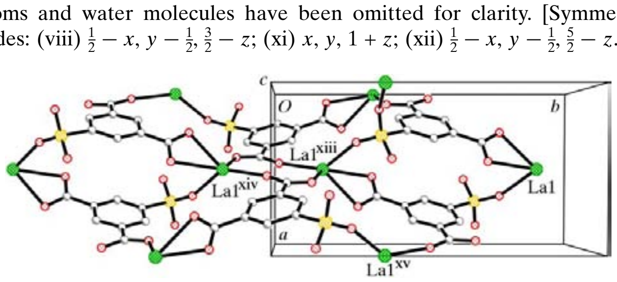


Figure 7
The two-dimensional layer of (II) in the crystallographic *ab* plane. H atoms and water molecules have been omitted for clarity. [Symmetry codes: (xiii) $1 - x, 1 - y, 1 - z$; (xiv) $x, y - 1, z$; (xv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

Experimental

The two title compounds were synthesized using hydrothermal methods. For (I), the starting mixture consisted of sodium 5-sulfoisophthalate (1 mmol, 0.27 g), $LaCl_3\cdot 6H_2O$ (1 mmol, 0.35 g), 1,10-phenanthroline (3 mmol, 0.54 g) and water (20 ml). For (II), the starting mixture consisted of sodium 5-sulfoisophthalate (1 mmol, 0.27 g), $LaCl_3\cdot 6H_2O$ (1 mmol, 0.35 g), 2-aminopyrimidine (3 mmol, 0.29 g) and water (20 ml). The mixtures were placed in 30 ml Teflon-lined stainless steel reactors. The solution for (I) was heated at 412 K for 3 d and the solution for (II) was heated at 408 K for 4 d. After slow cooling of the reaction systems to room temperature, colourless prism-shaped crystals of (I) and (II) were collected and washed with distilled water.

Compound (I)

Crystal data

$[La_2(C_8H_3O_7S)_2(C_{12}H_8N_2)_2(H_2O)_3]\cdot H_2O$
$M_r = 1196.62$
Monoclinic, $P2/n$
$a = 10.1655$ (5) Å
$b = 15.1560$ (7) Å
$c = 13.8914$ (6) Å
$\beta = 108.302$ (2)°
$V = 2031.96$ (16) Å^3
$Z = 2$

$D_x = 1.956$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6312 reflections
$\theta = 2.5$–$25.2°$
$\mu = 2.26$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.27 × 0.18 × 0.15 mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.531$, $T_{\max} = 0.718$
10 692 measured reflections
3661 independent reflections
3586 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25.2°$
$h = -12 \rightarrow 12$
$k = -18 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.115$
$S = 1.40$
3661 reflections
314 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 5.3444P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

La1—O1	2.474 (4)	La1—O9	2.538 (4)
La1—O4$^{\rm i}$	2.617 (4)	La1—N1	2.730 (5)
La1—O5$^{\rm i}$	2.577 (4)	La1—N10	2.712 (5)
La1—O6$^{\rm ii}$	2.442 (4)	S1—O1	1.457 (4)
La1—O7$^{\rm iii}$	2.475 (4)	S1—O2	1.434 (5)
La1—O8	2.9231 (9)	S1—O3	1.453 (5)

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8A···O4$^{\rm i}$	0.82 (11)	2.19 (9)	2.840 (7)	135 (11)
O8—H8B···O7$^{\rm ii}$	0.82 (5)	2.26 (11)	2.863 (5)	131 (13)
O9—H9A···O4$^{\rm iii}$	0.82 (3)	1.92 (4)	2.734 (6)	172 (7)
O9—H9B···O10	0.82 (5)	1.96 (5)	2.747 (6)	160 (6)
O10—H10A···O3	0.82 (8)	1.95 (8)	2.726 (6)	158 (8)

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

Compound (II)

Crystal data

$[\mathrm{La(C_8H_3O_7S)(H_2O)_3]\cdot H_2O}$
$M_r = 454.14$
Monoclinic, $P2_1/n$
$a = 7.9902$ (2) Å
$b = 15.4229$ (4) Å
$c = 10.5753$ (2) Å
$\beta = 92.606$ (1)°
$V = 1301.87$ (5) Å^3
$Z = 4$
$D_x = 2.317$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5538 reflections
$\theta = 2.3$–25.2°
$\mu = 3.50$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.35 × 0.28 × 0.10 mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.333$, $T_{\max} = 0.713$
6724 measured reflections
2345 independent reflections
2307 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25.2°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.047$
$S = 1.15$
2345 reflections
214 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 0.8212P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (II).

La1—O1	2.6260 (17)	La1—O8	2.5984 (18)
La1—O2$^{\rm i}$	2.5918 (17)	La1—O9	2.4726 (19)
La1—O4$^{\rm ii}$	2.6090 (18)	La1—O10	2.5937 (17)
La1—O5$^{\rm ii}$	2.6106 (18)	S1—O1	1.4654 (19)
La1—O6$^{\rm iii}$	2.4908 (17)	S1—O2	1.4478 (18)
La1—O7$^{\rm iv}$	2.5308 (17)	S1—O3	1.4576 (18)

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

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8A···O3	0.84 (2)	1.90 (2)	2.731 (2)	171 (3)
O8—H8B···O11$^{\rm i}$	0.83 (2)	1.86 (2)	2.648 (3)	159 (2)
O9—H9A···O11$^{\rm ii}$	0.81 (2)	1.90 (2)	2.690 (3)	164 (2)
O9—H9B···O8$^{\rm ii}$	0.82 (2)	1.91 (2)	2.726 (3)	176 (2)
O10—H10A···O3$^{\rm iii}$	0.84 (2)	2.07 (2)	2.872 (3)	159 (2)
O10—H10B···O5$^{\rm iv}$	0.84 (2)	2.41 (3)	2.970 (3)	125 (2)
O10—H10B···O7$^{\rm v}$	0.84 (2)	2.41 (2)	3.140 (3)	146 (2)
O11—H11A···O5$^{\rm vi}$	0.81 (2)	2.23 (2)	2.859 (3)	134 (2)
O11—H11B···O4	0.84 (2)	1.79 (2)	2.626 (3)	169 (2)

Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $1-x, 2-y, 1-z$; (iii) $1+x, y, z$; (iv) $1-x, 2-y, 2-z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (vi) $x-\frac{1}{2}, \frac{5}{2}-y, z-\frac{1}{2}$.

The water H atoms were refined subject to the restraint O—H = 0.82 (2) Å. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom). The 1.63 e Å^{-3} peak in the final difference Fourier map for (I) was adjacent to atom La1.

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 2002); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1760). Services for accessing these data are described at the back of the journal.

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