The Formation and the Structure of $(\eta^5\text{-}C_5H_5)_3Nd\cdot OC_4H_8$

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Received June 16, 1984

Recent studies have shown that the organolanthanide systems Cp_3Ln (Cp = $\eta^5\text{-}C_5H_5$, Ln = *e.g.* Pr or Nd) coordinate not only uncharged Lewis bases, but also various anionic nucleophiles (*e.g.* NCS^-, $NCBH_3^-$, BH_4^- or alkyl$^-$) [3]. While the existence of paramagnetic anionic adducts in solution (*e.g.* THF or CH_2Cl_2) has been confirmed by ^1H NMR spectroscopy [4], the chemical nature of some well-shaped, rod-like, pale-violet crystals that precipitated from a concentrated solution of Cp_3Nd and $Li(n\text{-}C_4H_9)$ in THF could not be determined by conventional analytical procedures owing to the scarcity of material. The crystals were characterized by single-crystal X-ray diffraction.

Experimental

C_4H_9Li in tetrahydrofuran was added to a solution of Cp_3Nd in tetrahydrofuran and crystals suitable for the X-ray study were obtained by slow cooling of the reaction mixture. All the handling was carried out in a dry box. The single crystals obtained were sealed in thin-walled glass capillaries. The unit cell parameters were obtained by least-squares refinement of the setting angles for 20 accurately-centered reflections (2θ = 12–28°) using a Philips PW 1100 four circle diffractometer with MoKα graphite-monochromated radiation. As a check on crystal and electronic stability the intensities of three reflections were monitored every three h. No significant decay in intensity was observed during data collection. Important crystal data are summarized in Table I. The intensities

TABLE I. Crystal Data.[a]

Formula	$NdOC_{19}H_{23}$
M	411.6
Crystal colour	pale-violet
Habit	prismatic
Crystal size/mm	0.5 × 0.2 × 0.1
Space group	$P2_1/n$
Crystal system	monoclinic
a/Å	8.386(4)
b/Å	24.651(9)
c/Å	8.301(4)
α/°	90
β/°	101.6(1)
γ/°	90
U/Å^3	1681
Z	4
Dc/Mg cm^{-3}	1.63
F(000)	820
Radiation (λ/Å)	[MoKα(0.7107)]
μ/cm^{-1}	29.05
Reflections measured	3572
T	293 K

(continued overleaf)

0020-1693/84/$3.00

TABLE I. *(continued)*

scan method	$\theta/2\theta$
scan speed/°	1.80
scan width/°	1.20
Background counts/s.	20
$2\theta_{max}$/°	50
σ limit $[I > n\sigma(I)]$	n = 3
Unique observed reflections	1378
Weighting scheme *w*	$5.1497[\sigma^2(Fo) + 0.002633(Fo)^2]^{-1}$
R, $R = \Sigma[\lvert Fo\rvert - \lvert Fc\rvert]/\Sigma\lvert Fo\rvert$	0.096
Rw, $Rw = \left[\frac{\Sigma w[\lvert Fo\rvert - \lvert Fc\rvert]^2}{\Sigma v\lvert Fo\rvert^2}\right]^{1/2}$	0.103

[a] The *a* and *c* cell parameters here reported are interchanged with respect to those of refs. [1] and [2].

TABLE II. Final Fractional Coordinates (×10^4) and Thermal Parameters (×10^3).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nd	4462(1)	6443.1(4)	5791(1)	40.5(6)	69.8(8)	28.4(6)	2.1(5)	0.1(4)	3.4(5)
O(1)	2562(15)	5812(6)	3842(15)	57(8)	90(10)	34(6)	−8(6)	8(6)	−6(7)
C(2)	903(26)	5673(14)	4155(36)	47(11)	119(22)	114(21)	−1(18)	1(12)	−35(14)
C(3)	−8(27)	5524(17)	2369(33)	44(12)	253(42)	69(16)	−55(22)	1(11)	−3(18)
C(4)	988(31)	5635(17)	1154(32)	75(16)	262(41)	59(15)	−25(22)	16(13)	−100(23)
C(5)	2682(28)	5751(14)	2119(28)	60(13)	140(25)	52(13)	−24(15)	−2(10)	−15(15)
C(6)	3514(40)	7500(12)	5934(28)	123(23)	100(20)	42(12)	−2(13)	2(13)	10(17)
C(7)	2068(45)	7255(13)	5198(55)	125(25)	69(19)	170(38)	6(22)	−10(26)	50(18)
C(8)	2280(41)	7078(12)	3635(37)	113(23)	91(20)	78(18)	−3(16)	−46(17)	23(18)
C(9)	3761(39)	7241(11)	3298(36)	113(22)	58(15)	87(18)	5(13)	−4(16)	18(15)
C(10)	4519(28)	7518(10)	4756(37)	63(14)	66(14)	105(20)	24(14)	−18(13)	−6(11)
C(11)	2495(32)	6297(23)	8238(58)	29(13)	374(66)	280(41)	249(44)	−40(18)	−20(24)
C(12)	3737(32)	6644(14)	8820(25)	68(16)	174(29)	28(10)	−3(14)	0(10)	28(18)
C(13)	5013(40)	6362(16)	9204(29)	101(20)	154(32)	36(13)	7(15)	−26(12)	−21(20)
C(14)	5034(37)	5831(13)	8749(32)	107(20)	108(23)	52(14)	37(14)	0(14)	−2(17)
C(15)	3322(51)	5755(18)	8002(29)	167(31)	219(39)	31(12)	41(18)	19(16)	−117(29)
C(16)	6810(36)	5706(13)	5204(59)	81(18)	80(19)	180(38)	18(23)	73(23)	20(16)
C(17)	7525(46)	6085(29)	6394(40)	94(24)	447(85)	58(18)	4(35)	34(18)	141(39)
C(18)	7622(37)	6599(25)	5286(55)	50(15)	459(87)	123(32)	−164(46)	56(19)	−74(28)
C(19)	7006(61)	6472(14)	4903(80)	161(39)	65(19)	302(62)	57(28)	186(45)	35(22)
C(20)	6578(36)	6026(19)	3861(34)	76(18)	167(33)	62(15)	7(19)	26(13)	59(21)

were corrected for Lorentz, polarization and absorption effects following the North *et al.* method [5].

The structure was solved using three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares allowing all the non-hydrogen atoms to vibrate anisotropically. Hydrogen atoms were not located or included in the calculations. Atomic scattering factors and anomalous dispersion corrections (applied to Nd only) were obtained from ref. [6]. The function $w\Delta^2$ ($\Delta = |Fo| - |Fc|$) was minimized and in the last refinement cycles a weighting scheme was introduced (see Table I).

The final discrepancy indices were $R = 0.096$ and $Rw = 0.103$. The poor quality of the crystals, obtained directly from the reaction mixture, did not allow accurate molecular parameter determination but it was good enough to enable us to identify the product obtained: the title compound. The final values of the positional and thermal parameters are listed in Table II. Observed and calculated structure factors are available as supplementary material. Calculations were carried out with the SHELX system of computer programs [7].

Discussion

Bond lengths and angles are reported in Table III. A view of the molecule parallel to a Cp ring is shown in Fig. 1. The compound is isostructural with

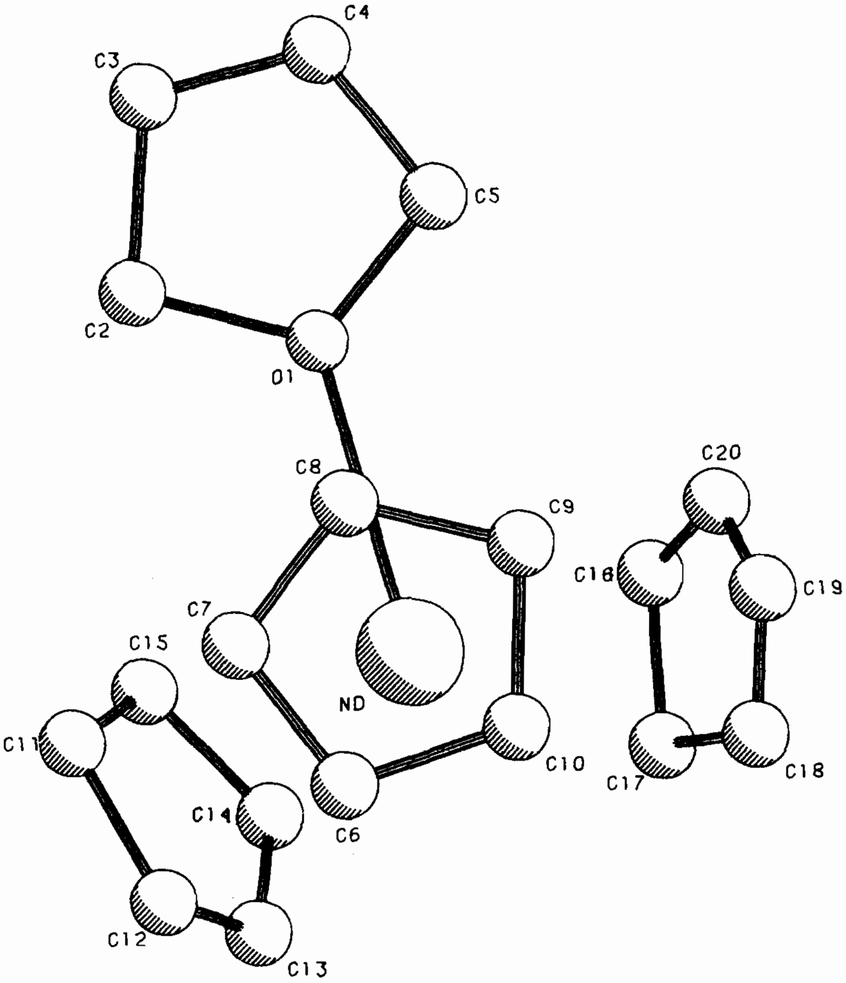

Fig. 1. View of the Cp$_3$Nd•THF molecule parallel to the C(6)–C(10) ring.

TABLE III. Bond Lengths (A) and Bond Angles (°).

Nd–O(1)	2.56(4)	O–C(2)	1.50(3)
Nd–C(6)	2.73(3)	O–C(5)	1.46(3)
Nd–C(7)	2.81(3)	C(2)–C(3)	1.57(4)
Nd–C(8)	2.77(3)	C(3)–C(4)	1.46(4)
Nd–C(9)	2.83(3)	C(4)–C(5)	1.51(4)
Nd–C(10)	2.79(3)	C(6)–C(7)	1.38(5)
Nd–C(11)	2.88(5)	C(6)–C(10)	1.41(4)
Nd–C(12)	2.75(2)	C(7)–C(8)	1.41(5)
Nd–C(13)	2.78(3)	C(8)–C(9)	1.39(5)
Nd–C(14)	2.84(3)	C(9)–C(10)	1.42(4)
Nd–C(15)	2.80(2)	C(11)–C(12)	1.36(6)
Nd–C(16)	2.79(3)	C(11)–C(15)	1.54(7)
Nd–C(17)	2.67(3)	C(12)–C(13)	1.26(4)
Nd–C(18)	2.79(3)	C(13)–C(14)	1.36(5)
Nd–C(19)	2.78(3)	C(14)–C(15)	1.46(5)
Nd–C(20)	2.81(3)	C(16)–C(17)	1.40(7)
		C(16)–C(20)	1.35(5)
Nd–Cent1[a]	2.52	C(17)–C(18)	1.58(9)
Nd–Cent2	2.55	C(18)–C(19)	1.07(8)
Nd–Cent3	2.54	C(19)–C(20)	1.16(6)
Cent1–Nd–O(1)	96.4	Cent1–Nd–Cent2	117.1
Cent2–Nd–O(1)	102.7	Cent1–Nd–Cent3	115.0
Cent3–Nd–O(1)	98.1	Cent2–Nd–Cent3	120.5
Nd–O(1)–C(2)	121(1)	Nd–O(1)–C(5)	122(1)
O(1)–C(2)–C(3)	100(2)	C(11)–C(12)–C(13)	107(4)
C(2)–C(3)–C(4)	112(2)	C(12)–C(13)–C(14)	121(3)
C(3)–C(4)–C(5)	106(2)	C(13)–C(14)–C(15)	100(3)
C(4)–C(5)–O(1)	107(2)	C(14)–C(15)–C(11)	105(3)
C(5)–O(1)–C(2)	113(2)	C(15)–C(11)–C(12)	105(3)
C(6)–C(7)–C(8)	106(4)	C(16)–C(17)–C(18)	101(3)
C(7)–C(8)–C(9)	112(3)	C(17)–C(18)–C(19)	104(5)
C(8)–C(9)–C(10)	103(3)	C(18)–C(19)–C(20)	120(6)
C(9)–C(10)–C(6)	110(3)	C(19)–C(20)–C(16)	115(5)
C(10)–C(6)–C(7)	108(3)	C(20)–C(16)–C(17)	99(4)

[a] Cent 1 is the centroid of the C(6)–C(10) ring, Cent 2 of the C(11)–C(15) ring and Cent 3 of the C(16)–C(20) ring.

TABLE IV. Significant Structural Parameters in the Isostructural Series $Cp_3Ln \cdot THF$ (Ln = Y, La, Nd and Gd).

Compound	Ln^{3+} crystal[a] radii [8]	Ln–O	Ln–Cent 1	Ln–Cent 2	Ln–Cent 3	Ln–C (average)
$Cp_3Y \cdot THF$ [1]	1.16	2.451(4)	2.438	2.453	2.454	2.71(3)
$Cp_3La \cdot THF$ [1]	1.36	2.57(1)	2.575	2.575	2.576	2.82(4)
$Cp_3Nd \cdot THF$[b]	1.30	2.56(1)	2.52	2.55	2.54	2.79(4)
$Cp_3Gd \cdot THF$ [2]	1.25	2.494(7)	2.47	2.49	2.49	2.74(3)

[a] These values are for c.n. 8 for Y and c.n. 9 for the other metal ions. [b] Present work.

the gadolinium, lanthanum and yttrium derivatives for which synthesis and structure have been recently reported [1, 2]. The molecule presents high libration, particularly for the Cp ligands as in the lanthanum derivative [1], where this effect was justified both with the poor quality of the crystals and with the larger ionic radium of the lanthanum with respect to that of yttrium (where this effect is lower). Table IV compares some significant structural parameters along the isostructural series $Cp_3Ln \cdot THF$ (Ln = Y, La, Nd and Gd) with the crystal radii according to ref. [8]. It can be noted that both the Nd–O bond distance and the Nd–Cp bond distances are in good agreement with the trend to be expected when the Ln element is varied.

In addition, it is interesting to note that the Nd–C distances are comparable with those found in the tetrameric neodimium tris(methylcyclopentadienide) [9], confirming the electrostatic nature of the bonding between the metal ion and the Cp ligands. Here the coordinated THF molecule prevents the formation of polynuclear species, as the requirement for the metal ion to have the maximum number of cation–anion contacts in relation with its size is satisfied with the further coordination of the THF oxygen.

The X-ray crystallographic result described above indicates that the equilibrium:

$$Cp_3Nd \cdot THF + Li(n\text{-}C_4H_9) \overset{THF}{\rightleftarrows} [Li(THF)_4]\,[Cp_3Nd(n\text{-}C_4H_9)]$$

may not be completely on the right hand side and that the uncharged THF-adduct is less soluble in THF than the salt-like product.

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