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Tetrakis(μ-anthracene-9-carboxylato)-κ^4O:O';κ^3O,O':O';κ^3O:O,O'-bis-[(anthracene-9-carboxylato-κ^2O,O')-(1,10-phenanthroline-κ^2N,N')-erbium(III)]: effects of a noncoordinating anthracene ligand ring system on the final structure of a coordination complex

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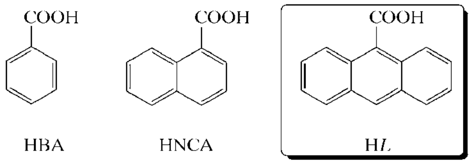
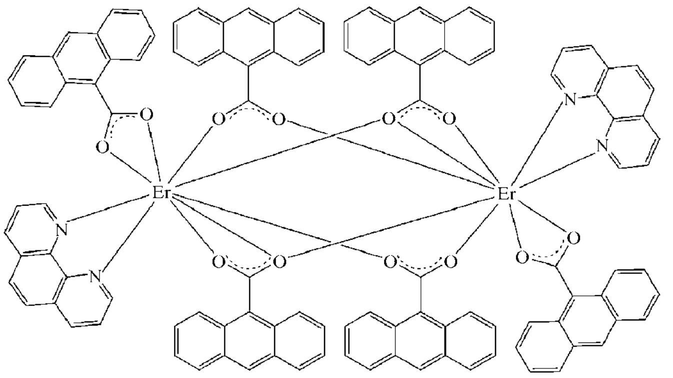
The title complex, $[Er_2(C_{15}H_9O_2)_6(C_{12}H_8N_2)_2]$, has a centrosymmetric binuclear cage structure in which the two Er^{III} atoms are both nine-coordinated and are bridged by four bulky anthracene-9-carboxylate (L) ligands, with a nonbonding Er$\cdots$Er separation of 3.9041 (2) Å. The L groups coordinate each Er^{III} atom in three different ways. The results reported here reveal that the bulky anthracene skeleton of the L ligand plays an important role in the formation of the complex by virtue of intra- and intermolecular π–π stacking and C—H$\cdots\pi$ interactions.

Comment

The rational design and synthesis of functional rare-earth coordination complexes has attracted great interest because of their fascinating structural diversities and potential uses as functional materials (Bünzli, 2006; Cheng *et al.*, 2006; Fu *et al.*, 2005; Suárez *et al.*, 2004). The most effective and facile approach for the synthesis of such complexes is still the appropriate choice of well designed organic ligands as bridges or terminal groups (building blocks), with metal ions or metal clusters as nodes (Ye *et al.*, 2005). Among various ligands, versatile carboxylic acid ligands exhibiting diverse coordination modes, such as benzoic (HBA) and naphthalene-1-carboxylic (HNCA) acids, have been well used in the preparations of various functional rare-earth complexes (Bußkamp *et al.*, 2007; Deacon *et al.*, 2007; Murugesu *et al.*, 2006; Roh *et al.*, 2005; Shi *et al.*, 2001; Wan *et al.*, 2003; Wang *et al.*, 1999, 2006; Yang *et al.*, 2003). In comparison with the aforementioned benzene- and naphthalene-based carboxylic acid ligands, however, far less common has been the use of anthracene-based carboxylic acids, such as the acid used herein, anthracene-9-carboxylic acid (HL).



In our recent research, HNAC and HL have been successfully used to construct a series of novel Ag^I, Cu^{II}, Co^{II}, Ni^{II}, Mn^{II}, Cd^{II} and La^{III} complexes having mononuclear, dinuclear, tetranuclear, hexanuclear and one-dimensional chain structures; these complexes also exhibit interesting magnetic and luminescent properties (Liu, Chang & Wang, 2007; Liu, Chen *et al.*, 2008; Liu *et al.*, 2006; Liu, Wang *et al.*, 2007; Liu, Yan *et al.*, 2008; Zou *et al.*, 2005). To further explore the coordination architectures of the HL ligand bearing the bulky anthracene skeleton in this research, a new Er^{III} complex with L has been synthesized by taking advantage of the carboxylate-bridging coordination abilities of the ligand and the steric bulk of its anthracene ring system, while also incorporating 1,10-phenanthroline (phen) as a chelating co-ligand. We report here the synthesis and the crystal structure of the title complex, (I).



(I)

The structure of (I) consists of a centrosymmetric dinuclear $[Er_2L_6(phen)_2]$ unit, in which each Er^{III} ion is nine-coordinated by two N-atom donors from one chelating phen ligand and seven O atoms from five distinct L ligands (Fig. 1). The Er—O distances [2.2721 (16)–2.6123 (16) Å; Table 1] are in the normal range and are in agreement with those found in other carboxylate-containing Er^{III} complexes (Cheng *et al.*, 2006). The phen ligand acts as a typical chelating ligand, coordinating to the Er^{III} ion with Er—N bond distances of 2.558 (2) and 2.6132 (19) Å, and an N1—Er1—N2 angle of 63.63 (7)°. For L there exist three different forms of carboxyl coordination mode with the Er^{III} centre, namely bidentate *syn–syn* bridging (μ_2-η^1:η^1-bridging), symmetric bidentate chelating (μ_1-η^1:η^1-chelating) and tridentate chelating/

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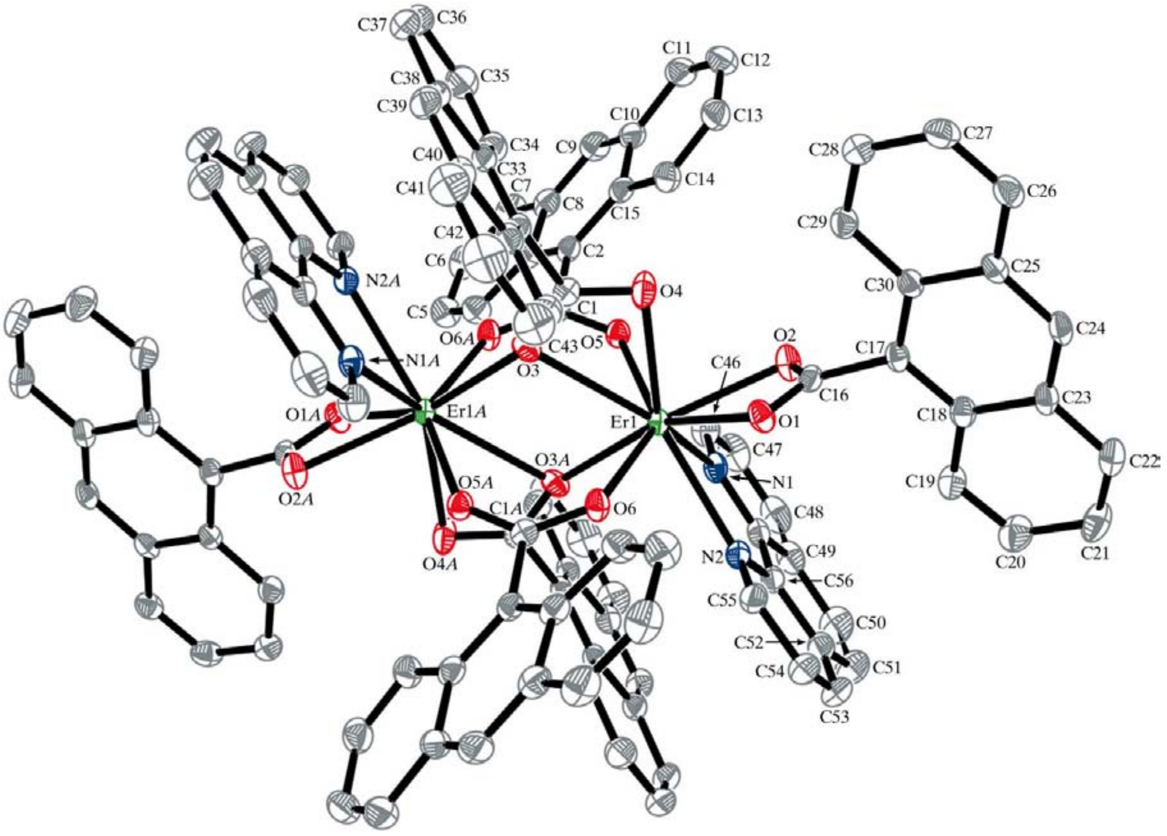

Figure 1
The molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix *A* are generated by the symmetry operation ($-x + 1$, $-y + 1$, $-z + 1$). For the sake of clarity, all H atoms have been omitted.

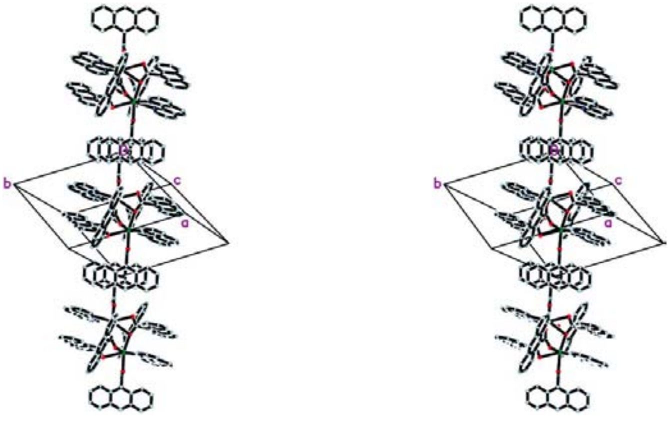

Figure 2
Part of the crystal packing of (I), rendered in stereostyle, showing a π–π stacking chain along the [111] direction. All H atoms have been omitted for clarity.

bridging (η-*O*,*O*′-μ-*O*,*O*) coordination modes, which jointly connect the two Er^{III} atoms to form an eight-membered ring composed of atoms Er1, O5, C1, O6*A*, Er1*A*, O5*A*, C1*A* and O6, as well as a four-membered ring composed of atoms Er1, O3, Er1*A* and O3*A*, with a nonbonding Er1···Er1*A* separation of 3.9041 (2) Å [the suffix *A* denotes the symmetry operation ($-x + 1$, $-y + 1$, $-z + 1$)]. Intramolecular face-to-face π–π stacking is observed between the anthracene and phenanthroline ring systems in the dinuclear unit, with a centroid–centroid separation of 3.636 (5) Å, an average interplanar separation of 3.486 Å and a dihedral angle of 4.8° (Janiak, 2000). In addition, adjacent dinuclear $[Er_2L_6(phen)_2]$ units are arranged into a one-dimensional chain along the [111] direction by intermolecular π–π stacking interactions (symmetry operation: $-x + 2$, $-y + 2$, $-z + 2$; see Fig. 2) between the completely parallel anthracene ring systems of distinct *L* ligands, with a centroid–centroid separation of 3.743 (2) Å.

Moreover, complex (I) contains intra- and intermolecular C—H···π interactions (Table 2) involving the C25–C30 (centroid *Cg*1) and C10–C15 (centroid *Cg*2) benzene rings of the *L* ligands and the C52–C56/N2 (centroid *Cg*3) pyridine rings of the phen ligands, with an edge-to-face orientation that interlinks the dinuclear subunits into two different one-dimensional chains along the [100] and [110] directions, respectively (Fig. 3). The result is a two-dimensional network running parallel to the (001) plane (Sony & Ponnuswamy, 2006). As we have found previously (Liu, Wang *et al.*, 2007), such bulky anthracene-based carboxylate ligands have a large conjugated π system, and thus π–π stacking and/or C—H···π interactions play an important role in the formation of the supramolecular framework. Isolation of complex (I), therefore, is a new proof of the coordination versatility of simple

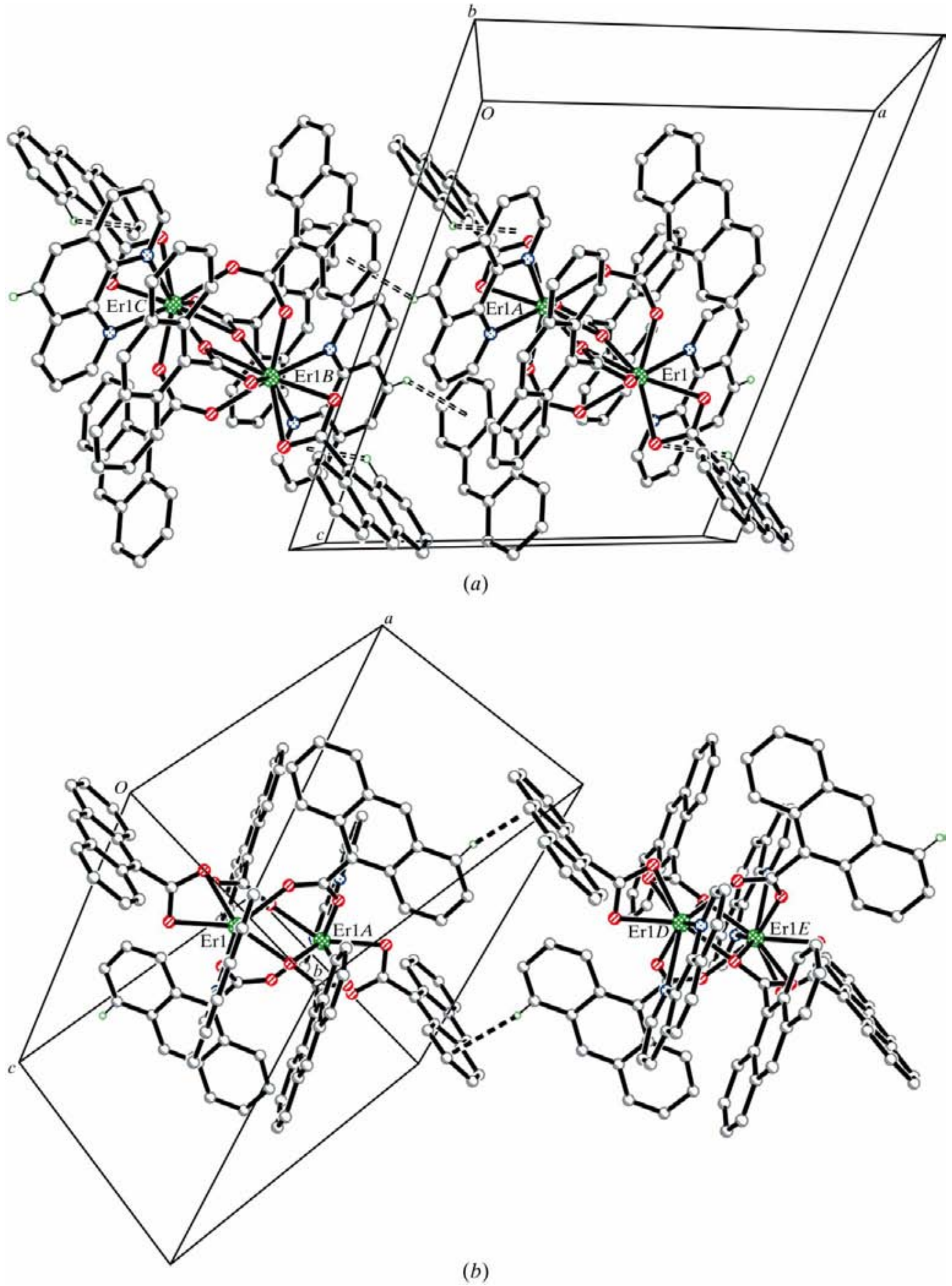

Figure 3
Views of the intra- and intermolecular C—H$\cdots\pi$ interactions in (I), showing two different hydrogen-bonded chains, *viz*. (*a*) along the [100] direction (interactions are shown as dashed open lines) and (*b*) along the [110] direction (interactions are shown as dashed solid lines). The Er^{III} atoms labelled with the suffixes *A*, *B*, *C*, *D* and *E* are generated by the symmetry operations ($-x + 1, -y + 1, -z + 1$), ($x - 1, y, z$), ($-x, -y + 1, -z + 1$), ($x - 1, y - 1, z$) and ($-x, -y, -z + 1$), respectively. Only H atoms involved in the interactions are shown for clarity.

monocarboxylic acid ligands bearing a bulky anthracene ring skeleton.

Experimental

A mixed solution of H*L* (0.05 mmol) and phen (0.05 mmol) in CH_3OH (10 ml) in the presence of excess 2,6-dimethylpyridine (*ca* 0.05 ml for adjusting the pH value to basic conditions) was carefully layered on top of an aqueous solution (15 ml) of $Er(NO_3)_3$ (0.1 mmol) in a test tube. Yellow single crystals of (I) suitable for X-ray analysis appeared on the tube wall after *ca* two weeks at room temperature (yield ~30% based on H*L*). Elemental analysis calculated for $C_{114}H_{70}Er_2N_4O_{12}$: C 67.71, H 3.49, N 2.77%; found: C 67.85, H 3.57, N 2.69%.

Crystal data

$[Er_2(C_{15}H_9O_2)_6(C_{12}H_8N_2)_2]$
$M_r = 2022.26$
Triclinic, $P\overline{1}$
$a = 12.4951$ (2) Å
$b = 13.3839$ (2) Å
$c = 14.9579$ (2) Å
$\alpha = 110.9348$ (8)°
$\beta = 103.1758$ (8)°
$\gamma = 106.6669$ (8)°
$V = 2079.97$ (6) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 2.08$ mm^{-1}
$T = 273$ (2) K
0.20 × 0.14 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\min} = 0.681$, $T_{\max} = 0.789$

24533 measured reflections

7308 independent reflections

6534 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.049$

$S = 1.06$

7308 reflections

595 parameters

H-atom parameters constrained

$\Delta\rho_{\max} = 0.96$ e Å^{-3}

$\Delta\rho_{\min} = -0.43$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Er1—O3^{i}	2.2721 (16)	Er1—O4	2.5222 (18)
Er1—O5	2.2727 (16)	Er1—N2	2.558 (2)
Er1—O6	2.3510 (16)	Er1—O3	2.6123 (16)
Er1—O2	2.3727 (17)	Er1—N1	2.6132 (19)
Er1—O1	2.4024 (17)	Er1—Er1^{i}	3.9041 (2)
O3^{i}—Er1—O5	76.39 (6)	O2—Er1—N2	83.73 (6)
O3^{i}—Er1—O6	74.83 (6)	O1—Er1—N2	71.19 (6)
O5—Er1—O6	137.12 (6)	O4—Er1—N2	140.11 (6)
O3^{i}—Er1—O2	148.50 (6)	O3^{i}—Er1—O3	74.08 (6)
O5—Er1—O2	87.07 (6)	O5—Er1—O3	70.39 (5)
O6—Er1—O2	131.90 (6)	O6—Er1—O3	71.56 (5)
O3^{i}—Er1—O1	150.34 (6)	O2—Er1—O3	125.40 (6)
O5—Er1—O1	132.78 (6)	O1—Er1—O3	107.57 (5)
O6—Er1—O1	77.74 (6)	O4—Er1—O3	49.98 (5)
O2—Er1—O1	54.65 (6)	N2—Er1—O3	144.79 (6)
O3^{i}—Er1—O4	123.26 (6)	O3^{i}—Er1—N1	76.23 (6)
O5—Er1—O4	76.72 (6)	O5—Er1—N1	73.71 (6)
O6—Er1—O4	93.44 (6)	O6—Er1—N1	127.65 (6)
O2—Er1—O4	77.13 (6)	O2—Er1—N1	73.44 (6)
O1—Er1—O4	69.17 (6)	O1—Er1—N1	113.22 (6)
O3^{i}—Er1—N2	90.41 (6)	O4—Er1—N1	138.86 (7)
O5—Er1—N2	137.24 (6)	N2—Er1—N1	63.63 (7)
O6—Er1—N2	73.94 (6)	O3—Er1—N1	137.60 (6)

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

Table 2

Hydrogen-bond geometry (Å, °).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C25–C30, C10–C15 and C52–C56/N2 rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$\cdots$*Cg*1^{ii}	0.93	2.75	3.642 (5)	162
C50—H50$\cdots$*Cg*2^{iii}	0.93	2.91	3.668 (5)	140
C19—H19$\cdots$*Cg*3	0.93	2.86	3.567 (4)	134

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

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms [C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3217). Services for accessing these data are described at the back of the journal.

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