Triclinic
$P\bar{1}$
$a = 7.356\,(1)$ Å
$b = 8.986\,(2)$ Å
$c = 9.544\,(2)$ Å
$\alpha = 74.37\,(3)°$
$\beta = 89.69\,(3)°$
$\gamma = 89.34\,(3)°$
$V = 607.5\,(2)$ Å^3
$Z = 2$
$D_x = 1.851$ Mg m^{-3}
D_m not measured

Cell parameters from 25
reflections
$\theta = 10–25°$
$\mu = 1.666$ mm^{-1}
$T = 294$ K
Cube
$0.28 \times 0.26 \times 0.22$ mm
Red

Data collection

Siemens *P4* diffractometer
ω scans
Absorption correction: none
2452 measured reflections
1996 independent reflections
1499 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.0115$

$\theta_{max} = 24.0°$
$h = -1 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$
3 standard reflections
  every 100 reflections
  intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.194$
$S = 1.091$
1990 reflections
159 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 1.10$ e Å^{-3}
$\Delta\rho_{min} = -0.88$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co(1)—O(1)	1.917 (3)	Co(1)—N(4)	1.965 (4)
Co(1)—O(2)	1.919 (3)	O(1)—C(1)	1.306 (5)
Co(1)—N(1)	1.949 (3)	O(2)—C(1)	1.300 (5)
Co(1)—N(2)	1.942 (3)	O(3)—C(1)	1.227 (5)
Co(1)—N(3)	1.941 (3)		
O(1)—Co(1)—O(2)	68.4 (1)	N(2)—Co(1)—N(1)	86.6 (1)
O(1)—Co(1)—N(3)	166.6 (1)	O(1)—Co(1)—N(4)	91.1 (1)
O(2)—Co(1)—N(3)	98.7 (1)	O(2)—Co(1)—N(4)	90.6 (1)
O(1)—Co(1)—N(2)	92.3 (1)	N(3)—Co(1)—N(4)	85.4 (2)
O(2)—Co(1)—N(2)	90.9 (1)	N(2)—Co(1)—N(4)	176.6 (2)
N(3)—Co(1)—N(2)	91.3 (2)	N(1)—Co(1)—N(4)	92.8 (2)
O(1)—Co(1)—N(1)	97.6 (1)	O(3)—C(1)—O(2)	125.2 (4)
O(2)—Co(1)—N(1)	165.7 (1)	O(3)—C(1)—O(1)	123.0 (4)
N(3)—Co(1)—N(1)	95.5 (1)	O(2)—C(1)—O(1)	111.7 (3)

The O atoms of the disordered perchlorate anion were divided into two sets, each having 0.5 occupancy, and refined isotropically. All H atoms were fixed at ideal positions with a fixed U_{iso} of 0.08 Å^2. The largest difference peak (1.10 e Å^{-3}) lies 1.01 Å from the Co atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1995). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

References

Bailar, J. C. Jr (1946). *Inorg. Synth.* **2**, 222–228.
Dasgupta, T. P. & Harris, G. M. (1969). *J. Am. Chem. Soc.* **91**, 3207–3211.
Dasgupta, T. P. & Harris, G. M. (1971). *J. Am. Chem. Soc.* **93**, 91–95.
Dasgupta, T. P. & Harris, G. M. (1974). *Inorg. Chem.* **13**, 1275–1278.
Francis, D. J. & Jordan, R. B. (1972). *Inorg. Chem.* **11**, 461–466.
Harris, G. M. & Hyde, K. E. (1978). *Inorg. Chem.* **17**, 1892–1896.
Holden, J. S. & Harris, G. M. (1955). *J. Am. Chem. Soc.* **77**, 1934–1938.
Hyde, K. E., Fairchild, G. H. & Harris, G. M. (1976). *Inorg. Chem.* **15**, 2631–2634.
Nakahara, A., Saito, Y. & Kuroya, H. (1952). *Bull. Chem. Soc. Jpn*, **25**, 331.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1995). *SHELXTL. Structure Determination Programs.* Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Van Eldik, R., Dasgupta, T. P. & Harris, G. M. (1975). *Inorg. Chem.* **14**, 2573–2575.
Van Eldik, R., Palmer, D. A. & Harris, G. M. (1980). *Inorg. Chem.* **19**, 3679–3683.

catena-Diaquatris(α-furancarboxylato)-lanthanum(III)

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Abstract

Each La^{3+} ion in *catena*-poly[[diaqua(2-furancarboxylato-*O,O'*)lanthanum(III)]-μ-(2-furancarboxylato-*O,O'*:-*O'*)], [La(C$_5$H$_3$O$_3$)$_3$(H$_2$O)$_2$]$_n$, is coordinated to seven O atoms from furancarboxylato groups and to two O atoms of water molecules in a distorted monocapped square-

antiprism configuration. The rare earth metal ions are bridged by the carboxylate groups to form an infinite two-dimensional polymeric network.

Comment

Rare earth carboxylates have been widely studied in recent years as a result of the variety of structure types exhibited by these compounds (Ma, Jin & Ni, 1994a,b). The carboxylate groups may be coordinated simultaneously to metal ions in three different modes, namely bridging, chelating and bridging-chelating modes. As a result, the complexes are often in dinuclear dimer, polymeric chain or network structures. As part of our study on rare earth metal complexes containing unsaturated carboxylic acid, we report here the preparation and crystal structure of the title compound, (I) (Fig. 1).

(I)

The La atoms are coordinated to nine O atoms, seven of which (O11, O12, O12^{ii}, O21, O22, O31 and O32^i) are from five different carboxylate groups and two (OW1 and OW2) from two independent water molecules. They adopt an irregular monocapped square-antiprism arrangement, in which atoms O12^{ii}, O22, O31 and OW1 form one square plane, and atoms O12, O21, O32^i and OW2 form another, with O11 as a capped site on the latter plane (see Table 1 for symmetry codes). Both planes are almost planar with average atomic deviations of 0.166(15) and 0.147(9) Å, respectively, and a dihedral angle between them of 6.5(1)°. A similar coordination environment has been observed previously for Ln^{3+} in complexes such as [Ln(NO₃)₃(OH₂)₃]₂.L₃ [Ln = La, Nd, Sm, Er and Y; L = 1,8-bis(quinolyl-oxy)-3,6-dioxaoctane; Tang, Gan, Liu, Tang, Tan & Yu, 1996].

None of the furylic O atoms are coordinated to the La^{3+} ions and none of the atoms of the furancarboxylic acid ligands deviate significantly from the least-squares plane through each ligand. The carboxylate ligands adopt three different coordination modes in the crystal: O31—C3—O32 groups are in a bridging mode in which two O atoms coordinate to two different La^{3+} ions, forming a conventional carboxylate bridge; O21—C2—O22
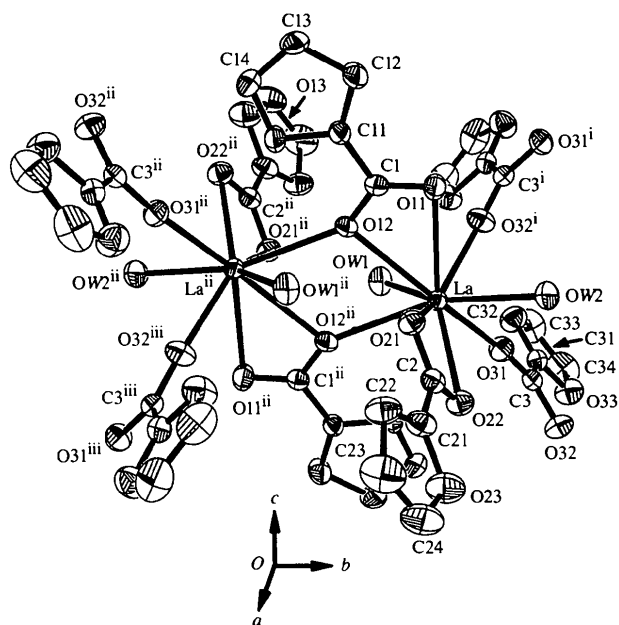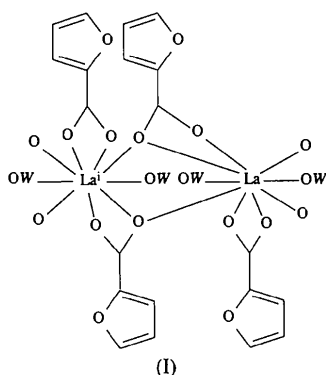

Fig. 1. A drawing of the title compound showing the dimeric units. H atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

groups are in a chelating mode in which two O atoms coordinate to the same La^{3+} ion, forming an unstable four-membered ring; O11—C1—O12 groups are in a bridging-chelating mode in which two O atoms chelate one La^{3+} ion, with O12 also linked to another La^{3+} ion to form a tridentate bridge. Two central La^{3+} ions are connected by two bridging-chelating O11—C1—O12 carboxylate groups to form a dimeric unit around the ($\frac{1}{2}$,0,$\frac{1}{2}$) crystallographic inversion centre. These dimeric units are linked to one another along the [011] direction by one simple bridging carboxylate group (O31—C3—O32) to form an infinite one-dimensional polymer chain. Laterally, in the (100) plane, these polymer chains are connected to one another by the other symmetrically related (O31—C3—O32) bridging carboxylate group to form an infinite two-dimensional polymeric network. The distances between two adjacent La^{3+} ions in the polymer network are 4.538(1) Å (symmetry code: $-x + 1$, $-y$, $-z + 1$) within the dimeric unit, and 6.175(2) and 6.175(2) Å (symmetry codes: x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$ and x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$, respectively) between the dimeric units. These La···La distances are considerably longer than the corresponding distances observed in the one-dimensional chain structure of the La^{3+}–methacryl-ato complex [4.268(2) and 5.524(1) Å, respectively; Lu, Wu, Dong, Chun, Gu & Liang, 1995]. The La—O$_{carboxyl}$ distances range from 2.451(3) to 2.780(3) Å, with a mean value of 2.592(116) Å, and the La—O$_{water}$ distances are between 2.570(3) and 2.575(3) Å, with a mean value of 2.573(4) Å. Both of the aver-

age La—O bond lengths are in good agreement with the corresponding distances found in other lanthanide complexes {2.56(10) and 2.57(3) Å, respectively, in [La₂(C₄H₅O₂)₆(H₂O)₄]; Lu, Wu, Dong, Chun, Gu & Liang, 1995}.

Since the H-atom positions of the coordinated water molecules can not be determined exactly, the presence of hydrogen bonding may be inferred from the close O···O non-bonded contacts listed in Table 2. We observed that the carboxylate O atoms can form hydrogen bonds with the OH group of the coordinated water molecules, and some weak hydrogen bonds may also exist between the O atoms on the furyl rings and the coordinated water molecules. These intermolecular interactions enhance the stability of the crystal packing.

Experimental

[La(NO₃)₃].6H₂O (0.1 mmol) and α-furancarboxylic acid (0.32 mmol) were first dissolved separately in appropriate amounts of ethanol. The ethanolic solution of α-furan-carboxylic acid was adjusted to pH 6–7 with 3 *M* NaOH solution, then the ethanolic solution of [La(NO₃)₃].6H₂O was added dropwise and the resulting mixture was refluxed and stirred for 4 h. The precipitate which formed was filtered off and colourless crystals suitable for X-ray diffraction analysis were obtained by evaporating the filtrate at room temperature for three weeks.

Crystal data

[La(C₅H₃O₃)₃(H₂O)₂]
$M_r = 508.16$
Monoclinic
$P2_1/c$
$a = 10.3727(8)$ Å
$b = 16.812(2)$ Å
$c = 9.496(5)$ Å
$\beta = 92.585(14)°$
$V = 1654.2(9)$ Å³
$Z = 4$
$D_x = 2.040$ Mg m⁻³
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 5.0–12.5°$
$\mu = 2.645$ mm⁻¹
$T = 293$ K
Plate
$0.8 \times 0.5 \times 0.2$ mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction:
  ψ scan (*XEMP*; Siemens, 1991*b*)
  $T_{min} = 0.313$, $T_{max} = 0.593$
6169 measured reflections
4825 independent reflections

3843 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 30°$
$h = -14 \to 14$
$k = -23 \to 1$
$l = -1 \to 13$
3 standard reflections
  every 97 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.100$

$(\Delta/\sigma)_{max} = 0.024$
$\Delta\rho_{max} = 1.351$ e Å⁻³
$\Delta\rho_{min} = -2.241$ e Å⁻³

$S = 1.149$
3843 reflections
246 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:
  SHELXL93
Extinction coefficient:
  0.0014(3)
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 1. *Selected bond lengths (Å)*

La—O32ⁱ	2.451(3)	O13—C14	1.365(5)
La—O31	2.453(3)	O13—C11	1.372(4)
La—OW1	2.570(3)	O21—C2	1.279(5)
La—O21	2.570(3)	O22—C2	1.256(5)
La—OW2	2.575(3)	O23—C21	1.361(6)
La—O12	2.614(3)	O23—C24	1.375(6)
La—O12ⁱⁱ	2.622(3)	O31—C3	1.253(5)
La—O22	2.653(3)	O32—C3	1.254(5)
La—O11	2.780(3)	O33—C34	1.366(6)
O11—C1	1.240(4)	O33—C31	1.376(5)
O12—C1	1.290(4)		

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

Table 2. *Contact distances (Å)*

OW1···O21ⁱ	2.697(4)	OW1···O12ⁱ	2.919(4)
OW1···O32ⁱⁱ	2.824(4)	OW2···O11ⁱⁱⁱ	3.050(5)
OW2···O22ⁱⁱ	2.878(4)	OW1···O33ⁱⁱ	3.064(5)

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

All non-H atoms were refined anisotropically. H atoms on the furyl rings were placed at calculated positions with an average C—H distance of 0.93 Å. Final difference Fourier maps showed the highest and lowest electron densities to be 1.35 and -2.24 e Å⁻³, respectively, which were too close to the La-atom position (0.81 and 1.11 Å, respectively) to be suitable for the accommodation of any additional atoms.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1991*a*). Software used to prepare material for publication: *SHELXL93*.

References

Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Lu, W.-M., Wu, J.-B., Dong, N., Chun, W.-G., Gu, J.-M. & Liang, K.-L. (1995). *Acta Cryst.* C51, 1568–1570.
Ma, J.-F., Jin, Z.-S. & Ni, J.-Z. (1994*a*). *Acta Cryst.* C50, 1008–1010.
Ma, J.-F., Jin, Z.-S. & Ni, J.-Z. (1994*b*). *Acta Cryst.* C50, 1010–1012.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1991*a*). *XP. Molecular Graphics Program*. Version 4.27. Siemens Analytical X-ray Instrument Inc., Madison, Wisconsin, USA.
Siemens (1991*b*). *XEMP. Empirical Absorption Correction Program*. Siemens Analytical X-ray Instrument Inc., Madison, Wisconsin, USA.
Tang, Y., Gan, X.-M., Liu, W.-S., Tang, N., Tan, M.-Y. & Yu, K.-B. (1996). *Polyhedron*, 15, 2607–2612.