

catena-Poly[europium(III)-tri- μ -2,3-dimethoxybenzoato]Xia Li,^a Ying-Quan Zou,^{b*} Bo Zheng^c and Huai-Ming Hu^c^aDepartment of Chemistry, Capital Normal University, Beijing 100037, People's Republic of China, ^bDepartment of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China, and ^cDepartment of Chemistry, Northwest University, Xi'an 710069, People's Republic of China
Correspondence e-mail: zouyq@263.net

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The title compound, $[\text{Eu}(\text{C}_9\text{H}_9\text{O}_4)_3]_n$ or $[\text{Eu}(2,3\text{-DMOBA})_3]_n$, where 2,3-DMOBA is 2,3-dimethoxybenzoate, is an infinite one-dimensional non-centrosymmetric coordination polymer. The unique Eu^{III} atom is bridged by six carboxylate ligands; it is *enea*-coordinated and has a distorted tricapped trigonal prism geometry. The $\text{Eu}-\text{O}$ distances are in the range 2.315 (3)–2.959 (5) Å.

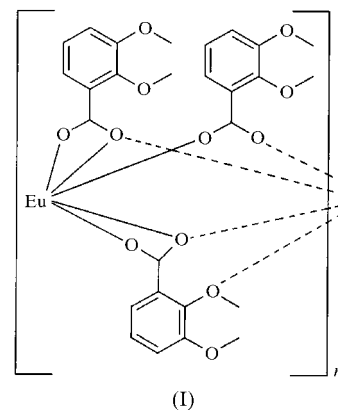
Comment

The variety of coordinating structures of lanthanide(III) carboxylates and their potential chemical and biological applications in luminescent probes and labels are interesting themes of coordination chemistry. Lanthanide(III) carboxylates are found to form many kinds of one-, two- and three-dimensional coordination polymers, where the carboxylate ligands act as bridges between the metal atoms. In *enea*-coordinated lanthanide(III) complexes, the central metal atom is in a monocapped square antiprism or tricapped trigonal prism geometry. The geometries of these 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. We report here the preparation and crystal structure of the title compound, (I).

Compound (I) is an infinite one-dimensional non-centrosymmetric coordination polymer. The unique Eu^{III} atom is bridged by six carboxylate ligands (Fig. 1); each Eu^{III} atom is coordinated to nine O atoms of six carboxylate ligands. A distorted tricapped trigonal prism arrangement is found. Atoms $\text{O1}^i/\text{O6}/\text{O9}$ and $\text{O2}^i/\text{O7}^i/\text{O10}^i$ form the upper and lower triangles of the prism, respectively, and the dihedral angle between them is 6.0° [symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$]. Atoms O1, O5 and O6ⁱ occupy the three cap positions (Fig. 2). A similar coordination environment has been observed previously for lanthanide(III) complexes such as cerium(III) acetate (Sadikov *et al.*, 1967), neodymium(III) (methylthio)acetate (Kondo *et al.*, 1982), and $[\text{Eu}_3(\text{ClCH}_2\text{CO}_2)_9(\text{H}_2\text{O})_5]_n$,

$[\text{Nd}_3(\text{ClCH}_2\text{CO}_2)_9(\text{H}_2\text{O})_5]_n$ and $[\text{La}_3(\text{ClCH}_2\text{CO}_2)_9(\text{H}_2\text{O})_5]_n$ (Imai *et al.*, 1987).

All the carboxylate ligands are coordinated to the Eu^{III} atom and can be classified into three different coordination modes in the crystal structure of (I). In the first of these, the carboxylate ligand is in a tridentate coordination mode: carboxyl group O1–C1–O2 is in a bridging–chelating mode, in which both O atoms chelate one Eu^{III} atom and one of them is also simultaneously linked to another Eu^{III} atom, forming a tridentate bridge. In the second coordination mode, the carboxylate group acts in a bidentate manner: carboxyl group O9–C19–O10 is in a conventional bridging mode, in which two O atoms coordinate to two different Eu^{III} atoms to form a bidentate bridge. In the third coordination mode, the carboxylate group acts in a tetradentate manner: carboxyl group O5–C10–O6 is in a bridging–chelating mode, with the O atom of the methoxy group additionally coordinated to the Eu^{III} atom, forming a tetradentate bridge.



In the tridentate coordination mode, the two C–O bond lengths of the carboxyl group (C1–O1 and C1–O2) are not significantly different and the C–O double bond is delocalized. In the typical form of a bridging–chelating mode, the $\text{Ln}-\text{O}$, $\text{Ln}-\text{O}'$ and $\text{Ln}'-\text{O}'$ bond lengths (Ln and Ln' are adjacent lanthanide atoms, and O' is the O atom which is simultaneously bonded to two lanthanide atoms) are about the same, and the $\text{Ln}-\text{O}-\text{C}$, $\text{Ln}-\text{O}'-\text{C}$ and $\text{Ln}'-\text{O}'-\text{C}$ bond angles are in the ranges $90-100$, $90-100$ and $140-150^\circ$, respectively. Many complexes containing a bridging–chelating mode are deformed from the ideal shape. In the case of (I), the $\text{Eu1}-\text{O1}$ bond length and $\text{C1}-\text{O2}-\text{Eu1}$ bond angle increase, while the $\text{C1}-\text{O1}-\text{Eu1}$ bond angle decreases. This deformation of the tridentate coordination ligand is thought to tend toward the form of the bidentate one.

In the bidentate coordination mode, the two C–O bond lengths of the carboxyl group (C19–O9 and C19–O10) are not significantly different and the C–O double bond is probably delocalized. These angles in (I) are in the normal ranges and the difference between the two $\text{Eu}-\text{O}$ bonds is very small. Therefore, the deformation of this mode is thought to be small.

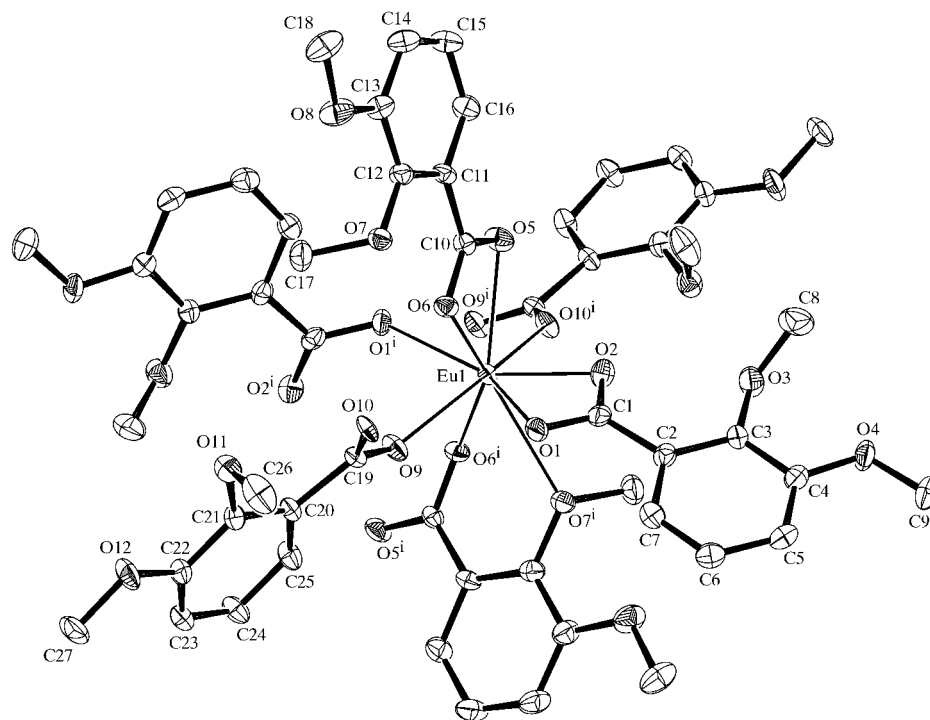


Figure 1
The coordination environment of the Eu^{III} atom in (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity [symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$].

In the tetradentate coordination mode, the $\text{Ln}-\text{O}$, $\text{Ln}-\text{O}'$ and $\text{Ln}'-\text{O}'$ bond lengths ($\text{Eu1}-\text{O5}$, $\text{Eu1}-\text{O6}$ and $\text{Eu1}^{\text{i}}-\text{O6}$) are in the range 2.409 (3)–2.500 (4) Å, and the $\text{Ln}-\text{O}-\text{C}$ and $\text{Ln}-\text{O}'-\text{C}$ bond angles ($\text{Eu1}-\text{O5}-\text{C10}$ and $\text{Eu1}-\text{O6}-\text{C10}$) are both 93.9 (3)–93.9 (3)°. These data show that this mode has the ideal shape for a bridging–chelating mode. Atom O7 of the methoxy group in one of the aromatic carboxylate ligands bonds with an adjacent Eu atom, similar to what is found in the complex $[\text{Nd}(\text{2-CH}_3\text{OC}_6\text{H}_4\text{COO})_3] \cdot 4\text{H}_2\text{O}$ (Poly-

nova *et al.*, 1987). The $\text{Eu}-\text{O}(\text{methoxy})$ bond length [2.703 (4) Å] is comparable with the corresponding values for analogous bonds in the complexes $[\text{Eu}(\text{2,2,6,6-tetramethylheptane-3,5-dione})_3]_2(\text{2,5,8,11-tetraoxadodecane})$ (Drake *et al.*, 1993), $[\text{Eu}(\text{hexafluoroacetylacetonato})_3(\text{diglyme})]$ (Kang *et al.*, 1997) and $[\text{Eu}_2(\text{5,11,17,23-tetrabutyl-25,27-dihydroxy-26-carboxymethoxy-28-diethylamidomethoxycalix(4)arene})_2 \cdot 3\text{EtOH} \cdot 2\text{CH}_2\text{Cl}_2]$ (Beer *et al.*, 1996).

Experimental

2,3-Dimethoxybenzoic acid (1.5 mmol, 255 mg) was dissolved in ethanol (20 ml). The pH of the solution was adjusted to 6 with 2 M NaOH solution. To the resulting solution was added a solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 223 mg) in water (5 ml). The reaction mixture was stirred for 4 h at 333 K. A white precipitate formed and was filtered off. Crystals of (I) suitable for X-ray analysis were obtained from the filtrate after several days at room temperature. Analysis found: C 46.21, H 3.74%; calculated for $\text{C}_{27}\text{H}_{27}\text{EuO}_{12}$: C 46.63, H 3.91%.

Crystal data

$[\text{Eu}(\text{C}_9\text{H}_9\text{O}_4)_3]$
 $M_r = 695.45$
 Orthorhombic, $P2_12_12_1$
 $a = 18.9555$ (14) Å
 $b = 8.0426$ (4) Å
 $c = 17.1475$ (10) Å
 $V = 2614.2$ (3) Å³
 $Z = 4$
 $D_x = 1.767$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 20 233 reflections
 $\theta = 2.5\text{--}27.5^\circ$
 $\mu = 2.47$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 $0.33 \times 0.21 \times 0.16$ mm

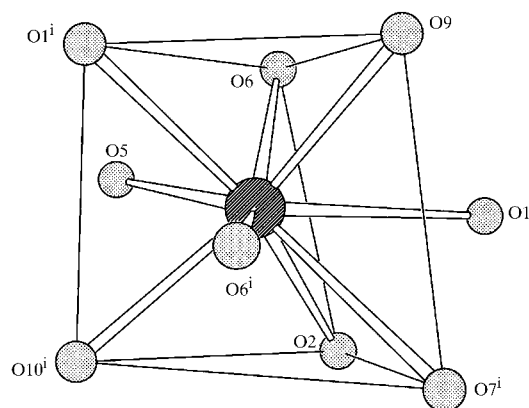


Figure 2
A schematic representation of the coordination geometry of the Eu^{III} atom in (I) [symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$].

Data collection

Rigaku R-AXIS RAPID image-plate diffractometer
Oscillation scans
Absorption correction: empirical (*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.543$, $T_{\max} = 0.674$
5640 measured reflections

5640 independent reflections
4984 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 27.5^\circ$
 $h = -24 \rightarrow 24$
 $k = -10 \rightarrow 10$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.067$
 $S = 1.03$
5640 reflections
367 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0212P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.86 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.80 \text{ e } \text{\AA}^{-3}$
Absolute structure: Flack (1983),
with 2495 Friedel pairs
Flack parameter = -0.011 (15)

Table 1

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

Eu1—O1	2.959 (5)	Eu1—O10 ⁱ	2.332 (3)
Eu1—O1 ⁱ	2.392 (4)	O1—C1	1.272 (6)
Eu1—O2	2.365 (4)	O2—C1	1.267 (7)
Eu1—O5	2.500 (4)	O5—C10	1.264 (6)
Eu1—O6	2.498 (4)	O6—C10	1.271 (6)
Eu1—O6 ⁱ	2.409 (3)	O9—C19	1.265 (5)
Eu1—O7 ⁱ	2.703 (4)	O10—C19	1.262 (6)
Eu1—O9	2.315 (3)		
O9—Eu1—O10 ⁱ	149.50 (11)	O1 ⁱ —Eu1—O5	77.04 (15)
O9—Eu1—O2	117.54 (14)	O6 ⁱ —Eu1—O5	137.94 (13)
O10 ⁱ —Eu1—O2	87.94 (12)	O6—Eu1—O5	52.02 (11)
O9—Eu1—O1 ⁱ	79.69 (14)	O9—Eu1—O7 ⁱ	84.93 (14)
O10 ⁱ —Eu1—O1 ⁱ	81.75 (13)	O10 ⁱ —Eu1—O7 ⁱ	90.94 (12)
O2—Eu1—O1 ⁱ	156.45 (15)	O2—Eu1—O7 ⁱ	66.72 (13)
O9—Eu1—O6 ⁱ	78.41 (12)	O1 ⁱ —Eu1—O7 ⁱ	134.17 (14)
O10 ⁱ —Eu1—O6 ⁱ	72.93 (12)	O6 ⁱ —Eu1—O7 ⁱ	62.60 (12)
O2—Eu1—O6 ⁱ	124.87 (15)	O6—Eu1—O7 ⁱ	130.67 (11)
O1 ⁱ —Eu1—O6 ⁱ	72.06 (16)	O5—Eu1—O7 ⁱ	144.27 (12)
O9—Eu1—O6	75.77 (12)	O9—Eu1—O1	71.58 (11)
O10 ⁱ —Eu1—O6	127.04 (13)	O10 ⁱ —Eu1—O1	134.54 (10)
O2—Eu1—O6	82.76 (13)	O2—Eu1—O1	46.85 (11)
O1 ⁱ —Eu1—O6	86.65 (15)	O1 ⁱ —Eu1—O1	141.19 (11)
O6 ⁱ —Eu1—O6	149.02 (4)	O6 ⁱ —Eu1—O1	124.65 (12)
O9—Eu1—O5	123.28 (14)	O6—Eu1—O1	61.65 (12)
O10 ⁱ —Eu1—O5	75.03 (12)	O5—Eu1—O1	97.28 (12)
O2—Eu1—O5	79.87 (15)	O7 ⁱ —Eu1—O1	69.26 (11)

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

H atoms were placed at calculated positions and refined using a riding model, with C—H distances in the range 0.93–0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; 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: FG1732). Services for accessing these data are described at the back of the journal.

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