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Synthesis and structure of (η^5-C_5H_5)$_3$Dy·OC_4H_8

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Abstract

Reaction of a 1/3 mole ratio of $DyCl_3$ and NaC_5H_5 in THF solution resulted in the formation of (η^5-C_5H_5)$_3$Dy·THF. The compound crystallized in the monoclinic space group $P2_1/n$ with unit cell constants $a=8.247(4)$, $b=24.582(5)$, $c=8.318(6)$ Å, $\beta=101.49(7)°$ and $D_c=1.69$ g cm^{-3} for $Z=4$. Full-matrix least-squares refinement has led to a final R value of 0.046 based on 2214 independent observed reflections. The THF molecule is coordinated to the dysprosium atom at a Dy–O distance of 2.522(5) Å. The Dy–C(cyclopentadienyl) bond lengths range from 2.649(2) to 2.816(9) Å. A comparison of some significant structural parameters along the isostructural series Cp_3Ln·THF (Ln = La, Pr, Nd, Gd and Dy) with the crystal radii was made.

Introduction

Crystal structures of tricyclopentadienyl lanthanide compounds obtained by sublimation, such as Cp_3Sc [1], Cp_3Sm [2], Cp_3Pr [3] and $(C_5H_4Me)_3Nd$ [4], have been reported. Due to their larger unsaturated coordination, they are all polymers, although both their structures and formal coordination numbers are different. To our knowledge, up till now investigations of crystal structures of four tricyclopentadienyl lanthanides in the form of THF adducts have been carried out. It was found that Cp_3La·THF [5], Cp_3Pr·THF [6], Cp_3Nd·THF [6, 7] and Cp_3Gd·THF [8] are monomeric units with a formal coordination number of 10. Within the series of Cp_3Ln·THF, the synthesis and structural study of Cp_3Dy·THF has not been reported [9]. In order to characterize the Dy–C(Cp) bond and to learn about the strength of coordination of the THF molecule, we synthesized Cp_3Dy·THF and determined its crystal and molecular structure by single crystal X-ray diffraction investigations. At the same time we attempted to compare some significant structural parameters along the isostructural series Cp_3Ln·THF (Ln = La, Pr, Nd, Gd and Dy).

Experimental

All transfers and handling were accomplished by the Schlenk technique. Tetrahydrofuran solvent was refluxed and distilled over finely divided $LiAlH_4$ or the sodium ketyl of benzophenone under argon immediately before use. Anhydrous $DyCl_3$ was prepared according to ref. 10. C_5H_5Na was prepared by a published procedure [11]. The title compound was produced by the room temperature reaction of a 1/3 mole ratio of anhydrous $DyCl_3$ and C_5H_5Na in THF for 36 h and purified by vacuum sublimation at 220 °C/10^{-3} torr. The yellow sublimate was soluble in THF at room temperature. Crystals suitable for the X-ray diffraction experiment were grown by slow cooling of the THF solution.

Single crystals of the title compound were sealed in thin-walled glass capilaries under an argon atmosphere. Diffraction data was collected on an Enraf-Nonius CAD4 type four circle diffractometer using Mo Kα radiation ($\lambda=0.71073$ Å), scan technique of θ–2θ and scan speed varied in the range of 1.03–5.49°/min. The total number of independent reflections amounts to 2214 in the range of $2° \leqslant \theta \leqslant 22°$, including 1547 reflections with $I > 3\sigma$. The intensity data was corrected for LP, absorption and decay factors. The crystal structure was determined by the heavy-atom method. From the three-dimensional Patterson map, we found the position of heavy atom Dy. After

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several cycles least-squares refinement for the position of Dy, the unweighted $R(=[\Sigma||F_o|-|F_c||]/\Sigma|F_o|)$ factor decreased to 0.1745. 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 0.049. After all the hydrogen atoms found by the difference Fourier syntheses, one cycle of refinement on all atoms with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms, reduced the R factor to 0.046. The final values of the positional and thermal parameters are listed in Table 1.

Results and discussion

The crystal of $(\eta^5\text{-}C_5H_5)_3Dy\cdot OC_4H_8$ is monoclinic, space group $P2_1/n$, $Z=4$, $D_{calc}=1.69$ g cm^{-3}. Cell constants are $a=8.247(4)$, $b=24.582(5)$, $c=8.318(6)$ Å, $\beta=101.49(7)$°; cell volume $V=1652.5$ Å^3. The molecular structure and atom numbering schemes are shown in Fig. 1. Bond lengths and angles are presented in Table 2. It is obvious that the molecule has a coordination sphere consisting of three η^5-cyclopentadienyl ligands and one σ-bonded tetrahydrofuran ligand. The THF molecule appears firmly coordinated at a Dy–O distance of 2.522(5) Å. The three cyclopentadienyl ligands are coordinated to the dysprosium atom in an η^5-fashion with an average Dy–C length of 2.74(8) Å. The range extends from 2.649(12)–2.816(9) Å. Baker and Raymond [12] have pointed out that Cp_3Ln–X compounds are structurally similar to those formulated as Cp_3U–X. Thus, the centroid–U–centroid angles in $Cp_3UC{\equiv}CPh$ [13] average 117°, while the centroid–U–C(σ) angles are close to 100°. In $Cp_3Dy\cdot THF$ the corresponding averages are 118 and 99°.

The very fact that there are fifteen lanthanide metals which have such a close mutual resemblance means that we can study fairly closely the influence of ionic radius (the main variable factor) on coordination geometry and crystal structure. Table 3 compares some significant structural parameters along the isostructural series $Cp_3Ln\cdot THF$ (Ln = La [5], Pr [6], Nd [6, 7], Gd [8] and Dy) with the crystal radii according to ref. 14. It is interesting to note that both the bond lengths of Ln–O and Ln–C(Cp) and the Ln–centroid distances in the isostructural series $Cp_3Ln\cdot THF$ present a decreasing trend as crystal radii of Ln^{3+} decrease. However neither the bond lengths of Dy–O and Dy–C(Cp) nor the Dy–centroid distances in $Cp_3Dy\cdot THF$ are in agreement with the above trend. We postulated that this result was due to severe steric cause and 'gadolinium break'. Three cyclopentadienyl groups and one tetrahydrofuran ligand are perhaps overcrowded to the smaller Dy^{3+} while they are available to the other four Ln^{3+}.'Gadolinium break' is an important phenomenon and cannot be neglected in the 4f series. It means that there is a discontinuity near

TABLE 1. Final fractional coordinates (×10^3) and thermal parameters (×10^3)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Dy	77.67(7)	144.27(3)	−54.84(8)	27.1(3)	37.1(3)	30(3)	2.0(3)	7.9(2)	2.7(4)
O(1)	388(1)	418.3(4)	253(1)	42(4)	60(6)	50(5)	9(4)	21(4)	14(5)
C(1)	477(2)	250.0(7)	454(2)	70(1)	54(9)	70(1)	5(9)	6(9)	14(9)
C(2)	581(2)	249.2(6)	351(2)	70(1)	50(8)	90(1)	0.(8)	11(9)	−22(8)
C(3)	515(3)	277.7(8)	207(2)	150(2)	70(1)	42(9)	10(1)	−10(1)	−8(9)
C(4)	358(2)	294.2(7)	228(3)	110(1)	42(9)	140(1)	−23(9)	−90(1)	−10(1)
C(5)	165(2)	777.2(7)	121(3)	35(8)	64(9)	160(2)	16(8)	−(1)	10(1)
C(6)	812(2)	374(1)	248(2)	70(1)	240(2)	5(6)	−90(1)	−3(7)	(1)
C(7)	381(2)	160.9(8)	868(2)	35(7)	120(1)	83(9)	4(8)	34(6)	41(9)
C(8)	410(2)	136.2(8)	4(2)	14(6)	140(1)	68(9)	−1(9)	−6(7)	−40(1)
C(9)	373(2)	83.6(7)	−2(2)	70(1)	60(1)	90(1)	15(9)	23(9)	10(9)
C(10)	302(2)	73.8(8)	843(2)	28(7)	140(1)	130(1)	15(8)	25(7)	−7(1)
C(11)	406(2)	430.0(8)	90(2)	52(8)	110(1)	45(8)	30(9)	24(6)	21(9)
C(12)	745(2)	47(1)	499(2)	90(1)	240(2)	60(1)	−100(1)	10(9)	−4(1)
C(13)	629(2)	64(1)	593(3)	29(9)	300(2)	130(1)	−40(1)	20(1)	−140(1)
C(14)	716(2)	74.3(7)	768(2)	33(7)	90(1)	62(9)	−23(7)	10(7)	−25(9)
C(16)	382(2)	370(1)	683(2)	12(6)	360(3)	44(8)	50(1)	−16(6)	−30(1)
C(17)	553(3)	582(1)	336(2)	230(2)	240(2)	72(8)	200(1)	113(8)	110(1)
C(18)	594(3)	427.5(8)	704(2)	280(2)	120(1)	148(9)	−110(1)	18(8)	−63(8)
C(19)	637(2)	379(1)	763(2)	47(9)	350(3)	42(9)	110(1)	−6(7)	−50(1)
C(20)	495(2)	657.0(8)	255(2)	18(1)	80(1)	65(8)	−20(1)	77(7)	−2(9)

TABLE 2. Bond lengths (Å) and bond angles (°) for $(\eta^5\text{-}C_5H_5)_3Dy\cdot OC_4H_8$

Atoms	Distance	Atoms	Distance
Dy–O(1)	2.522(5)	O(1)–C(11)	1.425(9)
Dy–C(1)	2.733(9)	O(1)–C(14)	1.462(8)
Dy–C(2)	2.736(9)	C(1)–C(2)	1.326(13)
Dy–C(3)	2.730(9)	C(1)–C(5)	1.388(14)
Dy–C(4)	2.741(8)	C(2)–C(3)	1.394(14)
Dy–C(5)	2.759(9)	C(3)–C(4)	1.40(2)
Dy–C(6)	2.812(9)	C(4)–C(5)	1.37(2)
Dy–C(7)	2.736(7)	C(6)–C(7)	1.35(2)
Dy–C(8)	2.691(7)	C(6)–C(10)	1.52(2)
Dy–C(9)	2.812(10)	C(7)–C(8)	1.268(13)
Dy–C(10)	2.791(8)	C(8)–C(9)	1.327(15)
Dy–C(16)	2.816(9)	C(9)–C(10)	1.325(15)
Dy–C(17)	2.756(14)	C(11)–C(12)	1.498(14)
Dy–C(18)	2.768(10)	C(12)–C(13)	1.41(2)
Dy–C(19)	2.649(12)	C(13)–C(14)	1.514(15)
Dy–C(20)	2.698(10)	C(16)–C(17)	1.31(3)
		C(16)–C(20)	1.24(2)
Dy–Cent1[a]	2.4772	C(17)–C(18)	1.22(4)
Dy–Cent2	2.5158	C(18)–C(19)	1.31(3)
Dy–Cent3	2.5071	C(19)–C(20)	1.38(3)

Atoms	Angles	Atoms	Angles
Cent1–Dy–O(1)	96.2	Cent1–Dy–Cent2	118.8
Cent2–Dy–O(1)	101.1	Cent1–Dy–Cent3	118.9
Cent3–Dy–O(1)	99.0	Cent2–Dy–Cent3	115.5
Dy–O(1)–C(11)	123.9(5)	Dy–O(1)–C(14)	120.9(4)
C(11)–O(1)–C(14)	110.0(6)	C(6)–C(10)–C(9)	107.0(1)
C(2)–C(1)–C(5)	108.0(1)	O(1)–C(11)–C(12)	107.8(7)
C(1)–C(2)–C(3)	111.0(1)	C(11)–C(12)–C(13)	104.0(1)
C(2)–C(3)–C(4)	105.0(1)	C(12)–C(13)–C(14)	110.0(1)
C(3)–C(4)–C(5)	109.0(1)	O(1)–C(14)–C(13)	102.9(7)
C(1)–C(5)–C(4)	107.0(1)	C(17)–C(16)–C(20)	103.0(1)
C(7)–C(6)–C(10)	102.2(8)	C(16)–C(17)–C(18)	123.0(2)
C(6)–C(7)–C(8)	109.0(1)	C(17)–C(18)–C(19)	96.0(1)
C(7)–C(8)–C(9)	116.0(1)	C(18)–C(19)–C(20)	113.0(1)
C(8)–C(9)–C(10)	105.0(1)	C(16)–C(20)–C(19)	105.0(2)

[a] Cent1 is the centroid of the C(1)–C(5) ring, Cent2 of the C(6)–C(10) ring and Cent3 of the C(16)–C(20) ring.

TABLE 3. Significant structural parameters in the isostructural series $Cp_3Ln\cdot THF$

Compound	Ln^{3+} crystal radii (Å)		Ln–O (Å)	Ln–Cent1 (Å)	Ln–Cent2 (Å)	Ln–Cent3 (Å)	Ln–C(av.) (Å)
$Cp_3La\cdot THF$	[5]	1.36	2.57(1)	2.575	2.575	2.576	2.84(4)
$Cp_3Pr\cdot THF$	[6]	1.32	2.555(9)	2.54	2.55	2.51	2.80(2)
$Cp_3Nd\cdot THF$	[6]	1.30	2.54(1)	2.51	2.51	2.51	2.78(2)
$Cp_3Nd\cdot THF$	[7]	1.30	2.56(1)	2.52	2.55	2.54	2.79(4)
$Cp_3Gd\cdot THF$	[8]	1.25	2.494(7)	2.47	2.49	2.49	2.74(3)
$Cp_3Dy\cdot THF$	[a]	1.22	2.522(5)	2.4772	2.5158	2.5071	2.74(8)

[a] Present work.

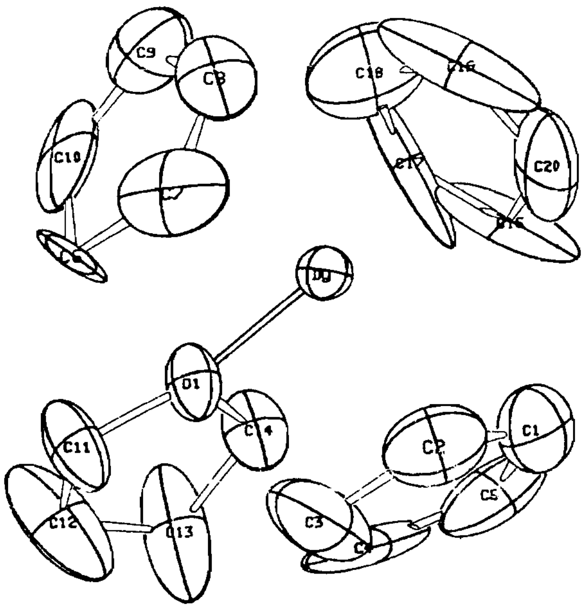

Fig. 1. Molecular structure and atom numbering scheme of $(\eta^5\text{-}C_5H_5)_3Dy\cdot OC_4H_8$.

Gd in both chemical and physical properties of lanthanide compounds as an element varies from La to Lu. Our results are consistent with the 'gadolinium break'. In view of the above-mentioned two reasons we deduce that in the isostructural series $Cp_3Ln\cdot THF$, the bond lengths of Ln–O and Ln–C(Cp) and the Ln–centroid distance of the succeeding elements (Ho, Er, Tm, Yb, Lu) may be much greater.

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