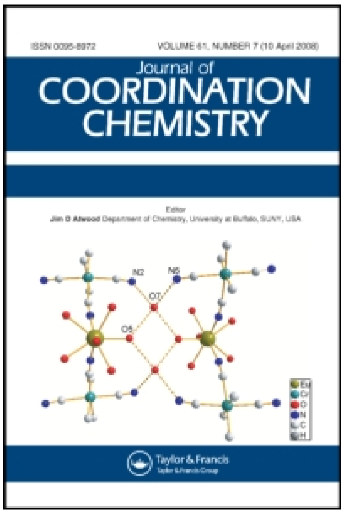

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Crystal Structure of (Cyclopentadienyl)-Dichlorogadolinium(III)-Tris(Tetrahydrofuran)

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CRYSTAL STRUCTURE OF (CYCLOPENTADIENYL)-DICHLOROGADOLINIUM(III)-TRIS(TETRAHYDROFURAN)

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The compound $CpGdCl_2 \cdot 3THF$ has been successfully prepared from NaCp ($Cp = C_5H_5$) and $GdCl_3$ (2:1 molar ratio) in THF and characterized by elemental analysis, IR and MS spectra and a single crystal X-ray diffraction study, showing that the compound is monomeric in both vapour and solid states. Crystals are monoclinic, space group $P2_1/n$, with $a = 7.818$, $b = 17.139(2)$, $c = 15.203(2)$ Å, $\beta = 95.88(2)°$, and $D_c = 1.678\,g/cm^3$ for $Z = 4$; 1876 reflections were considered observed. The structure was solved by heavy-atom methods. Least-squares refinement converged to a final value of $R = 0.041$. The gadolinium has a distorted octahedral geometry coordinated by one Cp ring centroid, three THF oxygen atoms and two chloride anions. The average Gd–O(THF) distance is 2.397(3) Å. The Gd–C(Cp) bond lengths range from 2.673(6) to 2.691(6) Å, and average 2.683(6) Å.

Keywords: Gadolinium(III), cyclopentadienyl, chloride, X-ray structure

INTRODUCTION

Syntheses of cyclopentadienyl dichlorides of lanthanides and determinations of crystal structures of $CpLnCl_2 \cdot 3THF$ (Ln = Nd, Er and Yb)[1–3] have been reported. To our knowledge, however, no structure information on the middle lanthanide cyclopentadienyl dichlorides has been reported. Rogers *et al.*[4] once attempted to obtain the title compound by reaction of 1:1 molar ratios of NaCp and anhydrous $GdCl_3$ in THF, but $Cp_3Gd \cdot THF$ was obtained instead of $CpGdCl_2.3THF$, owing to disproportionation. In order to verify the existence of the title compound, we herein report preparation of $CpGdCl_2 \cdot 3THF$ from NaCp and $GdCl_3$ (2:1 molar ratio) in THF as well as its crystal structure.

EXPERIMENTAL

All procedures were performed under prepurified argon using Schlenk techniques or in a glovebox. Anhydrous $GdCl_3$ was prepared according to a literature method.[5]

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THF was refluxed and distilled over sodium benzophenone ketyl under argon before use.

Measurements

Carbon and hydrogen analysis was carried out with a Perkin Elmer 240C microanalyser. The IR spectra were recorded over the 4000–200 cm^{-1} range on a Perkin Elmer 983G spectrometer using nujol and fluorolube mulls and examined between disc-shaped CsI crystals. Mass spectra were recorded on a Shimadzu QP-1000A spectrometer; EI mode, T = 50 – 350°C, EM = 1.3 kV. Mass data are based on ^{158}Gd, ^{35}Cl, ^{16}O, ^{12}C and ^{1}H. Analysis of gadolinium was accomplished using a titration procedure with disodium EDTA.[6]

Preparation

Freshly distilled cyclopentadiene (3.0 cm^3, 36 mmol) and anhydrous $GdCl_3$ (3.16 g, 12 mmol) were dissolved together in 40 cm^3 THF. To this suspension was added dispersed sodium metal (0.55 g, 24 mmol), and the reaction mixture was allowed to stir overnight at −2°C. After reaction was complete, the solution/suspension was centrifuged to remove the solution. To the residue was added 30 cm^3 THF and the resulting mixture was left to stand overnight at −2°C. Consequently, a number of colourless crystals suitable for X-ray analysis were grown at the interface of the solution/deposit system. Anal., Calcd. for $CpGdCl_2 \cdot 3THF$ ($C_{17}H_{29}O_3Cl_2Gd$): C, 40.07; H, 5.74; Cl, 13.92; Gd, 30.85%. Found: C, 39.85; H, 5.68; Cl, 14.03; Gd, 30.92%. IR (cm^{-1}): 212s, 242m, 363m, 436m, 756s, 778s, 860w, 914m, 1046s, 1445s, 1602s, 2882s, 2953s, 3075s. MS: *m/z* (relative intensity %): (M)$^+$, 509(10.5); M-Cl)$^+$, 474(1.02); (M-Cp)$^+$, 444(35.6); (M-Cp-Cl)$^+$, 409(6.5); (M-Cp-2Cl)$^+$, 373(4.3); (C_5H_6)$^+$, 66(100.0).

Crystal structure determination

Crystal of *Ca* 0.20 × 0.45 × 0.55 mm was used for the X-ray analysis and was apparently unchanged during the measurements (no decay of intensities was observed). Intensities were collected on an Enraf-Nonius CAD4 four-circle diffractometer at room temperature using MoKα radiation (0.71073 Å) with θ–2θ scan techniques. All the reflections in the range of $4° < 2\theta < 46°$ were measured for the compound. Of 2853 independent reflections collected, 1876, having $|F_o| \geqslant 3\sigma(|F_o|)$, were used in the analysis. The intensities were corrected for Lorentz and polarixation factors; corrections for absorption were not applied.

Crystal data

$C_{17}H_{29}O_3Cl_2Gd$, $M = 509.25$; monoclinic, $P2_1/n$, $a = 7.818(2)$, $b = 17.139(2)$, $c = 15.203(2)$ Å, $\beta = 95.88(2)°$, $V = 2015.53$ Å^3, $Z = 4$, $D_c = 1.678$ g/cm^3, μ(MoKα) = 36.70 cm^{-1}.

The structure was solved by Patterson and Fourier techniques by use of the SHELXTL program system. The position of the gadolinium atom was located from the initial Patterson map. Least-square refinement was carried out for the gadolinium atom with isotropic thermal parameters. The unweighted R $(= [\Sigma \| F_o| - |F_c\|]/\Sigma |F_o|)$

TABLE I
Final fraction atomic coordinates ($\times 10^3$) and thermal parameters ($\times 10^3$).†

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Gd	55.9(7)	50.23(4)	234.31(4)	10.66(9)	3.38(2)	3.12(2)	−0.54(9)	1.18(8)	−0.21(5)
Cl1	252.4(2)	29.8(1)	363.5(1)	16.8(3)	5.7(1)	4.25(8)	−0.0(3)	−4.1(3)	−0.4(1)
Cl2	201.7(2)	982.4(1)	858.3(1)	14.1(3)	6.42(9)	4.09(8)	−2.7(3)	−1.5(3)	−0.1(2)
O1	579.0(6)	437.2(3)	186.9(3)	13.6(8)	4.1(2)	5.3(3)	2.3(7)	0.4(8)	−3.0(4)
O2	293.9(5)	445.1(3)	338.6(3)	12.1(7)	4.0(2)	3.9(2)	−0.3(7)	1.9(7)	2.5(4)
O3	348.5(5)	391.9(3)	838.9(3)	13.7(8)	5.2(2)	3.2(2)	−4.5(7)	0.3(7)	0.7(4)
C1	492(1)	366.5(5)	168.2(7)	29(2)	5.7(4)	9.4(6)	−2(1)	9(2)	−7.2(7)
C2	619(1)	311.0(5)	122.7(7)	36(2)	6.7(4)	9.2(6)	9(2)	1(2)	−4.6(8)
C3	279(1)	142.3(6)	606.6(9)	43(2)	6.2(5)	20(1)	−7(2)	27(2)	2(1)
C4	756(1)	427.9(6)	156.5(8)	18(2)	7.5(5)	16.7(8)	−0(2)	14(2)	−13(1)
C5	616(1)	78.9(6)	821.5(7)	12(1)	7.0(5)	10.0(6)	5(1)	1(2)	−5.6(9)
C6	561(1)	125.8(6)	899.0(7)	26(2)	12.5(5)	11.6(6)	13(2)	−1(2)	−12.2(9)
C7	208(1)	346.9(6)	442.9(6)	35(2)	9.2(5)	8.8(5)	−14(2)	−7(2)	7.8(8)
C8	352(1)	400.6(5)	412.0(5)	28(2)	7.0(4)	6.0(4)	−7(1)	−6(1)	5.2(6)
C9	184.4(9)	356.3(5)	818.0(5)	23(1)	7.3(4)	6.6(4)	−14(1)	0(1)	1.8(7)
C10	624(1)	190.8(6)	399.2(6)	36(2)	11.5(5)	8.4(5)	21(2)	−2(2)	−4.3(9)
C11	216(1)	339.9(7)	972.0(6)	42(2)	13.4(6)	5.2(5)	−28(2)	−2(2)	−4.5(9)
C12	374(1)	377.0(6)	930.8(5)	37(2)	14.9(6)	4.7(4)	−23(2)	−4(1)	6.9(8)
C13	756(1)	321.8(5)	719.8(6)	27(2)	4.9(4)	6.9(5)	9(1)	−5(1)	−1.2(7)
C14	317.7(9)	129.5(5)	149.9(6)	15(1)	4.0(3)	7.5(5)	−3(1)	6(1)	2.4(7)
C15	195(1)	125.1(5)	89.5(5)	29(2)	5.0(4)	4.2(4)	−4(1)	4(1)	2.2(6)
C16	555(1)	329.4(5)	621.4(5)	26(2)	3.9(3)	5.4(4)	2(1)	−3(1)	−2.4(6)
C17	591(1)	296.0(4)	702.8(5)	27(2)	3.8(3)	7.2(5)	2(1)	2(1)	0.2(6)

†The thermal parameters are defined by $\exp[-1/4(B_{11}h^2a*^2+B_{22}k^2b*^2+B_{33}l^2c*^2+2B_{12}hka*b*+2B_{13}hla*c*+2B_{23}klb*c*)]$.

factor decreased to 0.39. Further refinement and a series of difference Fourier syntheses yielded the locations of all non-hydrogen atoms. Several cycles of isotropic block-matrix least-squares refinement and anisotropic full-matrix least-squares refinement for all non-hydrogen atoms reduced the unweighted R factor to 0.049. The hydrogen atomic positions were located by difference fourier syntheses. Further full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms using 1876 reflections with $|F_o| \geqslant 3\sigma(|F_o|)$ gave a final R factor of 0.041 and R_w 0.054, where $R_w=[\Sigma w(|F_o|-|F_o|)^2/\Sigma w|F_o|^2]^{1/2}$, $w=1/\sigma^2(F)$. The final fractional atomic coordinates are listed in Table I. Bond lengths and angles are given in Table II.

RESULTS AND DISCUSSION

Preparation and spectroscopic characterization

Rogers *et al.*[4] have reported that crystallization from reaction solution of a 1:1 molar ratio of NaCp and $GdCl_3$ in THF gave only $Cp_3Gd{\cdot}THF$, due to the following

TABLE II
Bond lengths (Å) and angles (°).

Bond lengths

Atoms	Distance	Atoms	Distance	Atoms	Distance
Gd-Cl1	2.638(1)	Gd-Cl2	2.633(1)	Gd-O1	2.458(3)
Gd-O2	2.364(3)	Gd-O3	2.370(3)	Gd-C13	2.691(6)
Gd-C14	2.673(6)	Gd-C15	2.681(5)	Gd-C16	2.684(6)
Gd-C17	2.687(6)	O1-C1	1.434(8)	O1-C4	1.419(8)
O2-C5	1.483(8)	O2-C8	1.462(6)	O3-C9	1.484(6)
O3-C12	1.453(7)	C1-C2	1.496(9)	C2-C3	1.480(11)
C3-C4	1.425(13)	C5-C6	1.459(11)	C6-C7	1.468(10)
C7-C8	1.490(9)	C9-C10	1.508(10)	C10-C11	1.476(11)
C11-C12	1.469(9)	C13-C14	1.398(10)	C13-C17	1.414(8)
C14-C15	1.398(9)	C15-C16	1.367(8)	C16-C17	1.415(8)
Gd-Cent[a]	2.404(6)				

Bond angles

Atoms	Angles	Atoms	Angles
Cl1-Gd-Cl2	154.93(5)	Cl1-Gd-O1	77.63(8)
Cl1-Gd-O2	87.06(8)	Cl1-Gd-O3	88.07(8)
Cl2-Gd-O1	77.30(9)	Cl2-Gd-O2	87.58(8)
Cl2-Gd-O3	86.55(8)	O1-Gd-O2	78.2(1)
O1-Gd-O3	76.9(1)	O2-Gd-O3	155.1(1)
C1-O1-C4	108.0(6)	C5-O2-C8	110.8(5)
C9-O3-C12	109.8(4)	O1-C1-C2	108.6(6)
C1-C2-C3	104.1(7)	C2-C3-C4	108.1(7)
O1-C4-C3	109.5(8)	O2-C5-C6	103.0(7)
C5-C6-C7	110.6(6)	C6-C7-C8	105.2(6)
O2-C8-C7	106.3(5)	O3-C9-C10	104.4(5)
C9-C10-C11	106.7(6)	C10-C11-C12	106.6(6)
O3-C12-C11	107.1(6)	C14-C13-C17	107.3(6)
C13-C14-C15	109.0(6)	C14-C15-C16	108.0(6)
C15-C16-C17	108.4(6)	C13-C17-C16	107.4(6)
O1-Gd-Cent	179.0(6)	O2-Gd-Cent	102.4(6)
O3-Gd-Cent	102.5(6)	Cl1-Gd-Cent	103.2(6)
Cl2-Gd-Cent	101.9(6)		

[a] Cent is defined as the centroid of the C13-C17 ring.

disproportionation.

$$3\text{NaCp}+3\text{GdCl}_3 \xrightarrow{\text{THF}} 3(\text{CpGdCl}_2) \xrightarrow{\text{THF}} \text{Cp}_3\text{Gd}\cdot\text{THF}+2\text{GdCl}_3$$

In order to obtain $\text{CpGdCl}_2\cdot 3\text{THF}$, we have improved conditions of preparation and crystallization. In contrast to the traditional method of crystallization, we obtained crystals of $\text{CpGdCl}_2\cdot 2\text{THF}$ from a precipitate of NaCp and GdCl_3 (2:1 molar ratio) in THF (see experimental section). Thus, we suppose that this may be due to the following disproportionation.

$$4NaCp + 2GdCl_3 \xrightarrow{THF} 2(Cp_2GdCl) \xrightarrow[-2°C]{THF} CpGdCl_2{\cdot}3THF + Cp_3Gd{\cdot}THF$$

The disproportionation product $Cp_3Gd{\cdot}THF$ has been proved to exist in the above reaction solution by elemental analysis and mass spectra.

The IR spectra of $CpGdCl_2{\cdot}3THF$ show characteristic absorptions of the η^5-Cp group at about 250, 780, 1010, and 3080 cm^{-1} and coordinated THF molecules near 890 and 1046 cm^{-1}.[7,8] Mass spectra showed clearly the molecular ion and main fragments of $CpGdCl_2{\cdot}3THF$. The molecular ion is characterized by the ready loss of a Cp group with a strong relative intensity ion $(M\text{-}Cp)^+$ in the spectra. However, no ion peaks for $(M\text{-}THF)^+$ formed by direct loss of the coordinated THF molecule of the molecular ion are observed. This indicates that the Gd–O(THF) bond is stronger than Gd–C(Cp) bond.

X-ray crystal structure

The molecular structure and atom numbering of $CpGdCl_2{\cdot}3THF$ are shown in Figure 1. The compound $CpGdCl_2.3THF$ is isostructural with known derivatives of Nd, Er and Yb.[1–3] The gadolinium ion is *pseudo*-octahedrally coordinated by an η^5-Cp group, two chloride anions and three THF molecules. In $CpGdCl_2{\cdot}3THF$, the Gd–C(Cp) bond lengths range from 2.673(6) to 2.691(6) Å and the average is 2.683(6) Å. The Gd–O(THF) bond lengths range from 2.36(3) to 2.458(3) Å (average

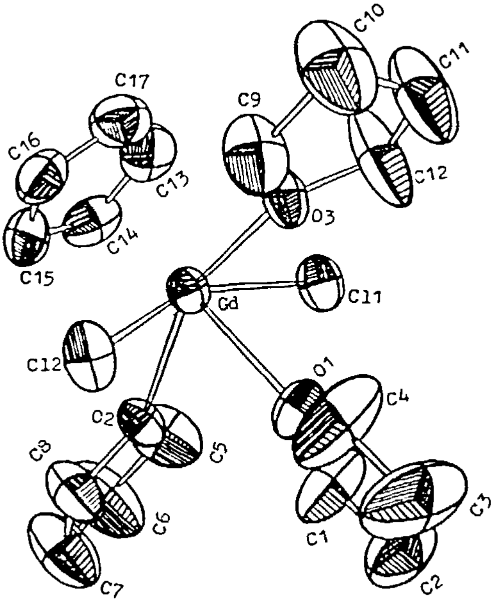

FIGURE 1 A view of the $CpGdCl_2{\cdot}3THF$ molecule showing the atom labelling scheme with hydrogen atoms omitted for clarity.

TABLE III

Significant structural parameters in the isostructural complexes $CpLnX_2 \cdot 3THF$ (Ln = Nd, Gd, Er, Yb; X = Cl, Br) and $Cp_3Gd \cdot THF$.

Compound	$CpNdCl_2 \cdot 3THF$	$CpGdCl_2 \cdot 3THF$	$CpErCl_2 \cdot 3THF$	$CpYbCl_2 \cdot 3THF$	$CpYbBr_2 \cdot 3THF$	$Cp_3Gd \cdot THF$
Ln^{3+} radii[10] Å	1.30	1.25	1.20	1.18	1.18	1.25
(Ln-C)ave	2.799(16)	2.683(6)	2.667(6)	2.641	2.640(16)	2.74(3)
Ln-Cent(Cp)	2.503(16)	2.404(6)	2.389(3)	—	2.358(16)	2.48†
Ln-X(1)	2.719(4)	2.638(1)	2.620(1)	2.598	2.779(2)	—
Ln-X(2)	2.712(4)	2.633(1)	2.613(1)	2.591	2.771(2)	—
Ln-O(1)	2.529(10)	2.458(3)	2.452(3)	2.417	2.438(9)	2.494(7)
Ln-O(2)	2.445(9)	2.364(3)	2.350(3)	2.335	2.335(8)	—
Ln-O(3)	2.448(9)	2.370(3)	2.365(3)	2.365	2.348(9)	—

† Average distance Gd-Cent.

2.397(3) Å) and are shorter than those reported for $Cp_3Gd{\cdot}THF$ with Gd–$C(Cp)_{av}$ = 2.74(3) Å, Gd–O(THF) = 2.494(7) Å. This deviation is due to steric contraction to form a close structure with the Cp group and three THF molecules in the present compound. However, the bond distances in the title compound are reasonable in comparison with corresponding values in the isostructural compounds CpLnX.3THF (Ln = Nd, Er, Yb; X = Cl, Br),[1–3,9] (Table III). It can be seen that all bond lengths Ln-$C(Cp)_{av}$, Ln-O, Ln-Cl and Ln-Cent(Cp) decrease with increasing atomic number of lanthanide. This is in agreement with the regular pattern of contraction of the ionic radius of the lanthanide elements. The O2–Gd–Cent, O3–Gd–Cent, Cl1–Gd–Cent, Cl2–Gd–Cent angles are all opened to *ca* 102°, owing to the steric bulk of the Cp ligand.

SUPPLEMENTARY MATERIAL

Atomic coordinates for the hydrogen atoms, full lists of bond lengths and angles, atomic thermal parameters and a list of calculated and observed structure factors for the compound are available from the authors on request.

REFERENCES

1. G. Yang, Y. Fan, Z. Jin, Y. Xing and W. Chen, *J. Organomet. Chem.*, **322**, 57 (1987).
2. C.S. Day, V.W. Day, R.D. Ernst and S.H. Vollmer, *Organometallics*, **1**, 998 (1982).
3. M. Adam, X.F. Li, W. Oroschin and R.D. Fischer, *J. Organomet. Chem.*, **296**, C19 (1985).
4. R.D. Rogers, R.V. Bynum and J.L. Atwood, *J. Organomet. Chem.*, **192**, 65 (1980).
5. M.D. Taylor and C.P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).
6. C. Ye and Y. Li, *Chinese J. Org. Chem.*, 210 (1981).
7. C. Qian, C. Ye, H. Lu, Y. Li, Y. Ge and M. Tsutsui, *J. Organomet. Chem.*, **247**, 161 (1983).
8. C. Qian, X. Wang, Y. Li and C. Ye, *Polyhedron*, **9**, 479 (1990).
9. G.B. Deacon, G.D. Fallon and D.L. Wilkinson, *J. Organomet. Chem.*, **293**, 45 (1985).
10. R.D. Shannon, *Acta Cryst.*, **A32**, 751 (1976).