ORGANOLANTHANOIDS

VII *. THE CRYSTAL AND MOLECULAR STRUCTURE OF DIBROMO-η^5-CYCLOPENTADIENYLTRIS(TETRAHYDROFURAN)YTTERBIUM(III)

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(Received March 21st, 1985)

Summary

Crystals of dibromo-η^5-cyclopentadienyltris(tetrahydrofuran)ytterbium(III) are monoclinic, $P2_1/n$ (C_{2n}^5, No. 14), with a 15.310(15), b 16.900(17), c 7.968(8) Å, β 96.66(5)° and $Z = 4$. The ytterbium is pseudo-octahedrally coordinated by a cyclopentadienyl ligand, *trans* bromines, and *mer* tetrahydrofuran ligands, and the ytterbium–oxygen distance *trans* to cyclopentadienyl is longer than the other ytterbium–oxygen bonds.

Introduction

We have recently reported the synthesis of bromobis(cyclopentadienyl)ytterbium(III) by the oxidation reaction (eq. 1) [1].

$$2(C_5H_5)_2Yb + HgBr_2 \rightarrow 2(C_5H_5)_2YbBr + Hg\downarrow \qquad (1)$$
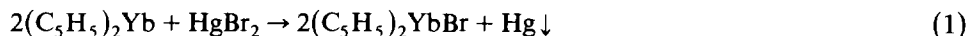
Attempted crystallization of the complex, $(C_5H_5)_2YbBr(thf)$ (thf = tetrahydrofuran), over a prolonged period gave some single crystals with the same space group and similar cell dimensions to those of $(\eta^5\text{-}C_5H_5)ErCl_2(thf)_3$ [2], suggesting formation of $(\eta^5\text{-}C_5H_5)YbBr_2(thf)_3$. To identify this compound unequivocally, and because no crystal structure of an organolanthanoid bromide appears to have been reported [3–5], we have determined the crystal and molecular structure of the compound. Unit-cell data have also been obtained for the product of a similar decomposition of $(C_5H_5)_2YbCl(thf)_{0.5}$.

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* Part VI: G.B. Deacon, A.J. Koplick and T.D. Tuong, Aust. J. Chem., 37 (1984) 517.

Experimental

A solution of an analytically pure sample of $(C_5H_5)_2YbBr(thf)$ [1] in tetrahydro-furan was allowed to stand under nitrogen for several months. A number of red crystals formed amidst a yellow-orange sludge. These were separated under nitrogen and transferred to an argon-filled recirculating dry box. A red wedge shaped crystal with approximate dimensions of $0.4 \times 0.2 \times 0.2$ mm was selected and sealed under argon in a glass Lindemann capillary. Decomposition of $(C_5H_5)_2YbCl(thf)_{0.5}$ over a similar prolonged period gave some orange single crystals which were similarly isolated and mounted.

Crystal data

(a) Dibromo-η^5-cyclopentadienyltris(tetrahydrofuran)ytterbium(III). $C_{17}H_{29}$-Br_2O_3Yb, $M = 614.03$, Monoclinic, space group $P2_1/n$ (C_{2n}^5, No. 14), a 15.310(15), b 16.900(17), c 7.968(8) Å, β 96.66(5)°, U 2047.7 Å^3, $Z = 4$, D_c 1.99 g cm^{-3}, $F(000) = 1180.8$, Mo-K_α radiation, λ 0.7107 Å, μ(Mo-K_α) 82.0 cm^{-1}. The unit-cell parameters were obtained by least-squares refinement of the angular settings of 25 medium-high angle reflections.

(b) Dichloro-η^5-cyclopentadienyltris(tetrahydrofuran)ytterbium(III). $C_{17}H_{29}$-Cl_2O_3Yb, $M = 535.12$, Monoclinic, space group $P2_1/n$ (C_{2n}^5, No. 14), a 15.124(15), b 17.049(17), c 7.803(8) Å, β 95.90(5), U 2001.3 Å^3.

TABLE 1

FINAL ATOMIC COORDINATES

Atom	x	y	z
Yb(1)	0.2358(1)	0.0517(1)	−0.0597(1)
Br(1)	0.1407(1)	0.0172(1)	0.2067(2)
Br(2)	0.3693(1)	0.0306(1)	−0.2639(2)
C(1)	0.2033(11)	0.2046(8)	−0.1039(22)
C(2)	0.1246(11)	0.1710(9)	−0.0606(19)
C(3)	0.0909(10)	0.1226(9)	−0.1927(23)
C(4)	0.1512(13)	0.1263(10)	−0.3177(18)
C(5)	0.2177(14)	0.1774(9)	−0.2623(22)
C(6)	0.0925(10)	−0.1007(10)	−0.1412(20)
C(7)	0.0626(14)	−0.1552(11)	−0.2858(26)
C(8)	0.0950(14)	−0.1219(13)	−0.4342(22)
C(9)	0.1772(13)	−0.0784(11)	−0.3729(17)
C(10)	0.3536(14)	−0.0604(11)	0.2502(20)
C(11)	0.3745(20)	−0.1444(11)	0.2844(25)
C(12)	0.3790(13)	−0.1844(10)	0.1309(23)
C(13)	0.3277(12)	−0.1340(9)	−0.0017(20)
C(14)	0.3164(11)	0.1521(11)	0.2974(18)
C(15)	0.3960(13)	0.1990(12)	0.3584(23)
C(16)	0.4700(13)	0.1635(13)	0.2827(25)
C(17)	0.4282(10)	0.1300(12)	0.1157(19)
O(1)	0.1648(6)	−0.0555(5)	−0.2015(10)
O(2)	0.3161(6)	−0.0592(5)	0.0764(10)
O(3)	0.3371(6)	0.1138(5)	0.1420(10)

Data collection, structure solution, and refinement for (η^5-C_5H_5)YbBr$_2$(thf)$_3$

Data were collected with a Philips PW1100 automatic four-circle diffractometer equipped with a graphite monochromator [6]. A total of 3205 unique reflections were collected of which 2413 were considered above background [$F_0 \geqslant 6\sigma(F_0)$]. Intensity data were collected for $6° \leqslant 2\theta \leqslant 48°$ at a speed of $0.06°$ s^{-1} and a scan width of $(1.20 + 0.2 \tan\theta)°$ in θ. Every 4 h, 3 standard reflections were measured and these showed no significant change in intensity over the data collection period. Intensity data were corrected for Lorentz and polarization effects [7]. A numerical absorption correction based on the indexed crystal faces was also applied [8].

The structure was solved by a three dimensional Patterson synthesis, which readily gave the position of the ytterbium atom. A difference Fourier synthesis revealed unambiguously the position of all remaining non-hydrogen atoms. The full matrix least squares refinement [8] converged at $R = 0.049$ and $R_w = 0.047$ [$R_w = \Sigma w^{1/2}(|| F_0 | - | F_c ||)/\Sigma w^{1/2} |F_0 |$; $w = [\sigma(F)]^{-2}$], with hydrogen atoms included in their geometrically calculated positions with one common isotropic temperature factor. The atomic scattering factors for neutral Yb, Br, C, H, and O atoms [9] were corrected for anomalous dispersion. Final positional and thermal parameters are given in Table 1. A complete list of bond lengths and angles and of observed and calculated structure factor amplitudes are available from the authors.

Results and discussion

The molecular structure of dibromo-η^5-cyclopentadienyltris(tetrahydrofuran)ytterbium(III) (Fig. 1) is a monomeric unit in which formally eight coordinate ytterbium is pseudo-octahedrally coordinated by a cyclopentadienyl group, *trans* bromines, and *mer* tetrahydrofuran ligands. Thus, it is similar to the structure of (η^5-C_5H_5)ErCl$_2$(thf)$_3$ [2]. Bond distances and angles relating to the stereochemistry of ytterbium are listed in Table 2 together with corresponding data for (η^5-C_5H_5)ErCl$_2$(thf)$_3$. Subtraction of the ionic radius (0.985 Å) [10] for eight coordinate Yb^{3+} from the average Yb–C(C_5H_5) bond distance gives 1.655 Å which is within the range 1.64 ± 0.4 Å for the effective ionic radius of cyclopentadienyl or substituted cyclopentadienyl ligands [11]. A similar calculation for the erbium compound gives 1.663 Å, indicating substantially ionic bonding in each case. Subtraction of the ytterbium ionic radius from the Yb–O(1), Yb–O(3), and Yb–O(2) distances gives 1.350, 1.363, and 1.443 Å respectively. The first two values are close to the average ether oxygen radius [1.34(5) Å] determined for a range of organolanthanoid-ether complexes [12], whilst the last reflects the substantial relayed steric effect on the ligand *trans* to the bulky cyclopentadienyl group (see also below). The erbium–oxygen distances (Table 2) conform to a similar pattern [12]. Different behaviour is observed for two stereochemically similar (η^5-L)UX$_3$L$_2'$ (X = Cl or Br) complexes. In (η^5-MeC$_5$H$_4$)UCl$_3$(thf)$_2$ [13], both the equatorial and axial U–O bonds are lengthened, and subtraction of the ionic radius (1.00 Å [10]) for eight-coordinate U^{4+} gives 1.449 and 1.451 Å respectively. With (η^5-C$_9$H$_7$)UBr$_3$(thf)(OPPh$_3$) [14], the equatorial U–O(thf) bond is elongated [2.479(14) Å], whereas the axial U–O(OPPh$_3$) distance [2.320(14) Å] is much shorter. The lengthening of the equatorial U–O(thf) bonds may be partly associated with steric effects derived from the methyl and benzo substituents on the cyclopentadienyl rings.

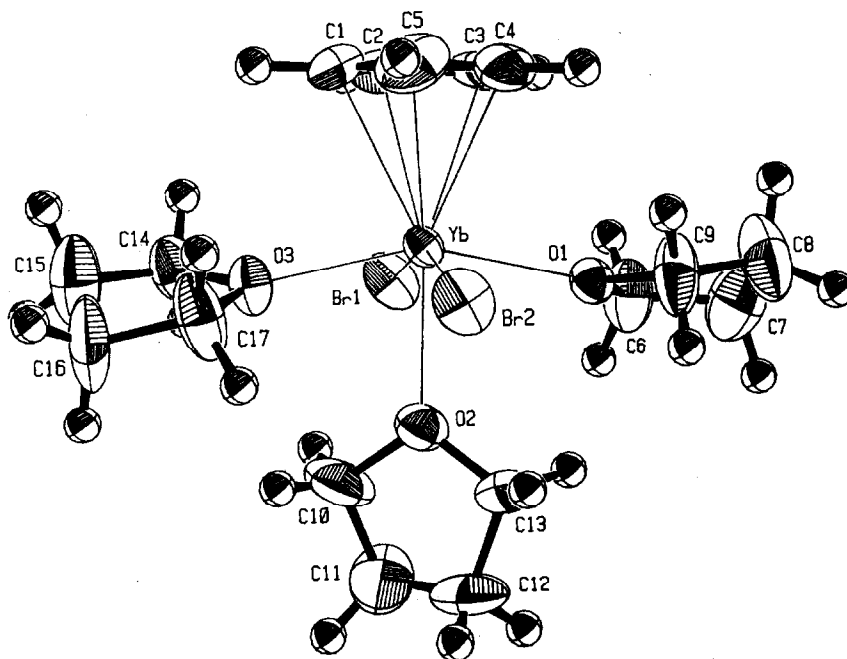The difference in metal–halogen distances between (η^5-C_5H_5)YbBr$_2$(thf)$_3$ and

Fig. 1. Molecular structure of $(\eta^5\text{-}C_5H_5)YbBr_2(thf)_3$.

$(\eta^5\text{-}C_5H_5)ErCl_2(thf)_3$ (after allowance for the slight difference in metal ion radii [10]) corresponds closely to the difference [10] in the halide ionic radii. However, the Yb–Br and Er–Cl distances (Table 2) are significantly less (ca. 0.17 Å) than the sum

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) RELATING TO COORDINATION OF THE METAL FOR $(\eta^5\text{-}C_5H_5)MX_2(thf)_3$ (M = Yb, X = Br (1) [a] or M = Er, X = Cl (2) [b])

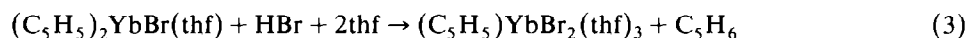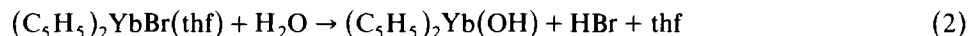| Bond	1	2	Difference	Angle	1	2
M–C(1)	2.647(16)	2.674(5)		X(1)–M–X(2)	155.31(5)	154.85(4)
M–C(2)	2.639(16)	2.663(7)		Cent–M–O(1)	102.2(2)	102.0(1)
M–C(3)	2.632(16)	2.665(7)		Cent–M–O(2)	179.0(2)	179.3(1)
M–C(4)	2.622(15)	2.664(6)		Cent–M–O(3)	102.1(2)	102.8(1)
M–C(5)	2.662(17)	2.663(6)		Cent–M–X(1)	102.0(5)	102.4(1)
(M–C)$_{ave}$ [c]	2.640(16)	2.667(6)	−0.027	Cent–M–X(2)	102.6(5)	102.8(1)
M–Cent [d]	2.358(16)	2.389(3)	−0.031	O(1)–M–O(2)	78.5(3)	78.1(1)
M–X(1)	2.771(2)	2.613(1)	0.158	O(1)–M–O(3)	155.7(3)	155.18(1)
M–X(2)	2.779(2)	2.620(1)	0.159	O(2)–M–O(3)	77.2(3)	77.1(1)
M–O(1)	2.335(8)	2.350(3)	−0.015	X(1)–M–O(1)	87.2(2)	87.7(1)
M–O(2)	2.428(9)	2.452(3)	−0.024	X(1)–M–O(2)	77.2(2)	77.0(1)
M–O(3)	2.348(9)	2.365(3)	−0.017	X(1)–M–O(3)	86.2(2)	86.2(1)
				X(2)–M–O(1)	87.1(2)	86.9(1)
				X(2)–M–O(2)	78.1(2)	77.9(1)
				X(2)–M–O(3)	89.2(2)	88.4(1)

[a] A complete set of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors. [b] From Ref. 2. [c] Average of preceding five bond lenghts. [d] Cent is the centre of the ring described by the cyclopentadienyl carbons.

of the appropriate lanthanoid(III) and halide ionic radii [10] suggesting some covalent character in the bonding. The only other available Yb–Br distances for solid compounds are those for six coordinate $YbBr_3$ (2.798 Å [15]) and $YbBr_2$ (ave. 2.92 Å [16]), which have bridging Yb–Br bonds. Subtraction of the appropriate ytterbium ionic radii gives values of 1.930 and 1.904 Å respectively. The corresponding value (1.790 Å) derived from the average of the Yb–Br distances of $(\eta^5\text{-}C_5H_5)YbBr_2(thf)_3$ is smaller as might be expected for terminal Yb–Br bonds. A more meaningful comparison can be made with the mutually *trans* U–Br bonds of $(\eta\text{-}C_9H_7)UBr_3(thf)(OPPh_3)$ [14], for which a similar calculation gives a comparable value of 1.754 Å.

For the metal coordination sphere, the bond angle differences between $(\eta^5\text{-}C_5H_5)YbBr_2(thf)_3$ and $(\eta^5\text{-}C_5H_5)ErCl_2(thf)_3$ are all less than 1° (Table 2), emphasizing the structural similarity. Thus, any increase in steric repulsion derived from the larger size of bromine appears to be substantially offset by the increase in bond length from Er–Cl to Yb–Br. The Cent–Yb–O(1), Cent–Yb–O(3), and Cent–Yb–Br angles are opened to ca. 102° owing to the steric bulk of the cyclopentadienyl ligands. Even with this distortion the C(2)–Br(1) and C(5)–Br(2) distances (3.352(15) and 3.398(19) Å respectively) are well within the sum of the $C(C_5H_5)$ and Br Van der Waals radii (3.65 Å) [17], whilst the C(3)–Br(1) and C(4)–Br(2) distances are very close to this value. Further distortion is hardly possible since the Br(1)–O(2) and Br(2)–O(2) distances (3.255(10) and 3.292(9) Å respectively) are already within the sum of the Van der Waals radii of oxygen and bromine (3.35 Å) [17]. Comparison of these non-bonding contacts with the corresponding data for $(\eta^5\text{-}C_5H_5)ErCl_2(thf)_3$ [2] suggests marginally greater steric crowding in the bromo complex.

The formation of $(\eta^5\text{-}C_5H_5)YbBr_2(thf)_3$ from $(C_5H_5)_2YbBr(thf)$ on standing (see Experimental) can be attributed to hydrolysis by adventitious water followed by protolysis of a cyclopentadienyl–ytterbium bond (reactions 2 and 3).

$$(C_5H_5)_2YbBr(thf) + H_2O \rightarrow (C_5H_5)_2Yb(OH) + HBr + thf \qquad (2)$$

$$(C_5H_5)_2YbBr(thf) + HBr + 2thf \rightarrow (C_5H_5)YbBr_2(thf)_3 + C_5H_6 \qquad (3)$$

The complex $(\eta^5\text{-}C_5H_5)YbCl_2(thf)_3$ has also been prepared in a similar manner and the unit-cell dimensions and space group (Experimental section) show it to be isostructural with the dibromo complex and with $(\eta^5\text{-}C_5H_5)ErCl_2(thf)_3$.

Acknowledgement

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