

SYNTHESIS AND STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{OC}_4\text{H}_8$

ROBIN D. ROGERS, R. VANN BYNUM, and JERRY L. ATWOOD *

Department of Chemistry, University of Alabama, University, AL 35486 (U.S.A.)

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Summary

Reaction of a 1/1 mole ratio of GdCl_3 and NaC_5H_5 in THF resulted in the formation of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{THF}$. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell constants a 8.220(4), b 24.650(9), c 8.317(4) Å, β 101.39(3)°, and D_c 1.71 g cm⁻³ for $Z = 4$. Full-matrix least-squares refinement has led to a final R value of 0.053 based on 2610 independent observed reflections. The THF molecule is coordinated to the gadolinium atom at a Gd—O distance of 2.494(7) Å. The Gd—C(cyclopentadienyl) bond lengths range from 2.68(2) to 2.80(1) Å, and average 2.74(3) Å.

Introduction

The first Cp_3Ln (Ln = lanthanide) compounds were reported by Birmingham and Wilkinson in 1955 [1]. Although the syntheses were carried out in THF (tetrahydrofuran), the final product was obtained by sublimation as solvent-free Cp_3Ln . The structure of these substances was unknown until 1969 when the results on Cp_3Sm were revealed [2]. An interesting polymeric arrangement was found, but the quality of the X-ray study was such that little faith could be placed in the result. The investigation of Cp_3Sc by our group [3] in 1973 substantiated the gross features of the Cp_3Sm work, but the most reliable Ln—C(Cp) bond lengths have subsequently been obtained from $[\text{Cp}_2\text{LnCl}]_2$, [4,5] $[\text{Cp}_2\text{Ln}(\text{CH}_3)]_2$ [4,6], $\text{Cp}_2\text{Ln}(\text{CH}_3)_2\text{Al}(\text{CH}_3)_2$ [7,8], $\text{Cp}_3\text{Ln} \cdot \text{L}$ [9,10] (L = donor ligand), and $(\text{MeCp})_3\text{Ln}$ [11]. Tetrahydrofuran adducts were reported by several groups [12,13], but no X-ray investigation has been forthcoming. In order to characterize the Gd—C(Cp) bond and to learn about the strength of coordination of the THF molecule, we decided to carry out a structural investigation of the title compound.

Experimental

All transfers and handling were accomplished either by Schlenk techniques or in a dry box. Anhydrous GdCl_3 was prepared by refluxing $\text{GdCl}_3 \cdot 6 \text{H}_2\text{O}$

TABLE 1
CRYSTAL DATA

Molecular formula:	GdOC ₁₉ H ₂₃
Molecular weight:	424.6
Cell constants ^a	
<i>a</i> (Å)	8.220(4)
<i>b</i> (Å)	24.650(9)
<i>c</i> (Å)	8.317(4)
β (°)	101.39(3)
Cell volume (Å ³)	1652.0
Linear absorption coefficient (cm ⁻¹)	41.5
Space group:	<i>P</i> 2 ₁ / <i>n</i>
Molecules/unit cell	4
Maximum crystal dimensions (mm)	0.42 × 0.70 × 1.10
Calculated density (g cm ⁻³)	1.71

^a Mo-*K*_α radiation, λ = 0.71069 Å. Ambient temperature of 23 ± 1°C.

(from Alpha) in thionylchloride for 24 h. The title compound was produced by the room temperature reaction of equimolar quantities of GdCl₃ and NaCp in THF. Crystals suitable for the X-ray diffraction experiment were grown by slow cooling of the reaction mixture after filtration and concentration.

Single crystals of the compound were sealed in thin-walled glass capillaries. Final parameters as determined from a least-squares refinement of the angular settings of 15 reflections (2θ > 30°) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table 1.

Data were collected on the diffractometer with graphite crystal monochromated Mo-*K*_α radiation. The diffracted intensities were collected in the usual manner [14]. As a check on the stability of the instrument and crystal, the (4 0 0), (0 0 4) and (0 14 0) reflections were measured every 50 reflections; no significant variation was noted.

One independent quadrant of data was measured out to 2θ = 50°, and a slow scan was performed on a total of 2610 unique reflections. (No reflections were subjected to a slow scan unless a net count of 40 was obtained in the prescan.) The data set of 2610 reflections used in the subsequent structure determination and refinement was considered observed, and consisted in the main of those for which *I* > 3σ(*I*). The intensities were corrected for Lorentz, polarization, and absorption effects. The latter was accomplished by the application of an empirical method based on ψ scans for χ = 90° reflections [15]. The minimum/maximum transmission factor ratio was 3.1/1.

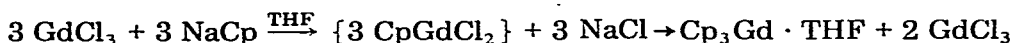
Full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS [16]. The function $w(|F_o| - |F_c|)^2$ was minimized. No correction was made for extinction. Neutral atom scattering factors were taken from the compilation of Cromer and Waber [17] for Gd, O and C; the scattering for Gd was corrected for the real and imaginary components of anomalous dispersion with the table of Cromer and Liberman [18]. Values for H were from ref. 19.

Structure solution and refinement

The existence of four molecules in the unit cell (space group $P2_1/n$) indicated that there was no crystallographically imposed symmetry. The position of the gadolinium atom was located by inspection of a Patterson map. A difference Fourier map phased on the metal atom readily revealed the positions of the 20 remaining non-hydrogen atoms. Refinement with isotropic thermal parameters led to a discrepancy factor of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma |F_o| = 0.075$. The conversion of all non-hydrogen atoms to anisotropic temperature factors and further refinement led to an R_1 value of 0.060. The placement of the hydrogen atoms at calculated positions with B set at $5.5 \text{ \AA}^2$ and additional cycles of least-squares refinement led to final R values of $R_1 = 0.053$ and $R_2 = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2\}^{1/2} = 0.053$. The largest parameter shifts in the final cycle of refinement were less than 0.20 of their estimated standard deviations. The error in an observation of unit weight was 3.52. The final difference Fourier map showed no unaccounted electron density. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table 2. Observed and calculated structure factor amplitudes are available as supplementary material *.

Discussion

The reaction of a 1/1 mole ratio of GdCl_3 and NaCp in THF produced $\text{Cp}_3\text{Gd} \cdot \text{THF}$ and GdCl_3 as the only identified products. Since after the initial filtration a pure solution was obtained, it seems likely that the title compound is the result of the disproportionation reaction shown below



The molecule, shown in Figure 1, has a coordination sphere consisting of three η^5 -cyclopentadienyl ligands and one σ -bonded tetrahydrofuran ligand. In overall geometry $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{OC}_4\text{H}_8$ bears a remarkable resemblance to $(\eta^5\text{-C}_5\text{H}_5)_3\text{Zr}(\eta^1\text{-C}_5\text{H}_5)$ [20].

The THF molecule appears firmly coordinated at a Gd—O distance of $2.494(7) \text{ \AA}$ (Table 3). There is a dearth of appropriate gadolinium compounds with oxygen-donor ligands available for comparison. The Gd—O distance appears short contrasted to the average Ce—O length of $2.58 \text{ \AA}$ in $[\text{Ce}(\text{C}_8\text{H}_8)\text{Cl} \cdot 2 \text{ THF}]_2$ [21]: the correction for $3+$ ionic radii is only $0.01 \text{ \AA}$ [22]. On the other hand, Gd^{3+} in the title compound is only $0.08 \text{ \AA}$ larger than Y^{3+} in $\text{Y}(\text{BH}_4)_3(\text{THF})_3$ [23], but the Y—O bond lengths average $2.37 \text{ \AA}$. Clearly, more structural studies are necessary before an understanding of the Ln^{3+} —O distances is available.

The three cyclopentadienyl ligands are coordinated to the gadolinium atom in an η^5 -fashion with an average Gd—C length of $2.74(3) \text{ \AA}$. The range extends from $2.68(2)$ to $2.80(1) \text{ \AA}$. As can be seen with the aid of the data in Table 4,

(Continued on p. 71)

* See NAPS document no. 03612 for 18 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only \$ 5.00 for photocopies or \$ 3.00 for microfiche. Outside the U.S. and Canada add postage of \$ 3.00 for photocopy and \$ 1.00 for microfiche.

TABLE 2
FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS ^a FOR $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{OC}_4\text{H}_8$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Gd	0.92324(6)	0.14397(2)	0.05512(6)	0.01042(8)	0.001171(8)	0.00863(7)	-0.00012(3)	0.00168(5)	-0.00020(2)
O	1.1108(9)	0.0822(3)	0.2447(9)	0.014(1)	0.0016(2)	0.011(1)	0.0006(4)	0.004(1)	0.0011(3)
C(1)	1.090(2)	0.0679(7)	0.409(2)	0.019(3)	0.0030(4)	0.013(2)	0.0020(8)	0.006(2)	0.0017(7)
C(2)	1.253(2)	0.047(1)	0.496(2)	0.027(4)	0.0060(7)	0.013(2)	0.006(1)	0.005(2)	0.002(1)
C(3)	1.367(2)	0.062(1)	0.405(3)	0.015(3)	0.008(1)	0.040(5)	0.001(1)	-0.000(3)	0.012(2)
C(4)	1.283(2)	0.0736(7)	0.236(2)	0.015(2)	0.0031(4)	0.020(3)	0.0025(8)	0.008(2)	0.0040(8)
C(5)	1.025(2)	0.2483(5)	0.046(2)	0.022(3)	0.0012(2)	0.019(3)	-0.0004(7)	0.001(2)	0.0002(6)
C(6)	1.166(2)	0.2221(8)	0.125(3)	0.015(3)	0.0025(4)	0.039(5)	-0.0015(8)	0.003(3)	-0.003(1)
C(7)	1.142(3)	0.2057(7)	0.273(3)	0.036(5)	0.0013(3)	0.032(4)	-0.000(1)	-0.021(4)	0.0000(9)
C(8)	0.987(3)	0.2224(7)	0.292(2)	0.047(6)	0.0020(3)	0.013(2)	-0.002(1)	0.000(3)	-0.0010(7)
C(9)	0.916(2)	0.2498(6)	0.146(2)	0.023(3)	0.0012(2)	0.020(3)	0.0007(7)	0.003(2)	-0.0003(6)
C(10)	0.698(2)	0.121(1)	0.249(2)	0.017(3)	0.0070(9)	0.012(2)	-0.003(1)	0.007(2)	-0.000(1)
C(11)	0.620(2)	0.1622(7)	0.131(2)	0.016(3)	0.0027(4)	0.033(4)	0.0012(8)	0.013(3)	0.000(1)
C(12)	0.586(2)	0.1379(6)	-0.007(2)	0.018(2)	0.0019(3)	0.016(2)	0.0010(7)	0.005(2)	0.0011(6)
C(13)	0.530(2)	0.0835(7)	0.004(2)	0.015(3)	0.0024(4)	0.035(4)	-0.0026(8)	0.008(3)	-0.002(1)
C(14)	0.703(2)	0.076(1)	0.163(3)	0.013(3)	0.0051(7)	0.041(6)	0.001(1)	0.010(3)	0.009(2)
C(15)	0.851(2)	0.103(2)	-0.258(2)	0.014(3)	0.010(1)	0.016(3)	0.001(2)	-0.002(2)	-0.009(2)
C(16)	0.977(3)	0.0724(7)	-0.181(2)	0.047(6)	0.0021(3)	0.018(3)	-0.001(1)	0.016(3)	-0.0016(8)
C(17)	1.112(2)	0.101(1)	-0.154(2)	0.016(3)	0.0048(6)	0.019(3)	0.002(1)	0.005(2)	-0.002(1)
C(18)	1.080(5)	0.1477(6)	-0.207(4)	0.11(1)	0.0002(2)	0.063(8)	-0.004(1)	0.071(9)	-0.003(1)
C(19)	0.928(6)	0.156(1)	-0.264(2)	0.13(2)	0.0054(9)	0.012(3)	0.023(4)	0.027(6)	0.004(1)

b

H(1)[C(1)]	1.060	0.100	0.466
H(2)[C(1)]	0.998	0.041	0.403
H(3)[C(2)]	1.247	0.004	0.497
H(4)[C(2)]	1.276	0.057	0.613
H(5)[C(3)]	1.462	0.038	0.415
H(6)[C(3)]	1.419	0.099	0.457
H(7)[C(4)]	1.329	0.104	0.183
H(8)[C(4)]	1.292	0.040	0.167
H(9)[C(5)]	1.007	0.264	-0.067
H(10)[C(6)]	1.270	0.215	0.080
H(11)[C(7)]	1.223	0.186	0.357
H(12)[C(8)]	0.934	0.216	0.390
H(13)[C(9)]	0.802	0.267	0.120
H(14)[C(10)]	0.742	0.124	0.369
H(15)[C(11)]	0.602	0.201	0.160
H(16)[C(12)]	0.532	0.156	-0.111
H(17)[C(13)]	0.610	0.056	-0.089
H(18)[C(14)]	0.753	0.039	0.205
H(19)[C(15)]	0.727	0.096	-0.301
H(20)[C(16)]	0.956	0.033	-0.155
H(21)[C(17)]	1.220	0.080	-0.098
H(22)[C(18)]	1.187	0.174	-0.180
H(23)[C(19)]	0.886	0.189	-0.317

a Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. b Hydrogen atoms were placed in calculated positions 1.00 Å from the bonded carbon atoms. Isotropic thermal parameters of 5.5 Å² were assumed.

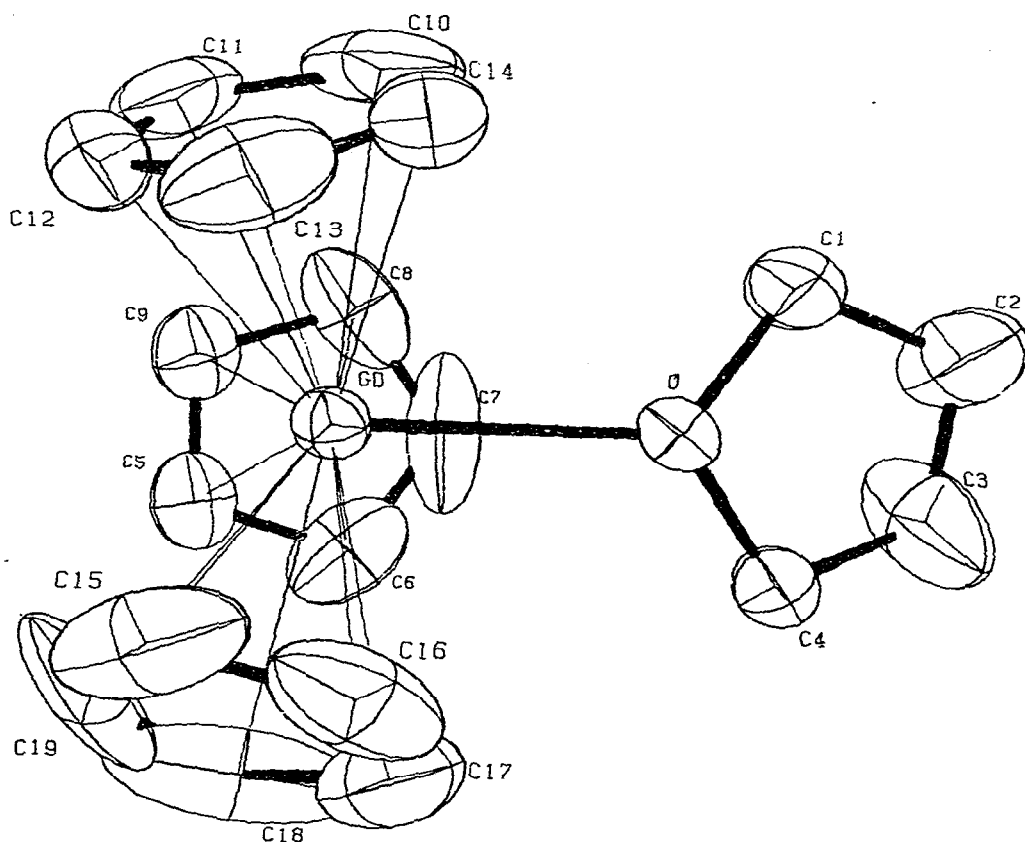


Fig. 1. Molecular structure and atom numbering scheme for $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{OC}_4\text{H}_8$ with the atoms represented by their 50% probability ellipsoids for thermal motion.

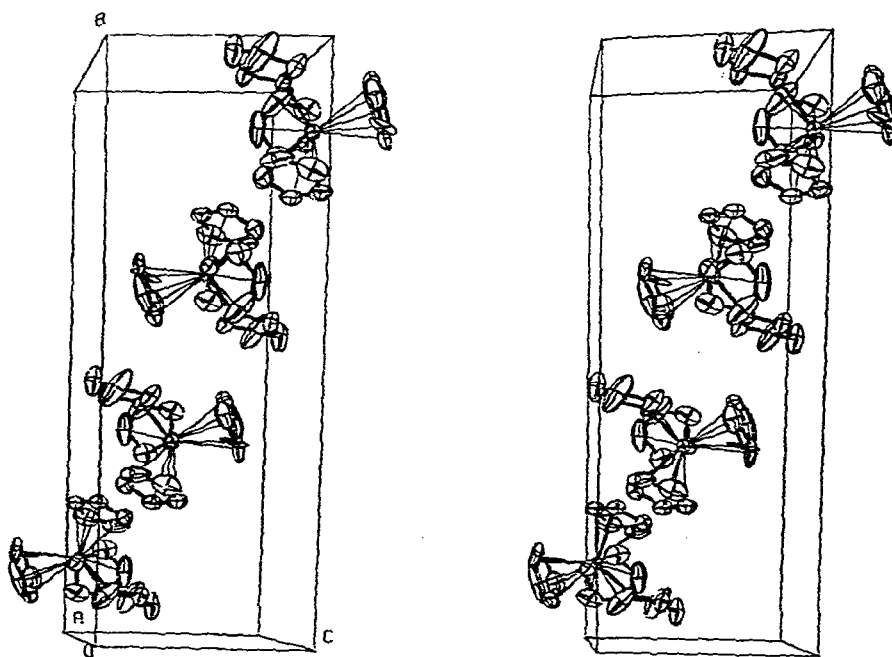


Fig. 2. Stereoscopic view of the unit cell packing for $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{OC}_4\text{H}_8$.

TABLE 3

BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd} \cdot \text{OC}_4\text{H}_8$

Bond Lengths			
Atoms	Distance	Atoms	Distance
Gd—O	2.494(7)	O—C(1)	1.45(1)
Gd—C(5)	2.71(1)	O—C(4)	1.45(1)
Gd—C(6)	2.75(2)	C(1)—C(2)	1.48(2)
Gd—C(7)	2.75(1)	C(2)—C(3)	1.37(2)
Gd—C(8)	2.74(1)	C(3)—C(4)	1.47(2)
Gd—C(9)	2.72(1)	C(5)—C(6)	1.38(2)
Gd—C(10)	2.74(1)	C(5)—C(9)	1.34(2)
Gd—C(11)	2.73(1)	C(6)—C(7)	1.35(3)
Gd—C(12)	2.72(1)	C(7)—C(8)	1.37(3)
Gd—C(13)	2.80(1)	C(8)—C(9)	1.41(2)
Gd—C(14)	2.74(2)	C(10)—C(11)	1.47(3)
Gd—C(15)	2.74(1)	C(10)—C(14)	1.32(3)
Gd—C(16)	2.74(1)	C(11)—C(12)	1.28(2)
Gd—C(17)	2.76(2)	C(12)—C(13)	1.39(2)
Gd—C(18)	2.74(2)	C(13)—C(14)	1.35(3)
Gd—C(19)	2.68(2)	C(15)—C(16)	1.34(3)
		C(15)—C(19)	1.45(4)
Gd—Cent1 ^a	2.47	C(16)—C(17)	1.30(2)
Gd—Cent2	2.49	C(17)—C(18)	1.24(3)
Gd—Cent3	2.49	C(18)—C(19)	1.26(5)

Bond Angles			
Atoms	Angle	Atoms	Angle
Cent1—Gd—O	96.3	Cent1—Gd—Cent2	118.6
Cent2—Gd—O	101.0	Cent1—Gd—Cent3	117.0
Cent3—Gd—O	100.3	Cent2—Gd—Cent3	117.0
Gd—O—C(1)	124.8(7)	Gd—O—C(4)	123.1(6)
C(1)—O—C(4)	107.9(9)	C(11)—C(10)—C(14)	105(2)
O—C(1)—C(2)	107(1)	C(10)—C(11)—C(12)	106(2)
C(1)—C(2)—C(3)	107(1)	C(11)—C(12)—C(13)	113(1)
C(2)—C(3)—C(4)	110(1)	C(12)—C(13)—C(14)	104(2)
C(3)—C(4)—O	105(1)	C(13)—C(14)—C(10)	112(2)
C(6)—C(5)—C(9)	109(1)	C(16)—C(15)—C(19)	103(2)
C(5)—C(6)—C(7)	108(2)	C(15)—C(16)—C(17)	109(2)
C(6)—C(7)—C(8)	109(1)	C(16)—C(17)—C(18)	109(2)
C(7)—C(8)—C(9)	106(2)	C(17)—C(18)—C(19)	114(3)
C(8)—C(9)—C(5)	108(1)	C(18)—C(19)—C(15)	104(2)

^a Cent1 is defined as the centroid of the cyclopentadienyl ring comprised of C(5)—C(9).

the Ln—C bond lengths for all the known cyclopentadienyl structures agree rather well after the correction for ionic radius is applied. This is in spite of the varied nature of the compounds themselves and more particularly of the use of substituted cyclopentadienyl groups.

It has been previously [10] pointed out that $\text{Cp}_3\text{Ln}-\text{X}$ compounds are structurally similar to those formulated as $\text{Cp}_3\text{U}-\text{X}$. Thus, the centroid—U—centroid angles in $\text{Cp}_3\text{UC}\equiv\text{CPh}$ [24] average 117° , while the centroid—U—C(σ) angles are near 100° . In $\text{Cp}_3\text{Gd} \cdot \text{THF}$ the corresponding averages are 117° and 99° .

A stereoscopic view of the unit cell packing is shown in Figure 2. No unusually close intermolecular contacts are noted.

TABLE 4
COMPARISON OF Ln-C(CYCLOPENTADIENYL) BOND LENGTHS

Compound	Ln-C Distance, <i>D</i> (Å)	Ln ³⁺ Radius ^a	Δ(<i>R</i> - <i>R</i> Gd ³⁺)	Δ'(<i>D</i> - <i>D</i> Gd)	Δ-Δ'	Ref.
(η ⁵ -C ₅ H ₅) ₃ Pr · CNC ₆ H ₁₀	2.78	1.23	0.07	0.04	0.03	9
(η ⁵ -C ₅ H ₄ Me) ₃ Nd	2.79	1.20	0.04	0.05	0.01	11
(η ⁵ -C ₅ H ₅) ₃ Gd · OC ₄ H ₈	2.74(3)	1.16	0.00	0.00	0.00	this study
[(η ⁵ -C ₅ H ₄ SiMe ₃) ₂ YMe] ₂	2.68(1)	1.02	-0.14	-0.06	0.08	4
[(η ⁵ -C ₅ H ₄ SiMe ₃) ₂ YCl] ₂	2.65(1)	1.02	-0.14	-0.09	0.05	4
(η ⁵ -C ₅ H ₅) ₂ YMe ₂ AlMe ₂	2.58	1.02	-0.14	-0.16	0.02	8
[(η ⁵ -C ₅ H ₅) ₃ Yb] ₂ (NC ₄ H ₄ N)	2.68(1)	1.09	-0.07	-0.06	0.01	10
[(η ⁵ -C ₅ H ₅) ₂ YbMe] ₂	2.61(1)	0.98	-0.18	-0.13	0.05	6
(η ⁵ -C ₅ H ₅) ₂ YbMe ₂ AlMe ₂	2.61(1)	0.98	-0.18	-0.13	0.05	7
[(η ⁵ -C ₅ H ₄ Me) ₂ YbCl] ₂	2.585(8)	0.98	-0.18	-0.16	0.02	5

^a Ref. 21.

Acknowledgements

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References

- 1 J.M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, **78** (1956) 42.
- 2 C.H. Wong, T.Y. Less and Y.T. Less, *Acta Crystallogr. B*, **25** (1969) 2580.
- 3 J.L. Atwood and K.D. Smith, *J. Amer. Chem. Soc.*, **95** (1973) 1488.
- 4 R. Shakir, J.L. Atwood and M.F. Lappert, unpublished results.
- 5 E.C. Baker, L.D. Brown and K.N. Raymond, *Inorg. Chem.*, **14** (1975) 1376.
- 6 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. Soc. Dalton Trans.*, (1979) 54.
- 7 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. Soc. Dalton Trans.*, (1979) 45.
- 8 G.R. Scollary, *Austral. J. Chem.*, **31** (1978) 411.
- 9 J.H. Burns and W.H. Baldwin, *J. Organometal. Chem.*, **120** (1976) 361.
- 10 E.C. Baker and K.N. Raymond, *Inorg. Chem.*, **16** (1977) 2710.
- 11 J.H. Burns, W.H. Baldwin and F.H. Fink, *Inorg. Chem.*, **13** (1974) 1916.
- 12 S. Manastyrskyj and M. Dubeck, *Inorg. Chem.*, **3** (1964) 1647.
- 13 E.O. Fischer and H. Fischer, *J. Organometal. Chem.*, **6** (1966) 141.
- 14 J.L. Atwood, W.E. Hunter, D.C. Hrnir, E. Samuel, H. Alt and M.D. Rausch, *Inorg. Chem.*, **14** (1975) 1757.
- 15 The empirical absorption correction was performed in a manner similar to that used by Churchill: M.R. Churchill and F.J. Hollander, *Inorg. Chem.*, **17** (1978) 1957.
- 16 Crystallographic programs used on a UNIVAC-1110 include ORFLS (structure factor calculation and least-squares refinement, by W.R. Busing, K.O. Martin and H.A. Levy), ORFFE (distances and angles with e.s.d.'s, by W.R. Busing, K.O. Martin and H.A. Levy), ORTEP (thermal ellipsoid drawings, by C.K. Johnson), FOURIER (D.J. Hodgson's version of Dellaca and Robinson's program), and BPL least-squares planes, by W.E. Hunter).
- 17 D.T. Cromer and J.T. Waber, *Acta Cryst.*, **18** (1965) 104.
- 18 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, **53** (1970) 1891.
- 19 International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1962, p. 202.
- 20 R.D. Rogers, R.V. Bynum and J.L. Atwood, *J. Amer. Chem. Soc.*, **100** (1978) 5238.
- 21 K.O. Hodgson and K.N. Raymond, *Inorg. Chem.*, **11** (1972) 171.
- 22 R.D. Shannon, *Acta Crystallogr. A*, **32** (1976) 751.
- 23 B.G. Segal and S.J. Lippard, *Inorg. Chem.*, **17** (1978) 844.
- 24 J.L. Atwood, C.F. Hains, M. Tsutsui and A.E. Gebala, *J. Chem. Soc. Chem. Commun.*, (1973) 452.