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catena-Poly[europium-tri-μ-4-methylbenzoato]

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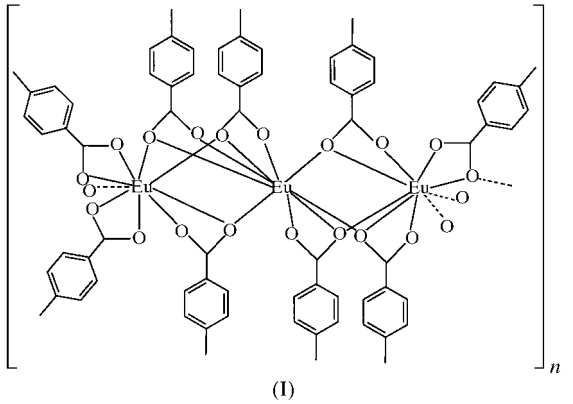
Each Eu^{3+} ion in the title compound, *catena*-poly[europium(III)-tri-μ-4-methylbenzoato-*O*:*O*,*O*′;*O*:*O*,*O*′;*O*,*O*′:*O*′], $\{[Eu(C_8H_7O_2)_3]_3\}_n$, is coordinated by nine O atoms, and three Eu atoms form a trimeric unit. These trimeric units are linked by bridging–chelating carboxylates to form an infinite one-dimensional polymer chain.

Comment

Rare earth carboxylate complexes have many special structures and interesting luminescent properties. The carboxylate groups may be coordinated simultaneously to metal ions in three modes, *viz*. bridging, chelating and bridging–chelating. The europium luminescent probe has been widely used in the local structure determination of crystalline materials. Our interest has focused on the crystal structures of europium complexes and their high-resolution laser-excited excitation and emission spectra. We report here a new europium complex, $\{[Eu(C_8H_7O_2)_3]_3\}_n$, (I) (Fig. 1).



(I)

In (I), each Eu atom is coordinated by nine O atoms from six different carboxylate groups, and all the carboxylate groups are coordinated in bridging–chelating modes, with two O atoms chelating one Eu^{3+} ion to form a tridentate bridge. Three Eu^{3+} ions, each pair linked by three carboxylate groups, form a trimeric unit. These trimeric units are then linked to one another along the *n*-glide face by three bridging–chelating carboxylates to form an infinite one-dimensional polymer chain.

Most of the Eu—O bond lengths [range 2.343 (3)–2.963 (5) Å] agree with those in the similar compound $[Eu_2(p\text{-}CH_3C_6H_4COO)_6(2,2'\text{-bipy})]$, (II) (Wang *et al.*, 1995; 2,2′-bipy is 2,2′-bipyridine), but the Eu2—O7 bond length is significantly longer than the Eu—O bond in (II) [2.315 (5)–2.505 (5) Å]. The difference may be due to their different chelating modes.

The O—Eu—O angles in (I) vary from 49.58 (10) to 159.60 (14)°, in agreement with those in (II).

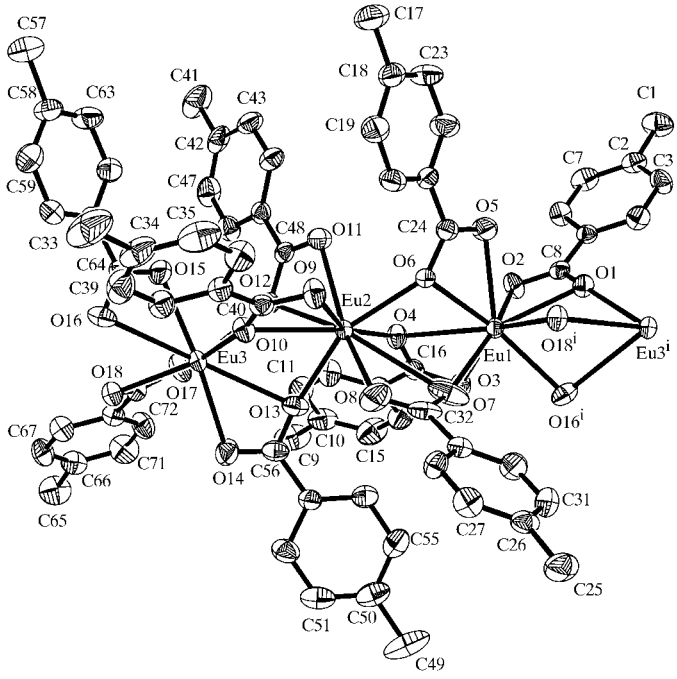


Figure 1
View of the title complex with displacement ellipsoids shown at the 30% probability level. Phenyl-ring atoms are numbered sequentially around each ring and some labels have been omitted for clarity. [Symmetry code: (i) $-\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.]

In most complexes containing MBA or MOBA (MBA is methylbenzoic acid and MOBA is methoxybenzoic acid), the Eu atoms are eight-coordinated by bidentate carboxylate ligands, as in (II), $[Eu_2(p\text{-MBA})_6(phen)_2]$ [(III); Jin *et al.*, 1994; phen is phenanthroline], $[Eu(m\text{-MOBA})_3(2,2'\text{-bipy})]$ [(IV); Li, Zheng *et al.*, 2000], $[Eu(m\text{-MOBA})_3(H_2O)_2]\cdot\frac{1}{2}(4,4'\text{-bipy})$ [(V); Li, Bian *et al.*, 2000; 4,4′-bipy is 4,4′-bipyridine] and $[Eu(m\text{-MBA})_3(H_2O)_2]$, (VI). Complex (I) may be a unique complex where europium is nine-coordinated.

It should also be noted that there are no hydrogen bonds in (I), while many other Eu complexes, such as (V) and (VI), contain hydrogen bonds which can stabilize the complexes.

Complexes (I)–(IV) show that the coordinating abilities of phen, 2,2′-bipy, *p*-MBA and *p*-MOBA are stronger than that of H_2O; (V) and (VI) show that *m*-MOBA, *m*-MBA and H_2O may have similar coordinating abilities; and (IV) and (V) show that 4,4′-bipy is a very weak ligand because it cannot form a five-membered chelate ring.

Experimental

4-Methylbenzoic acid (3 mmol) was dissolved in 95% ethanol (25 ml) and its pH was maintained in the range 6–7 with NaOH (2 mol l^{-1}) solution. Then $Eu(NO_3)_3$ (1 mmol) dissolved in H_2O (5 ml) was added to the solution. The mixture was heated at 353 K under reflux with stirring for 6 h. A white precipitate was formed which was then filtered off. White prism-shaped crystals were obtained from the mother liquor after two weeks.

Crystal data

$[Eu_3(C_8H_7O_2)_9]$
M_r = 1672.10
Monoclinic, $P2_1/n$
a = 12.9880 (10) Å
b = 21.823 (2) Å
c = 23.542 (4) Å
β = 90.840 (10)°
V = 6672.0 (14) Å^3
Z = 4
D_x = 1.665 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
θ = 3.2–16.4°
μ = 2.86 mm^{-1}
T = 298 (2) K
Prism, white
0.32 × 0.20 × 0.18 mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: empirical (Kopfman & Huber, 1968)
T_{min} = 0.571, T_{max} = 0.629
13 082 measured reflections
11743 independent reflections
8293 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 25.0°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 25$
$l = -27 \rightarrow 27$
3 standard reflections every 97 reflections
intensity decay: 5.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.060
S = 0.90
11 743 reflections
848 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.000078 (6)

H atoms were placed at calculated positions with a C—H distance of 0.93 Å.

Table 1
Selected geometric parameters (Å, °).

Eu2—O13	2.343 (3)	Eu2—O9	2.422 (3)
Eu2—O6	2.353 (3)	Eu2—O12	2.573 (3)
Eu2—O8	2.382 (4)	Eu2—O10	2.581 (3)
Eu2—O4	2.393 (3)	Eu2—O7	2.963 (5)
Eu2—O11	2.415 (3)		
O5—Eu1—O6	52.10 (10)	Eu2—O6—Eu1	103.34 (10)
O15—Eu3—O14	159.60 (14)	O5—C24—O6	118.6 (4)

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; 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: VJ1129). Services for accessing these data are described at the back of the journal.

References

Fait, J. (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Jin, L.-P., Wang, Z.-M., Cai, G.-L., Liu, S.-X., Huang, J.-L. & Wang, R.-F. (1994). *Sci. China*, **24**, 577–583.
Kopfman, G. & Huber, R. (1968). *Acta Cryst.* A**24**, 348–357.
Li, X., Bian, Z.-Q., Jin, L.-P., Lu, S.-Z. & Huang, S.-H. (2000). *J. Mol. Struct.* **522**, 117–123.
Li, X., Zheng, X., Jin, L.-P., Lu, S.-Z. & Qin, W.-P. (2000). *J. Mol. Struct.* **519**, 85–91.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997*a*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*b*). *SHELXL*97. University of Göttingen, Germany.
Wang, R.-F., Jin, L.-P., Wang, M.-Z., Huang, S.-H. & Chen, X.-T. (1995). *Acta Chim. Sin.* **53**, 39–45.