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Preliminary communication

Synthesis and structural investigation of lanthanide organometallics involving cyclopentadienyl and 2-naphthoyltrifluoroacetonato chelate ligands

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Abstract

Four new di-η^5-cyclopentadienyl 2-naphthoyltrifluoroacetonato lanthanides, namely, $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$, $Cp_2Er(C_{10}H_7COCHCOCF_3) \cdot THF$, $Cp_2Pr(C_{10}H_7COCHCOCF_3)$, $Cp_2Sm(C_{10}H_7COCHCOCF_3)$ (Cp = cyclopentadienyl, THF = tetrahydrofuran) were synthesized and identified by elemental analysis and IR. The crystal structure of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ has been determined by single-crystal X-ray diffraction. The structural analysis showed that the holmium atom is surrounded by two cyclopentadienyl ligands, two oxygen atoms of the 2-naphthoyltrifluoroacetonato ligand and one oxygen atom of the solvated THF molecule.

Keywords: Holmium; Lanthanide complexes; Cyclopentadienyl; 2-Naphthoyltrifluoroacetonato; Crystal structure

1. Introduction

In recent years, organometallic chemistry of the rare earths has become an active area and thousands of articles covering this area of chemistry have appeared. However, to our knowledge, only a few articles [1–4] have focused on organolanthanide complexes involving both cyclopentadienyl and β-diketonato chelate ligands. In order to get more information about the properties and structural character of this type of complexes, we synthesized four new organolanthanide complexes and determined the X-ray structure of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$.

2. Experimental detail

All reactions and operations were carried out by use of Schlenk techniques under an atmosphere of ultrapure argon. THF, *n*-hexane and toluene were dried over sodium and distilled under argon from sodium benzophenone ketyl before use. 2-Naphthoyltrifluoroacetone [5], anhydrous $LnCl_3$ [6] and Cp_3Ln [7,8] (Ln = Ho, Er, Pr, Sm) were all prepared by the published procedures. Decomposition temperatures were determined in sealed argon-filled capillaries and were uncorrected. IR spectra were recorded on a Perkin-Elmer 983 (G) spectrometer (CsI crystal plate, Nujol and Fluorolube mulls). Elemental analysis was carried out with a Yanaco MT-2 analyzer, and elemental analysis results for Ln were obtained by a published method [9].

2.1. Preparation

2.1.1. Preparation of $Cp_2Ln(C_{10}H_7COCHCOCF_3) \cdot THF$ (Ln = Ho, Er)

A mixture of Cp_3Ln (Ln = Ho, Er) and 2-naphthoyltrifluoroacetone in molar ratio 1 : 1 was stirred *n*-hexane at room temperature for 3 days. The *n*-hexane was removed in vacuum from the reaction mixture. The resulting solid was recrystallized twice from THF/*n*-hexane, the products of $Cp_2Ln(C_{10}H_7COCHCOCF_3) \cdot THF$ (Ln = Ho, Er) were obtained.

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2.1.2. Preparation of $Cp_2Ln(C_{10}H_7COCHCOCF_3)$ (Ln = Sm, Pr)

1 mmol Cp_3Ln (Ln = Sm, Pr) reacted with 1 mmol 2-naphthoyltrifluoroacetone in 40 ml toluene with stirring. After stirring for 3 days at room temperature, toluene was removed from the reaction mixture. The crude products were recrystallized twice from toluene/*n*-hexane to afford the products $Cp_2Ln(C_{10}H_7COCHCOCF_3)$ (Ln = Sm, Pr).

Physical data, elemental analyses and IR of the four complexes are presented in Table 1.

2.2. X-ray crystallography

Part of the product $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ was dissolved in THF, drops of *n*-hexane were added. Keeping the solution at −10°C for a few days, crystals of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ suitable for X-ray study were obtained. The single crystals of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ used for structural analysis were sealed under argon in thin-walled capillaries. A single crystal of dimensions 0.6 × 0.5 × 0.55 mm was selected. The crystal of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ is monoclinic with space group C_2/C, $M_r = 632.44$, $a = 25.413(5)$ Å, $b = 8.083(1)$ Å, $c = 24.912(5)$ Å, $\beta = 99.78(2)°$, $V = 5043(2)$ Å^3 and $D_c = 1.67$ g cm^{-3} for $Z = 8$, $\mu = 32.22$ cm^{-1} and $F(000) = 2496$.

Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 X-ray diffractometer with graphite monochromated Mo–Kα radiation ($\lambda = 0.71069$ Å). The monoclinic cell parameters were refined by least squares from angular data of 25 reflections in the range of $14.01° < \theta < 15.39°$.

The data were collected at a temperature of 296 K using the ω-2θ scan technique. The scan rate is less than 5.50° min^{-1} in Omega. A total of 4804 unique reflections were collected in the range of $2\theta \leqslant 49.9°$, of which 3863 reflections with $I > 3\sigma(I)$ were considered observed and used in the structure determination.

The structure was solved by direct methods using MITHRIL. Approximate positions of the Ho atom were obtained from the E map, and those of the remaining non-hydrogen atoms from the DF map. After convergence of the isotropic refinement, an empirical absorption correction using the DIFABS program was applied, H atoms were placed in geometrically calculated positions, but not included in the refinement. The convergence of the last stage of full-matrix least-squares refinement on F with anisotropic thermal parameters for non-hydrogen atoms reached to $R = 0.035$, $Rw = 0.044$ $[w = 1/\sigma^2(|F_o|)]$, $s = 1.40$, $(\Delta/\sigma)_{max} = 0.05$ and $\Delta\rho = -0.715$–0.850 e · Å^{-3}. The views of the molecule were produced by the ORTEP program. All calculations were made on a Micro VAX-3100 computer using the TEXSAN v.2.1 program package.

3. Results and discussion

The elemental analyses (Table 1) indicate that all four compounds are in agreement with the general formula $Cp_2Ln(C_{10}H_7COCHCOCF_3) \cdot THF$ (Ln = Ho, Er) or $Cp_2Ln(C_{10}H_7COCHCOCF_3)$ (Ln = Pr, Sm).

The IR spectra of these compounds show characteristic Cp absorption at about 780, 1010, 1440 and 3100 cm^{-1}, and an absorption peak at about 250 cm^{-1} for Ln–C of the π-bonded Cp group [9], All of them exhibit the characteristic C=O and C=C multiple absorption of O-chelate complexes at 1500–1600 cm^{-1} [10]. The IR spectra of $Cp_2Ln(C_{10}H_7COCHCOCF_3) \cdot THF$ (Ln = Ho, Er) also show characteristic absorption of THF at about 913 cm^{-1} and 1065 cm^{-1} [11].

The molecular structure of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ is shown in Fig. 1. The atomic coordinates and isotropic thermal parameters, selected bond distances and bond angles of all non-hydrogen atoms are listed in Tables 2–4, respectively.

Fig. 1 shows that $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ is a mononuclear holmium complex. The central metal Ho is coordinated by two cyclopentadienyl ligands in the η^5 mode, two oxygen atoms of the 2-naphthoyltrifluoroacetonato ligand in bidentate fashion and one oxygen atom of the solvated THF. All the O(1)–

Table 1
Analytical and some IR data of the four new compounds

Compound	Color	Yield (%)	D.T. [a] (°C)	Found (Calc.) Ln	C	H	IR (cm^{-1})		
$Cp_2HoL \cdot THF$	Orange	41.0	82	26.30 (26.08)	52.76 (53.18)	3.85 (4.14)	1597s 1517w	1571s 1507m	1530s
$Cp_2ErL \cdot THF$	Orange	38.7	106	26.27 (26.35)	52.56 (52.98)	4.18 (4.13)	1595s 1515w	1570s 1505m	1530s
Cp_2PrL	Yellow green	36.0	144	26.69 (26.27)	54.46 (53.75)	3.52 (3.38)	1595s 1515w	1570s 1505m	1530s
Cp_2SmL	Yellow	35.4	144	27.86 (27.55)	53.19 (52.82)	3.58 (3.32)	1595s 1515w	1569s 1505m	1530s

L = $C_{10}H_7COCHCOCF_3$. [a] D.T. = Decomposition temperature.

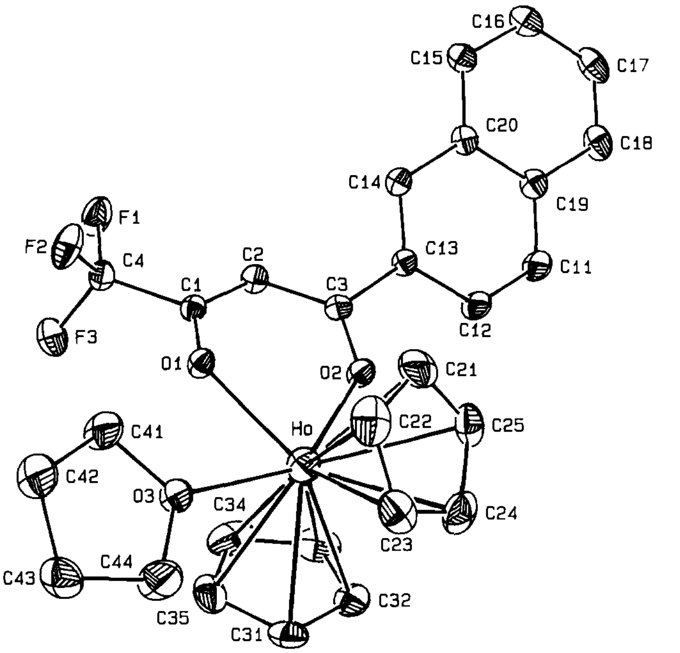

Fig. 1. Molecular structure of $Cp_2Ho(C_{10}H_7COCHCOCF_3)\cdot THF$.

Table 2
Atomic coordinates and isotropic thermal parameters

Atom	x	y	z	B_{eq}
Ho	0.351794(8)	0.17996(2)	0.163747(8)	3.14(1)
F(1)	0.4756(2)	−0.1500(4)	0.0304(2)	6.9(2)
F(2)	0.3906(2)	−0.1511(4)	0.0100(2)	6.6(2)
F(3)	0.4289(2)	−0.2715(4)	0.0804(2)	7.1(2)
O(1)	0.3820(1)	0.0318(4)	0.0988(1)	3.8(1)
O(2)	0.4335(1)	0.2902(4)	0.1545(1)	4.2(2)
O(3)	0.2782(1)	−0.0075(4)	0.1238(2)	4.6(2)
C(1)	0.4271(2)	0.0167(5)	0.0837(2)	3.3(2)
C(2)	0.4694(2)	0.1220(6)	0.0937(2)	3.7(2)
C(3)	0.4681(2)	0.2666(6)	0.1252(2)	3.4(2)
C(4)	0.4312(2)	−0.1400(6)	0.0506(2)	4.0(2)
C(11)	0.5491(3)	0.6447(7)	0.1682(2)	5.2(3)
C(12)	0.5164(2)	0.5139(7)	0.1689(2)	4.7(2)
C(13)	0.5085(2)	0.4002(6)	0.1251(2)	3.4(2)
C(14)	0.5340(2)	0.4233(6)	0.0818(2)	3.6(2)
C(15)	0.5914(2)	0.5980(7)	0.0334(2)	4.6(2)
C(16)	0.6217(2)	0.7371(8)	0.0316(3)	5.3(3)
C(17)	0.6291(3)	0.8475(7)	0.0757(3)	5.7(3)
C(18)	0.6066(3)	0.8186(6)	0.1199(3)	5.4(3)
C(19)	0.5749(2)	0.6758(6)	0.1237(2)	4.2(2)
C(20)	0.5676(2)	0.5640(6)	0.0789(2)	3.7(2)
C(21)	0.3237(4)	0.4524(8)	0.1056(3)	7.0(4)
C(22)	0.2766(3)	0.369(1)	0.1058(3)	7.0(4)
C(23)	0.2658(3)	0.3741(9)	0.1575(4)	6.6(4)
C(24)	0.3060(3)	0.4613(8)	0.1894(3)	7.0(4)
C(25)	0.3426(3)	0.5068(7)	0.1570(3)	6.0(3)
C(31)	0.3347(3)	0.0674(9)	0.2590(2)	5.5(3)
C(32)	0.3773(3)	0.1756(8)	0.2713(2)	5.8(3)
C(33)	0.4203(3)	0.116(1)	0.2546(3)	6.9(4)
C(34)	0.4077(4)	−0.037(1)	0.2295(3)	8.0(4)
C(35)	0.3540(4)	−0.0692(8)	0.2326(3)	6.9(4)
C(41)	0.2745(3)	−0.093(1)	0.0730(3)	6.7(3)
C(42)	0.2227(3)	−0.1829(8)	0.0639(3)	6.7(4)
C(43)	0.2041(3)	−0.1825(8)	0.1159(3)	6.6(4)
C(44)	0.2308(3)	−0.043(1)	0.1456(3)	8.3(4)

Table 3
Selected bond distances (Å)

Ho–O(1)	2.250(3)	C(1)–C(2)	1.362(7)
Ho–O(2)	2.306(4)	C(1)–C(4)	1.525(6)
Ho–O(3)	2.480(3)	C(2)–C(3)	1.411(7)
Ho–C(21)	2.666(6)	C(3)–C(13)	1.491(7)
Ho–C(22)	2.674(6)	C(21)–C(25)	1.36(1)
Ho–C(23)	2.674(6)	C(21)–C(22)	1.37(1)
Ho–C(24)	2.681(5)	C(22)–C(23)	1.36(1)
Ho–C(25)	2.655(6)	C(23)–C(24)	1.38(1)
Ho–C(31)	2.646(5)	C(24)–C(25)	1.38(1)
Ho–C(32)	2.648(6)	C(31)–C(32)	1.384(9)
Ho–C(33)	2.662(7)	C(31)–C(35)	1.42(1)
Ho–C(34)	2.646(6)	C(32)–C(33)	1.32(1)
Ho–C(35)	2.641(6)	C(33)–C(34)	1.40(1)
F(1)–C(4)	1.314(6)	C(34)–C(35)	1.40(1)
F(2)–C(4)	1.319(6)	C(41)–C(42)	1.485(9)
F(3)–C(4)	1.304(6)	C(42)–C(43)	1.45(1)
O(1)–C(1)	1.271(6)	C(43)–C(44)	1.45(1)
O(2)–C(3)	1.248(6)	Ho–Cent1 [a]	2.402
O(3)–C(44)	1.432(7)	Ho–Cent2 [b]	2.371
O(3)–C(41)	1.434(7)		

[a] Cent1 indicates the centroid of C(21) to C(25).
[b] Cent2 indicates the centroid of C(31) to C(35).

C(1)–C(2)–C(3)–O(2) plane and the other two cyclopentadienyl rings are situated in good planes with mean deviations of only 0.0605, 0.0069 and 0.0029 Å

Table 4
Selected bond angles (°)

O(1)–Ho–O(2)	73.2(3)	O(1)–C(1)–C(4)	112.8(4)
O(1)–Ho–O(3)	73.3(3)	C(2)–C(1)–C(4)	119.6(4)
O(2)–Ho–O(3)	145.7(3)	C(1)–C(2)–C(3)	121.7(4)
C(21)–Ho–C(22)	29.8(3)	O(2)–C(3)–C(2)	122.6(4)
C(21)–Ho–C(23)	48.9(3)	O(2)–C(3)–C(13)	116.4(4)
C(21)–Ho–C(24)	48.9(3)	C(2)–C(3)–C(13)	121.1(4)
C(21)–Ho–C(25)	29.7(3)	C(14)–C(13)–C(3)	121.4(4)
C(22)–Ho–C(23)	29.5(3)	C(12)–C(13)–C(3)	118.4(4)
C(22)–Ho–C(24)	48.9(3)	C(25)–C(21)–C(22)	108.8(7)
C(22)–Ho–C(25)	49.4(3)	C(23)–C(22)–C(21)	107.8(7)
C(23)–Ho–C(24)	29.8(3)	C(22)–C(23)–C(24)	108.1(7)
C(23)–Ho–C(25)	49.5(3)	C(23)–C(24)–C(25)	107.9(7)
C(24)–Ho–C(25)	30.0(3)	C(21)–C(25)–C(24)	107.4(7)
C(31)–Ho–C(32)	30.3(3)	C(32)–C(31)–C(35)	106.0(6)
C(31)–Ho–C(33)	49.7(3)	C(33)–C(32)–C(31)	110.9(7)
C(31)–Ho–C(34)	50.8(3)	C(32)–C(33)–C(34)	108.9(7)
C(31)–Ho–C(35)	31.1(3)	C(33)–C(34)–C(35)	106.7(7)
C(32)–Ho–C(33)	28.9(3)	C(34)–C(35)–C(31)	107.4(6)
C(32)–Ho–C(34)	49.5(3)	O(3)–C(41)–C(42)	107.1(6)
C(32)–Ho–C(35)	50.0(3)	C(43)–C(42)–C(41)	106.1(6)
C(33)–Ho–C(34)	30.6(3)	C(44)–C(43)–C(42)	105.1(6)
C(33)–Ho–C(35)	50.2(3)	O(3)–C(44)–C(43)	108.2(6)
C(34)–Ho–C(35)	30.8(3)	O(1)–Ho–Cent1 [a]	121.73
C(21)–Ho–C(31)	134.6(3)	O(1)–Ho–Cent2 [b]	109.71
C(1)–O(1)–Ho	134.3(3)	O(2)–Ho–Cent1	95.17
C(3)–O(2)–Ho	137.3(3)	O(2)–Ho–Cent2	97.40
C(41)–O(3)–Ho	125.6(3)	O(3)–Ho–Cent1	96.17
C(44)–O(3)–Ho	126.6(4)	O(3)–Ho–Cent2	100.52
C(44)–O(3)–C(41)	107.8(5)	Cent1–Ho–Cent2	128.53
O(1)–C(1)–C(2)	127.6(4)		

[a] Cent1 indicates the centroid of C(21) to C(25).
[b] Cent2 indicates the centroid of C(31) to C(35).

respectively. The three dihedral angles between the planes formed by O(1)–C(1)–C(2)–C(3)–O(2) and Cp1-[C(21)–C(25)], O(1)–C(1)–C(2)–C(3)–O(2) and Cp2-[C(31)–C(35)] and Cp1 and Cp2 are 37.57, 13.10 and 50.53°, respectively. The bond distances of two adjacent carbon atoms in each of the two cyclopentadienyl rings range from 1.32(1)–1.42(1) Å (an average of 1.38 Å), and the C–C–C angle in the cyclopentadienyl rings range from 106.0(6)–110.9(7)° (an average of 108.0°). The above mentioned C–C distances and C–C–C angles are similar to those of $Cp_2Yb(CH_3COCHCOCF_3)$ (an average of 1.37 Å and 108.0° respectively) [12]. The mean bond distance of Ho–O(1) and Ho–O(2) is 2.278 Å, which is 0.065 Å longer than that of the corresponding Yb–O in $Cp_2Yb(CH_3COCHCOCF_3)$. The O(1)–Ho–O(2) bond angle is 73.2°, which is 4.8° smaller than that of O(1)–Yb–O(2) in $Cp_2Yb(CH_3COCHCOCF_3)$. The average distance between the centre of the cyclopentadienyl ring and the holmium is 2.386 Å, which is 0.085 Å longer than that observed in Cp_2Yb-$(CH_3COCHCOCF_3)$. The vectors from the centre of either ring and from either oxygen atom of the β-diketonato to holmium form angles with an average of 106.0°, which is 2.7° smaller than that of Cp_2Yb-$(CH_3COCHCOCF_3)$. The longer bond distances and smaller bond angles compared with those of Cp_2Yb-$(CH_3COCHCOCF_3)$ may be a result of steric effects and lanthanide contraction effects.

The single crystal of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ obtained from solution is a monoclinic system with space group C_2/C. It is different to the reported structure of $Cp_2Yb(CH_3COCHCOCF_3)$ [12], which was obtained by sublimation. The structure of Cp_2Yb-$(CH_3COCHCOCF_3)$ is a monoclinic system with space group $P2_1/C$ without THF coordinating to it. The coordination number of $Cp_2Ho(C_{10}H_7COCHCOCF_3) \cdot THF$ is 9, while that of $Cp_2Yb(CH_3COCHCOCF_3)$ is 8. The geometry around the holmium atom in this structure can be described as a distorted trigonal bipyramid with the centres of the two cyclopentadienyl rings (Cent1, Cent2) and the three oxygen atoms forming the apices of the bipyramid, the Cent1, Cent2 and O(1) occupy equatorial positions. The Ho–Cent1, Ho–Cent2 and Ho–O(1) bond distances are 2.402, 2.371 and 2.250 Å respectively and the Cent1–Ho–Cent2, Cent1–Ho–O(1) and Cent(2)–Ho–O(1) bond angles are 128.53, 121.73 and 109.71° respectively. The O(2) and O(3) occupy axial positions with the Ho–O(2), Ho–O(3) bond distances of 2.306, 2.480 Å respectively and with the O(2)–Ho–O(3) bond angle of 145.7°. While the geometry around the Ytterbium atom in $Cp_2Yb(CH_3COCHCOCF_3)$ can be described as slightly distorted tetrahedral.

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