

Bis(μ -3-nitrobenzene-1,2-dicarboxylato)- $\kappa^8 O^1, O^2: O^2, O^3; O^3, O^2: O^2, O^1$ -bis[triaqua(2-carboxy-3-nitrobenzoato- $\kappa^2 O, O'$)]lanthanum(III) dihydrate

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The title compound, $[La_2(C_8H_3NO_6)_2(C_8H_4NO_6)_2(H_2O)_6] \cdot 2H_2O$, consists of dimeric units related by an inversion center. The two La^{III} atoms are linked by two bridging bidentate carboxylate groups and two monodentate carboxylate groups. Each La^{III} atom is nine-coordinated by six O atoms from five different carboxylate groups and three from water molecules. Hydrogen bonds between the water molecules and between the solvent water and a carboxylate O atom are observed in the structure. In the crystal packing, there are slipped π - π stacking interactions between the parallel benzene rings. Both hydrogen-bonding and π - π interactions

combine to stabilize the three-dimensional supramolecular network.

Comment

Rare-earth carboxylates show an intriguing variety of crystal structures as a result of the usually high coordination number of the metal ions and the many types of coordination displayed by carboxylate ligands in such complexes. Dimeric

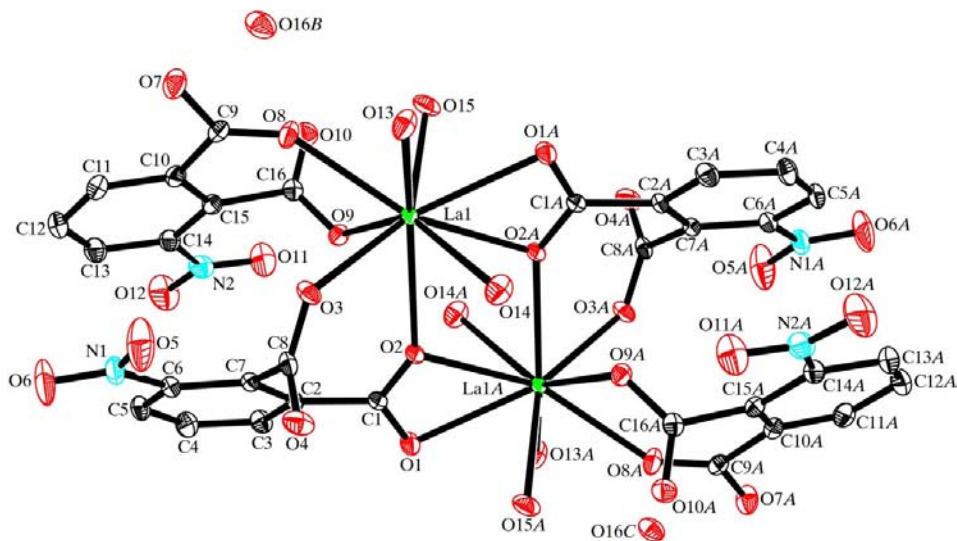
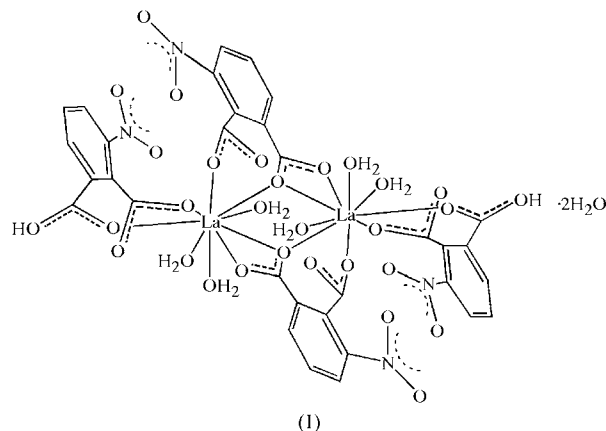


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. [Symmetry codes: (A) $-x + 1, -y + 2, -z + 1$; (B) $x - 1, y + 1, z$; (C) $-x + 2, -y + 1, -z + 1$.]

The asymmetric unit of complex (I) consists of two La atoms, two *L* ligands, two *HL* ligands, six coordinated water molecules and two solvent water molecules (Fig. 1). Each La atom is coordinated by six O atoms of five different carboxylate groups and by three O atoms of water molecules. They adopt a distorted tricapped trigonal-prismatic arrangement, with atoms O3, O9, O2A, O13, O14 and O15 filling the vertexes and atoms O1A, O2 and O8 capping the rectangular faces [symmetry code: (A) $-x + 1, -y + 2, -z + 1$] (Fig. 2). A similar coordination environment was observed previously for lanthanoid(III) complexes, such as $[\text{La}_2(\text{pyridine-3,4-dicarboxylate})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3]$ (Qin *et al.*, 2006) and $[\text{Ln}_2(\text{imidazole-4,5-dicarboxylate})_2(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}$ (Ln = Sm and Eu; Qin *et al.*, 2005). The La–O_{COO} bond distances range from 2.491 (2) to 2.622 (2) Å (mean 2.549 Å; Table 1), and those of the La–O_{aqua} bonds from 2.466 (2) to 2.615 (2) Å (mean 2.541 Å), all of which are within the range of those observed for other nine-coordinate La^{III} complexes with oxygen-donor ligands (Kiritsis *et al.*, 1998; Pan *et al.*, 2000; Qin *et al.*, 2006). The resulting La···La intradimer separation is 4.288 (7) Å. It is noteworthy that complex (I) contains both protonated (*HL*) and deprotonated (*L*) groups. The *HL* ligand adopts a bis(monodentate) coordination mode, in which the distances within the –COO groups are significantly different [C9–O7 = 1.300 (4) Å and C9–O8 = 1.216 (4) Å, and C16–O9 = 1.264 (4) Å and C16–O10 = 1.242 (4) Å], despite the fact that one is an acid group and the other is a carboxylate group. The *L* ligand adopts a bidentate chelating–monodentate coordination mode, which acts as a μ_2 -bridge through one bridging O atom [O2(1 – *x*, 2 – *y*, 1 – *z*)] and two monodentate O atoms (O1 and O3) to link two La^{III} atoms. The coordination mode contrasts with that in $[\text{La}_2(\text{pyridine-3,4-dicarboxylate})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3]$, in which the carboxylate groups adopt two kinds of coordination modes; one is monodentate–bidentate and the other is chelating–bidentate (Qin *et al.*, 2006).

In the *HL* ligand, one carboxylate group shows a distortion from the molecular plane; the dihedral angle between the

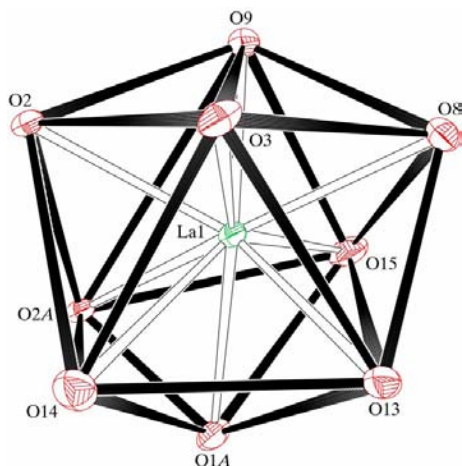


Figure 2

A schematic representation of the coordination geometry of the La^{III} atom. [Symmetry code: (A) $-x + 1, -y + 2, -z + 1$.]

planes of the benzene ring (C2–C7; plane 1) and the O1/C1/O2 carboxylate group is 30.5 (3)°. The other carboxylate group is almost perpendicular to the molecular plane; the dihedral angle between plane 1 and the plane of the O3/C8/O4 carboxylate group is 87.4 (4)°. These features are similar to those in the *L* ligand, in which the dihedral angle between the C10–C15 (plane 3) and O8/C9/O7 planes is 21.1 (4)°, and that between plane 3 and the O10/C16/O9 plane is 89.2 (4)°. Within each ligand, the nitro groups are almost coplanar with the benzene ring; the dihedral angle between plane 1 and the N1/O5/O6 plane is 6.4 (5)°, and that between plane III and the N2/O11/O12 plane is 2.7 (5)°. Finally, the dihedral angle between the two benzene rings (planes 1 and 3) is 12.38 (16)°.

Intermolecular hydrogen bonds (O3ⁱⁱ···O14, O4ⁱⁱ···O13, O7···O16 and O13···O16; symmetry codes and parameters are given in Table 2) bridge the molecules, forming an infinite chain along the *a* axis, and intermolecular hydrogen bonds between atoms O15 and O1ⁱⁱⁱ and between O16 and O4ⁱⁱⁱ generate an infinite chain along the *b* axis. The solvent water molecule O16 is in a tetrahedral environment with one water–water interaction, two water–carboxylate interactions involving O atoms of the *HL* ligand and one water–carboxylate interaction with an O atom of the *L* ligand. There are slipped π – π stacking interactions between the parallel benzene rings of the *HL* ligands with a distance of C13···C14 = 3.404 (5) Å (Fig. 3), which interlink molecules into an infinite one-dimensional chain along the *c* axis and further interconnect a two-dimen-

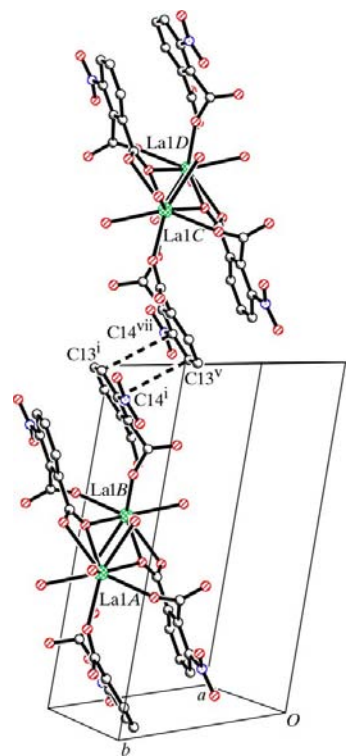


Figure 3

Part of the crystal structure of (I), showing π – π interactions as dashed lines. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (vii) *x*, *y*, *z* + 1; (A) $-x + 1, -y + 2, -z + 1$; (B) $-x + 1, -y + 2, -z + 1$; (C) *x*, *y*, *z* + 1; (D) $-x + 1, -y + 2, -z + 2$.]

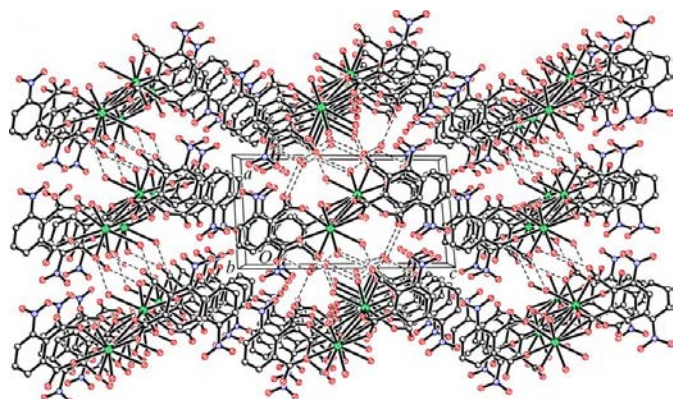


Figure 4
The crystal packing of (I), viewed down the *c* axis. Dashed lines indicate hydrogen bonds. H atoms have been omitted.

sional structure into a three-dimensional supramolecular network (Fig. 4).

Experimental

A solution of LaCl_3 (0.0245 g, 0.10 mmol) in water (5 ml) was added dropwise with constant stirring to an aqueous solution (5 ml) of 3-nitrobenzene-1,2-dicarboxylic acid (0.0211 g, 0.1 mmol). The pH of the mixture was adjusted to 3–4 with 0.1 M NaOH solution; the resulting mixture was then transferred into a Teflon-lined stainless steel vessel, which was sealed and heated to 423 K for 72 h, then cooled to room temperature. The reaction mixture was then filtered and single crystals were obtained from the filtrate after a few days by slow evaporation at room temperature.

Crystal data

$[\text{La}_2(\text{C}_8\text{H}_3\text{NO}_6)_2(\text{C}_8\text{H}_4\text{NO}_6)_2 \cdot (\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$	$\gamma = 104.581 (2)^\circ$
$M_r = 1260.42$	$V = 1054.1 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.1700 (12) \text{ \AA}$	$D_x = 1.986 \text{ Mg m}^{-3}$
$b = 8.9036 (13) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 15.279 (2) \text{ \AA}$	$\mu = 2.12 \text{ mm}^{-1}$
$\alpha = 100.828 (2)^\circ$	$T = 294 (2) \text{ K}$
$\beta = 90.935 (2)^\circ$	Block, colourless
	$0.24 \times 0.22 \times 0.18 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	5399 measured reflections
φ and ω scans	3711 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3350 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.593$, $T_{\max} = 0.683$	$R_{\text{int}} = 0.020$
	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.3043P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta\sigma)_{\text{max}} = 0.002$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.89 \text{ e \AA}^{-3}$
3711 reflections	$\Delta\rho_{\text{min}} = -0.90 \text{ e \AA}^{-3}$
316 parameters	
H-atom parameters constrained	

H atoms attached to C atoms were placed at calculated positions ($\text{C}-\text{H} = 0.93 \text{ \AA}$) and allowed to ride on their parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. Water and hydroxy H atoms were located in a difference map and refined with O–H distances restrained to $0.85 (3) \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Table 1
Selected bond lengths (\AA).

La1–O13	2.466 (2)	La1–O14	2.615 (2)
La1–O3	2.491 (2)	La1–O2 ⁱ	2.622 (2)
La1–O9	2.511 (2)	O7–C9	1.300 (4)
La1–O8	2.528 (2)	O8–C9	1.216 (4)
La1–O2	2.535 (2)	O9–C16	1.264 (4)
La1–O15	2.543 (2)	O10–C16	1.242 (4)
La1–O1 ⁱ	2.610 (2)		

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

Table 2
Hydrogen-bond geometry ($\text{ \AA}, ^\circ$).

<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>
O7–H7···O16	0.85	1.76	2.599 (4)	168
O13–H13A···O16	0.85	2.04	2.881 (4)	169
O13–H13B···O4 ⁱⁱ	0.85	1.82	2.659 (3)	169
O14–H14B···O3 ⁱⁱ	0.85	2.07	2.916 (4)	174
O15–H15B···O1 ⁱⁱⁱ	0.86	1.88	2.734 (4)	168
O16–H16A···O10 ^{iv}	0.85	2.04	2.756 (4)	142
O16–H16B···O4 ⁱⁱⁱ	0.85	1.91	2.747 (4)	169

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3048). Services for accessing these data are described at the back of the journal.

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