Lists of structure factors, anisotropic displacement parameters, H-centre coordinates and complete geometry have been deposited with the IUCr (Reference: CF1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1346–1348

Tetrakis(μ_3-2-methyl-5-thienyl)tetrakis(diethyl ether-*O*)-*tetrahedro*-tetralithium

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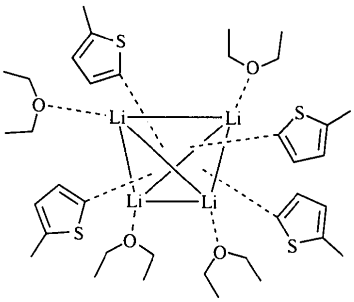
(Received 23 October 1995; accepted 15 January 1996)

Abstract

The lithium 2-methylthiophene complex, $[Li(C_5H_5S)(C_4H_{10}O)]_4$, crystallizes as a tetramer on a $\bar{4}$ symmetry site. The four Li atoms form a slightly distorted tetrahedron. The thiophene carbanions are each coordinated to a face of the lithium tetrahedron. One diethyl ether is also coordinated to each Li atom.

Comment

The crystal structure of the diethyl ether adduct of tetrameric lithium and 5-methylthiophene, the title compound (I), was determined as part of a study of the reaction mechanism of the lithium–iodine exchange reaction (Whipple, 1991; Reich, Green & Phillips, 1989, 1991; Bailey & Patricia, 1988).



(I)

The lithium reagent was prepared by metallation of 2-methylthiophene with *n*-butyllithium in ether at 273 K, and was recrystallized twice from ether at 253 K. The title compound, (I), crystallizes as discrete tetrameric units with $\bar{4}$ site symmetry. The four Li atoms form a slightly distorted tetrahedron. The twofold and non-twofold related Li—Li distances are 2.69 (2) and 2.75 (2) Å, respectively. Although these Li—Li distances are longer than usually seen, they are comparable with those found in the phenyllithium tetramer (Hope & Power, 1983), the (2,6-dimethoxyphenyl)-lithium tetramer (Harder *et al.*, 1988) and the *tert*-butylethynyllithium–thf tetramer (Geissler *et al.*, 1987). The thiophene carbanion C5 bonds to a face of the lithium tetrahedron, as is common in structures of this type.

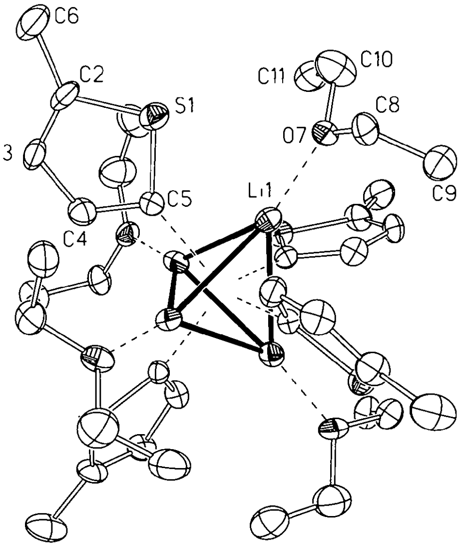


Fig. 1. Tetramer unit drawn with 30% probability displacement ellipsoids. H atoms have been removed for clarity.

Each diethyl ether is coordinated through its O atom to one Li atom. The bonding geometries in the 5-methylthiophene and diethyl ether groups are all within expected ranges. The S atom did not coordinate to any of the Li atoms; this is consistent with the structure of the dimeric benzothiophene–tmeda complex (Harder *et al.*, 1989)

Experimental

The title compound was prepared by metallation of 2-methylthiophene with *n*-butyllithium. Solutions of this compound were stable in Et_2O or thf at 253 K for long periods of time (at least six months).

Crystal data

$[Li(C_5H_5S)(C_4H_{10}O)]$
$M_r = 178.21$
Tetragonal
$I4_1/a$
$a = 19.649\,(3)$ Å
$c = 10.704\,(2)$ Å
$V = 4132.6\,(12)$ Å^3
$Z = 16$
$D_x = 1.146$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 22.5$–$25.0°$
$\mu = 2.361$ mm^{-1}
$T = 111\,(2)$ K
Prism
0.45 × 0.25 × 0.25 mm
Colorless

Data collection

Siemens *P*3*f* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1237 measured reflections
965 independent reflections
628 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.1217$

$\theta_{\rm max} = 50.0°$
$h = -19 \rightarrow 3$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 50 reflections
intensity decay: 3.2%

Refinement

Refinement on F^2
$R(F) = 0.0727$
$wR(F^2) = 0.1701$
$S = 1.243$
965 reflections
109 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0855P)^2 + 13.4262P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.024$
$\Delta\rho_{\rm max} = 0.315$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.286$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Li1	0.4663 (6)	0.3095 (6)	−0.0320 (11)	0.041 (3)
S1	0.59177 (10)	0.36337 (10)	0.0943 (2)	0.0495 (8)
C2	0.6756 (4)	0.3469 (5)	0.1316 (8)	0.057 (2)
C3	0.6959 (4)	0.2914 (5)	0.0659 (8)	0.052 (2)
C4	0.6435 (4)	0.2650 (4)	−0.0131 (8)	0.049 (2)
C5	0.5801 (4)	0.2968 (3)	−0.0117 (7)	0.035 (2)
C6	0.7138 (4)	0.3878 (5)	0.2246 (9)	0.084 (3)
O7	0.4284 (2)	0.3837 (3)	0.0791 (4)	0.0470 (15)
C8	0.4096 (4)	0.4495 (4)	0.0294 (8)	0.055 (2)
C9	0.3381 (4)	0.4489 (4)	−0.0185 (9)	0.066 (3)
C10	0.4160 (6)	0.3838 (6)	0.2099 (10)	0.092 (3)
C11	0.4210 (5)	0.3172 (5)	0.2605 (9)	0.079 (3)

Table 2. *Selected geometric parameters* (Å, °)

S1—C2	1.725 (8)	Li1—O7	2.024 (13)
S1—C5	1.748 (7)	Li1···S1	3.004 (12)
C2—C3	1.359 (11)	Li1—Li1$^{\rm ii}$	2.69 (2)
C2—C6	1.483 (11)	Li1—Li1$^{\rm iii}$	2.75 (2)
C3—C4	1.431 (10)	O7—C10	1.421 (11)
C4—C5	1.393 (10)	O7—C8	1.445 (9)
Li1—C5	2.260 (14)	C8—C9	1.496 (11)
Li1—C5$^{\rm i}$	2.259 (14)	C10—C11	1.420 (12)
Li1—C5$^{\rm ii}$	2.290 (15)		
C2—S1—C5	97.8 (4)	C11—C10—O7	111.2 (8)
C3—C2—C6	129.3 (8)	O7—Li1—C5	112.8 (6)
C3—C2—S1	108.2 (6)	O7—Li1—C5$^{\rm i}$	113.8 (6)
C6—C2—S1	122.5 (8)	C5$^{\rm i}$—Li1—C5	103.1 (5)
C2—C3—C4	112.7 (7)	O7—Li1—C5$^{\rm ii}$	117.0 (6)
C5—C4—C3	118.3 (7)	C5$^{\rm i}$—Li1—C5$^{\rm ii}$	102.2 (5)
C4—C5—S1	103.1 (5)	C5—Li1—C5$^{\rm ii}$	106.5 (5)
C10—O7—C8	108.5 (6)	Li1$^{\rm ii}$—Li1—Li1$^{\rm iii}$	60.8 (2)
C10—O7—Li1	130.1 (6)	Li1$^{\rm ii}$—Li1—Li1$^{\rm i}$	60.8 (2)
C8—O7—Li1	121.4 (6)	Li1$^{\rm iii}$—Li1—Li1$^{\rm i}$	58.5 (5)
O7—C8—C9	111.0 (6)		

Symmetry codes: (i) $\frac{3}{4} - y, x - \frac{1}{4}, -\frac{1}{4} - z$; (ii) $1 - x, \frac{1}{2} - y, z$; (iii) $\frac{1}{4} + y, \frac{3}{4} - x, -\frac{1}{4} - z$.

Crystal mounting was carried out in a glove bag under an argon atmosphere. Crystals were covered in Paratone-N oil and sealed in glass capillary tubes. Mounted crystals were kept on a plate in a dry-ice/acetone bath until they could be examined on the diffractometer. The intensity data were corrected for decay but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares on F^2. The H-atom positions were initially determined from geometric considerations and refined with a riding model. The U(H) values were set to 1.2 × U(C) for non-methyl groups and 1.5 × U(C) for methyl groups. The instability of the material led to poor quality crystals and prevented a better refinement.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

We thank the NSF (grant CHE9105497) and the University of Wisconsin for funds to purchase the computer used in this experiment.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1208). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1348–1350

Tetrakis(diphenylamido-*N*)hafnium

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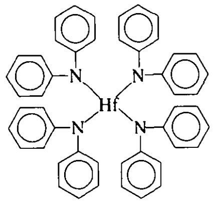
(*Received 6 November 1995; accepted 22 January 1996*)

Abstract

The hafnium coordination in the monomeric title molecule, [$Hf(C_{12}H_{10}N)_4$], is distorted tetrahedral, with Hf—N distances between 2.047 (4) and 2.085 (3) Å, and angles between 101.63 (14) and 121.33 (14)°. One molecule forms the asymmetric unit.

Comment

Since the structure of tetrakis(diethylamido)uranium(IV) was reported (Jones, Karmas, Martin & Gilman, 1956), the syntheses and spectroscopic properties of numerous homoleptic dialkylamido complexes have been reported (Bradley & Gitlitz, 1969). Relatively few crystal structures of this type of compound have been reported however. The structure of the monomeric homoleptic complex tetrakis(diphenylamido)niobium(IV) has been reported recently (Bott, Hoffman & Rangarajan, 1995) and the present hafnium complex seems to have a similar structure. Corresponding dialkylamido complexes having less bulky alkyl groups have a tendency to dimerize, as can be seen in the compound tetrakis(dimethylamido)zirconium (Chisholm, Hammond & Huffman, 1988). So far, no crystal structures of hafnium dialkylamides have been reported. The only hafnium complexes related to the title compound, (I), are bis(trimethylsilylamido) complexes, which have a similar N—Hf bonding pattern (Airoldi *et al.*, 1980).



(I)

The tetrahedral coordination of the title complex is distorted (Fig. 1). The N—Hf1—N angles vary between 101.63 (14) and 121.33 (14)°, whereas the Hf—N bond distances show only slight variations, from 2.047 (4) to 2.085 (3) Å (Table 2). This is in agreement with the geometry of chlorotris[bis(trimethylsilyl)amido]hafnium, for which Hf—N bond lengths of 2.040 (10) Å have been reported (Airoldi *et al.*, 1980). The positions of the amido N atoms deviate only slightly from their respective Hf–C_α–C_α planes, the largest deviation being 0.124 (4) Å for N3 from the Hf1–C25–C31 plane.

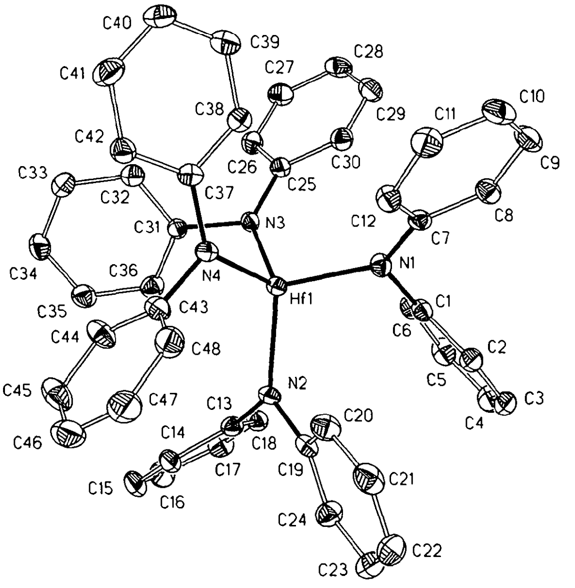


Fig. 1. View of the title molecule with 30% probability displacement ellipsoids. The H atoms have been omitted for clarity.

Experimental

The title complex was prepared by refluxing the lithium salt of the ligand precursor and hafnium(IV) chloride in toluene for 3 h. The lithium salt of the ligand precursor was prepared in tetrahydrofuran with butyl lithium as described in the literature (Jones, Karmas, Martin & Gilman, 1956).

Acta Crystallographica Section C
ISSN 0108-2701 © 1996