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{4,10-Bis[2-(2-oxidobenzylidene-amino-κ^2N,O)benzyl]-1,7-dioxa-4,10-diazacyclododecane-$\kappa^4O^1,N^4,O^3,N^{10}$}ytterbium(III) perchlorate acetonitrile solvate

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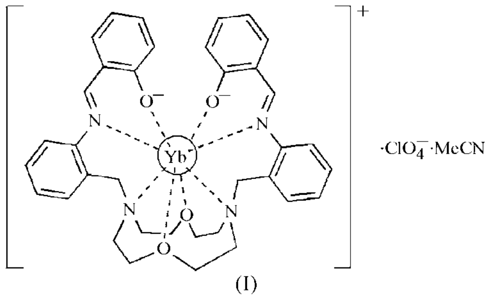
In the crystal structure of the title compound, $[\mathrm{Yb(C_{36}H_{38}N_4O_4)]ClO_4\cdot CH_3CN}$, the ytterbium ion is eight-coordinated and deeply buried in the cavity of the dianionic Schiff base ligand. The coordination polyhedron may be described as a distorted square antiprism that shows a twist angle of 29.5 (1)° between the two square planes. The receptor adopts a *syn* arrangement, with both pendent arms on the same side of the crown group, and there are two helicities (one associated with this layout of the pendent arms and the other with the conformation of the crown ring), which give rise to enantiomeric pairs of diastereoisomers, *viz*. $\Delta(\lambda\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta\delta)$.

Comment

Recently, we described the coordination ability of the dianionic Schiff base bibrachial lariat ether *N*,*N*′-bis(2-salicylaldiminatobenzyl)-4,10-diaza-12-crown-4 (H_2L) toward lanthanide(III) ions (González-Lorenzo *et al.*, 2005). We have found that this receptor shows a certain degree of selectivity toward the heaviest lanthanide(III) ions, only forming stable complexes with lanthanides from $\mathrm{Lu^{III}}$ to $\mathrm{Ho^{III}}$. Moreover, the luminescence properties of the corresponding $\mathrm{Yb^{III}}$ and $\mathrm{Er^{III}}$ complexes make them ideally suited for use as luminescent tags, even in protic media. They have been shown to be emissive in the near-IR and time-resolved studies revealed that the solvent is excluded from the inner coordination environment in solution.

The crystal structures of $[\mathrm{Ho}(L)]\mathrm{ClO_4}$, (II), and $[\mathrm{Er}(L)]\mathrm{ClO_4\cdot H_2O}$, (III), were reported previously (González-Lorenzo *et al.*, 2005). We describe here the crystal structure of the title compound, (I), which is the corresponding ytterbium complex, $[\mathrm{Yb}(L)]\mathrm{ClO_4\cdot CH_3CN}$. Some examples of X-ray crystal structures of $\mathrm{Yb^{III}}$ complexes with Schiff base ligands have been found in the literature. In those systems, the Schiff base function is incorporated within an acyclic ligand (Liu & Ding, 1998), within a macrocyclic receptor (Casellato *et al.*, 2000; Lisowski & Starinowick, 2003; Barge *et al.*, 2005), in a podand (Costes *et al.*, 1998; Bernhardt *et al.*, 2001; Kanesato *et al.*, 2004) or in a cryptand (Rodríguez-Cortiñas *et al.*, 2002). The X-ray crystal structure described here is the first example of a $\mathrm{Yb^{III}}$ complex with a lariat ether containing Schiff base pendent arms.



(I)

Although crystals of (II) and (III) are isomorphous in space group $P\overline{1}$, compound (I) crystallizes in the monoclinic space group $P2_1/c$. Figs. 1 and 2 show two different perspectives of the structure of the $[\mathrm{Yb}(L)]^+$ complex, while selected bond lengths and angles are given in Table 1. The structure of the complex in (I) is quite similar to those in (II) and (III) (González-Lorenzo *et al.*, 2005). The $\mathrm{Yb^{III}}$ ion is wrapped up in the Schiff base receptor, bound to its eight available donor atoms. The coordination environment of the metal may be described as a distorted square antiprism composed of two parallel pseudo-planes; atoms N1, O1, N4 and O4 define one of the pseudo-planes (the mean deviation from planarity is 0.21 Å), while atoms N2, O2, N3 and O3 define the other (the mean deviation from planarity is 0.10 Å). The angle between

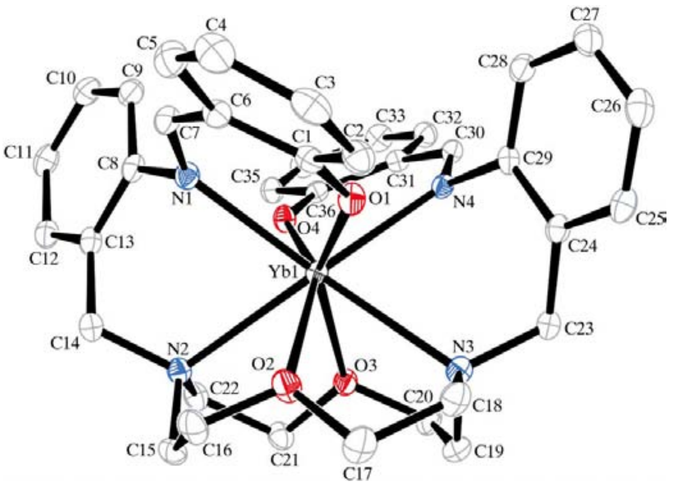


Figure 1
A front view of the $[\mathrm{Yb}(L)]^+$ cation, showing the $\Delta(\lambda\lambda\lambda\lambda)$ isomer. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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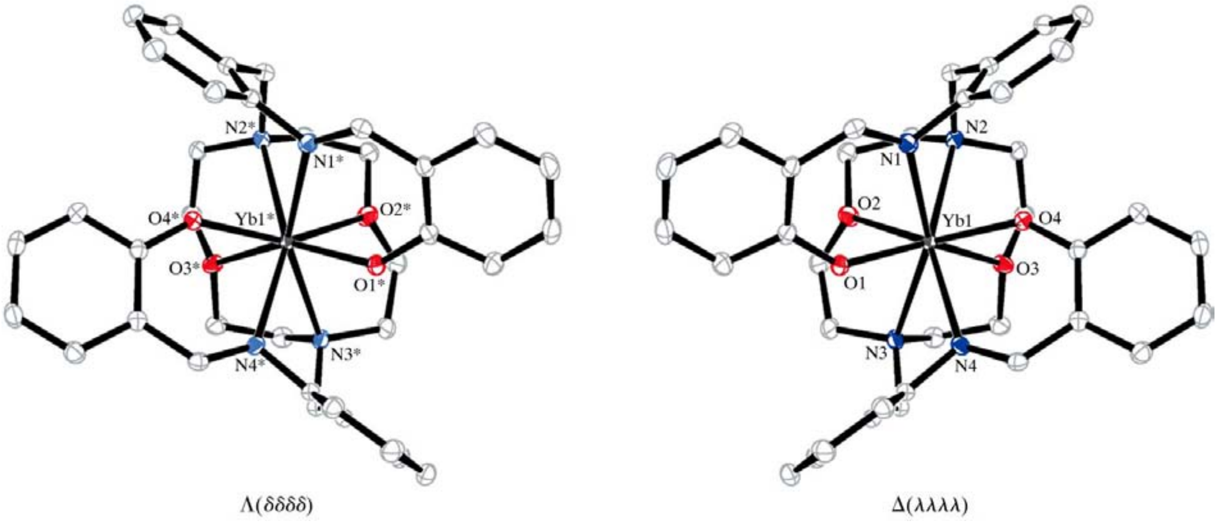

Λ(δδδδ)

Δ(λλλλ)

Figure 2
A top view of the $[Yb(L)]^+$ cation, showing the optical isomers Λ (left) and Δ (right). Atoms labeled with an asterisk (*) are at the symmetry position ($-x$, $-y$, $-z$).

these two least-squares planes is 0.91 (4)°, with the ytterbium ion located 1.1343 (2) Å from the first plane and 1.5809 (2) Å from the second. The twist angle between two square planes is 29.5 (1)°, showing a deformation of the coordination polyhedron from a square antiprism (ideal value 45°) toward a square prism (ideal value 0°).

Fig. 1 allows an appraisal of the conformation adopted by the bibrachial receptor. Both side arms are orientated on the same side of the crown ring, resulting in a *syn* conformation. Likewise, the lone pairs of both pivotal N atoms are directed into the receptor cavity in an *endo–endo* arrangement. In $[Yb(L)]^+$, there are two helicities (one associated with this layout of the pendent arms and the other with the conformation of the crown ring), which may give rise to two enantiomeric pairs of diastereoisomers. On the one hand, the coordination of the crown ring donor atoms to the Yb^{III} ion gives rise to five-membered chelate rings, Yb—N—C—C—O, adopting conformations that can be described as λ or δ. On the other hand, the *syn* conformation adopted by the receptor *L* leads to a chiral structure for the complex, with two possible optical isomers, labeled Λ or Δ (see Fig. 2), depending on the skew form of the pendent arms (Jacques & Desreux, 1994). The title compound is a racemic mixture of Δ(λλλλ) and Λ(δδδδ).

The N2—C14—C13 and N3—C23—C24 angles, related to the fold of the pendant arms in the receptor, are 114.28 (17) and 114.81 (17)°, respectively, while the planes defined by the benzene rings intersect at 20.04 (6)° and those formed by the phenol rings intersect at 54.81 (7)°. The benzene and phenol rings of the same pendant arm form angles of 70.98 (6) and 74.69 (7)°. The distances between the donor atoms give an idea about the shape and size of the receptor cavity. In (I), the pivotal N atoms are separated by 4.339 (3) Å, the imine N atoms by 4.042 (3) Å and the phenolate O atoms by 3.182 (2) Å.

Experimental

The synthesis of $[Yb(L)]ClO_4\cdot H_2O$ was described by González-Lorenzo *et al.* (2005). Crystals of (I) suitable for X-ray crystallographic analysis were grown by slow diffusion of diethyl ether into an acetonitrile solution of $[Yb(L)]ClO_4\cdot H_2O$. During this process, the crystal solvent was replaced with acetonitrile.

Crystal data

$[Yb(C_{36}H_{38}N_4O_4)]ClO_4\cdot C_2H_3N$
$M_r = 904.25$
Monoclinic, $P2_1/c$
$a = 11.901\ (2)$ Å
$b = 13.855\ (3)$ Å
$c = 21.936\ (4)$ Å
$\beta = 95.347\ (3)°$
$V = 3601.3\ (12)$ Å^3
$Z = 4$
$D_x = 1.668$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.73$ mm^{-1}
$T = 100.0\ (1)$ K
Prism, yellow
0.48 × 0.3 × 0.26 mm

Data collection

Siemens SMART CCD 1000 diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.347$, $T_{\max} = 0.49$
65102 measured reflections
8961 independent reflections
7644 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.046$
$S = 1.09$
8961 reflections
479 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0135P)^2 + 3.274P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.85$ e Å^{-3}

The positions of all H atoms were calculated geometrically and a riding model was used in their refinement, with C—H distances of 0.93–0.97 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C), or $1.5U_{\rm eq}$(C) for the methyl group.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to

Table 1
Selected geometric parameters (Å, °).

Yb1—O1	2.1254 (15)	Yb1—N1	2.4511 (18)
Yb1—O4	2.1383 (14)	Yb1—N4	2.4560 (18)
Yb1—O3	2.4039 (15)	Yb1—N3	2.6174 (18)
Yb1—O2	2.4184 (16)	Yb1—N2	2.6190 (18)
O1—Yb1—O4	126.76 (6)	O3—Yb1—N3	67.97 (5)
O1—Yb1—O3	150.70 (5)	O3—Yb1—N2	67.86 (5)
O1—Yb1—O2	75.81 (6)	O4—Yb1—O3	75.14 (5)
O1—Yb1—N1	74.01 (6)	O4—Yb1—O2	150.21 (5)
O1—Yb1—N4	78.00 (6)	O4—Yb1—N1	75.65 (6)
O1—Yb1—N3	82.75 (6)	O4—Yb1—N4	73.47 (6)
O1—Yb1—N2	127.79 (6)	O4—Yb1—N3	129.24 (5)
O2—Yb1—N1	95.96 (6)	O4—Yb1—N2	83.34 (6)
O2—Yb1—N4	135.16 (5)	N1—Yb1—N2	75.00 (6)
O2—Yb1—N3	66.30 (5)	N1—Yb1—N3	153.85 (6)
O2—Yb1—N2	66.86 (5)	N1—Yb1—N4	110.92 (6)
O3—Yb1—N1	134.68 (5)	N3—Yb1—N2	111.91 (6)
O3—Yb1—O2	92.59 (5)	N4—Yb1—N2	153.21 (6)
O3—Yb1—N4	92.87 (5)	N4—Yb1—N3	74.83 (6)

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3011). Services for accessing these data are described at the back of the journal.

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