Crystal Structure of Di[(μ-benzoato-O,O′)bis(η^5-methylcylopentadienyl)-ytterbium(III)]

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Dedicated to Professor Hanskarl Müller-Buschbaum on the occasion of his 70th birthday

Abstract. Transparent orange-red crystals of $[Yb(MeCp)_2(O_2CPh)]_2$ obtained by oxidation of $Yb(MeCp)_2$ with $Tl(O_2CPh)$ in tetrahydrofuran have a dimeric structure with bridging bidentate (O,O′)-benzoate groups and eight-coordinate ytterbium.

Keywords: Lanthanides; Benzoate; Crystal structure; Ytterbium; Methylcylopentadienyl

Considerable variety in carboxylate coordination has been observed in crystallographically characterized carboxylatobis(cyclopentadienyl)lanthanide(III) complexes, viz. O,O′-chelation (η^2) in monomeric $[Lu(\eta^5\text{-}C_5Me_4{}^tBu)_2(O_2CMe)]$ [1], $[Y(\eta^5\text{-}Cp)_2[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$ [2], $[Sc(\eta^5\text{-}Cp)_2(O_2C)\text{-}C_6H_4CH_3]$ [3], bridging bidentate (μ-η'(O),η'(O′)) in $[Yb(\eta^5\text{-}Cp)_2(O_2CC_6F_5)]_2$ [4], $[Y(\eta^5\text{-}C_5HMe_4)_2(O_2CMe)]_2$ [5], $[Sc(\eta^5\text{-}Cp)_2(O_2CSi(SiMe_3)_3)]_2$ [6] and bridging tridentate (μ_3-η^2-(O,O), η'(O′)) in $[Yb(\eta^5\text{-}C_5H_4X)_2Yb(O_2CMe)]_2$ (X = H or PPh_2) [7] and $[Ln(\eta^5\text{-}C_5HMe_4)_2(O_2CMe)]_2$ (Ln = La, Sm) [5]. In view of these possibilities, the coordination behaviour of the unsubstituted benzoate ion is of interest. Mass spectrometry suggests $Yb(Cp)_2(O_2CPh)$ to be dimeric, but single crystals have been elusive [8], and an incomplete, low resolution structure determination of $Yb(MeCp)_2(O_2CPh)$ suggested a dimer but no details could be provided [9]. We have now been able to successfully determine the structure, which reveals disorder problems that may have been the origin of the failure of an earlier study [9].

Experimental

Under an atmosphere of purified nitrogen $Yb(MeCp)_2$ and $Tl(O_2CPh)$ (each 0.89 mmol) were reacted in tetrahydrofuran (15 ml) to give an orange-red solution and a precipitate of thallium, which was removed by filtration. Large air-sensitive orange-red needles of the title product (yield 70%) were obtained from a mixture of dme/thf (3:1) by cooling over several days.

$$Yb(MeCp)_2 + Tl(O_2CPh) \xrightarrow{thf} Yb(MeCp)_2(O_2CPh) + Tl$$

Data collection for single crystal X-ray determination was carried out on a κ-CCD diffractometer (Enraf-Nonius).

Crystallographic data for $C_{38}H_{42}O_4Yb_2$: monoclinic, $P2_1/n$, Z = 4, T = 123(2) K, a = 2027.03(3), b = 900.76(2), c = 2054.90(4) pm, β = 119.43(3)°, μ = 57.28 cm^{-1}, MoKα, $5.08 \le 2\theta \le 56.85°$, $-27 \le h \le 27$, $-12 \le k \le 10$, $-27 \le l \le 27$, F(000) = 1768, R_1 = 0.443 for 5222 reflections [$I > 2\sigma(I)$], R_1 = 0.0922 and wR_2 = 0.0966 for 8041 unique reflections, GOOF on F^2 = 1.033. Structure solution: SHELXS-86 [10], structure refinement: SHELXL-97 [11].

IR (Nujol): 3070 w (ν(CH) MeCp), 1606 s and 1567 s ($\nu_{as}(CO_2)$), 1418 vs ($\nu_s(CO_2)$), 1306 m (ν(CC)), 1027 m (β(CH) MeCp), 776 s (γ(CH) MeCp), 717 s (ring def.) cm^{-1}.

UV/VIS/near IR (thf/dme): λ_{max} (E) 420(261), 876(4), 949(12), 966(27), 987 sh(19), 995(33) nm.

Discussion

$[Yb(MeCp)_2(O_2CC_6H_5)]_2$ crystallizes with the monoclinic crystal system in space group $P2_1/n$ with two crystallographically independent Yb positions. The structure consists of dimeric molecules, whose halves are related by symmetry centres. The coordination spheres of both ytterbium atoms are made up of two (η^5-MeCp) and two (μ-O_2CPh) ligands to yield a coordination number of eight (Fig. 1). This is similar to the structure of $[YbCp_2(O_2CC_6F_5)]_2$ [4] containing a fully substituted bridging bidentate benzoate ligand (cf. bridging tridentate leading to ninefold coordination for the less bulky acetate [7]). In $[Yb(MeCp)_2(O_2CPh)]_2$ the Yb–C distances average to 260 pm. Subtraction of the ionic radius of eight-coordinate Yb(III) [12] results in a radius of the Cp anion of 162 pm corresponding to the value derived from $[YbCp_2(O_2CC_6F_5)]_2$ [4] and being in the usual range [13]. With bridging bidentate coordination, the Yb1–Yb2 distances (484 and 509 pm) are much longer than in the bridging tridentate $[Yb(\eta^5\text{-}C_5H_4X)_2(O_2CMe)]_2$ (390 pm) [7]. The separations of the carboxylate oxygen atoms from the non-bonded Yb atoms are 372–409 pm, much longer than the 240 pm for the longest Yb–O bond in bridging tridentate coordination [7]. Despite the similarity of the Yb–O bond lengths in the present compound, the Yb–O–C angles

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show that the bonding of the benzoate ligands to the metal centres is unsymmetrical (for distances and angles between atoms, see legend to Figs. 1 and 2). The differences between corresponding angles, e. g. C1–O1–Yb1 and C1–O2–Yb1 (10–12°) are substantial but less than those (14–34°) of the marginally more crowded pentafluorobenzoate [4]. Further, this asymmetry in coordination foreshadows the intrinsic asymmetry of bridging tridentate coordination where the differences between corresponding pairs of Yb–O–C angles lie in the range of 50–70°. On both dimeric molecules, the MeCp ligands allow two equally probable positions for the methyl groups. Not related to this is a disorder of the Yb2 atoms which subsequently results in a disorder of one of the coordinated MeCp ligands in a ratio of one third to two thirds and an asymmetric coordination of the non-disordered MeCp ring to the weaker represented Yb2 positions (Fig. 2). All atoms, including the disordered ones, were refined anisotropically [14] giving a more reasonable result of the refinement than averaged atomic positions. The disorder might be explained by a block structure but not by intergrown individuals. Furthermore, no evidence of a suitable twinning law was found nor a possible lower symmetry. The close relation of the present compound to $YbCp_2(O_2CC_6H_5)$ [8] suggests a similar dimeric structure for the latter.

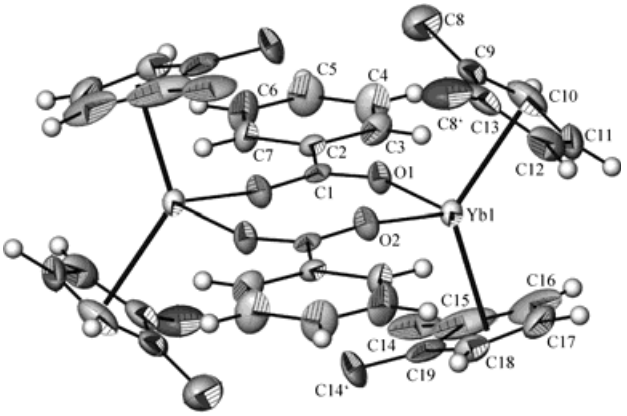

Fig. 1 Dimeric molecule **1** in the structure of $[Yb(MeCp)_2(O_2CC_6H_5)]_2$. The thermal ellipsoids are scaled to a probabilty density of 50%. The methyl groups C8 and C14 are disordered in a 1 : 1 ratio. Selected distances/pm and angles/°:

Yb1–O1 218.5(4), Yb1–O2 215.6(4), Yb1–C9 262.3(6), Yb1–C10 259.2(6), Yb1–C11 255.1(7), Yb1–C15 259.6(7), Yb1–C16 255.8(7), Yb1–C19 262.1(6), C1–O1 125.6(6), C1–O2 121.7(6); Yb1–O1–C1 151.6(4), Yb1–O2–C1 162.2(4), O1–Yb1–(centroid C9–C13) 105.3(6), O2–Yb1–(C9–C13) 107.7(6), (C9–C13)–Yb1–(centroid C15–C19) 130.4(6), O1–Yb1–(C15–C19) 107.1(6), O2–Yb1–(C15–C19) 105.3(6).

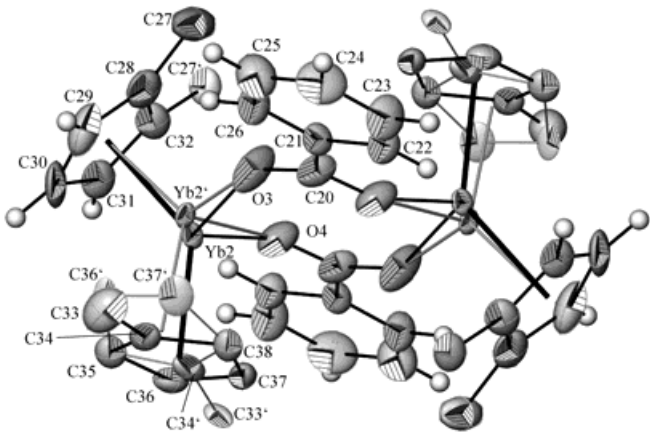

Fig. 2 Dimeric molecule **2** in the structure of $[Yb(MeCp)_2(O_2CC_6H_5)]_2$. The Yb2 atoms as well as one of the Cp rings are disordered in a 2 : 1 ratio. The individual with the higher occupation is shown by darker bonds and atoms. Methyl group C27 is disordered in a 1 : 1 ratio. Selected distances/pm and angles/°:

Yb2–O3 225.4(6), Yb2–O4 205.8(6), Yb2′–O3 199(1), Yb2′–O4 235(1), Yb2–C31 260.4(7), Yb2–C32 266.7(7), Yb2–C35 255.7(7), Yb2–C37 264(2), Yb2′–C29 233(2), Yb2′–C31 259.1(8), Yb2′–C36′ 255(2), Yb2′–C34′ 269(2), C20–O3 127.1(7), C20–O4 125.6(7); Yb2–O3–C20 139.2(5), Yb2–O4–C20 152.3(5), Yb2′–O3–C20 148.7(6), Yb2′–O4–C20 156.4(5), O3–Yb2–(centroid C28–C32) 100.0(7), O4–Yb2–(C28–C32) 105.2(7), (C28–C32)–Yb2–(centroid C34–C38) 134.7(9), O3–Yb2–(C34–C38) 108.4(8), O4–Yb2–(C34–C38) 104.7(8), O3–Yb2′–(centroid C28–C32) 117(1), O4–Yb2′–(C28–C32) 103(1), (C28–C32)–Yb2′–(centroid C34′–C38′) 129(2), O3–Yb2′–(C34′–C38′) 98(2), O4–Yb2′–(C34′–C38′) 107(2).

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[14] Further information about the crystal structure determination is deposited at the Cambridge data base and can be requested by giving the author names and the deposition number CCDC-160132.