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Tetra-μ-2-fluorobenzoato-bis[aqua(4,4′-bipyridine)(2-fluorobenzoato)lanthanum(III)]

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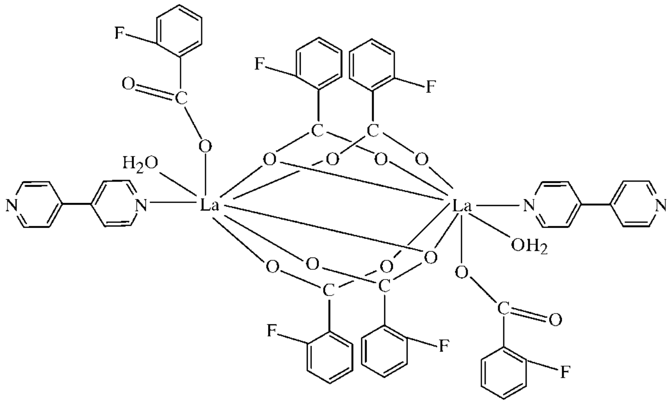
Each La^{3+} ion in the title complex, tetra-μ-2-fluorobenzoato-$\kappa^{10}O$:O';O:O,O';O:O';O,O':O'-bis[aqua(4,4′-bipyridine-κN)(2-fluorobenzoato-κO)lanthanum(II)], [La(C$_7$H$_4$FO$_2$)$_6$(C$_{10}$H$_8$N$_2$)$_2$(H$_2$O)$_2$], is coordinated by six O atoms from the carboxylate groups of five 2-fluorobenzoate ligands, one O atom from a water molecule and one N atom from a 4,4′-bipyridine molecule, thus forming a dimeric molecule. An infinite one-dimensional dimeric supramolecular chain is formed *via* intermolecular hydrogen bonds.

Comment

Rare earth carboxylate complexes with aromatic diamines, such as 1,10-phenanthroline and 2,2′-bipyridine, have been studied extensively. These lanthanide complexes display a variety of structural types, high stability and intense fluorescence characteristics. However, few rare earth carboxylate complexes with 4,4′-bipyridine have been reported. This paper



(I)

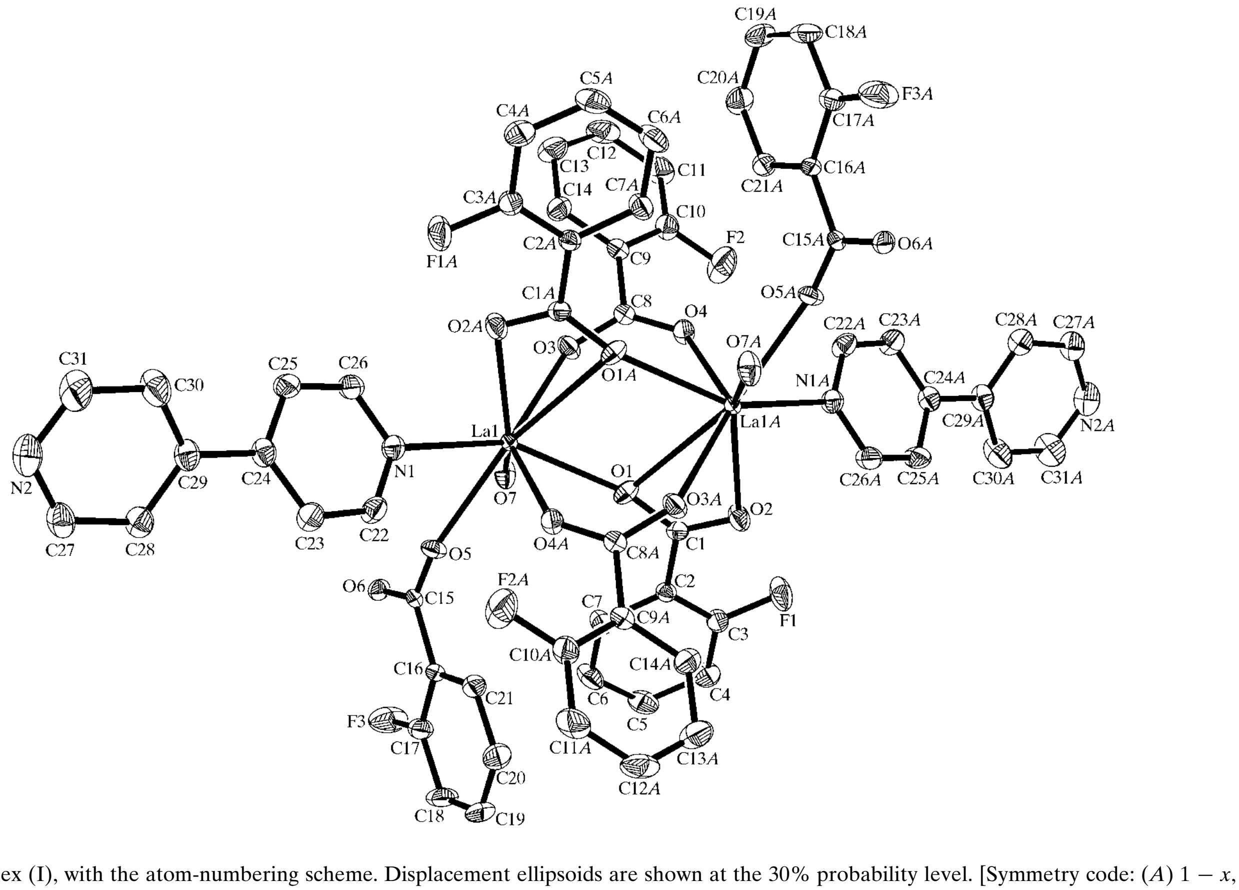


Figure 1
A view of complex (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (A) $1 - x$, $1 - y$, $1 - z$.]

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reports the structure of one such complex, (I), determined by single-crystal X-ray diffraction analysis.

Each La^{3+} ion is coordinated by seven O atoms and one N atom from a 4,4′-bipyridine molecule, where six of the O atoms (O1, O1*A*, O2*A*, O3, O4*A* and O5) are from five different 2-fluorobenzoate groups and the seventh (O7) is from a water molecule (Fig. 1). The carboxylate groups adopt three coordination modes, *viz*. monodentate, bidentate bridging and bidentate chelating. Two La^{3+} ions form a dimeric molecule, with four bridging carboxylate groups. The O5/C15/O6 carboxylate groups are monodentate, with one atom (O5) coordinated to the La^{3+} ion. The O3/C8/O4 groups are bridging, with the two O atoms coordinating to different La^{3+} ions. The O1/C1/O2 groups are in the chelating-bridging mode, in which two O atoms chelate one La^{3+} ion and one of the O atoms is linked to the other La^{3+} ion. The $La—O_{carboxy}$ distances in the title complex range from 2.471 (2) to 2.942 (3) Å (mean 2.569 Å) and the O—La—O angles range from 71.51 (9) to 143.64 (8)°. One N atom from a 4,4′-bipyridine molecule is coordinated to the La^{3+} ion, the La1—N1 bond distance being 2.852 (3) Å; this conformation contrasts with that in the $[\{Eu(DBM)_3\}_2(\mu\text{-}4,4'\text{-bipy})]$ complex (DBM is dibenzoylmethane), in which two N atoms from a 4,4′-bipyridine molecule link two Eu^{3+} ions, resulting in an infinite polymeric chain (Wang *et al.*, 1995). Each La^{3+} ion is also coordinated by a water molecule, the $La—O_{water}$ bond distance being 2.572 (3) Å.

Hydrogen bonds (Table 1) exist between two dimeric molecules, involving the non-coordinated N atom of the 4,4′-bipyridine group of one dimeric molecule and the H atom of the coordinated water molecule of another dimer (H···N = 2.02 Å and O—H···N = 168°; symmetry code: $1 + x$, $1 + y$, $1 + z$). An infinite one-dimensional dimeric supramolecular chain is formed, linked by the hydrogen bonds.

Experimental

$LaCl_3\cdot 6H_2O$ (0.5 mmol), 2-fluorobenzoic acid (1.5 mmol) and 4,4′-bipyridine (0.5 mmol) were dissolved separately in appropriate amounts of ethanol. The ethanol solution of 2-fluorobenzoic acid was adjusted to pH 6–7 with an aqueous solution of NaOH (2 mol dm^{-3}), and then the ethanol solutions of 4,4′-bipyridine and $LaCl_3$ were added dropwise. The mixture was heated under reflux with stirring for 2 h and the resulting white minor precipitate was filtered off. Single crystals were obtained from the mother liquor after it had been left to stand for one month at room temperature.

Crystal data

$[La(C_7H_4FO_2)_6(C_{10}H_8N_2)_2(H_2O)_2]$
$M_r = 730.42$
Triclinic, $P\bar{1}$
$a = 9.746$ (5) Å
$b = 12.780$ (7) Å
$c = 13.315$ (7) Å
$\alpha = 113.132$ (9)°
$\beta = 104.763$ (9)°
$\gamma = 96.916$ (9)°
$V = 1428.6$ (13) Å^3
$Z = 2$
$D_x = 1.698$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 986 reflections
$\theta = 3.2$–28.0°
$\mu = 1.57$ mm^{-1}
$T = 293$ (2) K
Prism, white
0.20 × 0.18 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.728$, $T_{max} = 0.834$
13 305 measured reflections
6871 independent reflections
5931 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 28.4°$
$h = -12 \rightarrow 13$
$k = -15 \rightarrow 16$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.080$
$S = 1.08$
6871 reflections
397 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$ where $P = (F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···N2^{i}	0.85	2.02	2.855 (4)	168
O7—H7*B*···O5^{ii}	0.85	2.50	3.158 (4)	135
C5—H5···F3^{iii}	0.93	2.52	3.379 (5)	153
C26—H26···O2^{iv}	0.93	2.44	2.950 (4)	115

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

H atoms were placed at calculated positions, with C—H distances of 0.93 Å and water O—H distances of 0.85 Å.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (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: AV1158). Services for accessing these data are described at the back of the journal.

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