Journal of Organometallic Chemistry, 339 (1988) 277–282
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Crystal and molecular structure of mixed ligand ytterbium organometallics: (dicyclopentadienyl)(acetylacetonato)ytterbium, $Yb(\eta^5\text{-}C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$

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(Received March 24th, 1987; in revised form July 31st, 1987)

Abstract

The crystal and molecular structure of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$ has been determined by a single crystal X-ray diffraction study. The crystal is triclinic with space group $P\bar{1}$, a 8.694, b 9.298, c 19.948 Å, α 100.08, β 91.89, γ 102.36°, V 1475.9 Å^3, and $Z = 4$ to give ρ_{calc} 1.81 g cm^{-3}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to an R factor of 0.028 based on 3961 independent reflections. The results showed that the crystal consists of discrete molecules of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$ and no direct interaction exists between Yb atoms. The Yb–O bond distances average 2.219 Å. The average Yb–C(η^5) bond distance is 2.611 Å.

Introduction

Up to now much has been published on the crystal structure of inorganic compounds involving β-diketonato chelate ligands [1]. However, to our knowledge, the crystal structure of organolanthanide compounds involving β-diketonato chelate ligands has not been reported. We have synthesized the compound $Cp_2Yb(acac)$ (where Hacac = acetylacetone) and other ytterbium organometallics involving both Cp (η^5-C_5H_5) and β-diketonato chelate ligands recently [2]. It was found that they tend to disproportionate at moderately high temperature. In order to clarify the cause of disproportionation, we determined the X-ray single crystal structure of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$.

0022-328X/88/$03.50

Experimental

Crystals of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$ suitable for X-ray diffraction studies were synthesized by use of Schlenk techniques. All operations were carried out under ultra-pure argon. Tricyclopentadienylytterbium was prepared by a published procedure [3]. After the reaction of tricyclopentadienylytterbium with acetylacetone in a solution of n-hexane at room temperature, the resulting solid was placed in a Schlenk-type sublimer and slowly sublimed at $70\,°C/10^{-3}$ Torr. Yellow single crystals grew. Several crystals were sealed in thin-wall glass capillaries under argon. Crystals of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$ are triclinic, $P\bar{1}$. The lattice constants, obtained by a CAD4 four-circle diffractometer, are summarized in Table 1.

Diffraction data were collected at room temperature on a CAD4 four-circle diffractometer using Mo-K_α radiation (λ 0.71073 Å). The total number of independent reflections was 3961 in the range of $2\theta \leqslant 45°$. The intensity data were corrected with LP and absorption factors.

The crystal structure was determined by the heavy-atom method and was refined by least-squares procedures. The positions of ytterbium were assigned from the highest non-origin peak in the initial Patterson map. Least-squares refinement was carried out for ytterbium atoms with isotropic thermal parameters. The unweighted R ($= [\Sigma \| F_0 | - | F_c \|] / \Sigma | F_0$) factor decreased to 0.197. Further refinement and a series of difference Fourier syntheses yielded the locations of all non-hydrogen atoms. Several cycles of isotropic least-squares refinement and anisotropic full-matrix least-squares refinement for all non-hydrogen atoms reduced the unweighted R factor to 0.032. The hydrogen atom positions were located by the difference Fourier syntheses. Two final cycles of refinement on all atoms, with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms, reduced R factor to 0.028. Final atomic positions and isotropic thermal parameters are listed in Table 2.

Results and discussion

All of the bond lengths and some important angles are given in Table 3 and Table 4. Figure 1 shows a view of the molecular structure. The results indicate that

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Table 1

Summary of crystal data

Molecular formula	$Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$
Mol wt. 402.30	
ρ_{calc}	1.81 g cm^{-3}
Crystal dimensions	0.42 × 0.25 × 0.3 mm
Space group $P\bar{1}$, $Z = 4$	Triclinic
Cell constants	
a 8.694(9) Å	α 100.08(2)°
b 9.298(2) Å	β 91.89(4)°
c 19.948(4) Å	ν 102.36(3)°
V 1485.9 Å^3	

Table 2

Atomic coordinates (fractional) and isotropic thermal parameters [a]

Atom	x	y	z	B_{eq} (Å)
Yb(1)	0.28652(5)	0.23361(5)	0.37562(2)	3.66(1)
Yb(2)	0.05789(5)	0.34614(5)	0.87156(2)	4.13(1)
O(1)	0.0754(8)	0.0116(8)	0.3632(4)	4.9(2)
O(2)	0.1643(7)	0.2832(8)	0.4670(3)	4.6(2)
O(3)	0.8932(9)	0.7201(8)	0.0325(4)	5.3(2)
O(4)	0.1648(8)	0.1702(8)	0.8334(4)	5.9(2)
C(1)	0.308(1)	0.317(1)	0.2575(5)	4.8(3)
C(2)	0.136(1)	0.253(1)	0.2632(5)	5.3(3)
C(3)	0.099(1)	0.351(1)	0.3168(6)	6.3(3)
C(4)	0.246(2)	0.481(1)	0.3433(6)	6.2(3)
C(5)	0.374(1)	0.458(1)	0.3071(6)	5.3(3)
C(6)	0.449(1)	0.074(2)	0.4205(8)	8.6(4)
C(7)	0.491(1)	0.898(1)	0.6407(7)	7.6(3)
C(8)	0.405(1)	0.736(2)	0.6323(7)	8.6(3)
C(9)	0.413(1)	0.671(2)	0.5629(8)	8.3(4)
C(10)	0.503(1)	0.791(2)	0.5351(6)	8.1(4)
C(11)	0.069(1)	0.014(1)	0.6147(6)	4.9(3)
C(12)	0.105(1)	0.914(1)	0.5621(6)	4.9(3)
C(13)	−0.011(1)	0.778(1)	0.5232(5)	4.4(2)
C(14)	0.203(1)	0.162(1)	0.6516(8)	7.1(4)
C(15)	0.045(1)	0.694(1)	0.4633(6)	5.7(3)
C(16)	0.221(1)	0.888(1)	0.1692(7)	6.3(3)
C(17)	0.249(1)	0.805(1)	0.1088(7)	5.9(3)
C(18)	0.246(1)	0.660(1)	0.1191(7)	6.3(3)
C(19)	0.218(1)	0.654(1)	0.1871(7)	7.3(3)
C(20)	0.199(1)	0.796(2)	0.2183(6)	7.3(4)
C(21)	0.192(2)	0.646(2)	0.9116(7)	7.7(4)
C(22)	0.146(2)	0.625(1)	0.8475(8)	8.0(4)
C(23)	0.238(2)	0.560(2)	0.8095(7)	9.3(5)
C(24)	0.352(2)	0.533(2)	0.854(1)	10.6(5)
C(25)	0.321(2)	0.595(2)	0.9212(7)	8.7(4)
C(26)	0.189(1)	0.197(1)	0.9819(6)	4.9(3)
C(27)	0.261(1)	0.117(1)	0.9347(6)	5.6(3)
C(28)	0.247(1)	0.107(1)	0.8638(6)	5.1(3)
C(29)	0.207(2)	0.192(2)	0.0557(6)	7.3(4)
C(30)	0.329(1)	0.016(1)	0.8194(8)	7.2(4)
H(1)	0.36(1)	0.278(9)	0.222(4)	4(2)*
H(2)	0.05(1)	0.135(9)	0.227(4)	7(2)*
H(3)	0.01(1)	0.342(9)	0.327(4)	5(2)*
H(4)	0.29(1)	0.580(9)	0.380(4)	7(2)*
H(5)	0.52(1)	0.456(9)	0.690(4)	7(2)*
H(6)	0.41(1)	0.944(9)	0.432(4)	11(2)*
H(7)	0.50(1)	−0.004(9)	0.318(4)	10(2)*
H(8)	0.34(1)	0.730(9)	0.667(4)	9(2)*
H(9)	0.34(1)	0.532(9)	0.546(4)	11(2)*
H(10)	0.45(1)	0.232(9)	0.527(4)	11(2)*
H(11)	0.22(1)	0.958(9)	0.553(4)	5(2)*
H(12)	0.14(1)	0.223(9)	0.665(4)	5(2)*
H(13)	0.30(1)	0.150(9)	0.648(4)	6(2)*
H(14)	0.25(1)	0.258(9)	0.627(4)	11(2)*
H(15)	0.11(1)	0.765(9)	0.428(4)	9(2)*
H(151)	0.15(1)	0.693(9)	0.471(4)	8(2)*
H(152)	0.98(1)	0.394(9)	0.531(4)	9(2)*

continued

Table 2 (continued)

Atom	x	y	z	B_{eq} (Å)
H(16)	0.22(1)	0.990(9)	0.176(4)	8(2)*
H(17)	0.28(1)	0.838(9)	0.052(4)	9(2)*
H(18)	0.28(1)	0.564(9)	0.079(4)	6(2)*
H(19)	0.22(1)	0.554(9)	0.205(4)	9(2)*
H(20)	0.20(1)	0.817(9)	0.270(4)	8(2)*
H(21)	0.15(1)	0.710(9)	0.949(4)	7(2)*
H(22)	0.93(1)	0.320(9)	0.164(4)	9(2)*
H(23)	0.23(1)	0.536(9)	0.768(4)	7(2)*
H(24)	0.41(1)	0.507(9)	0.839(4)	6(2)*
H(25)	0.37(1)	0.587(9)	0.969(4)	8(2)*
H(26)	0.32(1)	0.046(9)	0.949(4)	6(2)*
H(27)	0.24(1)	0.130(9)	0.060(4)	7(2)*
H(28)	0.10(1)	0.113(9)	0.066(4)	8(2)*
H(29)	0.18(1)	0.224(9)	0.088(4)	10(2)*
H(30)	0.24(1)	0.955(9)	0.770(4)	8(2)*
H(301)	0.35(1)	0.953(9)	0.831(4)	9(2)*
H(302)	0.39(1)	0.068(9)	0.803(4)	3(2)*

[a] Atoms with an asterisk were refined isotropically.

Table 3

Bond lengths (Å) [a]

Yb(1)–C(1)	2.194(4)	Yb(1)–C(2)	2.200(4)
Yb(1)–C(1)	2.598(7)	Yb(1)–C(2)	2.624(7)
Yb(1)–C(3)	2.606(7)	Yb(1)–C(4)	2.624(8)
Yb(1)–C(5)	2.599(7)	Yb(1)–C(6)	2.621(9)
Yb(1)–C(7)	2.624(8)	Yb(1)–C(8)	2.614(7)
Yb(1)–C(9)	2.625(8)	Yb(1)–C(10)	2.604(8)
Yb(2)–O(3)	2.183(5)	Yb(2)–O(4)	2.191(5)
Yb(2)–C(16)	2.609(8)	Yb(2)–C(17)	2.624(7)
Yb(2)–C(18)	2.639(8)	Yb(2)–C(19)	2.628(8)
Yb(2)–C(20)	2.605(8)	Yb(2)–C(21)	2.579(10)
Yb(2)–C(22)	2.571(10)	Yb(2)–C(23)	2.597(10)
Yb(2)–C(24)	2.614(10)	Yb(2)–C(25)	2.624(9)
C(1)–C(11)	1.297(8)	O(2)–C(13)	1.290(7)
O(3)–C(26)	1.278(8)	O(4)–C(28)	1.273(8)
C(1)–C(2)	1.421(10)	C(1)–C(5)	1.418(10)
C(2)–C(3)	1.400(11)	C(3)–C(4)	1.419(13)
C(4)–C(5)	1.400(11)	C(6)–C(7)	1.374(15)
C(6)–C(10)	1.327(15)	C(7)–C(8)	1.398(15)
C(8)–C(9)	1.427(15)	C(9)–C(10)	1.337(15)
C(11)–C(12)	1.398(10)	C(11)–C(14)	1.502(11)
C(12)–C(13)	1.382(10)	C(13)–C(15)	1.504(11)
C(16)–C(17)	1.388(11)	C(16)–C(20)	1.383(13)
C(17)–C(18)	1.394(11)	C(18)–C(19)	1.396(13)
C(19)–C(20)	1.417(13)	C(21)–C(22)	1.287(14)
C(21)–C(25)	1.379(15)	C(22)–C(23)	1.34(2)
C(23)–C(24)	1.43(2)	C(24)–C(25)	1.44(2)
C(26)–C(27)	1.399(11)	C(26)–C(29)	1.485(13)
C(27)–C(28)	1.399(11)	C(28)–C(30)	1.486(13)
Yb(1)---ring(1)	2.317	Yb(1)---ring(2)	2.343
Yb(2)---ring(3)	2.337	Yb(2)---ring(4)	2.319

[a] Numbers in parentheses are estimated standard deviation in the least significant digits.

Table 4

Bond angles (°) [a]

O(1)–Yb(1)–O(2)	79.8(2)	O(3)–Yb(2)–O(4)	80.3(2)
C(2)–C(1)–C(5)	106.9(7)	C(1)–C(2)–C(3)	108.2(8)
C(2)–C(3)–C(4)	108.6(8)	C(3)–C(4)–C(5)	107.3(7)
C(1)–C(5)–C(4)	109.0(7)	C(7)–C(6)–C(10)	108.0(1)
C(6)–C(7)–C(8)	108.0(1)	C(7)–C(8)–C(9)	105.9(9)
C(8)–C(9)–C(10)	106.0(1)	C(6)–C(10)–C(9)	112.0(1)
C(17)–C(16)–C(20)	108.8(8)	C(16)–C(17)–C(18)	108.9(9)
C(17)–C(18)–C(19)	106.9(8)	C(18)–C(19)–C(20)	108.6(8)
C(16)–C(20)–C(19)	106.8(8)	C(22)–C(21)–C(25)	111.0(1)
C(21)–C(22)–C(23)	110.0(1)	C(22)–C(23)–C(24)	109.0(1)
C(23)–C(24)–C(25)	103.0(1)	C(21)–C(25)–C(24)	106.0(1)
O(1)---Yb(1)---Ring(1)	106.4	O(1)---Yb(1)---Ring(2)	108.2
O(2)---Yb(1)---Ring(1)	106.2	O(2)---Yb(1)---Ring(2)	107.7
O(3)---Yb(2)---Ring(3)	107.4	O(3)---Yb(2)---Ring(4)	108.1
O(4)---Yb(2)---Ring(3)	107.6	O(4)---Yb(2)---Ring(4)	107.4
Ring(1)---Yb(1)---Ring(2)	119.3		
Ring(3)---Yb(2)---Ring(4)	130.1		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

bond lengths and angles involving the ytterbium ion are all normal. The Yb–O bond distances average 2.219 Å. The average Yb–C(η^5) bond distance is 2.611 Å. This is longer than the Lu–C(η^5) bond distance [4]. The average O–Yb–O bond angle is 80.0(2)°. There are two crystallographically independent molecules of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$ in an asymmetric unit. They have different orientations and no direct interaction exists between Yb atoms. The minimum non-bonded distance of Yb–Yb is 5.717 Å. This is in contrast to $[Yb(C_5H_5CH_3)Cl_2$ [5] and is probably due to the change in Yb–Yb separation caused by the formation of a stable six-membered chelate ring by the β-diketonato ligand.

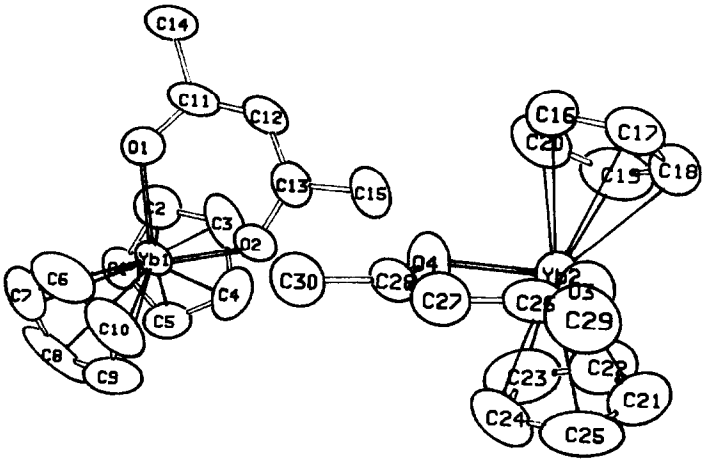

Fig. 1. Molecular structure of $Yb(C_5H_5)_2 \cdot (CH_3COCHCOCH_3)$.

Table 5

Deviations (Å) of atoms from the least-squares planes of cyclopentadienyl rings [a]

Atom	C(1)	C(2)	C(3)	C(4)	C(5)
Ring(1)	−0.01(1)	0.01(1)	−0.01(1)	0.01(1)	−0.00(1)
Atom	C(6)	C(7)	C(8)	C(9)	C(10)
Ring(2)	−0.11(1)	−0.36(1)	0.10(1)	0.35(1)	0.01(1)
Atom	C(16)	C(17)	C(18)	C(19)	C(20)
Ring(3)	−0.00(1)	−0.00(1)	0.01(1)	−0.01(1)	0.01(1)
Atom	C(21)	C(22)	C(23)	C(24)	C(25)
Ring(4)	−0.00(1)	−0.01(1)	0.01(2)	−0.01(2)	0.01(2)

Parameters of the plane's equations:

Parameter	Ring(1)	Ring(2)	Ring(3)	Ring(4)
A	−0.3658	−0.9158	−0.8936	0.3659
B	0.6545	−0.1428	−0.3507	0.9302
C	−0.6617	−0.3750	−0.2802	−0.0304
D	−2.7270	−5.9255	−2.4178	0.9378

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The geometry around the ytterbium atom in this structure can be described as slightly distorted tetrahedral, with the centers of the two cyclopentadienyl rings and the two oxygen atoms forming the apices of the tetrahedron. The average distance from the center of the ring to the ytterbium is 2.33(1) Å. The vectors from the center of either ring and from either oxygen atom to the ytterbium form angles that average 110.8°.

The five cyclopentadienyl carbons of each ring form very good planes (see Table 5). The rings are very well defined with carbon–carbon distances for adjacent carbon atoms ranging from 1.29 to 1.44 Å (an average of 1.39(2) Å) and with C–C–C angles within a ring ranging from 103 to 112°, an average of 108.(1)°. The rings are bound to the ytterbium with an average Yb–C distance of 2.61(1) Å.

References

1 R.A. Lalancette, M. Cefola, W.C. Hamilton and S.J.L. Placa, Inorg. Chem., 6 (1967) 2127.
2 H. Ma and Z. Ye, J. Organomet. Chem., 326 (1982) 369.
3 J.M. Birmingham, and G. Wilkinson, J. Am. Chem. Soc., 76 (1954) 6210.
4 C. Ni, Z. Zhang, D. Deng, and C. Qian, J. Organomet. Chem., 306 (1986) 209.
5 E.C. Baker, L.D. Brown and K.N. Raymond, Inorg. Chem., 14 (1975) 1376.