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catena-Poly[[[tetraaqualanthanum(III)]-di-μ-isoniconitinato-κ^2O:O'] nitrate]

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Key indicators

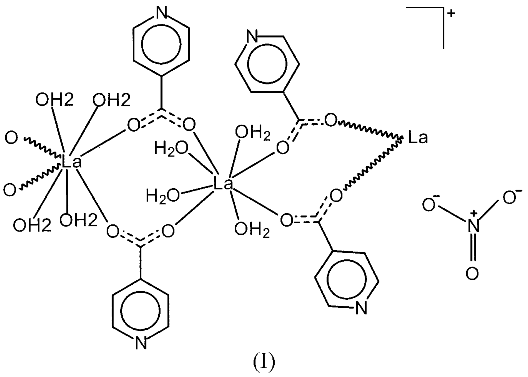
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
H-atom completeness 51%
R factor = 0.042
wR factor = 0.111
Data-to-parameter ratio = 12.6

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

The structure of the title compound, $\{[La(C_6H_4NO_2)_2(H_2O)_4](NO_3)\}_n$, consists of an infinite cationic chain, $[La(C_6H_4NO_2)_2(H_2O)_4]^+$, and well separated $(NO_3)^-$ anions. The La^{III} atom is eight-coordinated by four O atoms from four isonicotinate ligands and four water molecules. The coordination geometry around the La centre can be described as a distorted square antiprism. The La atoms are bridged by two carboxylate groups of two isonicotinate ligands to form an infinite chain along the **c** direction. The carboxylate-bridged chains are linked to each other *via* hydrogen bonds between pyridyl N atoms and coordinated water molecules to form a three-dimensional network with channels in which the nitrate anions are located, and the intermolecular hydrogen bonds are formed between the nitrate anions and cationic chains.

Comment

Lanthanide metal polynuclear compounds have attracted increasing interest due to their magnetic and luminescent properties. These compounds are usually prepared by the reaction of rare-earth metal ions with bi- or multidentate ligands, such as nicotinic acid (Starynowicz, 1991, 1993; Kay *et al.*, 1972; Ma *et al.*, 1996), isonicotinic acid (Ma *et al.*, 1999; Zeng *et al.*, 2000) and isonicotinic acid *N*-oxide (Mao *et al.*, 1998). In recent years, we have reported several complexes of this type with different bridging ligands (Zhang *et al.*, 1999; Cui *et al.*, 1999). We report here the synthesis and crystal structure of a new lanthanum complex with the isonicotinic ligand, namely *catena*-poly[[[tetraaqualanthanum(III)]-di-μ-isoniconitinato-κ^2O:O′] nitrate], (I). Since it contains a non-coordinated N atom on the pyridine ring, it can be used as a 'metallo ligand' to bind transition metals for the preparation of compounds of rare earth and transition metal.



(I)

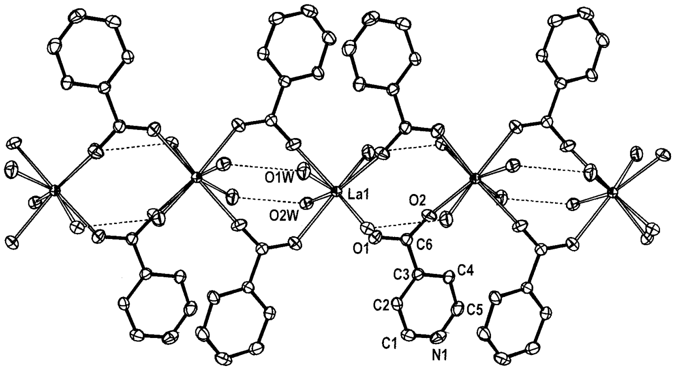


Figure 1
View of the polymeric cation of the title compound, with 40% probability ellipsoids. Hydrogen bonds are represented by dotted lines but H atoms have been omitted.

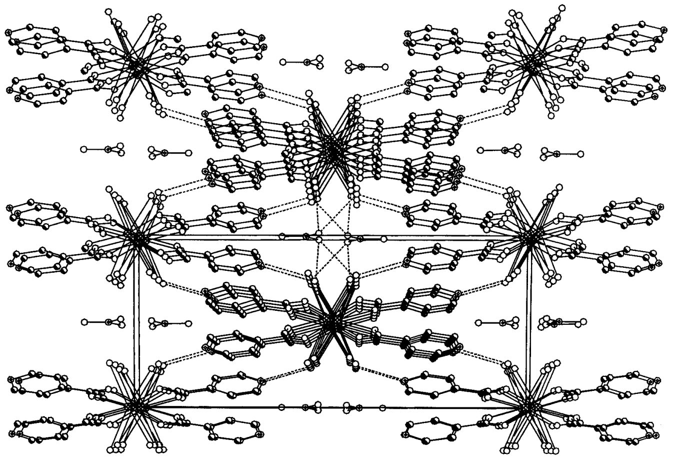


Figure 2
A packing diagram of the title compound. Dotted lines represent hydrogen bonds. For clarity, hydrogen bonding is shown only for a pair of nitrate anions interacting with coordinated water.

As shown in Fig. 1, the structure of (I) is composed of an infinite cationic chain $[La(C_6H_4NO_2)_2(H_2O)_4]^+$ and well separated $(NO_3)^-$ anions. La^{III} ions are eight-coordinated by four O atoms belonging to four different isonicotinate ligands [average La—O 2.441 (3) Å] and four water molecules [average La—O*W* 2.605 (3) Å]. The La centre has a distorted square anti-prism coordination geometry with O—La—O bond angles ranging from 70.14 (9) to 145.17 (10)°. One of the square faces comprises atoms O1, O1*A*, O2*W* and O2*WA*, with a mean deviation of 0.478 Å, and the other is defined by atoms O2, O2*A*, O1*W* and O1*WA*, with a mean deviation of 0.236 Å. The dihedral angle between the two planes is 2.04 (1)°. The La^{III} atom is displaced by 1.388 (3) and 1.370 (3) Å, respectively, from the above two faces. The La atoms are bridged by two *syn–syn* μ-*O,O′*-carboxylate groups of isonicotinate ligands to form an infinite chain with an La$\cdots$La separation of 5.154 (1) Å along the *c* axis. This alignment is similar to that found in $[\{Eu(L)_2(H_2O)_4\}]_n\cdot nH_2O$ (*L* = isonicotinic acid *N*-oxide; Mao *et al.*, 1998), but differs from those found in $Ln(isonicotinate)_3(H_2O)_2$ (Ln = Ce, Pr, Nd, Sm, Eu, Tb) (Ma *et al.*, 1999), in which the Ln^{III} atoms are bridged by four *syn–syn* μ-*O,O′*-carboxylate groups of isonicotinate ligands (Ln = Ce, Pr, Nd) or coordinated both by two *syn–syn* μ-*O,O′*-carboxylate groups and by the chelating carboxylate groups of isonicotinate ligands (Ln = Sm, Eu, Tb). To the best of our knowledge, the arrangement in the present complex is rare in lanthanide analogs.

There are two types of intermolecular hydrogen bonds and one intrachain hydrogen bond in the crystal structure. The intrachain hydrogen bond is formed by two waters coordinated to adjacent La^{III} ions with an O1*W*$\cdots$O2*W* distance of 2.862 (4) Å, as illustrated in Fig. 1. One of the two types of intermolecular hydrogen bonds, formed by the uncoordinated N atoms of isonicotinate ligands and coordinated water molecules between neighbouring chains, with an O2*W*$\cdots$N1 distance of 2.688 (4) Å, links the cationic chains into a three-dimensional network with channels along the *c* axis, in which the nitrate anions are located, as shown in Fig. 2. The other intermolecular hydrogen bonds are formed by the nitrate anions and coordinated water molecules with the O1*W*$\cdots$O4 distance of 2.860 (5) Å and O2*W*$\cdots$O4 distance of 2.818 (4) Å.

Experimental

The title complex was prepared by mixing a 1:1 molar ratio of $La(NO_3)_3\cdot xH_2O$ (43.2 mg, 0.1 mmol) and C_5H_4NCOOH (12.3 mg, 0.1 mmol) in a mixed solvent of H_2O/EtOH (*v*:*v* = 1:1). The pH of the solution was adjusted to 5.8 with $NH_3\cdot H_2O$. The reaction mixture was filtered and colourless single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

Crystal data

$[La(C_6H_4NO_2)_2(H_2O)_4](NO_3)$
M_r = 517.19
Monoclinic, *C*2/*c*
a = 9.2732 (12) Å
b = 19.963 (3) Å
c = 10.2565 (13) Å
β = 109.021 (2)°
V = 1795.0 (4) Å^3
Z = 4
D_x = 1.914 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2055 reflections
θ = 2.0–25.0°
μ = 2.44 mm^{-1}
T = 293 (2) K
Prism, colourless
0.40 × 0.22 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.530, T_{max} = 0.746
2844 measured reflections
1574 independent reflections
1406 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.0°
h = −9 → 11
k = −12 → 23
l = −12 → 12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.111
S = 1.01
1574 reflections
125 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 24.0948P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −1.51 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00285 (18)

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Table 1
Selected geometric parameters (Å, °).

La1—O2^{i}	2.423 (3)	La1—O1W^{iii}	2.602 (3)
La1—O2^{ii}	2.423 (3)	La1—O2W	2.608 (3)
La1—O1	2.460 (3)	La1—O2W^{iii}	2.608 (3)
La1—O1^{iii}	2.460 (3)	O2—La1^{ii}	2.423 (3)
La1—O1W	2.602 (3)		
O2^{i}—La1—O2^{ii}	96.94 (14)	O1W—La1—O1W^{iii}	128.39 (14)
O2^{i}—La1—O1	145.17 (10)	O2^{i}—La1—O2W	70.14 (9)
O2^{ii}—La1—O1	100.71 (10)	O2^{ii}—La1—O2W	143.36 (8)
O2^{i}—La1—O1^{iii}	100.71 (10)	O1—La1—O2W	77.87 (10)
O2^{ii}—La1—O1^{iii}	145.17 (10)	O1^{iii}—La1—O2W	71.36 (9)
O1—La1—O1^{iii}	81.22 (13)	O1W—La1—O2W	127.16 (9)
O2^{i}—La1—O1W	71.02 (9)	O1W^{iii}—La1—O2W	72.53 (9)
O2^{ii}—La1—O1W	75.40 (9)	O2^{i}—La1—O2W^{iii}	143.36 (8)
O1—La1—O1W	142.66 (10)	O2^{ii}—La1—O2W^{iii}	70.14 (9)
O1^{iii}—La1—O1W	82.30 (9)	O1—La1—O2W^{iii}	71.36 (9)
O2^{i}—La1—O1W^{iii}	75.40 (9)	O1^{iii}—La1—O2W^{iii}	77.87 (10)
O2^{ii}—La1—O1W^{iii}	71.02 (9)	O1W—La1—O2W^{iii}	72.53 (9)
O1—La1—O1W^{iii}	82.30 (9)	O1W^{iii}—La1—O2W^{iii}	127.16 (9)
O1^{iii}—La1—O1W^{iii}	142.66 (10)	O2W—La1—O2W^{iii}	139.15 (12)

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

H atoms bonded to carbon were positioned geometrically, with isotropic displacement parameters, riding on those of their carrier atoms. No H atoms were included for the water molecules.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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