

Heptaaqua(isonicotinato- κ^2O,O')lanthanum(III) 1,5-naphthalenedisulfonate

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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(C-C)$ = 0.007 Å
 R factor = 0.038
 wR factor = 0.125
 Data-to-parameter ratio = 15.0

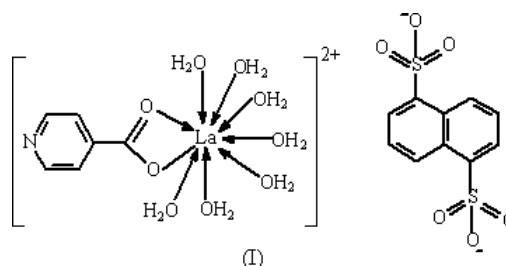
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[La(C_6H_4NO_2)(H_2O)_7](C_{10}H_6O_6S_2)$, consists of heptaaqua(isonicotinato)lanthanum(III) cations and 1,5-naphthalenedisulfonate dianions. The La^{III} atom is nine-coordinate, involving two carboxyl O atoms from one isonicotinate group and seven water molecules. The cations and anions are linked by $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds, generating a three-dimensional supramolecular framework.

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Comment

The study of the supramolecular chemistry of organo-sulfonates has received growing attention in recent years (Côté & Shimizu, 2003). The sulfonate groups are generally incorporated into inorganic-organic networks and are engaged in hydrogen-bond interactions. 1,5-Naphthalenedisulfonic acid (H_2NDS), with its rigid structure and two functionally active SO_3 groups in two well separated positions, can exhibit versatile binding modes and also form regular hydrogen bonds (Cai, 2004). To the best of our knowledge, only four metal complexes, $[M(H_2O)_6](1,5-NDS)$ ($M = Mg, Co, Cu$ and Ni) have been reported, in which the metal ions are coordinated by six water molecules, while the sulfonate dianions serve as hydrogen-bond acceptors (An *et al.*, 2004; Cai *et al.*, 2001; Chen *et al.*, 2002; Cai, 2004). However, there is little structural information about La^{III} complexes with 1,5-naphthalenedisulfonate. A search of the Cambridge Structural Database (Version of 2002; Allen, 2002) reveals one complex with this ligand, namely $La(OH)(1,5-NDS)(H_2O)$, in which the La^{III} atoms are eight-coordinate and bridged by 1,5-naphthalenedisulfonate ligands, forming a layer structure (Snejko *et al.*, 2002). In the present work, a new La^{III} complex, *viz.* $[La(isonicotinate)(H_2O)_7](1,5-NDS)$, (I), has been obtained from the self-assembly reaction of $La(NO_3)_3 \cdot 6H_2O$, isonicotinic acid and sodium 1,5-naphthalenedisulfonate. Its crystal structure is reported here.



As shown in Fig. 1, the asymmetric unit of (I) consists of an $[La(isonicotinate)(H_2O)_7]^{2+}$ cation and a 1,5-naphthalenedisulfonate dianion. In the cation, the La^{III} atom is nine-

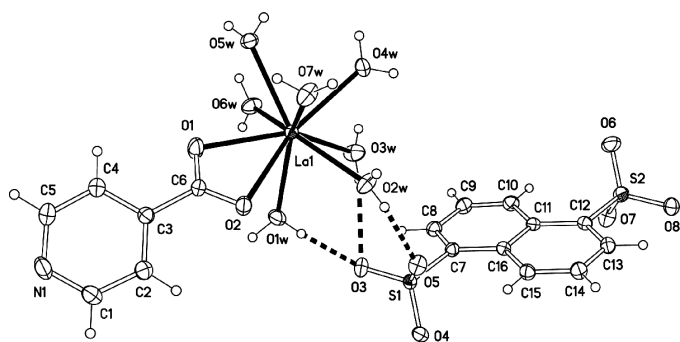


Figure 1
ORTEP plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

coordinate, involving two carboxyl O atoms from one bidentate chelate isonicotinate group and seven water molecules. The cation interacts with the 1,5-naphthalenedisulfonate dianion *via* hydrogen bonds (Table 1). The structure can be envisaged as one in which layers of anions alternate with layers of cations, the layers being linked *via* extensive intermolecular hydrogen bonds, giving rise to a three-dimensional network (Fig. 2 and Table 2).

Experimental

The title complex was prepared by the addition of an aqueous solution (10 ml) of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.33 g, 10 mmol) to an aqueous solution (20 ml) of sodium 1,5-naphthalenedisulfonate (3.32 g, 20 mmol) and isonicotinic acid (1.11 g, 10 mmol). Colorless prismatic single crystals were obtained from the filtrate at room temperature after several days. Analysis calculated for $\text{C}_{16}\text{H}_{24}\text{LaNO}_{15}\text{S}_2$: C 28.54, H 3.59, N 2.08%; found: C 28.57, H 3.55, N 2.11%.

Crystal data

$[\text{La}(\text{C}_6\text{H}_4\text{NO}_2)(\text{H}_2\text{O})_7](\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2)$	$D_x = 1.877 \text{ Mg m}^{-3}$
$M_r = 673.41$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 19908 reflections
$a = 6.4340 (13) \text{ \AA}$	$\theta = 3.1\text{--}27.5^\circ$
$b = 22.876 (5) \text{ \AA}$	$\mu = 2.04 \text{ mm}^{-1}$
$c = 16.273 (3) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 95.87 (3)^\circ$	Prism, colorless
$V = 2382.6 (8) \text{ \AA}^3$	$0.35 \times 0.26 \times 0.19 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-Axis RAPID diffractometer	5360 independent reflections
ω scans	4620 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.535$, $T_{\text{max}} = 0.677$	$\theta_{\text{max}} = 27.5^\circ$
20748 measured reflections	$h = -8 \rightarrow 8$
	$k = -29 \rightarrow 29$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0883P)^2 + 1.0026P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.27 \text{ e \AA}^{-3}$
5360 reflections	$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$
358 parameters	
H atoms treated by a mixture of independent and constrained refinement	

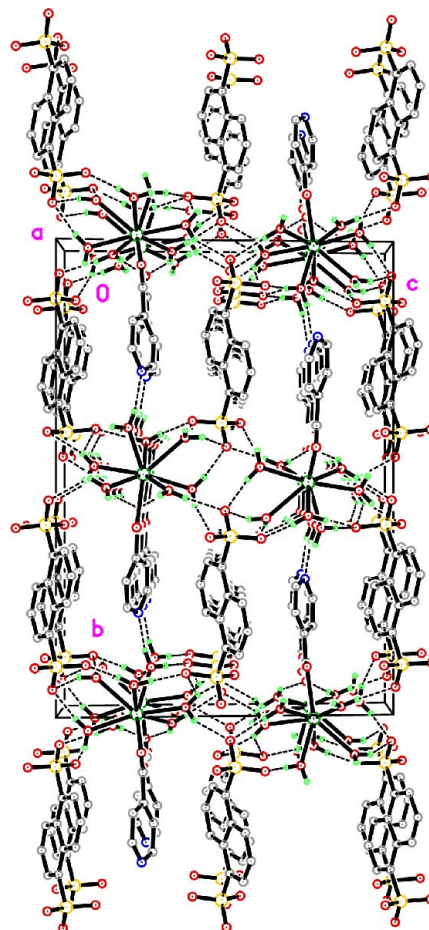


Figure 2
Packing diagram of the title complex. Hydrogen bonds are shown as dashed lines and H atoms attached to C atoms have been omitted.

Table 1

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

La1—O1	2.520 (4)	La1—O4W	2.524 (4)
La1—O2	2.740 (3)	La1—O5W	2.572 (3)
La1—O1W	2.568 (3)	La1—O6W	2.513 (4)
La1—O2W	2.514 (4)	La1—O7W	2.488 (4)
La1—O3W	2.624 (4)		
O1—La1—O2	48.96 (11)	O1W—La1—O5W	140.47 (13)
O1—La1—O1W	79.11 (13)	O1W—La1—O6W	78.25 (13)
O1—La1—O2W	123.40 (13)	O1W—La1—O7W	139.23 (14)
O1—La1—O3W	138.36 (15)	O2W—La1—O3W	72.86 (14)
O1—La1—O4W	147.53 (12)	O2W—La1—O4W	81.05 (14)
O1—La1—O5W	74.25 (12)	O2W—La1—O5W	138.15 (12)
O1—La1—O6W	79.68 (14)	O2W—La1—O6W	145.17 (13)
O1—La1—O7W	90.56 (15)	O2W—La1—O7W	71.96 (12)
O2—La1—O1W	68.08 (12)	O3W—La1—O4W	64.55 (13)
O2—La1—O2W	74.45 (13)	O3W—La1—O5W	121.53 (12)
O2—La1—O3W	125.78 (11)	O3W—La1—O6W	73.06 (14)
O2—La1—O4W	147.12 (14)	O4W—La1—O5W	73.37 (12)
O2—La1—O5W	111.78 (11)	O4W—La1—O6W	90.76 (15)
O2—La1—O6W	121.76 (13)	O4W—La1—O7W	76.38 (15)
O2—La1—O7W	75.40 (13)	O5W—La1—O6W	68.72 (12)
O1W—La1—O2W	81.15 (13)	O5W—La1—O7W	70.18 (13)
O1W—La1—O3W	65.09 (12)	O6W—La1—O7W	138.89 (12)
O1W—La1—O4W	129.50 (13)		

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

<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>
O1W—H1W1···O4 ⁱ	0.85 (4)	1.90 (5)	2.726 (5)	162 (5)
O1W—H1W2···O3	0.85 (5)	1.95 (5)	2.789 (5)	171 (7)
O2W—H2W1···O5	0.85 (6)	1.91 (6)	2.747 (5)	172 (7)
O2W—H2W2···O7 ⁱⁱ	0.85 (4)	1.96 (4)	2.800 (6)	175 (7)
O3W—H3W1···O3	0.85 (4)	2.41 (4)	3.111 (5)	140 (5)
O3W—H3W2···O5 ⁱⁱⁱ	0.85 (4)	2.03 (3)	2.878 (5)	173 (6)
O4W—H4W1···O7 ^{iv}	0.85 (5)	1.95 (3)	2.755 (6)	158 (7)
O4W—H4W2···N1 ^v	0.85 (3)	1.95 (4)	2.783 (6)	168 (7)
O5W—H5W1···O8 ^{iv}	0.85 (4)	1.99 (4)	2.833 (5)	177 (6)
O5W—H5W2···O2 ⁱⁱⁱ	0.85 (4)	2.12 (3)	2.891 (5)	151 (6)
O6W—H6W1···O2 ⁱⁱⁱ	0.85 (4)	1.97 (5)	2.791 (5)	164 (7)
O6W—H6W2···O3 ^{vi}	0.85 (4)	1.91 (4)	2.757 (5)	175 (7)
O7W—H7W1···O8 ^{vii}	0.85 (5)	1.95 (4)	2.682 (5)	143 (6)
O7W—H7W2···O6 ⁱⁱ	0.86 (5)	2.40 (3)	3.211 (7)	160 (7)
O7W—H7W2···O7 ⁱⁱ	0.85 (5)	2.51 (6)	2.998 (6)	117 (5)

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

C-bound H atoms were placed in calculated positions, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and were refined in the riding-model approximation. The H atoms of the aqua ligands were located in a difference map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The final difference Fourier map had a large peak at about 1 Å from La1.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK,

2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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