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Aquatris(1,10-phenanthroline)(*trans*-2,3-dimethylacrylato)ytterbium(III)

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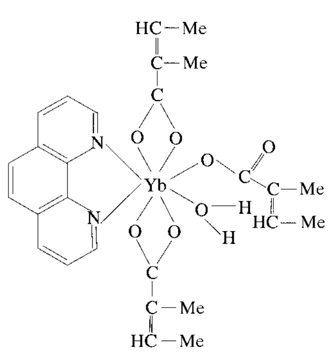
The title mononuclear complex, $[Yb(C_5H_7O_2)_3(C_{12}H_8N_2)(H_2O)]$, is a most uncommon carboxylate complex of a rare earth metal. Each Yb^{III} ion is eightfold coordinated, being bonded to five O atoms of three dimethylacrylate groups, both N atoms of a phenanthroline and one O atom of a water molecule, giving a distorted square antiprismatic coordination polyhedron.

Comment

The chemistry of rare earth complexes is a fascinating field because of the potential use of such complexes as extraction agents, luminescent compounds and catalysts (Richardson, 1982; Molander & Hoberg, 1992). Knowledge of the structures of lanthanide compounds is vital to the interpretation of their bonding and chemical properties. *trans*-2,3-Dimethylacrylic acid is a prochiral compound and has often been used as a model substrate in asymmetric hydrogenation catalysis (Ashby & Halpern, 1991). Information on the stereochemistry of its complexes can help to clarify the catalytic mechanism of asymmetric homogeneous hydrogenation. The present investigation of the title compound, (I), forms part of our studies of rare earth complexes with unsaturated carboxylic acids.



(I)

In (I) (Fig. 1), the Yb^{III} ion is eightfold coordinated by five O atoms from three *trans*-2,3-dimethylacrylate groups, two N atoms from a phenanthroline and one O atom from a water molecule. The phenanthroline forms a five-membered chelate ring (consisting of Yb, N1, N2, C11 and C12) and two *trans*-2,3-dimethylacrylate groups act as bidentate chelating ligands, forming two four-membered chelating rings (consisting of Yb, O3, C18 and O4, and of Yb, O5, C23 and O6). The two four-atom mean planes make a dihedral angle of 93.8 (2)° and form dihedral angles with the mean plane through atoms Yb, N1, C11, C12 and N2 of 100.8 (2) and 8.1 (2)°, respectively. The coordination polyhedron of Yb^{III} is a slightly distorted square antiprism. The two N atoms of a phenanthroline group, five carboxylate O atoms and the O atom from a water molecule occupy the ligand sites of two square faces of the antiprism. The least-squares plane through O3, O4, O5 and O6, and that through O1, O7, N1 and N2 are essentially parallel to each other [dihedral angle of about 3.4 (2)°] and the distances of Yb^{III} from the least-squares mean planes of the square faces are 1.3998 (6) and 1.2324 (6) Å, respectively.

Lanthanide carboxylate complexes have been widely studied and most are found to exhibit a variety of dimeric, trimeric or infinite chain structures in the solid state (Ma & Ni, 1996; Wei *et al.*, 1998). The title complex, however, is a monomer. We believe that two factors hinder the complex polymerization, one is the small radius of Yb^{III} (a consequence of lanthanide contraction) and the other is steric hindrance; the *trans*-2,3-dimethylacrylate group is larger than the methylacrylate ligand in the dimeric complex $[Yb(C_4H_5O_2)_3(C_{12}H_8N_2)]_2$, (II) (Lu *et al.*, 1999).

Carboxylate ligands exhibit various modes of coordination to rare earth metal ions (Ma & Ni, 1996). The title complex

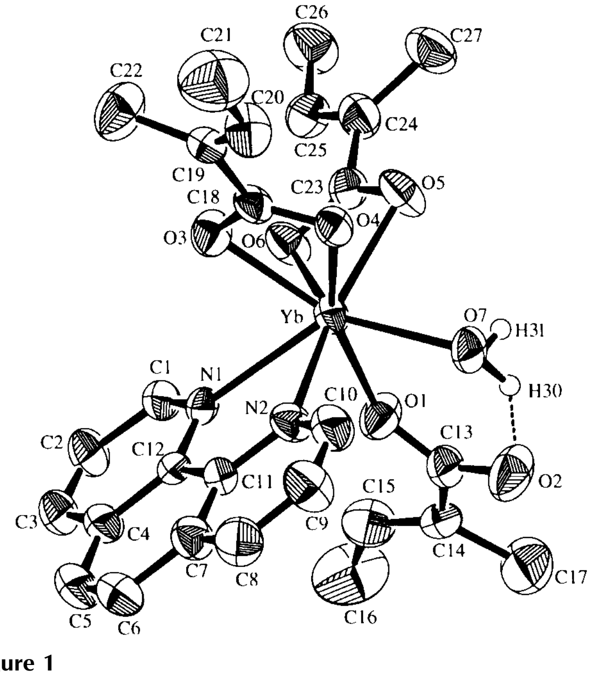


Figure 1
The molecular structure and atom-numbering scheme of the title complex. Displacement ellipsoids are shown at the 40% probability level and H atoms, except those of the aqua ligand, have been omitted for clarity.

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presents two modes, bidentate or monodentate, and also has two distinct Yb—O(chelating) distances. The average Yb—O(chelating) bond length (2.348 Å) in the title complex is nearly equal to the corresponding length (2.363 Å) in complex (II). This indicates that different carboxylate groups with the same mode of coordination with the Yb^{III} ion have essentially the same bond lengths. The Yb—O(monodentate) and Yb—O(water) distances are 2.233 (8) and 2.295 (7) Å, respectively, which are slightly larger than the average value (2.218 Å) of the Yb—O(bridging) bonds in complex (II). The Yb—N bond lengths are similar at 2.458 (8) and 2.478 (9) Å. The Yb—O(chelating) bond lengths are significantly longer than the sum of the covalent radii of the two atoms, which is to be expected because the angles O3—Yb—O4 and O5—Yb—O6 of about 55° indicate ring strain. This may be the reason why a water molecule also takes part in the coordination. The water ligand also forms an intramolecular hydrogen bond with the uncoordinated O atom of a carboxylate ligand.

The carboxyl groups give rise to very strong IR absorptions, which can in principle be used to distinguish between the different coordination modes of the ligands (*i.e.* ionic, monodentate or bidentate) by comparison of the band separation with that of the corresponding sodium compound (Deacon & Phillips, 1980). A separation between ν_{asym}(COO) and ν_{sym}(COO) that is substantially greater than the value of 170 cm^{-1} for the sodium salt is thought to be indicative of monodentate coordination. However, the value for the title complex, in which the carboxylate ligands are bidentate and monodentate, is 150 cm^{-1}, indicating that the spectroscopic technique could not correctly identify the coordination mode.

Experimental

trans-2,3-Dimethylacrylic acid (150 mg, 1.5 mmol) and Yb(NO$_3$)$_3$·6H$_2$O (130 mg, 0.3 mmol) were dissolved in aqueous ethanol (12 ml, 1:1 *v*/*v*) and adjusted to pH 4.3 by the addition of 10% NaOH solution. An ethanolic solution of 1,10-phenanthroline (60 mg, 0.3 mmol) was added with stirring to the solution. After filtration, the filtrate was allowed to stand at room temperature, whereupon single crystals suitable for X-ray work were obtained after a few days. Analysis: calculated C 48.50, H 4.67, N 4.19, Yb 25.88%; found C 49.06, H 4.91, N 4.13, Yb 26.08%. IR spectra: ν_{asym}(COO) 1578, ν_{sym}(COO) 1428, ν(C=C) 1658, ν(C—C, phen ring) 1520, ν(C—H, out of phen ring bend) 731 and 850 cm^{-1}.

Crystal data

$[Yb(C_5H_7O_2)_3(C_{12}H_8N_2)(H_2O)]$
$M_r = 668.59$
Monoclinic, $P2_1/n$
$a = 9.512\ (3)$ Å
$b = 20.472\ (10)$ Å
$c = 14.412\ (3)$ Å
$\beta = 99.92\ (2)^\circ$
$V = 2764\ (1)$ Å^3
$Z = 4$
$D_x = 1.606$ Mg m^{-3}
$D_m = 1.64$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 21 reflections
$\theta = 13.93$–25.18°
$\mu = 3.43$ mm^{-1}
$T = 293$ K
Square prism, colourless
0.30 × 0.20 × 0.20 mm

Data collection

AFC-7*R* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: part of the refinement model (Walker & Stuart, 1983)
$T_{min} = 0.377$, $T_{max} = 0.504$
5655 measured reflections
5384 independent reflections
3359 reflections with $I > 2.5\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 25.5^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 24$
$l = -17 \rightarrow 17$
3 standard reflections every 200 reflections intensity decay: 5.66%

Refinement

Refinement on *F*
$R = 0.052$
$wR = 0.063$
$S = 1.980$
3359 reflections
335 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o) + 4F_o^2/\sigma^2(F_o)^2$
$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -1.21$ e Å^{-3}
Extinction correction: secondary (Zachariasen, 1963)
Extinction coefficient: 1.690×10^{-7}

Table 1
Selected geometric parameters (Å, °).

Yb—O1	2.233 (8)	Yb—N2	2.480 (9)
Yb—O3	2.347 (8)	O1—C13	1.26 (1)
Yb—O4	2.396 (7)	O2—C13	1.22 (1)
Yb—O5	2.310 (8)	O3—C18	1.25 (1)
Yb—O6	2.342 (7)	O4—C18	1.27 (1)
Yb—O7	2.295 (7)	O5—C23	1.28 (1)
Yb—N1	2.458 (8)	O6—C23	1.25 (1)
O1—Yb—O3	147.9 (3)	O4—Yb—O6	116.3 (3)
O1—Yb—O4	156.3 (3)	O4—Yb—O7	79.5 (3)
O1—Yb—O5	98.9 (3)	O4—Yb—N1	121.1 (3)
O1—Yb—O6	82.2 (3)	O4—Yb—N2	77.4 (3)
O1—Yb—O7	76.9 (3)	O5—Yb—O6	56.1 (3)
O1—Yb—N1	74.4 (3)	O5—Yb—O7	84.3 (3)
O1—Yb—N2	95.3 (3)	O5—Yb—N1	137.3 (3)
O3—Yb—O4	54.9 (2)	O5—Yb—N2	155.4 (3)
O3—Yb—O5	93.8 (3)	O6—Yb—O7	131.4 (3)
O3—Yb—O6	80.7 (3)	O6—Yb—N1	81.2 (3)
O3—Yb—O7	133.9 (3)	O6—Yb—N2	146.6 (3)
O3—Yb—N1	76.3 (3)	O7—Yb—N1	132.1 (3)
O3—Yb—N2	84.6 (3)	O7—Yb—N2	79.4 (3)
O4—Yb—O5	81.5 (3)	N1—Yb—N2	66.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H30···O2	0.97	1.82	2.650 (12)	142
O7—H31···O4^i	0.95	2.14	2.706 (11)	117

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992) and *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1371). Services for accessing these data are described at the back of the journal.

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