

Lisette Hernández,^a Soraya Taboada,^a Lindora D'Ornelas,^a Teresa González^b and Reinaldo Atencio^{b*}

^aFacultad de Ciencias, Universidad Central de Venezuela, Apartado 47102, Caracas 1020-A, Venezuela, and ^bCentro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

Correspondence e-mail: ratencio@ivic.ve

Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.064
wR factor = 0.213
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(3,5-Dimethylpyrazole)[hydridotris(3,5-dimethylpyrazol-1-yl)borate]lithium 3,5-dimethylpyrazole solvate

In the title compound, $[\text{Li}(\text{C}_{15}\text{H}_{22}\text{BN}_6)(\text{C}_5\text{H}_8\text{N}_2)] \cdot \text{C}_5\text{H}_8\text{N}_2$, the lithium ion shows a LiN_4 distorted tetrahedral geometry with a tridentate TpMe_2 [$\text{TpMe}_2 = \text{tris}(\text{dimethylpyrazolyl})\text{borate}$] ligand and one 3,5-dimethylpyrazole molecule. A clathrated 3,5-dimethylpyrazole molecule appears to be attached to the Li complex through $\text{N}-\text{H} \cdots \text{N}$, $\text{N}-\text{H} \cdots \pi$ and $\pi-\pi$ interactions. The crystal packing is otherwise dominated by hydrophobic methyl–methyl interactions.

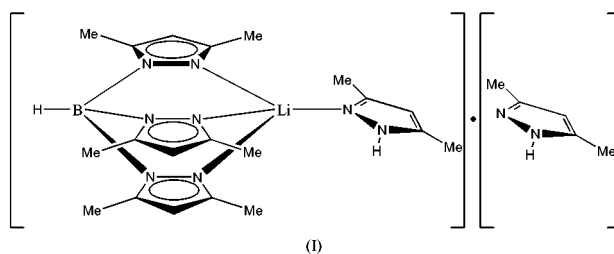
Received 2 June 2004

Accepted 10 June 2004

Online 26 June 2004

Comment

Trofimenko's tris(pyrazolyl)borate ligands (Tp) have been extensively used in the synthesis of metal-containing complexes (Trofimenko, 1993). They have played a prominent role in modern coordination chemistry, in particular, with Tp derivatives attached to an alkali metal. These ' TpM ' ($M =$ alkali metal) moieties are frequently used due to their potential as ligand transfer agents (Trofimenko, 1967). However, from the structural point of view, these salts have received little attention, as suggested from the very low number of crystal structures present in the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002). The majority of such structural studies have been centered on potassium and sodium compounds, and only two of them have been dedicated to lithium derivatives. The first is lithium phenyltris(3-*tert*-butylpyrazolyl)borate, $([\text{PhTp}^t\text{Bu}]\text{Li})$ (Kisko *et al.*, 1999), where the ligand exhibits an asymmetric tridentate coordination to the lithium center, with two long $\text{Li}-\text{N}$ distances [average $1.978(3) \text{ \AA}$] and one significantly shorter [$1.934(3) \text{ \AA}$]. The second lithium derivative is the centrosymmetric dimer $([\text{FcTp}]\text{Li})_2 \cdot 4\text{C}_6\text{H}_6$ (Fc = ferrocenyl; Guo *et al.*, 2001), in which each Li atom is bound to two Tp ligands. In this entity, the $\text{Li}-\text{N}$ distances [average $2.052(4) \text{ \AA}$] are longer than those found in the $([\text{PhTp}^t\text{Bu}]\text{Li})$ complex. Here, the preparation and structural characterization of the first hydridotris(pyrazolyl)borate derivative, (I) $\{[\text{TpMe}_2]\text{Li}(\text{pz})\} \cdot (\text{pz})$ [$\text{TpMe}_2 = \text{tris}(\text{dimethylpyrazolyl})\text{borate}$, $\text{pz} = 3,5\text{-dimethylpyrazole}$], (I), is described.



(I)

The asymmetric unit of (I) contains one $[\text{TpMe}_2]\text{Li}(\text{pz})$ complex and one clathrated 3,5-dimethylpyrazole molecule.

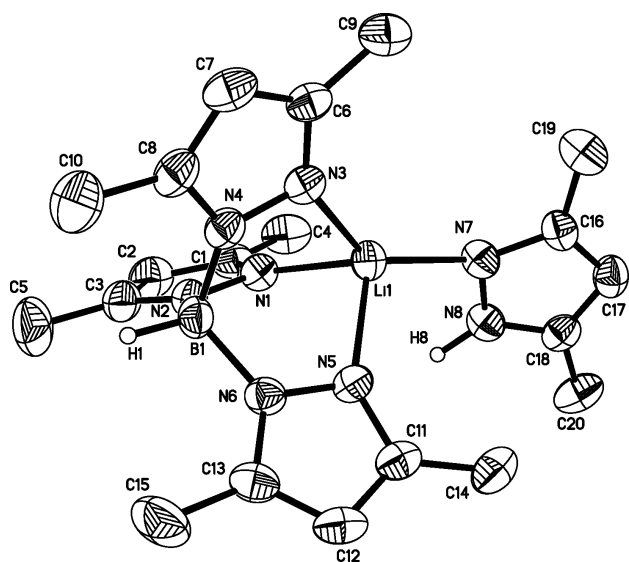


Figure 1
Displacement ellipsoid representation of the $[\text{TpMe}_2]\text{Li}(\text{pz})$ complex, showing anisotropic displacement parameters at the 35% probability level (the 3,5-dimethylpyrazole solvent molecule and most H atoms have been omitted for clarity).

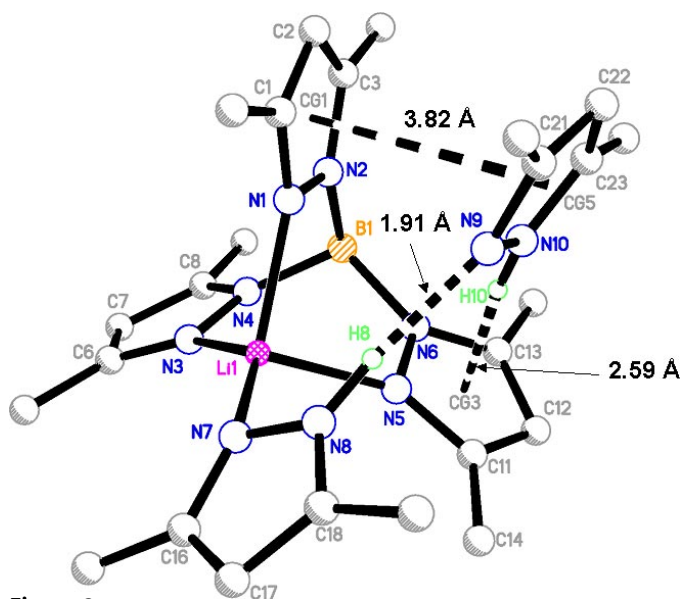


Figure 2
View of the interaction between the clathrated 3,5-dimethylpyrazole molecule and the $[\text{TpMe}_2]\text{Li}(\text{pz})$ complex.

The lithium ion shows a LiN_4 distorted tetrahedral geometry, in which three N atoms belong to the tridentate TpMe_2 ligand and the remaining position is occupied by a 3,5-dimethylpyrazole molecule coordinated through one of its N atoms (Fig. 1). As the $\text{N}_{\text{Tp}}-\text{Li}-\text{N}_{\text{Tp}}$ bite angles of the TpMe_2 ligand span a narrow range $[92.1(2)-94.7(2)^\circ]$, the bond angles $\text{N}_{\text{Tp}}-\text{Li}-\text{N}_{\text{pz}}$ involving the N atom of the pz ligand cover a wider range $[110.1(2)-138.3(3)^\circ]$. All the $\text{Li}-\text{N}$ bond lengths, however, are only marginally different from each other [range 2.045(5)–2.081(5) Å], and they are longer than those observed for the $[\text{PhTp}^t\text{Bu}]\text{Li}$ complex (Kisko *et al.*, 1999), but compare well with those reported for the compound $([\text{FcTp}]\text{Li})_2\cdot 4\text{C}_6\text{H}_6$ (Guo *et al.*, 2001).

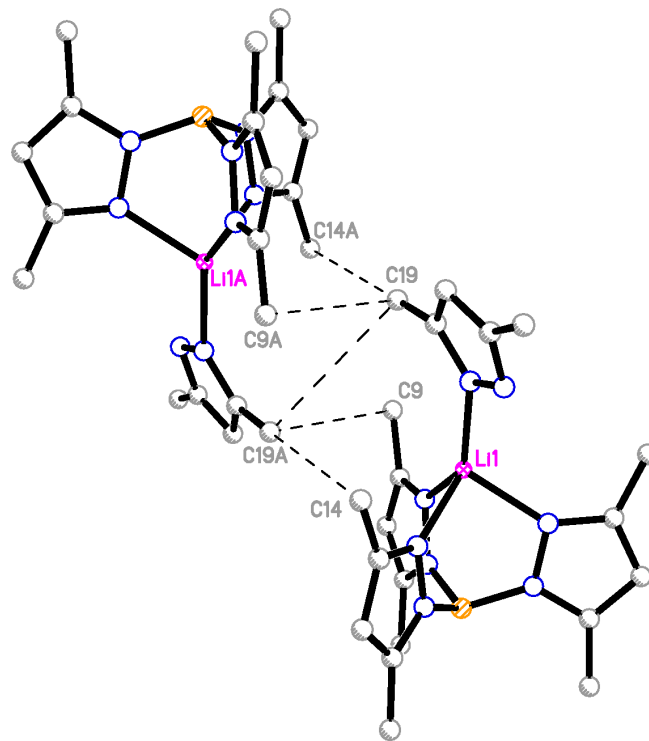


Figure 3
The dimeric moiety in the crystal structure, which is generated by hydrophobic methyl–methyl interactions. [Symmetry code: (A) $-x, -y, -z$.]

The clathrated pz molecule appears to be linked to the Li complex through three different interactions (Fig. 2). First, it forms an $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond with one N atom of the coordinated pz molecule [$\text{N}8\cdots\text{N}9 = 2.897(4)$ Å and $\text{N}8-\text{H}8\cdots\text{N}9 = 173^\circ$]. Second, the $\text{N}10-\text{H}10$ moiety is oriented just to one face of the $\text{N}5/\text{C}11/\text{C}12/\text{C}13/\text{N}6$ pyrazole ring, allowing an $\text{N}-\text{H}\cdots\pi$ interaction ($\text{N}10\cdots\text{Cg}3 = 2.59$ Å and $\text{N}10-\text{H}10\cdots\text{Cg}3 = 162^\circ$, where $\text{Cg}3$ is the centroid of the $\text{N}5/\text{C}11/\text{C}12/\text{C}13/\text{N}6$ ring). Finally, a $\pi-\pi$ interaction between the $\text{N}5/\text{C}11/\text{C}12/\text{C}13/\text{N}6$ ring and one pyrazolate group ($\text{N}1/\text{C}1/\text{C}2/\text{C}3/\text{N}2$) is also observed ($\text{Cg}3\cdots\text{Cg}1 = 3.82$ Å, where $\text{Cg}1$ is the centroid of the $\text{N}1/\text{C}1/\text{C}2/\text{C}3/\text{N}2$ ring).

The crystal packing is otherwise dominated by hydrophobic methyl–methyl interactions. The most striking one involves the methyl substituent of the coordinated pz molecule, which is accommodated between two pyrazolate ligand and one methyl group of a coordinated pz belonging to an adjacent complex. These methyl–methyl interactions lead to the formation of a supramolecular dimer that adopts a centrosymmetric head-to-tail configuration (Fig. 3), with $\text{C}(\text{methyl})\cdots\text{C}(\text{methyl})$ short contacts [range 3.70(1)–4.17(1) Å].

Experimental

Compound (I) was synthesized by mixing the potassium salt $\text{K}[\text{TpMe}_2]$ (1 g, 3 mmol) and a solution (3.1 ml) of butyllithium (1 M) in toluene at approximately 278 K. Evaporation of the mixture produced a white solid in good yield (90%). Recrystallization of this solid from pentane produced colorless crystals of (I).

Crystal data

[Li(C₁₅H₂₂BN₆)(C₅H₈N₂)]·C₅H₈N₂
M_r = 496.40
 Triclinic, *P* $\bar{1}$
a = 10.5773 (13) Å
b = 17.629 (3) Å
c = 8.0759 (9) Å
 α = 90.228 (11)°
 β = 102.521 (10)°
 γ = 81.179 (11)°
V = 1452.0 (3) Å³

Z = 2
D_x = 1.135 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 22 reflections
 θ = 20.8–37.1°
 μ = 0.07 mm⁻¹
T = 298 (2) K
 Prism, colorless
 0.60 × 0.40 × 0.20 mm

Data collection

Rigaku AFC-7S diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.934, *T_{max}* = 0.989
 5421 measured reflections
 5115 independent reflections
 3500 reflections with *I* > 2σ(*I*)

R_{int} = 0.018
 θ_{max} = 25.0°
h = 0 → 12
k = -20 → 20
l = -9 → 9
 3 standard reflections
 every 150 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.064
wR(*F*²) = 0.213
S = 1.04
 5115 reflections
 335 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1072P)^2 + 0.8283P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.010 (3)

Table 1

Selected geometric parameters (Å, °).

Li1–N1	2.045 (5)	Li1–N3	2.072 (5)
Li1–N7	2.068 (5)	Li1–N5	2.081 (5)
N1–Li1–N7	118.1 (2)	N1–Li1–N5	93.7 (2)
N1–Li1–N3	92.1 (2)	N7–Li1–N5	110.1 (2)
N7–Li1–N3	138.3 (3)	N3–Li1–N5	94.7 (2)

The H atoms on the N and B atoms were found in a difference map, while the C-bound H atoms were positioned geometrically (C–H = 0.93 Å). All H atoms were refined using a riding model, with *U*(H) = 1.2 (1.5 for methyl H atoms) times *U_{eq}*(parent atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

The financial support provided by CDCH from Universidad Central de Venezuela and FONACIT-MCT (project Nos. 03-12-3904-2000 and LAB-199700821, respectively), is gratefully acknowledged.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Bruker (1998). *SHELXTL-NT*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Guo, S., Peters, F., Frabizi de Biani, F., Bats, J. W., Herdtweck, E., Zanello, P. & Wagner, M. (2001). *Inorg. Chem.* **40**, 4928–4936.
 Kisko, J. L., Hascall, T., Kimblin, C. & Parkin, G. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1929–1935.
 Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Trofimenko, S. (1967). *J. Am. Chem. Soc.* **89**, 6288–6294.
 Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.