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Synthesis and crystal structure of $(C_9H_7GdCl_2 \cdot 3THF)THF$

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Abstract

The indenylgadolinium dichloride tristetrahydrofuranate $(C_9H_7GdCl_2 \cdot 3THF)THF$ was prepared and its crystal structure (monoclinic space group $P2_1$) determined by X-ray diffraction.

In $C_9H_7GdCl_2 \cdot 3THF$, Gd, O(1), O(2), O(3) and the centroid of the five-membered indenyl ring form a plane, and Cl(1) and Cl(2) are located at two opposite sides of the plane to give a pseudo-octahedron. The coordination number of Gd is eight.

Introduction

The synthesis of indenyl lanthanide dichlorides has been reported [1], but their crystal structures have not been determined, though crystal structures for $(C_9H_7)_3Sm$ [2], $(C_9H_7)_3Ce \cdot Py$ [3] (Py = pyridine), $(C_9H_7)_3Ln \cdot OC_4H_8$ [4] (Ln = Nd, Gd), $[(C_9H_7)_3Ln]_2(\mu\text{-}Cl)Na(THF)_6$ [5] (Ln = Nd, Sm) and $C_8H_8PrC_9H_7 \cdot 2THF$ [6] are known.

The crystal of $(C_9H_7GdCl_2 \cdot 3THF)THF$ was first obtained and its crystal structure was determined.

Experimental

The complexes described below are extremely sensitive to air and moisture. Therefore, all manipulations of the complexes were conducted under nitrogen with rigorous exclusion of air and water.

THF was refluxed over sodium strips and then distilled from sodium benzophenone ketyl. $GdCl_3$ was made by the literature method, and KC_9H_7 was prepared by treating indene with an excess of K pearls in THF at room temperature.

The rare earth element was determined by complexometric titration, chlorine by titration with $AgNO_3$ solution, and carbon and hydrogen by combustion. IR

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spectra were recorded as KBr pellets on a FTS-ZOE spectrometer. The thermogravimetry data were obtained on a TGS-2 thermogravimetric analyzer.

Synthesis of ($C_9H_7GdCl_2 \cdot 3THF$)THF

Anhydrous $GdCl_3$ (1.85 g, 7.0 mmol) was added to a 50 ml glass tube and heated under reduced pressure for several minutes until gas evolution had ceased, then the tube was cooled by filling it with nitrogen, 20 ml THF was added and the resulting solution was stirred overnight. A KC_9H_7 solution of THF (6.6 ml, 5.6 mmol) was then added with stirring for several hours. After reaction was completed, the solution/suspension was centrifuged to remove unused solid. The solution was concentrated appropriately and then placed in a refrigerator for crystallization to obtain yellowish granular crystals (1.96 g) in a yield of 63% (based on the amount of KC_9H_7).

Anal. Found (%) for $C_9H_7GdCl_2 \cdot 3THF$: Gd, 27.74; Cl, 12.25; C, 43.97; H, 6.29. Calc. (%): Gd, 28.11; Cl, 12.67; C, 45.04; H, 5.54. IR spectra (cm^{-1}): 3040m,

Table 1

Atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
Gd	2215(1)	5000	4174(1)	68(1)
Cl(1)	2160(3)	2848(3)	4445(3)	82(1)
Cl(2)	2118(4)	7229(3)	4712(3)	87(2)
O(1)	−193(6)	4963(13)	3490(6)	81(3)
O(2)	1620(7)	5019(15)	6068(6)	83(3)
O(3)	4409(6)	4963(15)	5694(7)	84(3)
O(4)	6093(31)	7381(22)	−123(37)	400(31)
C(11)	−1039(16)	3982(15)	3218(19)	83(8)
C(12)	−2382(13)	4491(13)	2869(21)	153(11)
C(13)	−2422(21)	5660(23)	3248(30)	178(14)
C(14)	−1037(18)	5956(19)	3431(32)	146(16)
C(21)	787(24)	5825(16)	6396(17)	145(11)
C(22)	581(24)	5483(20)	7475(18)	147(13)
C(23)	1160(32)	4373(28)	7748(29)	227(21)
C(24)	2094(20)	4317(16)	7063(15)	131(10)
C(31)	5160(17)	5976(14)	6046(21)	191(12)
C(32)	6438(16)	5552(12)	6803(17)	141(9)
C(33)	6459(16)	4404(13)	7174(15)	135(8)
C(34)	5290(14)	4026(13)	6248(17)	129(9)
C(41)	5054(34)	6529(25)	−382(37)	353(30)
C(42)	4025(32)	7179(25)	−128(32)	250(24)
C(43)	4284(38)	8217(33)	513(46)	348(30)
C(44)	5407(38)	8338(28)	116(55)	407(34)
C(1)	2091(17)	4443(10)	1926(14)	96(8)
C(2)	3216(20)	3803(14)	2519(18)	139(12)
C(3)	3870(16)	4793(18)	2957(15)	140(11)
C(4)	3239(18)	5800(11)	2518(14)	147(12)
C(5)	1845(15)	5665(15)	1793(12)	131(9)
C(6)	546(19)	6066(18)	1033(15)	113(11)
C(7)	−393(17)	5311(18)	375(12)	162(13)
C(8)	−96(19)	4164(16)	617(13)	147(10)
C(9)	1134(17)	3670(19)	1337(15)	109(9)

Table 2

Bond lengths (Å)

Gd–Cl(1)	2.581(3)	Gd–Cl(2)	2.735(4)
Gd–O(1)	2.392(6)	Gd–O(2)	2.513(8)
Gd–O(3)	2.429(6)	Gd–C(1)	2.709(17)
Gd–C(2)	2.876(23)	Gd–C(3)	2.594(20)
Gd–C(4)	2.691(19)	Gd–C(5)	2.838(14)
O(1)–C(11)	1.438(21)	O(1)–C(14)	1.463(26)
O(2)–C(21)	1.430(27)	O(2)–C(24)	1.401(21)
O(3)–C(31)	1.426(22)	O(3)–C(34)	1.463(20)
O(4)–C(41)	1.439(43)	O(4)–C(44)	1.421(53)
C(11)–C(12)	1.465(21)	C(12)–C(13)	1.466(33)
C(13)–C(14)	1.440(31)	C(21)–C(22)	1.421(33)
C(22)–C(23)	1.446(40)	C(23)–C(24)	1.458(45)
C(31)–C(32)	1.445(22)	C(32)–C(33)	1.432(21)
C(33)–C(34)	1.433(20)	C(41)–C(42)	1.442(53)
C(42)–C(43)	1.429(52)	C(1)–C(2)	1.391(23)
C(43)–C(44)	1.404(74)	C(1)–C(5)	1.475(21)
C(1)–C(9)	1.375(23)	C(2)–C(3)	1.377(26)
C(3)–C(4)	1.386(24)	C(4)–C(5)	1.450(21)
C(5)–C(6)	1.453(22)	C(6)–C(7)	1.377(26)
C(7)–C(8)	1.407(29)	C(8)–C(9)	1.427(24)

Gd–(centroid of five membered ring) 2.47
Gd–C av. 2.74

2960s, 2840s, 1600m, 1440s, 1380m, 1340w, 1320w, 1290w, 1180w, 1150w, 1100w, 1050s, 1020s, 1000s, 930w, 900m, 840s, 750s, 720m, 700s, 680m, 650m, 530w, 470w.

Determination of crystal structure

Data were collected on a Nicolet XRD corporation R3m/E four circle diffractometer at room temperature, using a graphite monochromator, Mo-K_α radiation. Scan type $\omega/2\theta$, $2\theta_{max} = 50°$. 2634 independent reflections were measured and 1537 reflections satisfying $I > 3\sigma(I)$ were accepted as observed. Corrections were made for Lorenz and polarisation effects. The structure was solved by the heavy atom method and parameters were refined by block-matrix least-squares analysis with refinement on $R = 0.042$, $R_w = 0.045$.

The crystallographic data of $(\eta^5\text{-}C_9H_7GdCl_2 \cdot 3THF)THF$ were as follows: monoclinic, space group $P2_1$. $a = 10.468(3)$, $b = 11.888(3)$, $c = 11.854(4)$ Å, $\beta = 108.46(2)°$, $V = 1399.3(7)$ Å^3, $Z = 2$, $F(000) = 638e$, $\mu = 26.6$ cm^{-1}, $D_c = 1.50$ g cm^{-3}.

The atomic coordinates, selected bond lengths and angles of all non-hydrogen atoms of complex $(\eta^5\text{-}C_9H_7GdCl_2 \cdot 3THF)THF$ are presented in Tables 1–3. The molecular and crystal structures of the complex and the packing of molecules in the unit cell are shown in Figs. 1 and 2, respectively.

Results and discussion

Crystals of $(C_9H_7GdCl_2 \cdot 3THF)THF$ were prepared by reaction of anhydrous $GdCl_3$ (1 mole) with C_9H_7Na (0.8 moles) in tetrahydrofuran (THF) at room

Table 3

Bond angles (deg)

Cl(1)-Gd-Cl(2)	158.0(1)	O(1)-Gd-O(2)	76.7(2)
O(1)-Gd-O(3)	154.0(3)	O(2)-Gd-O(3)	77.3(3)
Cl(1)-Gd-C(1)	83.3(3)	C(2)-Gd-C(3)	28.6(6)
C(1)-Gd-C(2)	28.6(5)	C(1)-Gd-C(4)	43.5(4)
C(1)-Gd-C(3)	42.4(5)	C(3)-Gd-C(4)	30.4(5)
C(2)-Gd-C(4)	50.4(5)	Cl(2)-Gd-C(5)	87.6(4)
C(2)-Gd-C(5)	54.8(5)	Cl(1)-Gd-C(5)	30.7(4)
C(4)-Gd-C(5)	30.3(4)	C(3)-Gd-C(5)	51.5(5)
C(11)-C(12)-C(13)	115.0(14)	C(12)-C(13)-C(14)	98.8(20)
C(21)-C(22)-C(23)	106.9(24)	C(32)-C(33)-C(34)	97.9(12)
C(31)-C(32)-C(33)	116.4(14)	C(42)-C(43)-C(44)	87.1(37)
C(41)-C(42)-C(43)	123.0(30)	C(2)-C(1)-C(9)	104.8(13)
C(2)-C(1)-C(5)	133.1(14)	C(5)-C(1)-C(9)	122.0(14)
C(1)-C(2)-C(3)	87.9(13)	C(3)-C(4)-C(5)	113.4(14)
C(2)-C(3)-C(4)	118.4(14)	C(4)-C(5)-C(6)	154.2(17)
C(1)-C(5)-C(4)	86.4(11)	C(6)-C(7)-C(8)	116.4(15)
C(1)-C(5)-C(6)	119.1(14)	C(1)-C(9)-C(8)	113.7(18)
C(5)-C(6)-C(7)	119.8(18)		
C(7)-C(8)-C(9)	128.3(17)		
Centroid(η^5)-Gd-Cl(1)		94.9	
Centroid(η^5)-Gd-O(1)		104.5	

temperature and separated out from the solution in a refrigerator. In this formula the THF outside the parentheses represents an interstitial molecule. When the crystal of the complex was isolated from the solution the interstitial THF molecule could escape to give $C_9H_7GdCl_2 \cdot 3THF$. The analytical values for the complex are consistent with those calculated as $C_9H_7GdCl_2 \cdot 3THF$.

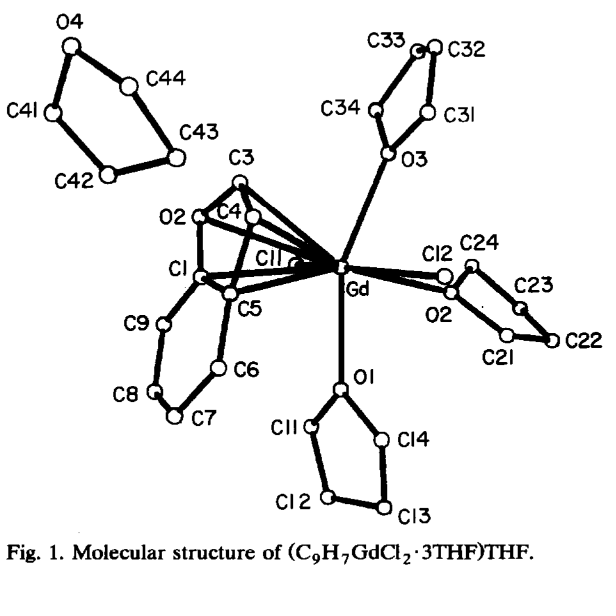

Fig. 1. Molecular structure of $(C_9H_7GdCl_2 \cdot 3THF)THF$.

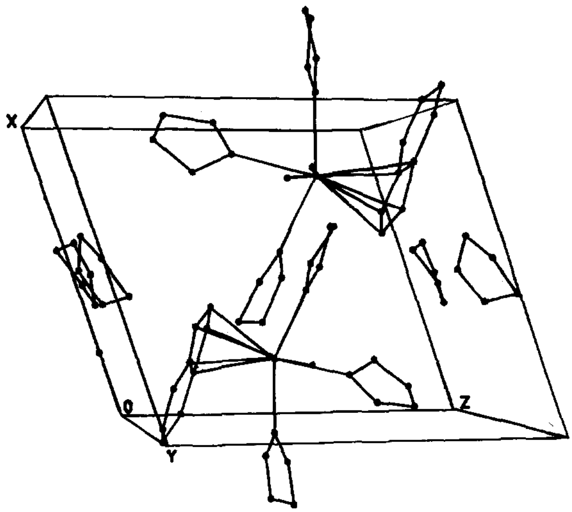

Fig. 2. The packing of $(C_9H_7GdCl_2 \cdot 3THF)THF$ in the unit cell.

In $C_9H_7GdCl_2 \cdot 3THf$ Gd, O(1), O(2), O(3) and the centroid of the indenyl ring form a plane, and Cl(1) and Cl(2) are located at two opposite sides of the plane to give a pseudo-octahedron. The Gd is in the centre of the octahedron and the coordination number is eight (Fig. 1).

The $C_5H_5NdCl_2 \cdot 3THF$ molecule has C_{2v} symmetry about Nd, Cl(1), Cl(2), O(1), O(2), O(3), which becomes C_s when the C_5H_5 group is taken into account [7]. However, $C_9H_7GdCl_2 \cdot 3THF$ does not have C_{2v} symmetry owing to the existence of the C_9H_7 group.

In $(C_9H_7)_3Gd \cdot OC_4H_8$ [4] the bond lengths of Gd–C(η^5) are 2.708(7)–C(1), 2.628(5)–C(2), 2.728(6)–C(3), 2.959(8)–C(4, bridging atom), 2.955(8)–C(5, bridging atom), respectively. The Gd–C(4,5) distances are greater than those of Gd–C, and

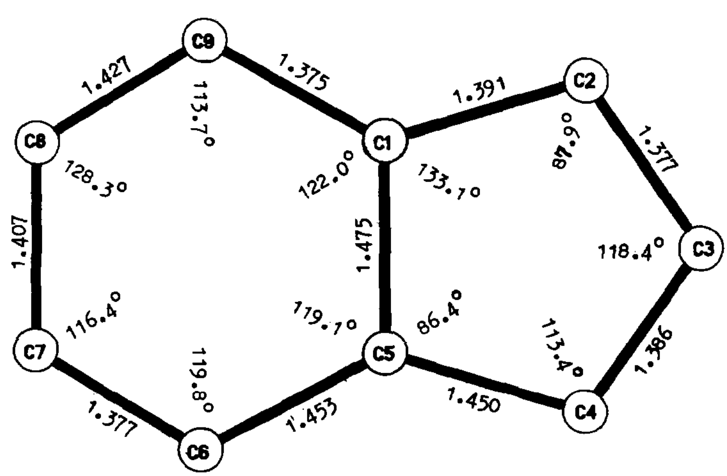

Fig. 3. Bond distances (Å) and angles (°) in the indenyl group of $(C_9H_7GdCl_2 \cdot 3THF)THF$.

in the indenyl groups of $(C_9H_7)_3Ce \cdot C_5H_5N$ [3] and $C_8H_8PrC_9H_7 \cdot (THF)_2$ [6] the bond distances Ce(Pr)–C(bridging atoms) are also greater than those of Ce(Pr)–C(nonbridging atoms). This may be related to the existence of the coordinated pyridine (or THF) molecule. In $C_5H_5GdCl_2 \cdot 3THF$ [8] the five Gd–C(η^5) bond lengths are almost equal. In $(C_9H_7GdCl_2 \cdot 3THF)THF$ the Gd–C(1, 2, 5) bond lengths are greater than those of Gd–C(3, 4), see Table 2, and the distances of C(1)–C(5) and C(4)–C(5) are also greater than those of C(1)–C(2), C(2)–C(3) and C(3)–C(4), which is caused by the effects of the benzene ring in indenyl group and the interstitial THF in the complex. In the case of $(C_9H_7)_3Ce \cdot C_5H_5N$ [3] the C(6)–C(7) and C(8)–C(9) bond distances are significantly shorter than all the others. This feature cannot be observed in the present complex (Fig. 3). The average bond length Gd–C(η^5) in the title complex is shorter than Gd–C(η^5) in $(C_9H_7)_3Gd \cdot OC_4H_8$ [4], which is caused by crowding of the three indenyls in $(C_9H_7)_3Gd \cdot OC_4H_8$ [4].

In $C_5H_5GdCl_2 \cdot 3THF$ [8] the angle of Cl(1)–Gd–Cl(2) is 154.8(1)°, about 3° larger than in $(C_9H_7GdCl_2 \cdot 3THF)THF$ where it is 158.0(1)° (Table 3). The angles of O(1)–Gd–O(2) and O(1)–Gd–O(3) in the former are 76.2(3)° and 154.7(3)°, respectively, and in the latter 76.7(2)° and 154.0(3)°, respectively.

In $C_5H_5GdCl_2 \cdot 3THF$ [8], C(1)–Gd–C(2) and C(1)–Gd–C(5) are 30.3(4)°; C(1)–Gd–C(3) and C(1)–Gd–C(4) are 49.9(4)°. In $(C_9H_7GdCl_3 \cdot 3THF)THF$ the angles of C(1)–Gd–C(2), C(2)–Gd–C(3), C(3)–Gd–C(4), C(4)–Gd–C(5) and C(1)–Gd–C(5) are 28.6(5)°, 28.6(6)°, 30.4(5)°, 30.3(4) and 30.7(4)°, respectively (Table 3). This shows that the five-membered ring in indenyl is distorted.

From Fig. 3 it can be seen that all the inner angles of the five-membered ring deviate from 108° and the angles of C(6)–C(7)–C(8) and C(1)–C(9)–C(8) deviate markedly from 120°. This is different from the complexes reported in the literatures [2–6], in which each inner angle of indenyl deviates slightly from 108° or 120°.

In Table 4 the equations for the best planes of the indenyl ring and atomic deviations of $(C_9H_7GdCl_2 \cdot 3THF)THF$ are listed. It can be seen that the atomic deviations in the planes of indenyl ring are very small.

Table 4

Equations for the best planes of indenyl ring, and atomic deviations

Plane	Equation, atoms and their deviation (Å)							
P(1)	$-6.289X + 0.025Y + 11.243Z = 0.8524$							
	C(1)	C(2)	C(3)	C(4)	C(5)			
	0.0089	−0.0325	0.0502	−0.0438	0.0173			
P(2)	$6.769X + 0.118Y - 11.003Z = -0.6624$							
	C(1)	C(5)	C(6)	C(7)	C(8)	C(9)		
	0.0112	0.0053	−0.0337	0.0471	−0.0320	0.0020		
P(3)	$6.532X - 0.049Y - 11.128Z = -0.7187$							
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
	−0.0368	0.0340	−0.0250	0.0606	−0.0436	−0.0450	0.0715	−0.0097
	C(9)							
	−0.0106							

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