Two New Benzoate-di(methylcyclopentadienyl)ytterbium(III) Complexes: $[Yb(MeCp)_2(O_2CC_6F_5)]_2$ and $[Yb(MeCp)_2(O_2C\text{-}o\text{-}HC_6F_4)]_2$

Glen B. Deacon[a], **Catharina C. Quitmann**[a,b], **Klaus Müller-Buschbaum**[b], **Gerd Meyer**[b]*

[a] Clayton/Australia, School of Chemistry, Monash University

[b] Köln, Institut für Anorganische Chemie, Universität zu Köln

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Abstract. Transparent orange crystals of $[Yb(MeCp)_2(O_2CC_6F_5)]_2$ and $[Yb(MeCp)_2(O_2C\text{-}o\text{-}HC_6F_4)]_2$ were obtained by oxidation of $Yb(MeCp)_2$ with $M(O_2CR)$ ($M = {}^1/_2$ Hg, Tl; $R = C_6F_5$, $o\text{-}HC_6F_4$) in tetrahydrofuran. They have a dimeric structure with bridging bidentate (O,O')-benzoate groups and eight coordinated ytterbium. Both crystallise isotypic in the orthorhombic space group *P*bca. Room temperature as well as low temperature single crystal X-ray investigations show the *o*-H/F positions in $[Yb(MeCp)_2(O_2C\text{-}o\text{-}HC_6F_4)]_2$ not to be ordered.

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

Carboxylatobis(cyclopentadienyl)lanthanide(III) complexes display a considerable variety in carboxylate coordination ranging from O,O'-chelation (η^2) in monomeric complexes [1−3] to bridging tridentate (μ_3-η^2(O,O), η^1(O')) [4, 5] and bridging bidentate (μ-η^1(O),η^1(O')) [4, 6, 7] in dimeric complexes. The nature of the respective type of coordination seems to be mostly dependant on the steric demand of the carboxylate group. The previously reported structures of $[Yb(MeCp)_2(O_2CPh)]_2$ with the unsubstituted benzoate [8] and the substituted $[Yb(Cp)_2(O_2CC_6F_5)]_2$ [6] showed them to be dimeric with bridging bidentate groups. In $[Yb(Cp)_2(O_2CC_6F_5)]_2$ the *ortho*-fluorine atoms of the carboxylate groups show close non-bonding contacts with ring carbon atoms of one cyclopentadienyl group, that could be minimized by an increased dihedral angle between the planes of the pentafluorophenyl groups and the plane formed by the ytterbium and oxygen atoms. From this it was of interest to investigate the coordination behaviour of the substituted benzoates $[Yb(MeCp)_2(O_2CR)]_2$ ($R = C_6F_5$, $o\text{-}HC_6F_4$) to determine the degree of substitution of a benzoate ligand needed to obtain a monomeric structure as well as to eliminate disorder problems observed for $[Yb(MeCp)_2(O_2CPh)]_2$ by substitution with fluorine atoms.

Experimental

$[Yb(MeCp)_2(O_2CC_6F_5)]_2$ (**1**) *and $[Yb(MeCp)_2(O_2C\text{-}o\text{-}HC_6F_4)]_2$* (**2**):

Under an argon atmosphere $Yb(MeCp)_2$ ((**1**): 0.36 g, 0.89 mmol; (**2**): 0.2 g, 0.5 mmol) and $M(O_2CR)$ (M = ‰ Hg, Tl; $R = C_6F_5$, $o\text{-}HC_6F_4$; (**1**):0.28 g, 0.45 mmol; (**2**): 0.2 g, 0.5 mmol) were reacted in tetrahydrofuran (20 ml) to give an orange solution and a precipitate of thallium/mercury, which was removed by filtration. Small air-sensitive orange plates of **1** and **2** were obtained from a mixture of dme/thf ((**1**): 4:1; (**2**): 3:1) by cooling ((**1**): 6-8 h; (**2**): 2 days). To improve the crystal quality of both complexes the crystals and their mother liquor were sealed in ampoules under vacuum and heated to 50 °C for of three months (Yields: (**1**) 0.34 g (72%);(**2**) 0.17 g (64%)).

$$n[(MeCp)_2Yb(THF)] + M(O_2CR)_n \xrightarrow{thf} n[(MeCp)_2Yb(O_2CR)] + M$$

$$(M = Hg,\ n = 2,\ R = o\text{-}HC_6F_4;\ M = Tl,\ n = 1,\ R = C_6F_5)$$

The data collections for the single crystal X-ray structure determinations were carried out on a IPDS-II diffractometer (STOE).

Crystallographic data for $C_{38}H_{28}O_4F_{10}Yb_2$: orthorhombic, Pbca, Z = 8, T = 173(2) K, a = 1293.2(3), b = 2340.3(5) c = 2305.8(5) pm, μ = 5.422 cm^{-1}, MoKα, $3.48 \leq 2\theta \leq 50.68°$, $-27 \leq h \leq 27$, $-15 \leq k \leq 15$, $-27 \leq l \leq 27$, F(000) = 4144, R_1 = 0.0613 for 3350 reflections [I>2sigma(I)], R_1 = 0.1104 and wR_2 = 0.1579 for all 6194 unique reflections, GOOF on F^2 = 0.880. Structure resolution: SHELXS-86 [10], structure refinement: SHELXL-97 [11].
IR (Nujol): 3075 w (ν(CH) MeCp), 1651 s and 1626 s ($\nu_{as}(CO_2)$), 1423 vs ($\nu_s(CO_2)$), 1236 m (ν(CC)), 1001 m (β(CH) MeCp), 772 s (γ(CH) MeCp), 744 s (ring def.) cm^{-1}.
UV/VIS/near IR (thf/dme): λ_{max} (E) 980(8) nm.

Crystallographic data for $C_{38}H_{30}O_4F_8Yb_2$: orthorhombic, Pbca, Z = 8, T = 173(2) K, a = 1280.72(13), b = 2343.47(9), c = 2327.94(9) pm, μ = 5.404 cm^{-1}, MoKα, $3.90° \leq 2\theta \leq 50.68°$, $-14 \leq h \leq 14$, $-25 \leq k \leq 24$, $-26 \leq l \leq 26$, F(000) = 4000, R_1 = 0.0616 for 1900 reflections [I>2sigma(I)], R_1 = 0.1833 and wR_2 = 0.1233 for all 5242 unique reflections, GOOF on F^2 = 0.766. Structure resolution: SHELXS-86 [10], structure refinement: SHELXL-97 [11].
IR (Nujol): 3070 w (ν(CH) MeCp), 1622 vs and 1593 vs ($\nu_{as}(CO_2)$), 1405 m ($\nu_s(CO_2)$), 1260 m (ν(CC)), 1037 m (β(CH) MeCp), 756 s (γ(CH) MeCp), 722 m (ring def.) cm^{-1}.
UV/VIS/near IR (thf/dme): λ_{max} (E) 982(13) nm.

Results and Discussion

$[Yb(MeCp)_2(O_2CC_6F_5)]_2$ (**1**) and $[Yb(MeCp)_2(O_2C\text{-}o\text{-}HC_6F_4)]_2$ (**2**) are isotypic and crystallise in the orthorhombic crystal system in the space group *P*bca with two crystallographically independent

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* Prof. Dr. G. Meyer
Institut für Anorganische Chemie
Universität zu Köln
Greinstraße 6
D-50939 Köln
Fax: 0221 4705083
E-mail: gerd.meyer@uni-koeln.de

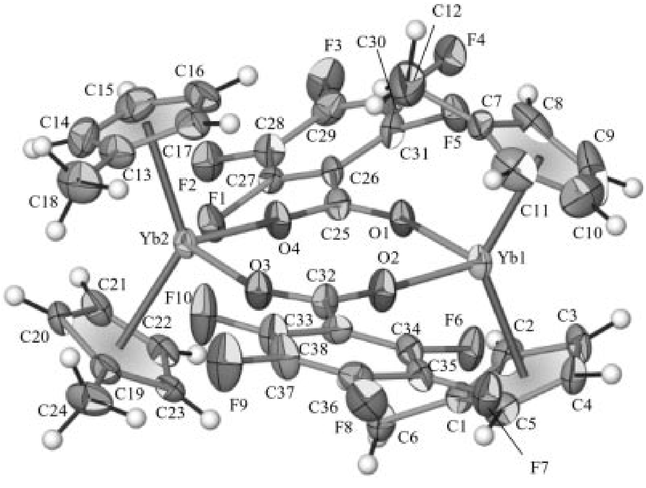

Fig. 1 The dimeric molecule of $[Yb(MeCp)_2(O_2CC_6F_5)]_2$ **1**. The thermal ellipsoids are scaled to a probability density of 30%. Selected distances/pm and angles/°:

Yb1-O1 222(1), Yb1-O2 220(1), Yb2-O3 221(1), Yb2-O4 220(1), O1-C1 122(2), O2-C1 124(2), O3-C8 123(2), O4-C8 124(2); O2-Yb1-O3 97(1), O4-Yb2-O1 92(1), C1-O1-Yb2 175(1), C1-O2-Yb1 146(1), C8-O3-Yb1 167(1), C8-O4-Yb2 152(1), O4-C8-O3 124(1), O1-C1-O2 124(1), O2-Yb1-(centroid C27-C31) 104, O2-Yb1-(C33-C37) 107, O3-Yb1-(C27-C31) 107, O3-Yb1-(C33-C37) 105, O1-Yb2-(centroid C15-C19) 107, O1-Yb2-(C21-C25) 108, O4-Yb2-(C15-C19) 104, O4-Yb2-(C21-C25) 106, (C21-C25)-Yb2-(C15-C19) 132.

In the isotypic dimeric molecule of $[Yb(MeCp)_2(O_2C\text{-}o\text{-}HC_6F_4)]_2$ **2**, the *ortho* positions of the $(O_2C\text{-}o\text{-}HC_6F_4)$ ligands are half-occupied by F and H. Selected distances/pm and angles/°:

Yb1-O1 219(2), Yb1-O2 212(2), Yb2-O3 223(2), Yb2-O4 216(2), O1-C25 128(2), O2-C32 124(2), O3-C32 128(2), O4-C25 122(2); O2-Yb1-O1 93(5), O4-Yb2-O3 97(5), C32-O2-Yb1 171(2), C32-O3-Yb2 145(2), C25-O1-Yb1 150(2), C25-O4-Yb2 165(2), O4-C25-O1 127(2), O2-C32-O3 127(2), O1-Yb1-(centroid C1-C5) 105, O1-Yb1-(C7-C11) 110, O2-Yb1-(C1-C5) 105, O2-Yb1-(C7-C11) 105, O3-Yb2-(centroid C13-C17) 105, O3-Yb2-(C19-C23) 106, O4-Yb2-(C13-C17) 105, O4-Yb2-(C19-C23) 107, (C13-C17)-Yb2-(C19-C23) 132.

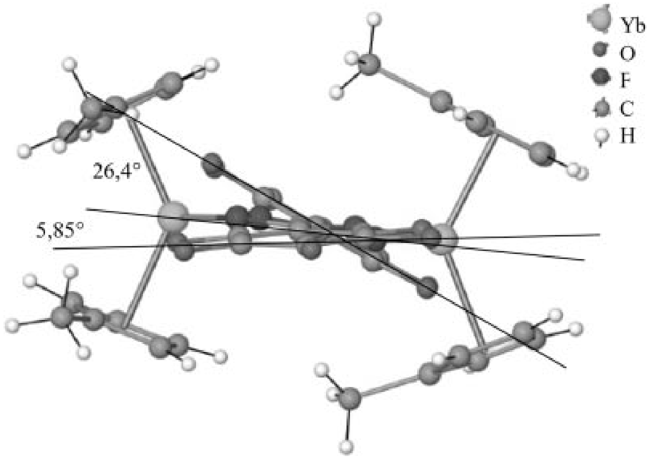

Fig. 2 Twist angles between planes made up of the polyfluorophenyl groups and the Yb_2O_2 plane in (**2**).

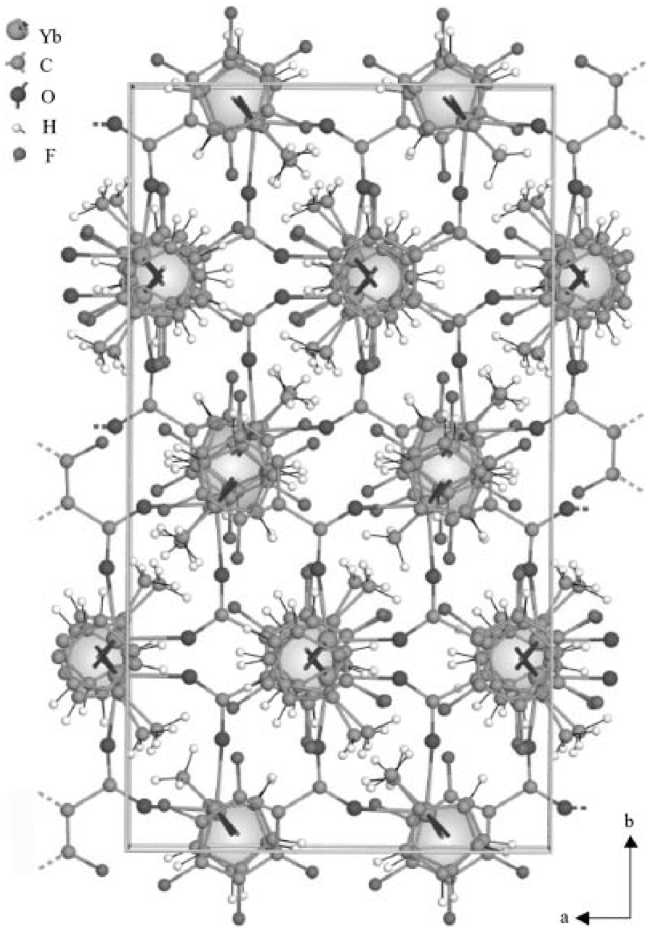

Fig. 3 The crystal structure of $[Yb(MeCp)_2(O_2CC_6F_5)]_2$ along [001].

Yb positions. The structures consist of dimeric molecules. The coordination spheres of both ytterbium atoms consist of two (η^5-MeCp) and two (μ-O_2CR) ($R = C_6F_5$, o-HC_6F_4) ligands giving a coordination number of eight (Fig. 1). This is similar to the structures of $[YbCp_2(O_2CC_6F_5)]_2$ [6] and $[Yb(MeCp)_2(O_2CPh)]_2$ [8]. Evidently the steric demand of the methyl group on the cyclopentadienyl ligand does not suffice to cause the formation of monomeric carboxylates with these substituting arrangements in the benzoates. The bridging carboxylate groups (μ-O_2CR) ($R = C_6F_5$, o-HC_6F_4) are twisted, resulting in a considerable dihedral angle between the planes of one of the polyfluorophenyl groups and the Yb_2O_2 plane, as opposed to the unsubstituted benzoate groups of $[Yb(MeCp)_2(O_2CPh)]_2$ that lie in the Yb_2O_2 plane. This distortion constitutes the essential difference between the two molecular structures **1** and **2** and other comparable benzoates [6, 8]. The resulting mean angle between the carboxylate groups amounts to 35° in **1** and 32° in **2**. It is made up from the two different angles that the two carboxylate groups form with the Yb_2O_2 plane. In both complexes the twist of one of the ligands is substantially bigger than that of the opposed ligand, 28° and 7° in **1** and 26° and 6° in **2** (Fig. 2). Thus they are in good accordance with $[YbCp_2(O_2CC_6F_5)]_2$ [6], whereas the unsubstituted benzoate $[Yb(MeCp)_2(O_2CPh)]_2$ [8] shows almost no twisting of the phenyl rings. The Yb-C distances average to 258 pm in **1** and 256 pm in **2**. Subtraction of the ionic radius of eight co-ordinate Yb(III) [12] results in a radius of the Cp anion of 162 pm corresponding to the value derived from $[YbCp_2(O_2CC_6F_5)]_2$ [6] and being in the usual range [9]. The bonding of the benzoate ligands to the metal centres is unsymmetrical (for distances and angles between atoms, see legend of

Fig. 1), the differences between corresponding C-O-Yb angles are substantial (15-28°) but less than those (14-34°) found in $[YbCp_2(O_2CC_6F_5)]_2$ [6]. The methyl groups of the MeCp ligands point in the direction opposite to the polyfluorophenyl groups.

Due to the long period of time the crystals were treated in the mother liquor, crystals of **1** and **2** did not show the same disorder problems for the methyl groups or even half dimers as observed in $[Yb(MeCp)_2(O_2CPh)]_2$ [8]. Independent from the temperature at which the data collection for the crystal structure determination was carried out the *o*-H/F of the (O_2C-*o*-HC_6F_4) ligands are not ordered in the crystal structure of **2**. The crystal structure of **1** arranged in π-stacking pillars is shown in Fig. 3. It can be concluded that a dimer is the most stable structure of Cp_2-Yb-benzoates and that either bulkier substitution or metals with smaller ionic radii, e.g. Sc, are necessary in order to obtain a monomeric structure.

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[13] Further information about the crystal structure determination is deposited at the Cambridge data base and can be requested by citing the names of the authors and the deposition number CCDC-199472, 199473, 199474, for (**1**) and (**2**) and the room temperature investigation of (**2**).