

# Formation of Tetrahydrofuran Adducts of $\text{LiZrCl}_5$ in the Reaction of $\text{Li}(\text{NPh}_2)$ and $\text{ZrCl}_4$ : Crystal Structures of $[\text{Li}(\text{thf})_4][\text{ZrCl}_5(\text{thf})]$ and $\text{Li}(\text{thf})_3\text{-}\mu\text{-Cl-ZrCl}_4(\text{thf})$

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Two different tetrahydrofuran adducts of lithium pentachlorozirconate(IV) were isolated in a reaction between diphenylamidolithium and zirconium(IV) chloride. The isolated complexes are  $[\text{Li}(\text{thf})_4][\text{ZrCl}_5(\text{thf})]$  (**1**), which decomposes at temperatures above  $-5^\circ\text{C}$ , and  $\text{Li}(\text{thf})_3\text{-}\mu\text{-Cl-ZrCl}_4(\text{thf})$  (**2**), which is thermally stable at  $20^\circ\text{C}$ . Both complexes crystallise in the monoclinic space group No. 14. The complexes share similar geometry and synthetic background. Both structures consist of an octahedral  $\text{ZrCl}_5^-(\text{thf})$  unit and a tetrahedrally coordinated lithium ion. In **1** the lithium tetrahedron is a distorted  $\text{Li}(\text{thf})_4^+$  unit, whereas in **2** the pseudo-tetrahedral coordination sphere around lithium comprises a bridging chloro ligand. The data sets were collected at 153 K (**1**), and 193 K (**2**).

Since the synthesis of tetrakis(diethylamido)uranium(IV)<sup>1</sup> was reported, lithium amides have widely been used in syntheses of homoleptic dialkylamido complexes. Mixed amido complexes containing halide ligands are not so easily obtained as the homoleptic ones in direct reaction of the lithium amides. Trimethylsilylalkylamides have successfully been used to replace lithium amides in these types of syntheses.<sup>2</sup>

An alternative route for mixed chloroamido complexes, such as dichlorobis(diethylamido)bis(tetrahydrofuran)zirconium(IV), is the direct reaction of homoleptic dialkylamido complex and metal halide in the presence of tetrahydrofuran.<sup>3</sup> When dimethylamido lithium was coupled with zirconium(IV) chloride  $\text{Zr}(\text{NMe}_2)_6\text{Li}_2(\text{thf})_2$  was obtained together with the dimeric  $[\text{Zr}(\text{NMe}_2)_4]_2$  complex.<sup>4</sup> Adduct formation and dimerisation is apparently related to the small non-bulky ligand. In the case of central metals with very high oxidation states, monomeric complexes such as hexakis(dimethylamido)tungsten(VI) have been obtained.<sup>5</sup>

In the present paper we report crystal structures of tetrakis(tetrahydrofuran)lithium tetrahydrofuranpentachlorozirconate(IV) (**1**) and tris(tetrahydrofuran)lithium  $\mu$ -chlorotetrahydrofuran tetrachlorozirconium(IV) (**2**) which are reaction products of diphenylamidolithium and zirconium(IV) chloride.

## Experimental

All the reaction steps were carried out under argon atmosphere using standard Schlenk techniques. The crys-

tals for the X-ray measurements were mounted to the glass fiber using the oil drop method.<sup>6</sup>

### Preparation of the compounds.

$[\text{Li}(\text{thf})_4][\text{ZrCl}_5(\text{thf})]$ : Diphenylamine (1.33 g, 7.87 mmol) was dissolved in tetrahydrofuran (thf) and cooled to  $-70^\circ\text{C}$ . An equivalent amount of butyl lithium (5.0 ml, 1.6 M in n-hexane) was added. The temperature of the solution was allowed to rise to room temperature. Thf was evaporated and replaced with 30 ml toluene. The lithium salt of the ligand precursor and 1.67 g (7.17 mmol) of zirconium(IV) chloride was refluxed in toluene for 2 h. The reaction mixture was filtered to remove the precipitated LiCl. The filtrate was then cooled down to  $-15^\circ\text{C}$ . Colourless, large, plate-like crystals were obtained in 48 h. The fragile crystals decomposed rapidly when mother liquor was removed or temperature of the solution was allowed to rise above  $-5^\circ\text{C}$ . Crystals were picked from mother liquor, which was cooled with dry ice/ethanol bath to prevent the decomposition of the crystals. Then the crystals were transferred to perfluoroether which was cooled with a cold nitrogen stream apparatus.<sup>6</sup> A specimen was cut from large plates and mounted on a glass fiber in perfluoroether. The mounted crystal was cooled by keeping it close to a liquid nitrogen surface when transferred to the diffractometer. Data were collected at  $-120^\circ\text{C}$ .

$\text{Li}(\text{thf})_3\text{-}\mu\text{-Cl-ZrCl}_4(\text{thf})$ : Diphenylamine (16.5 g, 97.1 mmol) was dissolved in tetrahydrofuran (thf) and cooled down to  $-70^\circ\text{C}$ . 60.8 ml (97.3 mmol) butyl lithium

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(1.6 M in n-hexane) was added. Temperature of the solution was allowed to rise to room temperature. Thf was replaced with 80 ml toluene. The lithium salt of the ligand precursor and 11.35 g (48.71 mmol) of zirconium(IV) chloride was added and the suspension was refluxed for 5 h. The reaction mixture was filtered to remove precipitated LiCl. Filtrate was then cooled to 5 °C. Yellow prismatic crystals were obtained in 12 h. A portion of these air sensitive but thermally stable crystals was transferred to perfluoroether. X-Ray diffraction data were collected at –80 °C.

**X-Ray crystallography.** Intensity data were recorded on an automated four-circle Rigaku AFC-7S diffractometer using graphite monochromatised MoK $\alpha$  ( $\lambda = 0.7173$  Å) radiation. Reflections with intensities over background were collected using  $2\theta$ - $\omega$  scans. Intensities of the three standard reflections, which were recorded after every 200 intensity scans, showed only slow decomposition of the crystals (<2.5%) in the both measurements. For both data sets  $\psi$ -scans were used for absorption correction. The data set was compressed to reflection files for structure determination and refinement with TEXSAN Single Crystal Structure Analysis Software.<sup>7</sup> Crystallographic data are presented in Tables 1 and 2.

**Structure determination and refinement.** Both structures were solved with SHELXTL PC 4.1 program package<sup>8</sup>

Table 1. Crystal data for [Li(thf)<sub>4</sub>][ZrCl<sub>5</sub>(thf)].

Compound	[Li(C <sub>4</sub> H <sub>8</sub> O) <sub>4</sub> ][ZrCl <sub>5</sub> (C <sub>4</sub> H <sub>8</sub> O)]
Formula	C <sub>20</sub> H <sub>40</sub> Cl <sub>5</sub> LiO <sub>5</sub> Zr
Formula mass	635.93
Colour, Habit	Colourless, Plate
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> , No. 14
Temperature/K	153(1)
<i>a</i> /Å	10.466(9)
<i>b</i> /Å	16.361(9)
<i>c</i> /Å	17.645(7)
$\beta$ /°	105.59(4)
<i>V</i> /Å <sup>3</sup>	2910(3)
<i>Z</i>	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.451
Crystal size/mm	0.45 × 0.35 × 0.20
<i>F</i> (000)	1312
$\mu$ /mm <sup>-1</sup>	0.863
Transmission range	0.5770–1.0000
$2\theta$ -range/°	5–55
Independent reflections	5922
Parameters	538
Refinement method on <i>F</i> <sup>2</sup>	Full-matrix least squares
Final <i>R</i> -indices [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.0695, <i>wR</i> <sub>2</sub> = 0.1711
<i>R</i> -indices (all data)	<i>R</i> <sub>1</sub> = 0.0942, <i>wR</i> <sub>2</sub> = 0.1862
<i>S</i> (Goodness of fit, <i>F</i> <sup>2</sup> )	1.011
Weights	$[\sigma^2(F_o^2) + (0.1048P)^2]^{-1}$ ; where $P = (F_o^2 + 2F_c^2)/3$
Residual e-density (e/Å <sup>3</sup> )	1.025 and –1.387

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$  with  $F > 4\sigma(F)$ , function minimized is  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]]^{0.5}$   
 $S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{0.5}$ .

Table 2. Crystal data for Li(thf)<sub>3</sub>- $\mu$ -Cl-ZrCl<sub>4</sub>(thf).

Compound	Li(C <sub>4</sub> H <sub>8</sub> O) <sub>3</sub> - $\mu$ -Cl-ZrCl <sub>4</sub> (C <sub>4</sub> H <sub>8</sub> O)
Formula	C <sub>16</sub> H <sub>32</sub> Cl <sub>5</sub> LiO <sub>4</sub> Zr
Formula mass	563.83
Colour, Habit	Yellow, Block
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> , No. 14
Temperature/K	193(1)
<i>a</i> /Å	11.320(6)
<i>b</i> /Å	17.686(7)
<i>c</i> /Å	12.622(9)
$\beta$ /°	90.37(5)
<i>V</i> /Å <sup>3</sup>	2527(2)
<i>Z</i>	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.482
Crystal size/mm	0.40 × 0.30 × 0.25
<i>F</i> (000)	1152
$\mu$ /mm <sup>-1</sup>	0.981
Transmission range	0.8624–1.0000
$2\theta$ -range/°	5–53
Independent reflections	4909
Parameters	261
Refinement method on <i>F</i> <sup>2</sup>	Full-matrix least squares
Final <i>R</i> -indices [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.0391, <i>wR</i> <sub>2</sub> = 0.0875
<i>R</i> -indices (all data)	<i>R</i> <sub>1</sub> = 0.0451, <i>wR</i> <sub>2</sub> = 0.0904
(Goodness of fit, <i>F</i> <sup>2</sup> )	1.039
Weights	$[\sigma^2(F_o^2) + (0.0314P)^2 + 2.4183P]^{-1}$ ; where $P = (F_o^2 + 2F_c^2)/3$
Residual e-density/e Å <sup>-3</sup>	0.401 and –0.335

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$  with  $F > 4\sigma(F)$ , function minimized is  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]]^{0.5}$   
 $S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{0.5}$ .

using direct methods which showed the positions of the nonhydrogen atoms. Further refinement with full matrix least-squares on *F*<sup>2</sup> was carried out with SHELXL 93<sup>9</sup> using all collected reflections. All non-hydrogen atoms were refined anisotropically. In compound 1 all hydrogen atoms were introduced with fixed C–H distance of 0.99 Å and 1.5 × thermal parameters of the parent atoms. In compound 2 C–H distances were allowed to refine. In both cases several carbon atoms of the tetrahydrofuran molecules showed relatively large thermal parameters, but only in the case of carbons C(21) to C(24) in compound 1 could these be suppressed when the tetrahydrofuran molecule was refined in two orientations. Fractional atomic coordinates for both complexes are presented in Tables 3 and 4. Structure factors and thermal parameters are available as supplementary material.

## Results and discussion

Assuming that the use of bulky dialkyl amine would lead to isolable mixed chloroamido complexes we studied the reaction of diphenylamido lithium and zirconium(IV) chloride. However, no desired products were obtained. Instead, we isolated two previously unknown tetrahydrofuran adducts of lithium pentachlorozirconate(IV). The first tetrahydrofuran adduct (1) was obtained from the reaction where equimolar amounts of diphenylamido lithium and zirconium(IV) chloride were allowed to

Table 3. Atomic coordinates ( $\times 10^4$ ) for  $[\text{Li}(\text{thf})_4][\text{ZrCl}_5(\text{thf})]$  (1).

Atom	x	y	z
Zr(1)	7978(1)	3460(1)	3745(1)
Li(1)	2601(10)	986(6)	5972(5)
Cl(1)	5571(1)	3629(1)	3313(1)
Cl(2)	8228(2)	4807(1)	3203(1)
Cl(3)	10382(1)	3400(1)	4338(1)
Cl(4)	7701(2)	2256(1)	4504(1)
Cl(5)	8098(2)	2702(1)	2601(1)
O(11)	7883(4)	4156(2)	4827(2)
C(11)	8676(7)	3985(5)	5628(3)
C(12)	8175(6)	4517(4)	6170(4)
C(13)	6953(7)	4933(4)	5652(4)
C(14)	7166(6)	4918(4)	4846(4)
O(21)	3779(5)	1763(3)	5692(3)
C(21) <sup>a</sup>	4993(47)	2114(26)	6233(18)
C(22) <sup>a</sup>	4975(49)	2975(18)	5770(20)
C(23) <sup>a</sup>	4344(31)	2753(20)	4968(16)
C(24) <sup>a</sup>	3561(25)	2138(14)	4935(11)
C(21A) <sup>b</sup>	4377(27)	2375(20)	6239(12)
C(22A) <sup>b</sup>	5431(40)	2708(21)	5885(20)
C(23A) <sup>b</sup>	4407(39)	2934(33)	5114(31)
C(24A) <sup>b</sup>	4135(35)	1886(29)	4973(15)
O(31)	3700(4)	115(2)	6534(2)
C(31)	5032(6)	-6(5)	6487(4)
C(32)	5358(8)	-857(5)	6729(7)
C(33)	4617(10)	-982(5)	7344(6)
C(34)	3365(8)	-516(4)	7013(4)
O(41)	1618(4)	546(2)	4968(2)
C(41)	2168(7)	-110(4)	4612(4)
C(42)	1253(9)	-244(5)	3830(4)
C(43)	676(8)	576(6)	3610(4)
C(44)	546(7)	927(4)	4383(4)
O(51)	1634(4)	1524(2)	6600(2)
C(51)	854(8)	2244(4)	6345(4)
C(52)	1233(8)	2852(4)	6996(4)
C(53)	1966(7)	2362(4)	7718(3)
C(54)	1825(6)	1481(4)	7437(3)

<sup>a</sup>Refined occupancy factor 0.56(4). <sup>b</sup>0.44(4).

react. Large glacial plate-like crystals started to grow after the reaction mixture was filtered and cooled down to  $-15^\circ\text{C}$ . The X-ray diffraction analysis showed the composition of the crystals as tetrakis(tetrahydrofuran)-lithium tetrahydrofuranpentachlorozirconium(IV).

When two molar equivalents of diphenylamidolithium was refluxed with zirconium chloride and the resulting filtrate was transferred to  $5^\circ\text{C}$  a different thf adduct was isolated, viz. tris(tetrahydrofuran)lithium- $\mu$ -chlorotetrahydrofuran tetrachlorozirconium(IV). This complex was crystallising as large yellow prisms. In both cases the previously known tetrakis(diphenylamido)zirconium, perhaps with the desired chloroamido species, remained in the solution.

Because it is most likely that the origin of LiCl is the reaction where a transition metal-nitrogen bond is formed, we continued the crystallisation of the filtrate obtained after the isolation of  $\text{Li}(\text{thf})_3\text{-}\mu\text{-Cl-ZrCl}_4(\text{thf})$ . When pentane was added to the filtrate new crystals started to grow. The unit-cell measurements showed that

Table 4. Atomic coordinates ( $\times 10^4$ ) for  $\text{Li}(\text{thf})_3\text{-}\mu\text{-Cl-ZrCl}_4(\text{thf})$  (2).

Atom	x	y	z
Zr(1)	2325(1)	4129(1)	8227(1)
Li(1)	-749(5)	3440(3)	6630(4)
Cl(1)	173(1)	4327(1)	7811(1)
Cl(2)	2795(1)	4927(1)	6718(1)
Cl(3)	4379(1)	4113(1)	8777(1)
Cl(4)	1757(1)	3509(1)	9871(1)
Cl(5)	2405(1)	2973(1)	7237(1)
O(11)	2156(2)	5206(1)	9132(2)
C(11)	1656(4)	5918(2)	8726(3)
C(12)	1531(3)	6419(2)	9671(3)
C(13)	2487(3)	6159(2)	10407(3)
C(14)	2512(3)	5316(2)	10250(3)
O(21)	-2404(2)	3681(1)	6708(2)
C(21)	-3379(3)	3163(2)	6747(3)
C(22)	-4250(4)	3451(2)	5951(3)
C(23)	-4053(3)	4295(2)	5969(3)
C(24)	-2854(4)	4406(2)	6414(4)
O(31)	-322(2)	3596(2)	5183(2)
C(31)	749(5)	3902(4)	4778(4)
C(32)	906(5)	3637(4)	3716(5)
C(33)	-58(4)	3085(3)	3524(4)
C(34)	-974(4)	3289(2)	4302(3)
O(41)	-644(2)	2420(1)	7097(2)
C(41)	-623(4)	2192(2)	8183(3)
C(42)	-396(6)	1359(2)	8201(4)
C(43)	-648(6)	1105(2)	7093(4)
C(44)	-331(4)	1782(2)	6449(3)

these crystals were tetrakis(diphenylamido)zirconium complex.<sup>10</sup>

The crystal structure of  $[\text{Li}(\text{thf})_4][\text{ZrCl}_5(\text{thf})]$  consists of a distorted tetrahedral  $\text{Li}(\text{thf})_4^+$  cation and an octahedral  $\text{ZrCl}_5(\text{thf})^-$  anion (Fig. 1). The axial chloride ion [Cl(5)] has clearly the shortest bond to zirconium, 2.400(2) Å, while the other distances vary between 2.444(2) Å [Zr(1)-Cl(1)] and 2.453(2) Å [Zr(1)-Cl(3)] (Table 5). These Zr-Cl distances are very close to those reported for 1:4 tetrahydrofuran adduct of dimeric *trans*-1,2-cyclohexanediol zirconium trichloro complex, where

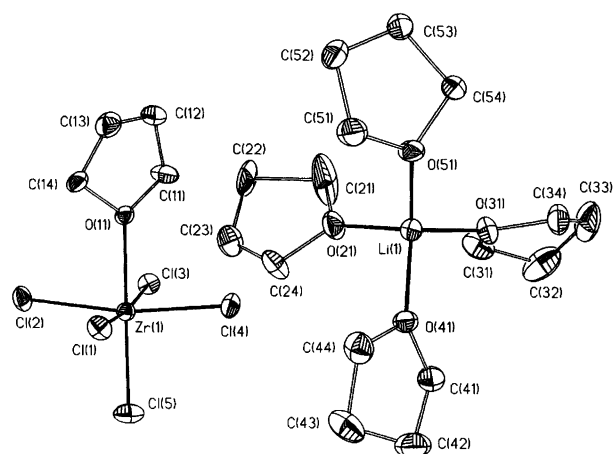


Fig. 1. A perspective view of  $[\text{Li}(\text{thf})_4][\text{ZrCl}_5(\text{thf})]$  showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

**Table 5.** Selected bond lengths (in Å) and angles (in °) in [Li(thf)<sub>4</sub>][ZrCl<sub>5</sub>(thf)] (1).

Zr(1)–Cl(1)	2.444(2)	Zr(1)–Cl(2)	2.444(2)
Zr(1)–Cl(4)	2.444(2)	Zr(1)–Cl(3)	2.453(2)
Zr(1)–Cl(5)	2.400(2)	Zr(1)–O(11)	2.248(4)
Li(1)–O(21)	1.925(10)	Li(1)–O(31)	1.929(11)
Li(1)–O(41)	1.933(10)	Li(1)–O(51)	1.904(10)
Cl(1)–Zr(1)–Cl(2)	89.19(6)	Cl(1)–Zr(1)–Cl(3)	172.13(5)
Cl(1)–Zr(1)–Cl(4)	89.86(6)	Cl(1)–Zr(1)–Cl(5)	94.49(6)
Cl(2)–Zr(1)–Cl(3)	89.90(5)	Cl(2)–Zr(1)–Cl(4)	169.28(6)
Cl(2)–Zr(1)–Cl(5)	95.83(7)	Cl(3)–Zr(1)–Cl(4)	89.59(6)
Cl(3)–Zr(1)–Cl(5)	93.38(6)	Cl(4)–Zr(1)–Cl(5)	94.89(7)
O(11)–Zr(1)–Cl(1)	86.03(10)	O(11)–Zr(1)–Cl(2)	84.82(10)
O(11)–Zr(1)–Cl(3)	86.10(10)	O(11)–Zr(1)–Cl(4)	84.46(10)
O(11)–Zr(1)–Cl(5)	179.17(10)	O(21)–Li(1)–O(31)	106.5(5)
O(21)–Li(1)–O(41)	103.3(5)	O(21)–Li(1)–O(51)	108.7(5)
O(31)–Li(1)–O(41)	107.0(5)	O(31)–Li(1)–O(51)	112.3(5)
O(41)–Li(1)–O(51)	118.1(5)		

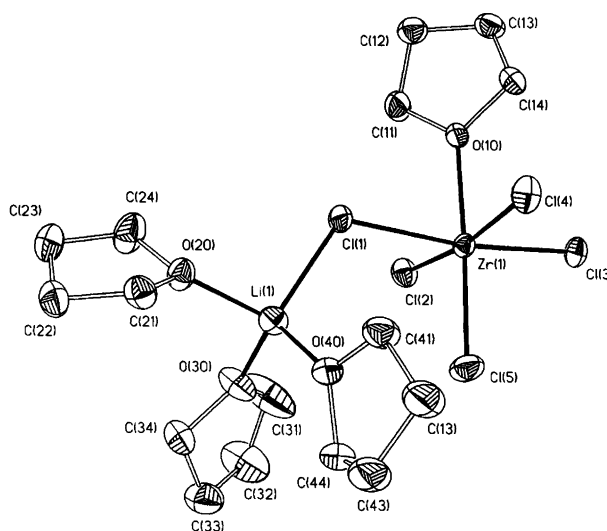
**Table 6.** Selected bond lengths (in Å) and angles (in °) in and Li(thf)<sub>3</sub>-μ-Cl-ZrCl<sub>4</sub>(thf) (2).

Zr(1)–Cl(1)	2.5134(9)	Zr(1)–Cl(2)	2.4309(10)
Zr(1)–Cl(3)	2.4225(9)	Zr(1)–Cl(4)	2.4371(10)
Zr(1)–Cl(5)	2.3979(10)	Zr(1)–O(11)	2.230(2)
Li(1)–Cl(1)	2.398(6)	Li(1)–O(21)	1.925(6)
Li(1)–O(31)	1.911(6)	Li(1)–O(41)	1.901(6)
Cl(1)–Zr(1)–Cl(2)	88.42(4)	Cl(1)–Zr(1)–Cl(3)	171.41(3)
Cl(1)–Zr(1)–Cl(4)	88.83(4)	Cl(1)–Zr(1)–Cl(5)	92.83(3)
Cl(2)–Zr(1)–Cl(3)	90.97(4)	Cl(2)–Zr(1)–Cl(4)	171.17(3)
Cl(2)–Zr(1)–Cl(5)	94.48(4)	Cl(3)–Zr(1)–Cl(4)	90.49(4)
Cl(3)–Zr(1)–Cl(5)	95.76(4)	Cl(4)–Zr(1)–Cl(5)	94.04(4)
O(11)–Zr(1)–Cl(1)	84.37(6)	O(11)–Zr(1)–Cl(2)	85.74(6)
O(11)–Zr(1)–Cl(3)	87.04(6)	O(11)–Zr(1)–Cl(4)	85.64(6)
O(11)–Zr(1)–Cl(5)	177.19(6)	O(21)–Li(1)–Cl(1)	104.1(3)
O(31)–Li(1)–Cl(1)	112.8(3)	O(41)–Li(1)–Cl(1)	113.7(3)
O(21)–Li(1)–O(31)	105.6(3)	O(21)–Li(1)–O(41)	104.7(3)
O(31)–Li(1)–O(41)	114.7(3)	Li(1)–Cl(1)–Zr(1)	117.16(14)

they range between 2.412(2) and 2.466(2) Å.<sup>11</sup> The octahedron in 1 is completed with an oxygen atom from the tetrahydrofuran molecule. O–Zr–Cl angles containing the equatorial chloride ions are significantly smaller, between 84.26(10) and 86.10(10)°, than the Cl–Zr–Cl angles involving the axial chloride ions, which vary between 93.38(6) and 95.83(7)°. The ZrCl<sub>5</sub>(thf)<sup>−</sup> anion is very similar to the one in [(thf)<sub>3</sub>Mg(μ-Cl)<sub>3</sub>Mg(thf)<sub>3</sub>][TiCl<sub>5</sub>(thf)].<sup>12</sup>

The cation part reveals distortion: tetrahedral O–Li–O angles vary from 106.5(5) to 118.1(5) in O(21)–Li(1)–O(31) and O(51)–Li(1)–O(41). Li–O distances vary between 1.904(10) and 1.933(10) Å in Li(1)–O(51) and Li(1)–O(41) bonds, respectively. A similar Li(thf)<sub>4</sub><sup>+</sup> unit has been found as a counterion in various compounds, such as in tetrakis(tetrahydrofuran)lithium pentacopperhexaphenyl<sup>13</sup> and tetrakis(tetrahydrofuran)-lithium bis(tris(trimethylsilyl)methyl)lithium.<sup>14</sup>

In Li(thf)<sub>3</sub>-μ-Cl-ZrCl<sub>4</sub>(thf) the coordination numbers of both metals are maintained, viz. 4 for lithium and 6 for zirconium (Fig. 2). All the bond lengths and angles, except those involving the bridging chloride ion, are similar to those found in compound 1 (Table 6). Bridging

**Fig. 2.** A perspective view of Li(thf)<sub>3</sub>-μ-Cl-ZrCl<sub>4</sub>(thf) showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

chloride ion has the longest bond to zirconium, 2.5134(9) Å. The Li(1)–Cl(1) distance is 2.398(6) Å and the Li(1)–Cl(1)–Zr(1) angle is 117.16(14).

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