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Structural investigation of the organolanthanide di-η^5-cyclopentadienyl 1,1,1-trifluoroacetylacetonato ytterbium

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Abstract

The crystal structure of $Cp_2Yb \cdot (CH_3COCHCOCF_3)$ has been determined by single-crystal X-ray diffraction. The ytterbium atom is η^5-coordinated to two cyclopentadienyl ligands and chelated with the two oxygen atoms of the 1,1,1-trifluoroacetylacetonato ligand. A structural comparison of this complex with $Cp_2Yb(CH_3COCHCOCH_3)$ is given.

1. Introduction

Organometallic chemistry of the lanthanide elements has become an area of vigorous activity within the last decade [1]. However, only little work [2–4] has focussed on organolanthanide complexes involving both cyclopentadienyl and β-diketonato chelate ligands. In our previous work [2–4], we reported that organolanthanide complexes with both cyclopentadienyl and other ligands are not stable to heat, and disproportionate (owing to rearrangement of ligands) at moderately high temperatures. In order to clarify the cause of disproportionation, we have determined the single-crystal X-ray structure of $Cp_2Yb \cdot (CH_3COCHCOCH_3)$ [5]. In the present work, we describe the molecular structure of $Cp_2Yb \cdot (CH_3COCHCOCF_3)$ and give a brief structural comparison between complexes $Cp_2Yb \cdot (CH_3COCHCOCF_3)$ and $Cp_2Yb \cdot (CH_3COCHCOCH_3)$.

2. Experimental details

All reactions, manipulations and crystallizations were conducted under an atmosphere of dry, deoxygenated argon, using standard Schlenk tube techniques. All glassware was warmed with a heat gun during the evacuation/filling cycles to ensure removal of traces of water. THF and n-hexane were dried over sodium and distilled under argon from sodium benzophenone. 1,1,1-Trifluoroacetylacetone was dried over anhydrous $MgSO_4$ and freshly distilled under argon before use. Anhydrous ytterbium trichloride was prepared according to the published procedure [6].

2.1. *Preparation of di-η^5-cyclopentadienyl (1,1,1-trifluoroacetylacetonato) ytterbium*

Tricyclopentadienyl ytterbium was prepared by reaction at room temperature of a 1:3 molar ratio of anhydrous ytterbium trichloride and cyclopentadienylsodium [7] in THF for 24 h and was purified by vacuum sublimation. To 80 ml of THF at room temperature was added with stirring 1 mmol of the dark green sublimate of tricyclopentadienyl ytterbium. To this solution was added dropwise 1 mmol of 1,1,1-trifluoroacetylacetone in 40 ml of THF over a period of 2 h. After stirring for 20 h, THF was removed under vacuum and the resulting solid was recrystallized twice from THF/n-hexane to afford the orange product $Cp_2Yb \cdot (CH_3COCHCOCF_3)$. Single crystal specimens suitable for X-ray study were obtained by slow sublimation of the product under high vacuum.

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2.2. X-Ray crystallography

The single crystals of $Cp_2Yb \cdot (CH_3COCHCOCF_3)$ used for structural analysis were sealed under argon in thin-walled glass capillaries. A single crystal of dimensions *ca.* $0.1 \times 0.4 \times 0.5$ mm was selected. All X-ray measurements were made with a Siemens R3m/v diffractometer operating in the $2\theta/\theta$ scan mode with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and the scan speed varying in the range of 4.88–29.3° min^{-1}. The structure was solved by direct methods and subsequently refined by full-matrix least-squares procedures. The non-hydrogen atoms were made anisotropic. Hydrogen atom positions were calculated from the riding model (fixed isotropic U) and isotropic thermal parameters were refined.

2.2.1. Crystal data

$C_5H_{15}F_3O_2Yb$, $M = 457.3$, monoclinic, space group $P2_1/c$, $a = 17.553(8)$, $b = 8.162(3)$, $c = 11.105(4)$ Å, $\beta = 90.52(3)°$, $V = 1590.9(11)$ Å^3, $Z = 4$, $D_c = 1.909$ g cm^{-3}, μ (Mo $K\alpha$) = 58.91 cm^{-1}, $F(000) = 872$.

2.2.2. Data collection

$3.0° \leq 2\theta \leq 50.0°$, $T = 293$ K, 2862 data recorded, 2516 unique, 1881 observed $[F > 4.0\sigma(F)]$. Semi-empirical absorption correction (transmission 0.2458–0.6282).

2.2.3. Refinement

190 parameters, $w = [\sigma^2(F) + 0.00001F^2]^{-1}$, $R = 0.061$, $R_w = 0.060$ (for observed data). All calculations were made on a Micro VAX-II computer using the Siemens SHELXTL-PLUS program package.

3. Results and discussion

A diagram of the molecular structure is shown in Fig. 1. The coordinates and equivalent isotropic temperature factors of non-hydrogen atoms are listed in Table 1. Bond distances and bond angles are given in Table 2 and Table 3, respectively.

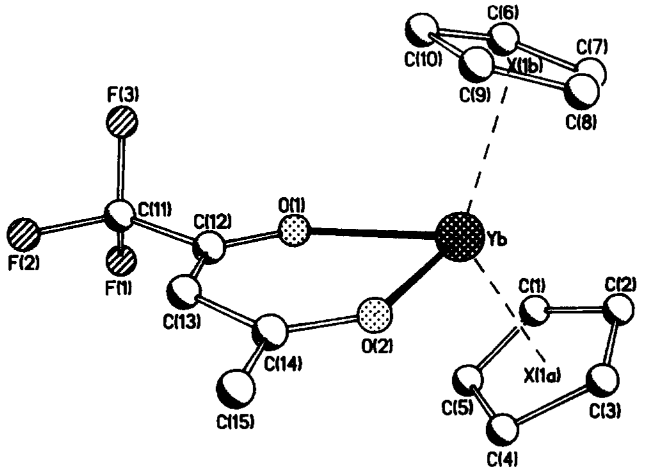

Fig. 1. Molecular structure of $Cp_2Yb \cdot (CH_3COCHCOCF_3)$.

The X-ray structure shows that the title compound is a mononuclear ytterbium complex with the central metal atom coordinated by two cyclopentadienyl ligands in the η^5 mode and by one 1,1,1-trifluoroacetylacetonato ligand in bidentate fashion with two oxygen atoms. The geometry around the ytterbium atom in this structure can be described as slightly distorted tetrahedral, with the centres of the two cyclopentadienyl rings and the two oxygens of the 1,1,1-trifluoroacetylacetonato ligand forming the apices of the tetrahedron. The two cyclopentadienyl rings are planar with mean deviation of 0.012 Å and 0.007 Å, respectively. The two planes form a dihedral angle of 49.3°.

The average distance of Yb–C (C_5H_5) is 2.58 Å. The effective ionic radii are 0.985 Å for eight-coordinated Yb^{3+} [8] and 1.60 Å for C_5H_5. The latter is smaller than that of $Cp_2Yb \cdot (CH_3COCHCOCH_3)$ (1.626 Å) [5]. These effective ionic radii of cyclopentadienyl ligands are consistent with the value suggested by Raymond [9] for predominantly ionic bonding, 1.64 ± 0.04 Å. On the basis of these structural data, the bonding in ytterbium(III) cyclopentadienyl complexes

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Yb	1854(1)	4917(1)	3424(1)	45(1)
O(1)	2888(7)	4012(13)	2534(10)	59(4)
O(2)	2767(8)	6294(13)	4390(11)	70(5)
F(1)	4045(13)	3358(28)	950(17)	193(12)
F(2)	4825(11)	3315(31)	2292(22)	218(12)
F(3)	3966(13)	1642(19)	2256(22)	208(13)
C(1)	1009(13)	5612(26)	1603(18)	73(7)
C(2)	601(13)	6172(37)	2582(28)	116(12)
C(3)	1001(22)	7414(33)	3090(21)	111(13)
C(4)	1668(21)	7698(22)	2382(30)	132(16)
C(5)	1639(19)	6538(31)	1438(19)	112(13)
C(6)	1289(15)	2092(20)	3952(19)	79(8)
C(7)	844(15)	3123(22)	4415(17)	71(9)
C(8)	1205(14)	3885(22)	5358(17)	71(8)
C(9)	1901(14)	3325(25)	5459(17)	78(8)
C(10)	2006(15)	2129(21)	4540(24)	96(10)
C(11)	4095(14)	3126(34)	2092(26)	92(10)
C(12)	3566(11)	4194(21)	2779(16)	62(6)
C(13)	3901(11)	5024(24)	3650(18)	81(7)
C(14)	3477(12)	6288(23)	4388(17)	69(7)
C(15)	3883(15)	7321(33)	5306(22)	147(14)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Bond distances (Å)

Yb–O(1)	2.202(12)	Yb–O(2)	2.225(12)
Yb–C(1)	2.561(21)	Yb–C(2)	2.593(25)
Yb–C(3)	2.554(31)	Yb–C(4)	2.567(22)
Yb–C(5)	2.596(22)	Yb–C(6)	2.580(19)
Yb–C(7)	2.557(23)	Yb–C(8)	2.582(20)
Yb–C(9)	2.608(19)	Yb–C(10)	2.604(20)
O(1)–C(12)	1.227(23)	O(2)–C(14)	1.246(24)
F(1)–C(11)	1.285(34)	F(2)–C(11)	1.309(30)
F(3)–C(11)	1.245(32)	C(1)–C(2)	1.385(36)
C(1)–C(5)	1.353(38)	C(2)–C(3)	1.353(41)
C(3)–C(4)	1.435(50)	C(4)–C(5)	1.413(36)
C(6)–C(7)	1.262(31)	C(6)–C(10)	1.412(36)
C(7)–C(8)	1.368(29)	C(8)–C(9)	1.309(34)
C(9)–C(10)	1.425(30)	C(11)–C(12)	1.489(32)
C(12)–C(13)	1.397(27)	C(13)–C(14)	1.420(27)
C(14)–C(15)	1.420(32)		
Yb–cent1 [a]	2.288	Yb-cent2 [b]	2.315

[a] cent1 indicates the centroid of C(1) to C(5). [b] cent2 indicates the centroid of C(6) to C(10).

appears to be largely ionic. The C–C distances within cyclopentadienyl ligands are in the range from 1.26(2) to 1.42(5) Å (an average of 1.37 Å, which is 0.02 Å shorter than the corresponding average in $Cp_2Yb \cdot (CH_3COCHCOCH_3)$). The C–C–C angles within a ring range from 103.1° to 110.5° (an average of 108.0°, which is 0.1° smaller than the corresponding average of 108.1° in $Cp_2Yb \cdot (CH_3COCHCOCH_3)$).

TABLE 3. Bond angles (°)

O(1)–Yb–O(2)	78.0(4)	C(1)–Yb–C(2)	31.2(8)
C(1)–Yb–C(3)	51.2(7)	C(2)–Yb–C(3)	30.5(10)
C(1)–Yb–C(4)	51.5(9)	C(2)–Yb–C(4)	52.0(10)
C(3)–Yb–C(4)	32.5(11)	C(1)–Yb–C(5)	30.4(9)
C(2)–Yb–C(5)	51.4(10)	C(3)–Yb–C(5)	52.4(8)
C(4)–Yb–C(5)	31.8(9)	C(1)–Yb–C(7)	93.9(7)
C(6)–Yb–C(7)	28.4(7)	C(6)–Yb–C(8)	49.1(6)
C(7)–Yb–C(8)	30.9(6)	C(6)–Yb–C(9)	50.7(7)
C(7)–Yb–C(9)	50.0(7)	C(8)–Yb–C(9)	29.2(7)
C(6)–Yb–C(10)	31.6(8)	C(7)–Yb–C(10)	50.4(8)
C(8)–Yb–C(10)	50.4(7)	C(9)–Yb–C(10)	31.7(7)
Yb–O(1)–C(12)	131.4(11)	Yb–O(2)–C(14)	135.5(12)
C(2)–C(1)–C(5)	110.5(21)	C(1)–C(2)–C(3)	107.7(24)
C(2)–C(3)–C(4)	108.4(23)	C(3)–C(4)–C(5)	105.9(25)
C(1)–C(5)–C(4)	107.4(25)	C(7)–C(6)–C(10)	110.4(20)
C(6)–C(7)–C(8)	109.4(23)	C(7)–C(8)–C(9)	109.4(19)
C(8)–C(9)–C(10)	107.7(20)	C(6)–C(10)–C(9)	103.1(20)
O(1)–C(12)–C(11)	115.0(17)	O(1)–C(12)–C(13)	128.8(17)
C(11)–C(12)–C(13)	116.1(18)	C(12)–C(13)–C(14)	123.2(18)
O(2)–C(14)–C(13)	122.2(17)	O(2)–C(14)–C(15)	117.8(18)
C(13)–C(14)–C(15)	119.7(19)		
O(1)–Yb–cent1	111.8	O(2)–Yb–cent1 [a]	107.8
O(1)–Yb–cent2	109.1	O(2)–Yb–cent2 [b]	106.0
cent1–Yb–cent2	131.1		

[a] cent1 indicates the centroid of C(1) to C(5). [b] cent2 indicates the centroid of C(6) to C(10).

The average distance between the centre of the cyclopentadienyl ring and the ytterbium is 2.315 Å, which is smaller than that observed in $Cp_2Yb \cdot (CH_3COCHCOCH_3)$ (2.33 Å) [5]. The vectors from the centre of either ring and either oxygen atom to the ytterbium form angles averaging 108.7°. This value is smaller than that of $Cp_2Yb \cdot (CH_3COCHCOCH_3)$ (110.8°) [5] and means the cyclopentadienyl ring is closer to the oxygen atom of the 1,1,1-trifluoroacetylacetonato ligand than to that of the acetylacetonato ligand.

The average distance of Yb–O in this complex is 2.219 Å, which is 0.03 Å longer than that of the corresponding Yb–O in $Cp_2Yb \cdot (CH_3COCHCOCH_3)$ [5*]. The longer distance is presumably because the 1,1,1-trifluoroacetylacetonato complex is sterically too crowded to form a shorter "normal" Yb–O bond and the oxygen atoms in $Cp_2Yb \cdot (CH_3COCHCOCF_3)$ are weaker electron donors, due to the strong electron-attracting effects of three fluorine atoms, which affect the formation of the coordinate bond Yb–O.

Crystals of $Cp_2Yb \cdot (CH_3COCHCOCF_3)$ crystallize in the monoclinic system with space group $P2_1/c$ while crystals of $Cp_2Yb \cdot (CH_3COCHCOCH_3)$ crystallize in the triclinic system with space group $P\bar{1}$. This is a good example of the effects of substitute group on crystal system and space group.

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