

Tetrakis(μ -2,3-dimethoxybenzoato)-bis[(2,2'-bipyridine)(2,3-dimethoxybenzoato)lanthanum(III)]

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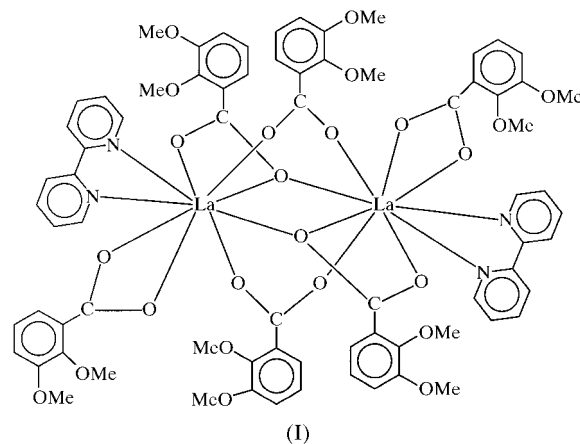
The title compound, tetrakis(μ -2,3-dimethoxybenzoato)- $\kappa^4 O:O';\kappa^6 O,O':O':O'$ -bis[(2,2'-bipyridine- N,N')(2,3-dimethoxybenzoato- O,O')lanthanum(III)], $[\text{La}_2(2,3\text{-DMOBA})_6(2,2'\text{-bpy})_2]$, where 2,3-DMOBA is 2,3-dimethoxybenzoate ($\text{C}_9\text{H}_9\text{O}_4$) and 2,2'-bpy is 2,2'-bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$), is a dimer with a centre of inversion between the La atoms bridged by four carboxylate ligands. The central La atom is ennea-coordinated and has a distorted monocapped square-antiprism geometry.

Comment

Lanthanoid(III) carboxylates have been widely studied in recent years due to the variety of structural types and their potential uses as fluorescent sensors. In ennea-coordinated lanthanoid(III) complexes, the central metal atom is in a monocapped square-antiprism or a tricapped trigonal-prism geometry. The geometries of the complexes are thought to depend on the size of the ligand compared with that of the metal atom, as well as on the substituted groups of the carboxylate. Herein, we report the preparation and crystal structure of the title compound, (I).

Complex (I) is a centrosymmetric dimer, with a centre of inversion between the metal atoms, bridged by four carboxylate ligands (Fig. 1). Each La atom is coordinated by seven O atoms of five different carboxylate ligands and by two N atoms of one 2,2'-bipyridine ligand. They adopt a distorted monocapped square-antiprism arrangement; atoms O22, O31, O32 and N2, and O12, O21ⁱ, O32ⁱ and N1, form lower and upper square planes with mean deviations of 0.0041 (4) and 0.1832 (4) Å, respectively, with a dihedral angle between them of 6.32 (3)°; atom O11 caps the upper plane (Fig. 2) [symmetry code: (i) 1 - x, -y, -z]. A similar coordination environment has been observed previously for lanthanoid(III) complexes

such as $[\text{Pr}_2(\text{pivalate})_6(2,2'\text{-bpy})_2]$ (Pisarevsky *et al.*, 1995), $[\text{La}_2(\text{propionato})_6(2,2'\text{-bpy})_2]$ (Brodkin *et al.*, 1996), $[\text{Ce}_2(\text{CH}_3\text{COO})_6(\text{phen})_2]$ (phen is phenanthroline; Panagiotopoulos *et al.*, 1995) and $[\text{Sm}_2(\text{PhCOO})_6(\text{phen})_2]$ (Niu *et al.*, 1999).



The carboxylate ligands adopt three different coordination modes in the crystal of (I). Firstly, O11–C11–O12 groups adopt a chelating mode, in which two O atoms coordinate to the same La atom to form a four-membered ring. Secondly, O21–C21–O22 groups adopt a bridging mode, in which two O atoms coordinate to two different La atoms to form a conventional carboxylate bridge. Thirdly, O31–C31–O32 groups adopt a bridging–chelating mode, in which both O atoms chelate one La atom and one of the two O atoms is also simultaneously linked to another La atom, to form a tridentate bridge.

In the chelating mode, the two C–O bond lengths of the carboxylate (C11–O11 and C11–O12) are not significantly different; the longer C–O bond has the longer La–O bond length (La1–O11), while the double-bonded O atom of the carboxyl group bonds with the La atom more strongly (La1–O12).

In the bridging mode, the two C–O bond lengths of the carboxylate (C21–O21 and C21–O22) are also not significantly different; the longer C–O bond has the shorter La–O bond length (La1–O21ⁱ), and this single-bonded O atom of the carboxyl group bonds with the La atom more strongly.

In the bridging–chelating mode, the two C–O bond lengths of the carboxylate (C31–O31 and C31–O32) are significantly different. This shows that the C–O double bond is localized. The O atom of the longer C–O bond bridges two La atoms (La1–O32 and La1ⁱ–O32), the O atom of the shorter C–O bond coordinates to one of the La atoms to form a chelate ring (La1–O31), and the single-bonded O atom of the carboxyl group (O32) bonds with the La atom more strongly.

The 2,2'-bipyridine ligand chelates to the La atom to form a five-membered ring. The two pyridine ring planes are not coplanar, the dihedral angle being 9.9 (3)°. The La–N bond lengths are comparable with the corresponding values found in the analogous complexes $[\text{La}_2(\text{propionato})_6(2,2'\text{-bpy})_2]$ (Brodkin *et al.*, 1996) and $[\text{La}_2(\text{Cl}_3\text{CCOO})_6(2,2'\text{-bpy})_2]$ (Cheng *et al.*, 1994).

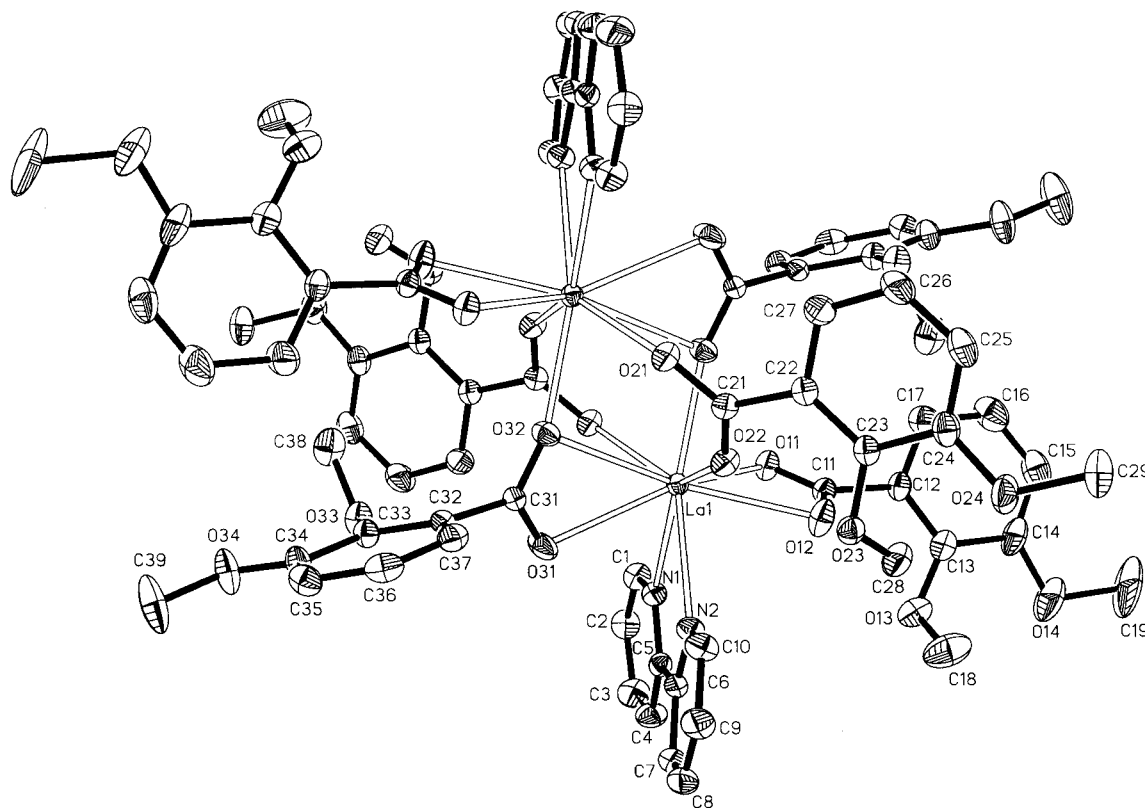


Figure 1

The molecular structure of (I) showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

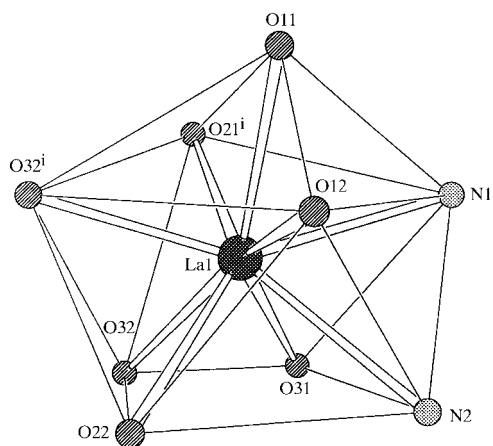


Figure 2

A schematic representation of the coordination geometry of the La atom [symmetry code: (i) $1 - x, -y, -z$].

Experimental

2,3-Dimethoxybenzoic acid (3 mmol, 510 mg) and 2,2'-bpy (1 mmol, 156 mg) were dissolved in ethanol (25 ml). The pH of the solution was adjusted to 7 with 2 M NaOH solution. To the resulting solution was added $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 433 mg) in water (5 ml). The reaction was stirred for 4 h at 343 K. A white precipitate was formed. Crystals of (I) suitable for X-ray analysis were obtained from the mother liquor at room temperature after a few days. Analysis found: C 52.61, H 4.34, N 3.14%; calculated for $\text{C}_{74}\text{H}_{76}\text{La}_2\text{N}_4\text{O}_{24}$: C 52.99, H 4.57, N 3.34%.

Crystal data

$[\text{La}_2(\text{C}_9\text{H}_9\text{O}_4)_6(\text{C}_{10}\text{H}_8\text{N}_2)_2]$

$M_r = 1677.16$

Triclinic, $P\bar{1}$

$a = 11.0203$ (11) Å

$b = 12.2390$ (13) Å

$c = 15.3540$ (15) Å

$\alpha = 66.785$ (7)°

$\beta = 83.551$ (5)°

$\gamma = 72.854$ (8)°

$V = 1818.6$ (3) Å³

$Z = 1$

$D_x = 1.531$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 25 reflections

$\theta = 5\text{--}16^\circ$

$\mu = 1.24$ mm⁻¹

$T = 293$ (2) K

Block, colourless

$0.60 \times 0.45 \times 0.28$ mm

Data collection

Siemens P4 diffractometer

ω scans

Absorption correction: empirical

via ψ scans (North *et al.*, 1968)

$T_{\min} = 0.521, T_{\max} = 0.707$

7311 measured reflections

6235 independent reflections

5830 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25^\circ$

$h = -1 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -18 \rightarrow 18$

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.091$

$S = 1.07$

6235 reflections

469 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.353P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 1.52 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.67 \text{ e \AA}^{-3}$

H atoms were placed at calculated positions and refined in riding mode, with $\text{C-H} = 0.93\text{--}0.96$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Final difference Fourier maps showed the maximum and minimum electron densities to be too close to the La-atom position to be suitable for the accommodation of any additional atoms.

Table 1

Selected geometric parameters (Å, °).

La1—O11	2.565 (2)	La1—N2	2.710 (3)
La1—O12	2.534 (3)	O11—C11	1.248 (4)
La1—O21 ⁱ	2.477 (2)	O12—C11	1.246 (4)
La1—O22	2.486 (2)	O21—C21	1.259 (4)
La1—O31	2.582 (3)	O22—C21	1.251 (4)
La1—O32	2.770 (2)	O31—C31	1.233 (4)
La1—O32 ⁱ	2.463 (2)	O32—C31	1.253 (4)
La1—N1	2.672 (3)		
O32 ⁱ —La1—O21 ⁱ	74.06 (8)	O12—La1—N1	84.92 (10)
O32 ⁱ —La1—O22	72.13 (8)	O11—La1—N1	73.33 (9)
O21 ⁱ —La1—O22	135.31 (8)	O31—La1—N1	72.07 (9)
O32 ⁱ —La1—O12	93.87 (10)	O32 ⁱ —La1—N2	150.22 (9)
O21 ⁱ —La1—O12	131.05 (8)	O21 ⁱ —La1—N2	134.07 (8)
O22—La1—O12	79.79 (9)	O22—La1—N2	78.79 (8)
O32 ⁱ —La1—O11	80.62 (8)	O12—La1—N2	74.50 (9)
O21 ⁱ —La1—O11	80.34 (8)	O11—La1—N2	110.04 (9)
O22—La1—O11	121.10 (8)	O31—La1—N2	66.13 (10)
O12—La1—O11	50.73 (8)	N1—La1—N2	60.47 (8)
O32 ⁱ —La1—O31	122.89 (8)	O32 ⁱ —La1—O32	76.58 (8)
O21 ⁱ —La1—O31	78.20 (11)	O21 ⁱ —La1—O32	72.50 (8)
O22—La1—O31	96.62 (11)	O22—La1—O32	71.91 (8)
O12—La1—O31	140.34 (11)	O12—La1—O32	151.67 (9)
O11—La1—O31	141.26 (10)	O11—La1—O32	148.33 (8)
O32 ⁱ —La1—N1	147.22 (9)	O31—La1—O32	47.55 (8)
O21 ⁱ —La1—N1	82.14 (8)	N1—La1—O32	117.49 (8)
O22—La1—N1	139.01 (8)	N2—La1—O32	100.59 (8)

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

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXTL* (Siemens, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1525). Services for accessing these data are described at the back of the journal.

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