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Journal of Organometallic Chemistry 490 (1995) C8–C13

Journal of Organometallic Chemistry

Preliminary communication

Syntheses and crystal structures of $(C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$ and $[(C_8H_8)Gd(C_5H_9C_4H_4(THF)][(C_8H_8)Gd(C_5H_9C_5H_4(THF)_2]$

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Received 28 September 1994; in revised form 22 November 1994

Abstract

$LnCl_3$ (Ln = Nd, Gd) reacts with $C_5H_9C_5H_4Na$ (or $K_2C_8H_8$) in THF ($C_5H_9C_5H_4$ = cyclopentylcyclopentadienyl) in the ratio of 1 : 1 to give $(C_5H_9C_5H_4)LnCl_2(THF)_n$ (or $(C_8H_8)LnCl_2(THF)_n$], which further reacts with $K_2C_8H_8$ (or $C_5H_9C_5H_4Na$) in THF to form the title complexes. If Ln = Nd the complex $(C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$ (**a**) was obtained: when Ln = Gd the 1 : 1 complex $[(C_8H_8)Gd(C_5H_9C_5H_4)(THF)]$ $[(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2]$ (**b**) was obtained in crystalline form.

The crystal structure analysis shows that in $(C_8H_8)Ln(C_5H_9C_5H_4)(THF)_2$ (Ln = Nd or Gd), the Cyclopentylcyclopentadienyl (η^5), cyclooctatetraenyl (η^8) and two oxygen atoms from THF are coordinated to Nd^{3+} (or Gd^{3+}) with coordination number 10.

The centroid of the cyclopentadienyl ring (Cp′) in $C_5H_9C_5H_4$ group, cyclooctatetraenyl centroid (COT) and two oxygens (THF) form a twisted tetrahedron around Nd^{3+} (or Gd^{3+}). In $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)$, the cyclopentyl-cyclopentadienyl (η^5), cyclooctatetraenyl (η^8) and one oxygen atom are coordinated to Gd^{3+} with the coordination number of 9 and Cp′, COT and oxygen atom form a triangular plane around Gd^{3+}, which is almost in the plane (dev. −0.0144 Å).

Keywords: Neodymium; Gadolinium

1. Introduction

The cyclopentadienyl and cyclooctatetraenyl lanthanide complexes were prepared by Jamerson et al. in 1974 [1]. In subsequent years complexes of this kind were not reported further, nor were the structures determined. In 1989 Schumann et al. reported the syntheses and X-ray crystal structures of $(\eta^5\text{-}C_5Me_5)Lu(\eta^8\text{-}C_8H_8)$ [2] and $(\eta^5\text{-}C_5(CH_2Ph)_5)Lu(\eta^8\text{-}C_8H_8)$ [3]. In 1991 we reported the syntheses of the complexes of $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot nTHF$ [4], $(\eta^5\text{-}C_9H_7)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF$ [4] and $(2,4\text{-}C_7H_{11})Sm(C_8H_8)(THF)$ [5], and the crystal structure determinations of $(\eta^5\text{-}C_5H_5)Pr(\eta^8\text{-}C_8H_8)(THF)_2$, $(\eta^5\text{-}C_9H_7)Pr(\eta^8\text{-}C_8H_8)(THF)_2$, and $(\eta^5\text{-}2,4\text{-}C_7H_{11})Sm(\eta^8\text{-}C_8H_8)(THF)$. In this paper we report the syntheses and crystal structure determination of $(\eta^5\text{-}C_5H_9C_5H_4)Nd(\eta^8\text{-}C_8H_8)(THF)_2$ (**a**) and $[(\eta^5\text{-}C_5H_9C_5H_4)Gd(\eta^8\text{-}C_8H_8)(THF)_2][(\eta^5\text{-}C_5H_9C_5H_4)Gd(\eta^8\text{-}C_8H_8)(THF)]$ (**b**).

2. Experimental

All operations on the lanthanide complexes were performed under nitrogen using Schlenk techniques. All solvents were purified. Anhydrous lanthanide chlorides were prepared by a literature method [6]. Infrared spectra were recorded on a Digilab FTS-ZOE spectrometer as KBr pellets. Metal analysis was carried out by complexometric titration and the combustion method was used for the carbon and hydrogen analysis.

2.1. *Preparation of crystals* ***a*** *and* ***b***

Crystal **a**: Solid $NdCl_3$ (0.9 g, 2.59 mmol) was placed in a glass bottle, which was predried and filled with nitrogen. THF (15 ml) was added at room temperature with stirring, which was continued for several hours. To the solution was added $K_2C_8H_8$ (3.51 mmol) in THF at −78°C with stirring. The reaction temperature of solution rose to room one, at which temperature the reaction mixture was kept for 12 h. To the solution was added $C_5H_9C_5H_4Na$ (3.49 mmol) in THF at room temperature and the reaction was carried out for 12 h

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SSDI 0022-328X(94)05354-5

again. The solution suspension was centrifuged to remove unused solid. The resulting clear solution was concentrated and hexane added until it went slightly turbid. The solution was then placed in a refrigerator for crystallization, giving green crystals in the yield of 40% with mp 74–76°C. Found: Nd 27.50; Calc. for $(C_5H_9C_5H_4)Nd(C_8H_8)(THF)_2$: Nd 27.46%. IR ($cm^{-1}$): 3000(w), 2950(m), 2865(m), 1650(w), 1590(m), 1450(m), 1335(m), 1055(s), 1030(s), 945(w), 895(s), 815(m), 800(m), 755(s), 700(w), 670(m).

Crystal **b**: solid $GdCl_3$ (1.0 g, 3.79 mmol) was placed in a glass bottle, which was predried and filled with nitrogen. THF (15 ml) was added at room temperature with stirring, which was continued for several hours. $C_5H_9C_5H_4Na$ (3.73 mmol) in THF at −78°C was added to the solution with stirring.

The temperature of the reaction mixture rose to room one, at which temperature the reaction was kept for 12 h. To the solution was added $K_2C_8H_8$ (3.72 mmol) in THF at room temperature and the reaction carried out again for 12 h. The solution suspension was centrifuged to remove unused solid. The resulting clear solution was concentrated and hexane was added until the solution went slightly turbid. The solution was then placed in a refrigerator for crystallization to give yellow crystals with mp 68–70°C. IR (cm^{-1}): the same as above.

2.2. Crystal structure determination

A single crystal of dimensions 0.12 × 0.36 × 0.42 (**a**) (or 0.16 × 0.42 × 1.02 (**b**)) mm was selected for structural analysis. Diffraction data were collected on a Nicolet R3m/E four-circle diffractometer using a graphite monochromatized, Mo K_α radiation (λ = 0.71069 Å), scan mode ω, scan speed of 7° min^{-1} and scan width of 1.6° (**a**) (or 1.3° (**b**)). A total of 4386(**a**) (or 7016(**b**)) reflections were measured within the range of $3° < 2\theta < 50°$ (**a**) (or $3° < 2\theta < 48°$ (**b**)), of which 3440 (**a**) (or 4689 (**b**)) reflections with $I > 3\sigma(I)$ were considered observed. Intensities were corrected for Lp factors and absorption. The crystallographic data are listed in Table 1. The coordinates of the neodymium (or gadolinium) atoms were derived from Patterson analysis and other non-hydrogen atoms were found by difference Fourier synthesis. The atomic coordinates and anisotropic temperature factors for all non-hydrogen atoms were refined by block-matrix least squares. The coordinates of hydrogen atoms were calculated according to theoretical models. Further refinements led to final $R = 0.043$ (**a**) (or 0.032 (**b**)), $R_w = 0.033$ (**a**) (or 0.029 (**b**)). The calculations were performed on an Eclipse s/140 computer using SHELXTL programs.

Atomic coordinates and equivalent isotropic temperature factors, main bond lengths and bond angles are listed in Tables 2, 3, and 4. The molecular structures are shown in Figs. 1, 2, 3 and 4; the packing of crystals (**a** and **b**) in the unit cell in Figs. 5 and 6.

Table 1
Crystal data for crystals **a** and **b**

formula	$C_{26}H_{37}O_2Nd$ (**a**)	$C_{48}H_{66}O_3Gd_2$ (**b**)
Mw	525.85	1005.65
Crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.434(3)	14.094(4)
b, Å	13.218(5)	18.100(4)
c, Å	8.222(2)	8.455(2)
α, deg	95.13(2)	96.93(2)
β, deg	102.17(2)	92.83(2)
γ, deg	64.27(2)	86.82(2)
V, $Å^3$	1189.9(5)	2136(1)
Dc, g/cm^a	1.47	1.56
μ, cm^{-1} (Mo-K_α)	22.1	32.2
F(000)	538	1012
Z	2	2
$R = \Sigma \Vert Fo \vert - \vert Fc \Vert \Sigma \vert Fo \vert$	0.043	0.032
$Rw = [\Sigma w \Vert Fo \vert - \vert Fc \Vert^2 / \Sigma w \vert Fo \vert^2]^{1/2}$	0.033	0.029
$W = [\sigma^2(Fo) + 0.0004(Fo)^2]^{-1}$		
(Δ/σ)max	0.29	0.42
$\Delta\rho$, $e/Å^3$	−0.75–1.16	−0.88–0.48
No. of parameters	262	478

3. Results and discussion

Solid $LnCl_3$ (Ln = Nd or Gd) reacts with $C_5H_9C_5H_4Na$ (or $K_2C_8H_8$) in THF at the ratio of 1 : 1 and then with $K_2C_8H_8$ (or $C_5H_9C_5H_4Na$) in THF to give $(C_8H_8)Ln(C_5H_9C_5H_4)(THF)_n$. The reaction equations are as follows:

$$LnCl_3 + C_5H_9C_5H_4Na$$
$$\xrightarrow{THF} (C_5H_9C_5H_4)LnCl_2(THF)_n$$
$$\xrightarrow{K_2C_8H_8} (C_8H_8)Ln(C_5H_9C_5H_4)(THF)_n$$

The elementary analysis values are consistent with the calculated ones. In IR spectra the bands of 2955, 2865, 1450 cm^{-1} are assigned to the absorption characteristics of cyclopentyl; 1030 cm^{-1} to cyclopentadienyl; 900, 755, 670 cm^{-1} to cyclooctatetraenyl [1]; 1055 cm^{-1} to THF [7].

3.1. Crystal a

Cyclopentylcyclopentadienyl (η^5), cyclooctatetraenyl (η^8) and two oxygen atoms (THF) are coordinated to Nd^{3+} with the coordination number 10. The centroid of cyclopentadienyl ring (Cp′) in $C_5H_9C_5H_4$ group, centroid of C_8H_8 (COT) and two oxygen atoms form a twisted tetrahedron around Nd^{3+}. The distances from

Table 2
Atomic coordinates ($\times 10^4$) and isotropie thermal parameters (Å$^2 \times 10^3$) for non-hydrogen atoms

	X	Y	Z	U_{eq}
Gd(1)	1753(1)	3559(1)	1925(1)	37(1)
Gd(2)	3067(1)	9134(1)	794(1)	43(1)
O(1)	678(3)	2948(2)	3838(5)	56(2)
O(2)	2887(3)	2800(2)	3724(5)	55(2)
O(3)	2254(4)	9646(3)	−1519(5)	66(2)
C(11)	615(7)	2159(4)	3885(8)	85(4)
C(12)	143(7)	2081(4)	5379(9)	92(4)
C(13)	−559(6)	2748(4)	5517(10)	83(4)
C(14)	−40(6)	3317(4)	4835(10)	92(4)
C(21)	3845(5)	2565(4)	3329(9)	78(3)
C(22)	4298(6)	2207(4)	4674(8)	85(4)
C(23)	3513(6)	2162(4)	5796(8)	86(4)
C(24)	2840(6)	2775(4)	5422(8)	82(3)
C(31)	1467(7)	9334(5)	−2477(11)	118(5)
C(32)	1152(7)	9860(5)	−3607(10)	112(5)
C(33)	1715(8)	10515(5)	−3225(10)	128(5)
C(34)	2550(7)	10278(4)	−2245(9)	90(4)
C(41)	2585(5)	4908(3)	2896(7)	54(2)
C(42)	2605(6)	4528(3)	4249(7)	59(3)
C(43)	1674(6)	4460(3)	4703(7)	65(3)
C(44)	1056(6)	4813(3)	3637(8)	69(3)
C(45)	1609(5)	5085(3)	2529(8)	61(3)
C(46)	3413(6)	5187(4)	2145(8)	72(3)
C(47)	4357(6)	4787(5)	2437(12)	116(5)
C(48)	5107(8)	5339(6)	2340(13)	158(6)
C(49)	4611(9)	6073(6)	2306(17)	192(8)
C(40)	3609(8)	5994(5)	2683(11)	117(5)
C(51)	2292(6)	2334(4)	8(7)	77(3)
C(52)	1333(7)	2259(4)	123(8)	85(4)
C(53)	505(7)	2733(5)	34(9)	88(4)
C(54)	339(6)	3468(5)	−300(8)	87(4)
C(55)	903(6)	4007(4)	−710(7)	78(3)
C(56)	1871(7)	4066(4)	−887(7)	76(4)
C(57)	2674(6)	3625(4)	−666(7)	75(3)
C(58)	2862(6)	2903(4)	−287(7)	79(3)
C(61)	3846(5)	7959(4)	−1092(9)	68(3)
C(62)	4425(6)	8031(4)	288(9)	84(3)
C(63)	4879(5)	8694(4)	356(10)	89(4)
C(64)	4608(5)	9015(4)	−956(10)	85(3)
C(65)	3961(5)	8578(4)	−1857(8)	70(3)
C(66)	3249(8)	7317(6)	−1667(17)	199(7)
C(67)	3590(8)	6709(5)	−2685(15)	198(7)
C(68)	2800(9)	6164(6)	−2923(15)	183(7)
C(69)	2139(8)	6385(5)	−1709(13)	126(5)
C(60)	2356(7)	7170(5)	−1058(13)	141(6)
C(71)	3210(7)	8701(4)	3613(8)	91(4)
C(72)	3686(6)	9332(5)	3760(8)	96(4)
C(73)	3194(7)	10029(5)	3266(9)	116(5)
C(74)	2717(10)	10393(5)	2548(11)	132(6)
C(75)	1801(9)	10147(6)	2007(11)	127(6)
C(76)	1348(6)	9483(6)	1856(10)	121(5)
C(77)	1599(6)	8769(5)	2202(9)	102(4)
C(78)	2377(7)	8460(4)	2950(9)	92(4)
Nd	1916(1)	1754(1)	903(1)	50(1)
O(1)	2363(3)	−176(3)	2241(4)	71(2)
O(2)	481(3)	2493(3)	3079(4)	69(2)
C(11)	2242(6)	−395(5)	3861(6)	96(4)
C(12)	3175(7)	−1496(6)	4369(8)	139(6)
C(13)	3743(8)	−2000(6)	3013(8)	164(6)
C(14)	3158(6)	−1226(4)	1600(7)	87(3)
C(21)	137(5)	3601(5)	3765(7)	85(3)
C(22)	−1096(6)	3981(6)	4072(10)	128(5)
C(23)	−1321(7)	2998(7)	3984(11)	156(6)
C(24)	−312(7)	2096(6)	3515(11)	135(6)
C(31)	2182(9)	628(8)	−1942(9)	121(6)
C(32)	1200(11)	568(7)	−1600(9)	114(6)
C(33)	117(10)	1331(11)	−1146(10)	129(8)
C(34)	−409(7)	2473(9)	−887(11)	116(6)
C(35)	−54(7)	3315(6)	−965(8)	153(5)
C(36)	907(8)	3381(6)	−1393(8)	148(5)
C(37)	1952(9)	2628(9)	−1874(9)	143(8)
C(38)	2488(7)	1476(9)	−2093(9)	134(7)
C(41)	3634(6)	2703(6)	2028(8)	95(4)
C(42)	4303(5)	1579(8)	1742(7)	90(5)
C(43)	4190(5)	949(6)	2890(9)	103(4)
C(44)	3422(6)	1696(7)	3858(7)	131(6)
C(45)	3102(7)	2744(8)	3362(10)	134(6)
C(46)	3284(9)	4037(10)	1272(15)	223(10)
C(47)	4153(9)	3570(10)	394(13)	209(9)
C(48)	5335(7)	3507(7)	1386(10)	132(6)
C(49)	5002(6)	4274(6)	2790(10)	120(5)
C(40)	3699(7)	4805(7)	2463(14)	208(7)

Nd^{3+} to the apices of tetrahedron are: Nd–Cp′ 2.540, Nd–COT 2.011, Nd–O(1) 2.654, Nd–O(2) 2.619Å; the angles of Cp′-Nd-COT, COT-Nd-O(1), COT-Nd-O(2), Cp′-Nd-O(1), Cp′-Nd-O(2) and O(1)-Nd-O(2) are 140.3, 114.8, 114.5, 94.0, 96.1 and 79.9°, respectively.

It can be seen from above data that the distance of Nd–COT is evidently smaller than that of Nd–Cp′. This is due to C_8H_8 having two negative charges and $C_5H_9C_5H_4^-$ only one. In addition, the angle of COT-Nd-O(1) (or O(2)) is greater than that of Cp′-Nd-O(1) (or O(2)). This is due to $C_8H_8^{2-}$ having larger steric effect than that of $C_5H_9C_5H_4^-$.

The bond lengths of Nd–O (2.654 and 2.619 Å) are not equal, which is consistent with that observed in $(C_8H_8)Gd(C_5H_4CH_2C_6H_5)DME$ [8]. From Fig. 1 it can be seen that the five carbon atoms of the cyclopentyl in $C_5H_9C_5H_4$ are located on one side of cyclopentadienyl plane, that is, the cyclopentyl is far from the cyclooctatetraenyl. This is caused by the repulsion between the cyclooctatetraenyl and cyclopentyl groups. The cyclopentadienyl in $C_5H_9C_5H_4$ is coordinated to Nd^{3+} with η^5-fashion. Owing to the steric effect C(41)–Nd bond length is the longest, the bond lengths from Nd to C(42), and C(45) near the C(41) are mediated and from Nd to C(43) and C(44) far from the C(41) the shortest. The bond lengths of Nd–C (η^5) range from 2.722 ~ 2.876 Å (av. 2.794 Å); Nd–C (η^8) from 2.656 ~ 2.739 Å (av. 2.691 Å).

If the difference between Nd^{3+} and Pr^{3+} radii is considered the average distance of Nd–C(η^8) is comparable to that in $(C_8H_8)Pr(C_5H_5)(THF)_2$ [4], but although the difference between Nd^{3+} and Lu^{3+} radii was subtracted the average distance is greater than that in $(C_8H_8)Lu(C_5Me_5)(THF)_2$ [2] and (C_8H_8)Lu-

Table 3
Selected bond lengths (Å)

Nd–O(1)	2.654	Nd–O(2)	2.619(4)
Nd–C(31)	2.660(8)	Nd–C(32)	2.710(10)
Nd–C(33)	2.736(12)	Nd–C(34)	2.739(7)
Nd–C(35)	2.685(6)	Nd–C(36)	2.673(7)
Nd–C(37)	2.666(10)	Nd–C(38)	2.656(8)
Nd–C(41)	2.876(9)	Nd–C(42)	2.812(8)
Nd–C(43)	2.747(6)	Nd–C(44)	2.722(6)
Nd–C(45)	2.814(9)		
Gd(1)–O(1)	2.629(4)	Gd(1)–O(2)	2.617(4)
Gd(1)–C(41)	2.795(6)	Gd(1)–C(42)	2.758(6)
Gd(1)–C(43)	2.695(6)	Gd(1)–C(44)	2.695(6)
Gd(1)–C(45)	2.746(6)	Gd(1)–C(51)	2.687(6)
Gd(1)–C(52)	2.716(7)	Gd(1)–C(53)	2.690(8)
Gd(1)–C(54)	2.653(7)	Gd(1)–C(55)	2.660(7)
Gd(1)–C(56)	2.669(7)	Gd(1)–C(57)	2.632(7)
Gd(1)–C(58)	2.641(7)	Gd(2)–O(3)	2.469(5)
Gd(2)–C(61)	2.714(7)	Gd(2)–C(62)	2.698(8)
Gd(2)–C(63)	2.662(8)	Gd(2)–C(64)	2.673(8)
Gd(2)–C(65)	2.687(7)	Gd(2)–C(71)	2.592(7)
Gd(2)–C(72)	2.603(7)	Gd(2)–C(73)	2.554(8)
Gd(2)–C(74)	2.601(9)	Gd(2)–C(75)	2.638(11)
Gd(2)–C(76)	2.643(9)	Gd(2)–C(77)	2.593(9)
Gd(2)–C(78)	2.569(8)		

$(C_5(CH_2C_6H_5)_5)$ [8]. This is caused by the coordination space crowded with two THFs in $(C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$. The dihedral angle between cyclopentadienyl and cyclooctatetraenyl planes is 37.90^0 (Table 5), which is equal to that in $(C_8H_8)Gd(C_5H_4CH_2C_6H_5)DME$ [8].

3.2. Crystal b

Structural analysis shows that the crystal of **b** consists of two complexes of $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$ and $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)$ (Fig. 2).

Table 4
Selected bond angles (°)

a			
O(1)–Nd–O(2)	79.9(1)	C(31)–Nd–C(32)	29.0(4)
C(31)–Nd–C(33)	56.0(3)	C(31)–Nd–C(34)	76.0(3)
C(31)–Nd–C(35)	84.2(2)	C(31)–Nd–C(36)	76.7(2)
C(31)–Nd–C(37)	56.7(3)	C(31)–Nd–C(38)	29.5(4)
C(41)–Nd–C(42)	28.0(2)	C(41)–Nd–C(43)	47.1(2)
C(41)–Nd–C(44)	46.7(3)	C(41)–Nd–C(45)	28.1(2)
b			
O(1)–Gd(1)–O(2)	72.9(1)	C(41)–Gd(1)–C(42)	29.2(2)
C(41)–Gd(1)–C(43)	49.3(2)	C(41)–Gd(1)–C(44)	49.4(2)
C(41)–Gd(1)–C(45)	29.7(2)	C(51)–Gd(1)–C(52)	29.5(3)
C(51)–Gd(1)–C(53)	57.4(3)	C(51)–Gd(1)–C(54)	78.0(2)
C(51)–Gd(1)–C(55)	85.0(2)	C(51)–Gd(1)–C(56)	76.8(2)
C(51)–Gd(1)–C(57)	57.6(2)	C(51)–Gd(1)–C(58)	30.3(2)
C(61)–Gd(2)–C(62)	29.7(2)	C(61)–Gd(2)–C(63)	49.3(2)
C(61)–Gd(2)–C(64)	48.9(2)	C(61)–Gd(2)–C(65)	29.6(2)
C(71)–Gd(2)–C(72)	30.1(3)	C(71)–Gd(2)–C(73)	58.4(3)
C(71)–Gd(2)–C(74)	79.5(3)	C(71)–Gd(2)–C(75)	85.7(3)
C(71)–Gd(2)–C(76)	77.8(3)	C(71)–Gd(2)–C(77)	58.1(3)
C(71)–Gd(2)–C(78)	30.3(3)		

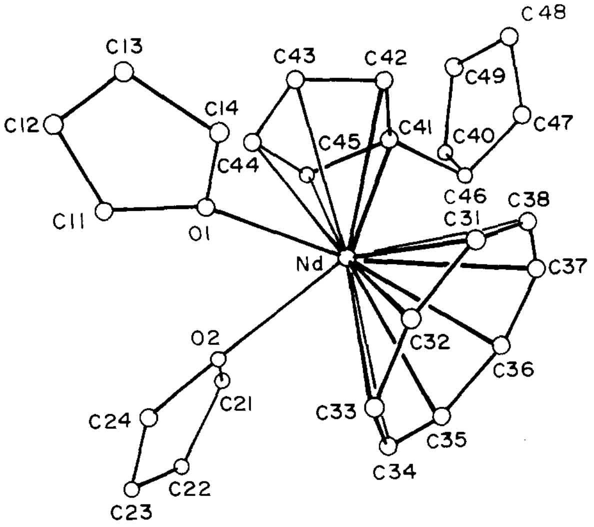

Fig. 1. Molecular structure of $((C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$.

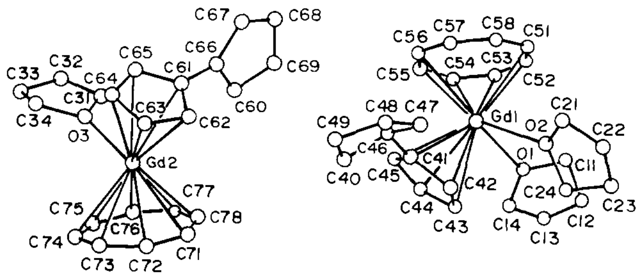

Fig. 2. Molecular structure of $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)$ and $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$.

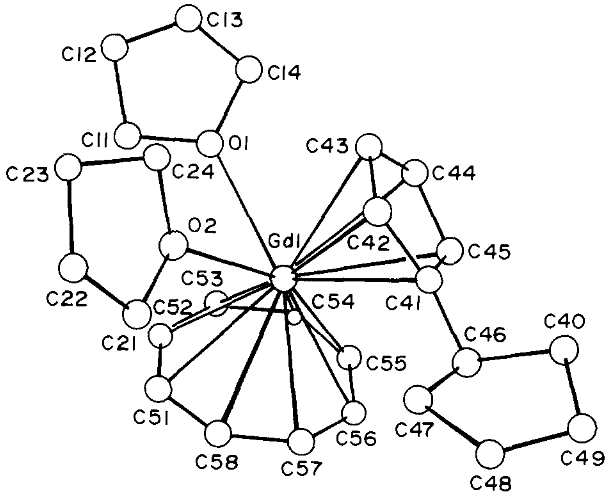

Fig. 3. Molecular structure of $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$.

In the complex $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$ cyclooctatetraenyl (η^8), cyclopentadienyl ring (η^5) of $C_5H_9C_5H_4$ and two oxygen atoms (THF) are coordinated to Gd^{3+} with the coordination number 10.

OCT, Cp′ and two oxygen atoms form a twisted tetrahedron around Gd^{3+}. The distances from Gd(1) to

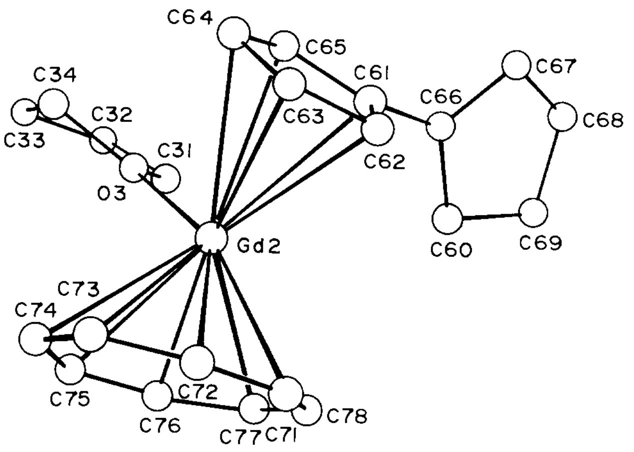

Fig. 4. Molecular structure of $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)$.

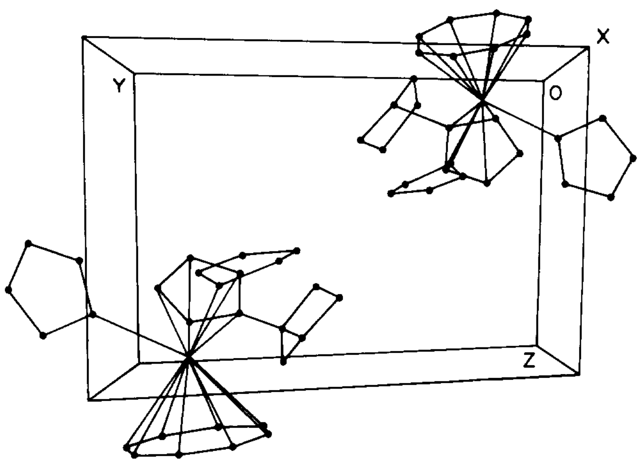

Fig. 5. The packing of crystal **a** in the unit cell.

Table 5
The equations of the best planes, atomic deviations and their dihedral angles

Planes		Equations, atoms and their deviations/Å				dihedral angle/deg P(1)	
$(C_8H_89)Nd(C_5H_9C_5H_4)(THF)_2$							
P(1)		2.986X − 0.191Y + 7.311Z = −0.812					
	C(31) *	C(32) *	C(33) *	C(34) *			
	0.0320	−0.0096	−0.016	−0.0058			
	C(35) *	C(36) *	C(37) *	C(38) *			
	0.0272	0.0002	−0.0250	−0.0031 *			
P(2)		9.637X + 4.842Y + 3.729Z = 5.567				37.9	
	C(41) *	C(42) *	C(43) *	C(44) *	C(45) *		
	0.0002	−0.0052	0.0082	−0.0083	0.0051		
	C(46)	C(47)	C(48)	C(49)	C(40)		
	0.0274	0.3110	1.7893	2.3635	1.2435		
$(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$							
P(1)		1.057X + 14.573Y + 4.135Z = 8.626					
	C(41) *	C(42) *	C(43) *	C(44) *	C(45) *		
	−0.0028	0.0046	−0.0046	0.0029	0.0000		
	C(46)	C(47)	C(48)	C(49)	C(40)		
	0.1810	−0.1815	0.6627	1.6643	1.6000		
P(2)		0.876X + 4.126Y + 7.904Z = 1.185				40.4	
	C(51) *	C(52) *	C(53) *	C(54) *			
	−0.0141	−0.0388	0.0141	0.0392			
	C(55) *	C(56) *	C(57) *	C(58) *			
	−0.0132	−0.0437	0.0193	0.0371			
$(C_8H_5)Gd(C_5H_9C_5H_4)(THF)$							
P(1)		10.609X − 7.060Y − 4.044Z = −1.098					
	C(61) *	C(62) *	C(63) *	C(64) *	C(65) *		
	−0.0001	0.0052	−0.0086	0.0086	−0.0051		
	C(66)	C(67)	C(68)	C(69)	C(60)		
	0.0525	1.2553	0.8976	−0.4502	−1.0367		
P(2)		−5.916X + 2.585Y + 7.491Z = 3.016				146.2	
	C(71) *	C(72) *	C(73) *	C(74) *			
	0.0404	0.0315	−0.0440	−0.0288			
	C(75) *	C(76) *	C(77) *	C(78) *			
	0.0441	0.0282	−0.0455	−0.0258			
P(3)		8.360X + 14.876Y + 0.277Z = 16.180				88.4	88.7
	Cp′•	COT•	Gd(2)•	O(3)•			
	0.0018	0.0048	−0.0144	0.0028			

* The atoms which are marked by asterisks are used to define a given plane.

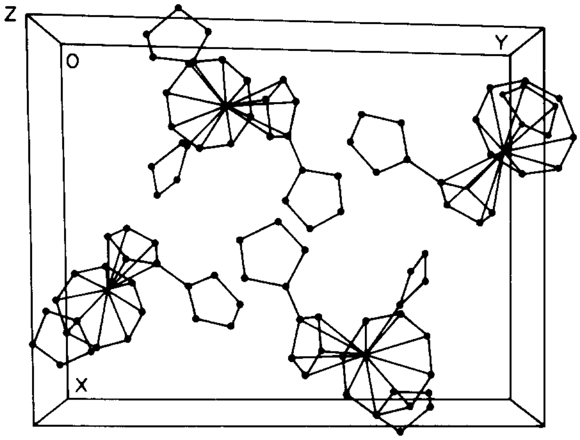

Fig. 6. The packing of crystal **b** in the unit cell.

the apices of tetrahedron are Gd(1)–Cp′ 2.464, Gd(1)–COT 1.958, Gd(1)–O(1) 2.629, Gd(1)–O(2) 2.617 Å; the angles of COT–Gd(1)–Cp′, COT–Gd(1)–O(1), COT–Gd(1)–O(2), Cp′–Gd(1)–O(1), Cp′–Gd(1)–O(2) and O(1)–Gd(1)–O(2) are 139.1, 115.4, 117.2, 97.2, 94.9 and 72.9°, respectively. The cyclopentadienyl in $C_5H_9C_5H_4$ is coordinated to Gd^{3+} (1), Gd(1)–C(41) bond length is the longest, the bond lengths from Gd(1) to C(42) and C(45) near the C(41) are mediated and from Gd(1) to C(43) and C(44) far from the C(41) the shortest. The difference between Gd(1)–C(41) and Gd(1)–C(43) distances is 0.1 Å. The bond lengths of Gd(1)–C(η^5) range from 2.695 ~ 2.795 Å (av. 2.738 Å); the bond lengths of Gd(1)–C(η^8) range from 2.632–2.716 Å (av. 2.668 Å). If the difference between Nd^{3+} and Gd^{3+} radii was subtracted the av. bond length Gd(1)–C(η^5) is approached to that of Nd–C(η^5) in $(C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$, but the av. bond length of Gd(1)–C(η^8) is greater than that of Nd–C(η^8) in $(C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$. From Table 5 it can be seen that except for one carbon atom in cyclopentyl in $C_5H_9C_5H_4$, the rest of the carbon atoms are located on one side of cyclopentadienyl plane, that is, the cyclopentyl is far from the cyclooctate-traenyl.

The dihedral angle between cyclopentadienyl and cyclooctate-traenyl planes is 40.4°, which is larger than that in $(C_8H_8)Nd(C_5H_9C_5H_4)(THF)_2$.

In $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)$ C_8H_8, $C_5H_9C_5H_4$ and oxygen atom (THF) are coordinated to Gd^{3+} (2) with the coordination number of 9. COT, Cp′ and one oxygen atom form a triangle around Gd(2), which is almost in the triangular plane. The distances from Gd(2) to the apices of the triangle are Gd(2)–Cp′ 2.419, Gd(2)–COT 1.875, Gd(2)–O(3) 2.469 Å; the relative angles of COT–Gd(2)–Cp′, COT–Gd(2)–O(3), Cp′–Gd(2)–O(3) are 147.6, 116.3 and 96.6°, respectively. From the angular data it can be seen that the bulk of ligands is in the following order: $C_8H_8 > C_5H_9C_5H_4 >$ THF.

The cyclopentadienyl in $C_5H_9C_5H_4$ is coordinated to Gd^{3+} (2) with η^5-fashion. Owing to the steric effect C(61)–Gd bond length is the longest, the bond lengths from Gd(2) to C(62) and C(65) near the C(61) are mediated and from Gd(2) to C(63) and C(64) far from the C(41) the shortest. The difference between Gd(2)–C(61) and Gd(2)–C(63) distances is 0.05 Å, which is smaller than that in $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$ (0.1 Å). This shows that the coordination space in $(C_8H_8)Gd(C_5H_9C_5H_4)(THF)_2$ is more crowded. The bond lengths of Gd(2)–C(η^5) range from 2.662 ~ 2.714 Å (av. 2.687 Å); Gd(2)–C(η^8) from 2.554 ~ 2.643 Å (av. 2.599 Å). If the difference between Gd(1) and Gd(2) radii [9] is subtracted the av. bond length of Gd(2)–C(η^5) or Gd(2)–C(η^8) is comparable to that of Gd(1)–C(η^5) or Gd(1)–C(η^8).

From Table 5 it can be seen that the four carbons of the cyclopentyl in $C_5H_9C_5H_4$ are symmetrically located on the two sides of cyclopentadienyl plane.

For $(C_8H_8)Ln(C_5H_9C_5H_4)(THF)_n$ when Ln = Nd Nd can reach coordination saturation with two THFs; when Ln = Gd Gd can reach coordination saturation with one THF or two THFs. This is due to Nd radius being larger than that of Gd.

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