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Tetrakis(tetrahydrofuran-*κO*)lithium *mer*-tris(carbazolyl-*κN*)-*trans*-dichloro(tetrahydrofuran-*κO*)zirconate

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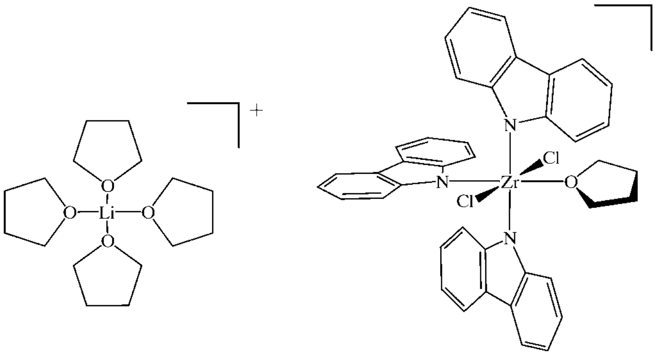
In the title compound, $[Li(C_4H_8O)_4][ZrCl_2(C_{12}H_8N)_3(C_4H_8O)]$, the environment of the Zr atom is pseudo-octahedral, with the three carbazolyl ligands in a *mer* configuration. The counter-ion of the zirconium complex is composed of an Li atom surrounded by four tetrahydrofuran (THF) molecules. The THF molecule attached to the Zr atom is disordered over two sites, as are two of the THF molecules in the lithium moiety. All bond distances and angles are consistent with those in complexes with similar structural entities. The Zr—N bond distances are 2.2185 (18) and 2.167 (3) Å.

Comment

Tris-amide complexes of transition metals show a wide and varied reactivity, and the synthesis and exploration of this class of compound have been the focus of considerable research in recent years in the inorganic community (Cummins *et al.*, 1988, 1991; Cummins, 1998*a*; Yandulov & Schrock, 2002). These studies have used electronically hard ligands, often for the formation of low-coordinate metal complexes, with a view to small-molecule activation (Cummins, 1998*a*,*b*). The merit of the study of complexes of this type has been demonstrated by the catalytic reduction of N_2 to NH_3 (Yandulov & Schrock, 2002, 2003). Recently, complexes with softer non-innocent ligands have been reported (Nygren *et al.*, 2003, 2004; Tanski & Parkin, 2003).

Structurally characterized carbazolyl complexes of transition metals that are σ-bound are rare (Lopez *et al.*, 2002); most of the known examples (Riley *et al.*, 1998, 1999, 2001) are for groups 4B and 5B. In most previous reports of group 4B metal complexes containing carbazolyl ligands, the metal center is surrounded by other nitrogen-containing ligands, such as dimethylamine (Riley *et al.*, 1999, 2001).

The molecular structure of the zirconium moiety of the title compound, (I), is shown in Fig. 1. Examination of the Cambridge Structural Database (CSD; Allen, 2002; Bruno *et al.*, 2002) revealed that the Zr—N bond lengths [mean Zr—N = 2.202 (3) Å; Table 1] of the carbazolyl ligands in (I) are well within the range of normal Zr—N bond lengths (mean Zr—N = 2.241 Å) reported in the literature. The Zr—Cl bond lengths are also well within the typical range (2.287–2.734 Å) reported for the first coordination sphere of zirconium consisting of two Cl atoms, three N atoms and one O-containing ligand. This search also revealed that the first coordination sphere of zirconium, consisting of three N atoms, one O atom and two Cl atoms, is rare in the structural chemistry of group 4B metals, with only eight examples in the database.



(I)

In the tetrahydrofuran (THF) molecule (Fig. 2) that ligates the zirconium center, atoms C20 and C20*A* are disordered over two sites, with relative occupancies of ~0.4 and ~0.6. Similarly, in the $Li(THF)_4$ moiety, the THF molecule containing atoms C25–C28, and the symmetry-generated THF molecule, are disordered over two sites, hereafter termed the THF and THF′ molecules, where the prime denotes a separate molecule with fractional population. The disorders in the C25 and C28 positions were treated identically, *i.e.* as a group, and the disorders in the C26 and C27 positions were treated in a similar manner. Atoms C25 and C28, and C25′ and C28′, were modeled with opposing populations, leading to occupancies of ~0.6 and ~0.4, respectively, for both atom sets. Atoms C26 and C27 were also modeled as being distributed over two sites, giving the pairs C26/C26′ and C27/C27′. The occupancies in this case are 0.5 for both sites of both atom pairs. The THF molecule composed of atoms O3 and C25–C28 has a bent conformation, the C25—C26—C27—C28 torsion angle being 4 (2)°, whereas for the second component of the disordered model, THF′, the torsion angle is 36 (3)°. These torsion angles are well within the normal range for THF coordinated to a metal center, as shown by a search of the CSD. For this torsion angle, 94.9% of the reported angles lie between +40 and −40° [mean 0.487 (8)°]. Although this solution may not be a perfect disorder model, it is the best fit given the quality of the data.

Recently, we reported the crystal structure of the related potassium salt (tetrahydrofuran)potassium *mer*-tris(carbazolyl)-*trans*-dichloro(tetrahydrofurano)zirconate (Nygren *et al.*, 2003). The *trans*-carbazolyl ligands in (I) deviate from linearity [167.49 (9)°] to a greater extent than those in the

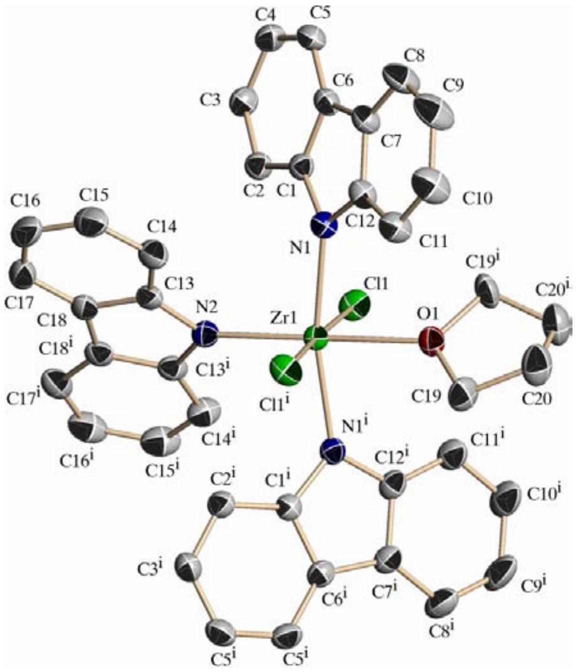


Figure 1
A view of the structure of the anion of (I), showing the atomic numbering scheme. All H atoms have been omitted for clarity, and only one of the disordered positions for each of atoms C20 and C20′ is shown. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. [Symmetry code: (i) $-x, y, \frac{3}{2} - z$.]

corresponding potassium complex [171.90 (7)°]. However, the Cl—Zr—Cl angle is closer to linearity [176.08 (3)°] in (I) than in the potassium analog [171.38 (2)°]. In (I), there is very little interaction between the tetrakis(tetrahydrofuran)lithium moiety of the structure and the zirconium fragment. The closest contact distance between the carbazolyl ligands and the cation is ~4.44 Å. By contrast, in the potassium complex, the cation is bound to two of the carbazolyl ligands in η^2 and η^6 fashions. This interaction, however, has very little effect on the structure of the zirconium anion. A slight difference may be seen in the intramolecular angles. The *cis*-carbazolyls that are most affected by the presence of the cation differ in their N—Zr—N angles by 3.03° [96.26 (5) and 93.23 (7)° for lithium and potassium, respectively]. Further comparison of the structures of the anions in the two structures shows that the type of cation has little influence on the overall anion structure. Given the close coordination of the K(THF) ion to the Zr complex, this result is surprising. However, the site between the rings that is occupied by the K atom is occupied by a THF moiety of the Li(THF)$_4$ cation in (I).

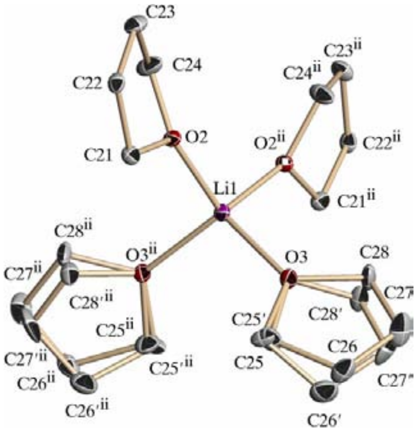


Figure 2
A view of the structure of the anion of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (ii) $1 - x, y, \frac{3}{2} - z$.]

Experimental

Treatment of a suspension of $ZrCl_4$ (0.153 g, 0.656 mmol) in THF, chilled to 195 K, with a solution of lithiated carbazole (0.500 g, 2.00 mmol) in THF, previously formed by deprotonation of carbazole with a fourfold molar excess of lithium hydride, resulted in a reaction that, on warming to room temperature, afforded a yellow solution. After filtration and removal of solvent, a yellow powder was recovered. THF was added to a small portion of the yellow powder until a saturated solution resulted and, over a period of a week, large crystals grew from the recrystallization solution. The compound has been characterized by one- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy at variable temperatures in solution. The spectroscopic data fully support the formation of this compound.

Crystal data

$[Li(C_4H_8O)_4][ZrCl_2(C_{12}H_8N)_3(C_4H_8O)]$
$M_r = 1028.16$
Monoclinic, $C2/c$
$a = 14.984$ (5) Å
$b = 27.435$ (9) Å
$c = 13.574$ (4) Å
$\beta = 113.220$ (5)°
$V = 5128$ (3) Å^3
$Z = 4$

$D_x = 1.332$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 112 reflections
$\theta = 2.7$–26.1°
$\mu = 0.37$ mm^{-1}
$T = 173$ (2) K
Block, yellow
0.22 × 0.19 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.946$, $T_{max} = 0.946$
24 554 measured reflections

5069 independent reflections
4128 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 26.1°$
$h = -18 \rightarrow 18$
$k = -33 \rightarrow 33$
$l = -16 \rightarrow 16$

Table 1
Selected geometric parameters (Å, °).

Li1—O2	1.939 (4)	O1—Zr1	2.261 (2)
Li1—O3	1.952 (4)	Zr1—N1	2.2185 (18)
N2—Zr1	2.167 (3)	Zr1—Cl1	2.4488 (9)
N2—Zr1—N1^{i}	96.26 (4)	Cl1—Zr1—Cl1^{i}	176.07 (3)
N1—Zr1—N1^{i}	167.49 (9)		
C25—C26—C27—C28	−4 (2)	C25′—C26′—C27′—C28′	−36 (3)

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.07$
5069 reflections
357 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 5.9992P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

All H atoms were introduced at calculated positions and treated by applying a riding model [$U_{iso}(H) = 1.2U_{eq}(C)$, and C—H = 0.99 ($CH_2$) and 0.95 Å (aromatic)].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1141). Services for accessing these data are described at the back of the journal.

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