metal-organic compounds

Tris(acetylacetonato-κ²O,O′)(1,10-phenanthroline-κ²N,N′)erbium(III)

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The title compound, $[Er(C_5H_7O_2)_3(C_{12}H_8N_2)]$, is a mixed-ligand metal–organic precursor for chemical vapour deposition, with the Er atom being eight-coordinate. The coordination polyhedron, described as a distorted square antiprism, is formed by three bidentate (chelating) acetylacetonate residues and a phenanthroline ligand in the apical positions. Molecular assembly via C—H···O hydrogen bonds generates a sheet structure in the ac plane. Weak co-operative C—H···π interactions form molecular dimers and contribute to the stability of the intersheet packing. The supramolecular assembly contains voids which form hydrophobic porous channels, surrounded by a cluster of dimers.

Comment

Metal–organic (MO) complexes have been widely employed as precursors for chemical vapour deposition (CVD) for the growth of various thin films (Williams, 1989). Several such MOCVD precursors have been previously synthesized and characterized (Patnaik *et al.*, 1996; Urs *et al.*, 2000; Urs, Anitha *et al.*, 2001; Urs, Shalini *et al.*, 2001; Urs *et al.*, 2003*a*,*b*; Dharmaprakash *et al.*, 2006). In continuation of this work, the title complex, (I), has been synthesized from its less volatile hydrate precursor *i.e.* tris(acetylacetonato)erbium(III) trihydrate, (II). The structure and packing of (I) are discussed here.

(I)
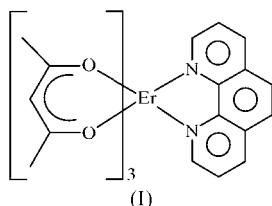
In this eight-coordinate Er^III complex, six O atoms and two N atoms form the primary coordination sphere, lying at the apices of a distorted square antiprism (Fig. 1). The antiprismatic arrangement is common among rare earth metal complexes and has previously been observed in analogous complexes of europium(III) (Watson *et al.*, 1972), lanthanum(III) (Kuz'mina *et al.*, 1997), cerium(III) and praseodymium(III) (Christidis *et al.*, 1998), and samarium(III) (Urs, Shalini *et al.*, 2001). The Er—O and Er—N bond distances are in the ranges 2.287 (4)–2.324 (4) and 2.523 (5)–2.568 (5) Å, respectively, in good agreement with their average values (Orpen *et al.*, 1989). Selected geometric parameters are given in Table 1. The metal atom is displaced by 1.38 (1) and 1.19 (1) Å, respectively, out of the planes of the square faces N1/N2/O1/O2 and O3/O4/O5/O6. The angle between the coplanar square faces is 2.2 (1)°.
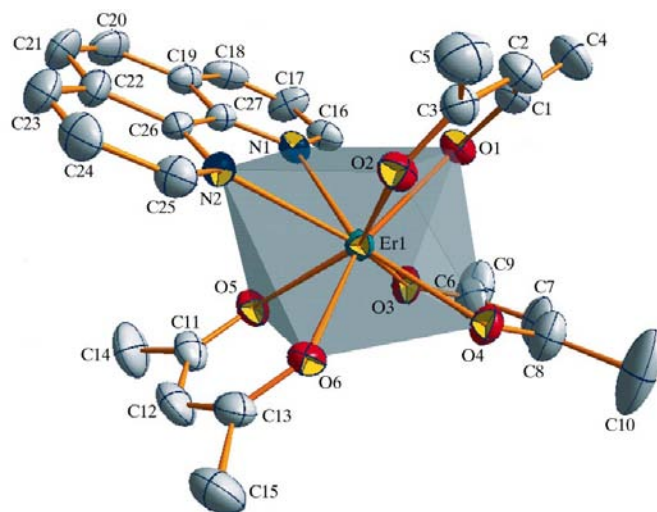

Figure 1
A perspective view of the eightfold coordination polyhedron of (I), possessing a distorted square-antiprismatic geometry. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.
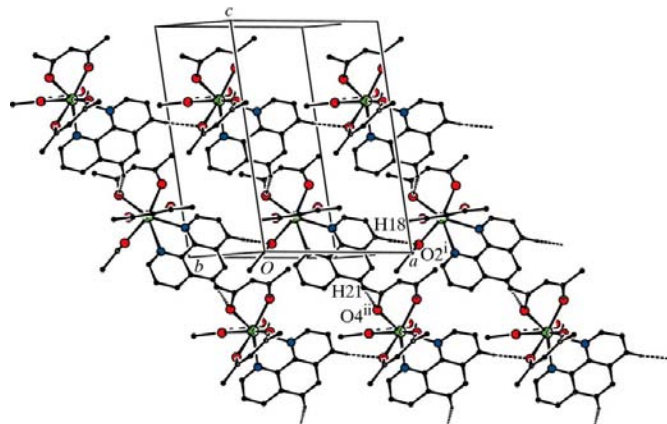

Figure 2
The crystal packing of (I), viewed in the ac plane, showing the sheet structure formed by C—H···O hydrogen bonds. H atoms are represented as small spheres of arbitrary radii, but those not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $1 + x, y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

The ligands span opposite *s*-edges of the polyhedron, with O···O and N···N bite distances of 2.750 (6)–2.775 (7) and 2.708 (6) Å, respectively, and O—Er—O and N—Er—N bite angles of 73.0 (2)–74.1 (2) and 64.3 (2)°, respectively. The six-membered chelate rings formed by Er^{III} and the acetylacetone residues are slightly puckered. The angles between the pairs of planes Er1/O1/O2 and C1/C2/C3, Er1/O3/O4 and C6/C7/C8, and Er1/O5/O6 and C11/C12/C13 are 10.4 (8), 21.0 (7) and 12.2 (9)°, respectively. The mean plane defined by the phenanthroline ring (N1/N2/C16–C27) has a maximum atomic deviation of 0.08 (1) Å for atom C24.

Compound (I) is isostructural with previously reported eight-coordinate complexes of europium(III), (III) (Watson *et al.*, 1972), praseodymium(III), (IV) (Christidis *et al.*, 1998), and samarium(III), (V) (Urs, Shalini *et al.*, 2001). The values of the unit-cell similarity index, Π, indicating the degree of isostructurality (Kálmán *et al.*, 1993), between (I) and (III), (I) and (IV), and (I) and (V) are 0.015, 0.004 and 0.002, respectively.

Geometric parameters and symmetry codes for the weak intermolecular interactions in (I) are listed in Table 2. Intermolecular associations *via* C18—H18···O2^i and C21—H21···O4^{ii} result in the formation of one-dimensional chains along the [100] direction and an approximate [202] direction. Combining such intermolecular linkages gives rise to a sheet structure in the *ac* plane (Fig. 2). Co-operative C2—H2···Cg1^{iii} (Cg1 is the centroid of the N1/C16–C19/C27 ring) interactions between molecules related by a centre of inversion aggregate the molecules to form dimers and stabilize the intersheet packing. The intersheet packing is not very efficient and consists of significant solvent-accessible voids with approximate volumes of 51 (1) and 49 (1) Å^3 (*PLATON*;

Spek, 2003). The voids are located at $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 1, 1)$, respectively, and are surrounded by clusters of dimers with the methyl groups of the acetylacetone residues exposed to the empty spaces. The voids form hydrophobic porous channels along the *a* axis, as illustrated in Fig. 3. The presence of nanometre-sized porous frameworks in the supramolecular assembly of metal–organic complexes has implications for chemical storage, separation and heterogeneous catalysis (Kitagawa *et al.*, 2004).

Experimental

The title compound, (I), was synthesized from its precursor trihydrate complex, (II). Acetylacetone (15 mmol, 1.55 ml) was added to an erbium chloride hexahydrate ($ErCl_3 \cdot 6H_2O$) solution (5 mmol, 1.9 g; 30% ethanol–water mixture). Ammonia (5 *M*) was added gradually to achieve a pH of 6–7. After stirring at room temperature for 2 h, the mixture yielded a precipitate which was filtered off, washed with water and dried in a vacuum. The resulting crude product was recrystallized from an aqueous ethanol solution, giving the pure trihydrate complex, (II). To obtain (I) from (II), a solution of 1,10-phenanthroline in ethanol was added to an ethanolic solution of (II) in a 1:1 molar ratio. After stirring at room temperature for 3 h, the adducted compound precipitated out. The precipitate thus formed was filtered off, repeatedly washed with water and dried in a vacuum. Single crystals of (I) suitable for X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

$[Er(C_5H_7O_2)_3(C_{12}H_8N_2)]$	$Z = 4$
$M_r = 644.78$	$D_x = 1.487$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.4660 (10)$ Å	$\mu = 2.95$ mm^{-1}
$b = 21.025 (3)$ Å	$T = 295 (2)$ K
$c = 14.643 (2)$ Å	Plate, pale green
$\beta = 98.670 (2)°$	$0.26 \times 0.14 \times 0.10$ mm
$V = 2881.0 (6)$ Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	21859 measured reflections
φ and ω scans	5638 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	4604 reflections with $I > 2\sigma(I)$
$T_{min} = 0.565$, $T_{max} = 0.747$	$R_{int} = 0.034$
	$\theta_{max} = 26.0°$

Refinement

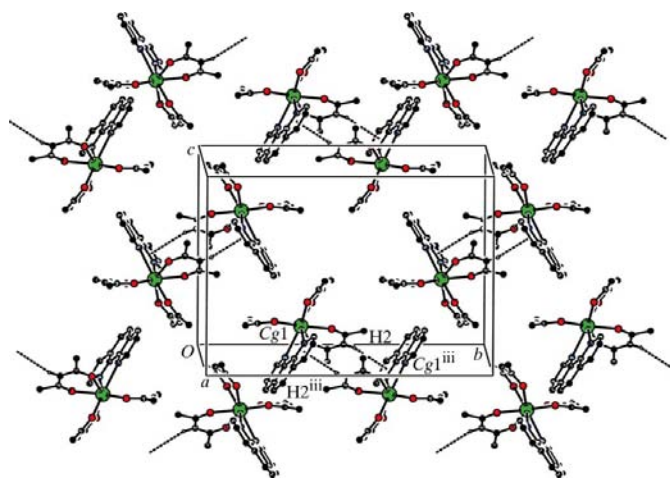|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + 7.0644P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{max} = 0.005$
$S = 1.26$	$\Delta\rho_{max} = 0.92$ e Å^{-3}
5638 reflections	$\Delta\rho_{min} = -0.71$ e Å^{-3}
331 parameters	
H-atom parameters constrained	

Figure 3
The packing of (I), viewed down the *a* axis, illustrating the putative hydrophobic porous channels in the middle and at the corners of the unit cell. The empty channels are surrounded by a cluster of molecular dimers, which are formed by co-operative C—H···π interactions. H atoms are represented as small spheres of arbitrary radii, but those not involved in hydrogen bonding have been omitted for clarity. Cg1 is the centroid of the N1/C16–C19/C27 ring. [Symmetry code: (iii) $1 - x$, $1 - y$, $-z$.]

All H atoms were placed in calculated positions, with aryl C—H = 0.93 Å and methyl C—H = 0.96 Å, and allowed to ride on their parent C atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms. The features in the residual electron density are possibly due to disorder in the crystal. The inclusion of the corresponding peaks, however, did not yield satisfactory results.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

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Table 1
Selected geometric parameters (Å, °).

Er1—O2	2.287 (4)	O2—C3	1.274 (7)
Er1—O3	2.297 (4)	O3—C6	1.261 (8)
Er1—O6	2.300 (4)	O4—C8	1.272 (9)
Er1—O1	2.302 (4)	O5—C11	1.257 (8)
Er1—O4	2.318 (4)	O6—C13	1.257 (8)
Er1—O5	2.324 (4)	N1—C16	1.317 (7)
Er1—N1	2.523 (5)	N1—C27	1.358 (8)
Er1—N2	2.568 (5)	N2—C25	1.324 (7)
O1—C1	1.260 (8)	N2—C26	1.359 (8)
O3—Er1—O6	116.83 (17)	C1—O1—Er1	135.2 (4)
O2—Er1—O1	74.05 (15)	C3—O2—Er1	136.2 (4)
O3—Er1—O4	73.92 (17)	C6—O3—Er1	131.7 (5)
O6—Er1—O4	77.30 (16)	C8—O4—Er1	131.1 (5)
O3—Er1—O5	74.69 (16)	C11—O5—Er1	134.2 (5)
O6—Er1—O5	72.99 (17)	C13—O6—Er1	135.9 (5)
O4—Er1—O5	119.57 (17)	C16—N1—C27	117.5 (6)
O2—Er1—N1	108.94 (15)	C16—N1—Er1	122.4 (5)
O1—Er1—N1	73.54 (16)	C27—N1—Er1	119.6 (4)
O2—Er1—N2	70.91 (16)	C25—N2—C26	117.2 (5)
O1—Er1—N2	110.19 (16)	C25—N2—Er1	124.0 (4)
N1—Er1—N2	64.25 (15)	C26—N2—Er1	118.7 (3)

Table 2
Hydrogen-bond geometry (Å, °).

$Cg1$ is the centroid of the N1/C16–C19/C27 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C18—H18$\cdots$O2[i]	0.93	2.39	3.242 (8)	153
C21—H21$\cdots$O4[ii]	0.93	2.58	3.416 (10)	150
C2—H2$\cdots$Cg1[iii]	0.93	2.98	3.879 (9)	163

Symmetry codes: (i) $x + 1, y, z$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$.

DIAMOND (Brandenburg & Berndt, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3035). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. & Berndt, M. (2006). *DIAMOND*. Release 3.1d. Crystal Impact GbR, Bonn, Germany.
Bruker (2003). *SMART* (Version 5.631) and *SAINT-Plus* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
Christidis, P. C., Tossidis, I. A., Paschalidis, D. G. & Tzavellas, L. C. (1998). *Acta Cryst.* C**54**, 1233–1236.
Dharmaprakash, M. S., Thamotharan, S., Neelgund, G. M. & Shivashankar, S. A. (2006). *Acta Cryst.* E**62**, m434–m436.
Kálmán, A., Párkányi, L. & Argay, G. (1993). *Acta Cryst.* B**49**, 1039–1049.
Kitagawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
Kuz'mina, N. P., Chugarov, N. V., Pisarevsky, A. P. & Martynenko, L. I. (1997). *Koord. Khim.* **23**, 450–454.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.
Patnaik, S., Guru Row, T. N., Raghunathan, L., Devi, A., Goswami, J., Shivashankar, S. A., Chandrasekaran, S. & Robinson, W. T. (1996). *Acta Cryst.* **52**, 891–894.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Urs, U. K., Anitha, K. C., Raghunathan, K. L., Shivashankar, S. A., Robinson, W. T. & Guru Row, T. N. (2001). *Acta Cryst.* E**57**, m242–m243.
Urs, U. K., Dharmaprakash, M. S., Shivashankar, S. A. & Guru Row, T. N. (2003a). *Acta Cryst.* E**59**, m1–m2.
Urs, U. K., Dharmaprakash, M. S., Shivashankar, S. A. & Guru Row, T. N. (2003b). *Acta Cryst.* E**59**, m83–m84.
Urs, U. K., Shalini, K., Cameron, T. S., Shivashankar, S. A. & Guru Row, T. N. (2001). *Acta Cryst.* E**57**, m457–m458.
Urs, U. K., Shalini, K., Shivashankar, S. A. & Guru Row, T. N. (2000). *Acta Cryst.* C**56**, e448–e449.
Watson, W. H., Williams, R. J. & Stemple, N. R. (1972). *J. Inorg. Nucl. Chem.* **34**, 501–508.
Williams, J. O. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1110–1120.