



Crystal structure of a three-coordinate lithium complex with monodentate phenyloxazoline and hexamethyldisilylamide ligands

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Received 6 February 2024

Accepted 8 May 2024

Edited by G. Ferrence, Illinois State University, USA

Keywords: 4,4-dimethyl-2-phenyl-2-oxazoline; trigonal planar; lithium(I); hexamethyldisilylamide; crystal structure.

CCDC reference: 2354028

Supporting information: this article has supporting information at journals.iucr.org/e

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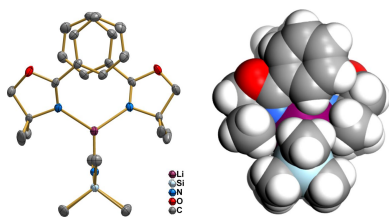
The reaction of lithium hexamethyldisilylamide, $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}]$ (LiHMDS), with 4,4-dimethyl-2-phenyl-2-oxazoline (Phox, $\text{C}_{11}\text{H}_{13}\text{NO}$) in hexane produced colourless crystals of bis(4,4-dimethyl-2-phenyl-2-oxazoline- κN)(hexamethyldisilylamido- κN)lithium, $[\text{Li}(\text{C}_6\text{H}_4\text{N}_2\text{Si}_2)(\text{C}_{11}\text{H}_{13}\text{NO})_2]$ or $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$ in high yield (89%). Despite the 1:1 proportion of the starting materials in the reaction mixture, the product formed with a 1:2 amide:oxazoline ratio. In the unit cell of the $C2/c$ space group, the neutral molecules lie on twofold rotation axes coinciding with the Li–N(amide) bonds. The lithium(I) centre adopts a trigonal–planar coordination geometry with three nitrogen donor atoms, one from the HMDS anion and two from the oxazolines. All ligands are monodentate. In the phenyloxazoline units, the dihedral angle defined by the five-membered heterocyclic rings is $35.81(5)^\circ$, while the phenyl substituents are approximately face-to-face, separated by $3.908(5) \text{ \AA}$. In the amide, the methyl groups assume a nearly eclipsed arrangement to minimize steric repulsion with the analogous substituents on the oxazoline rings. The non-covalent interactions in the solid-state structure of $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$ were assessed by Hirshfeld surface analysis and fingerprint plots. This new compound is attractive for catalysis due to its unique structural features.

1. Chemical context

Oxazolines are a family of cyclic aminoethers characterized by five-membered heterocyclic rings containing one unsaturation. They can be prepared using various methods that typically involve the cyclization of an aminoalcohol as a general process (Mulahmetovic & Hargaden, 2019). These compounds have been widely used in synthesis, catalysis, and as proligands in coordination chemistry (Connon *et al.*, 2021; Liu *et al.*, 2016; Rasappan *et al.*, 2008; McManus & Guiry, 2004; Gómez *et al.*, 1999).

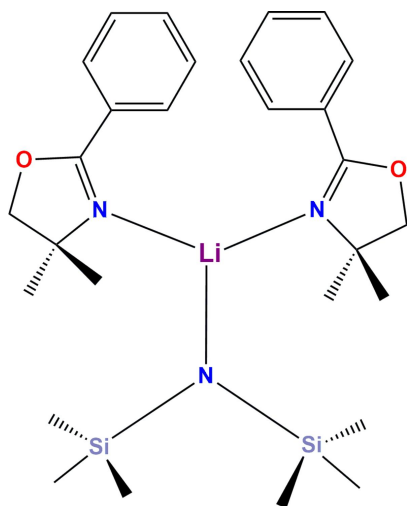
Metal complexes containing monodentate, *N*-donor monooxazoline ligands are reasonably frequent in the solid state (Huang *et al.*, 2014; Del Río & Gossage, 2009; Barclay *et al.*, 2003; Valk *et al.*, 1994; Michelin *et al.*, 1991). In the case of 2-phenyloxazolines (Phox), which are of interest to this work, the chelating behaviour is more common and involves a second donor atom, generally N, O, S or Se, in the *ortho* position of the aromatic ring (Volpe *et al.*, 2010; Bottini *et al.*, 2010). Phox complexes of *d*-block metals have been studied as catalysts (Abu-Elfotouh, 2017; Bagherzadeh *et al.*, 2008; Kandasamy *et al.*, 2004).

Lithium hexamethyldisilylamide (LiHMDS), in turn, was first crystallographically characterized as a cyclic, trimeric compound with alternating nitrogen and lithium atoms in a



planar six-membered ring (Mootz *et al.*, 1969). This complex and other bulky $MN(\text{Si}R_3)_2$ bis(trialkylsilyl)amides (M = alkali metal; R = Me, Et, ^iPr , ^tBu , Ph, *etc.*) are widely used in organic synthesis as deprotonating agents due to their low nucleophilicity and strong Brønsted basicity (Neufeld *et al.*, 2016; Tang *et al.*, 2005; Beak *et al.*, 1996), and in coordination chemistry as sterically demanding starting materials to impose low coordination numbers (Mohamed, 2010; Power, 2004). In both fields, the high solubility conferred by the trimethylsilyl substituents in a wide range of non-polar organic solvents is an advantage of working with HMDS^- in synthetic procedures (Ojeda-Amador *et al.*, 2016).

In this paper, we report the synthesis, crystal and molecular structures of the mononuclear, three-coordinate lithium(I) complex $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$ (Phox = 4,4-dimethyl-2-phenyl-2-oxazoline). The product crystallized directly from the reaction mixture at 253 K, following an attempt to deprotonate the oxazoline by reaction between $[\text{LiN}(\text{Si}(\text{CH}_3)_3)_2]$ and Phox in hexane.



2. Structural commentary

The $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$ complex crystallizes in the $C2/c$ space group as a discrete molecular unit with no solvent in the unit cell. The asymmetric unit comprises half of the anionic hexamethyldisilylamide ligand, $\{\text{N}_{0.5}(\text{Si}(\text{CH}_3)_3)\}^{0.5-}$, and one neutral 4,4-dimethyl-2-phenyl-2-oxazoline molecule, both coordinated to the lithium centre solely by the nitrogen atoms. Proper rotation about a twofold axis passing through the $\text{Li}-\text{N1}$ bond (symmetry operation $-x + 1, y, -z + \frac{1}{2}$) leads to the complete, neutral lithium complex molecule. The coordination sphere of lithium(I) presents a trigonal-planar geometry with no deviation from planarity, Fig. 1. In this environment, the two five-membered oxazoline rings (each with a planarity deviation of 0.082°) form a dihedral angle (α) of $35.81(5)^\circ$. At the same time, the distance between the approximately face-to-face phenyl substituents equals $3.908(5)$ Å, Fig. 2.

The $\text{Li}-\text{N}$ bonds are $2.126(2)$ and $1.942(3)$ Å long for the oxazoline and amide ligands, respectively. Such a significant

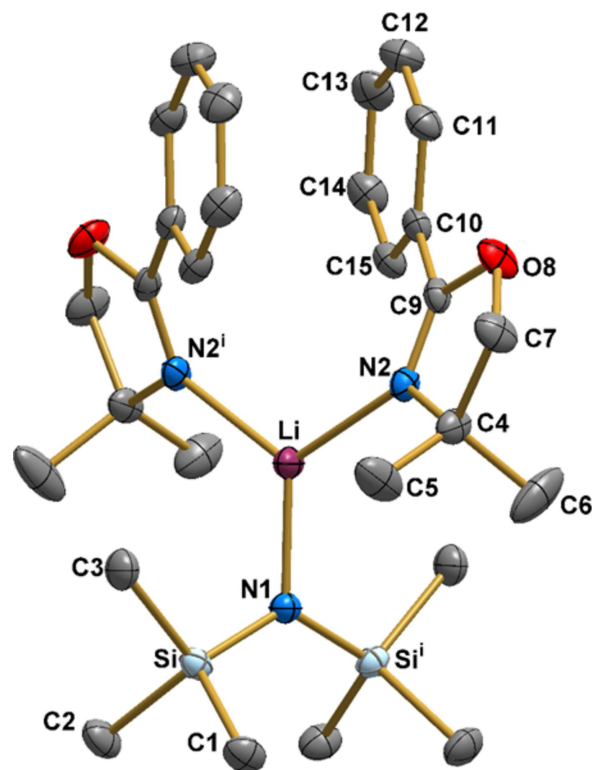


Figure 1

View of the molecular structure of $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$, with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

bond-length variation comes from the stronger interaction of the lithium centre with the anionic amide nitrogen (higher negative density charge) compared to the neutral oxazoline. Similar 0.1 – 0.2 Å bond-distance differences have been used to distinguish ‘ionic’ from ‘dative’ $\text{Li}-\text{N}$ bonds (Henderson *et al.*, 1997; Gregory *et al.*, 1991) and were reported earlier for other mononuclear, trigonal planar Li complexes containing

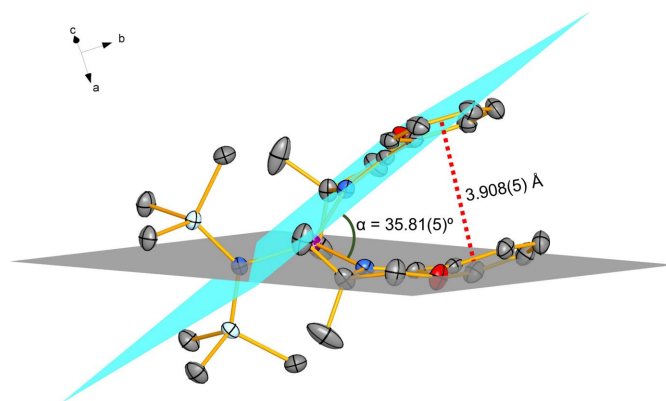


Figure 2

Distance between the phenyl rings (red dashed line) and dihedral angle (α) between the five-membered oxazoline rings. Grey: carbon; red: oxygen; blue: nitrogen; light blue: silicon; purple: lithium. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are excluded for clarity.

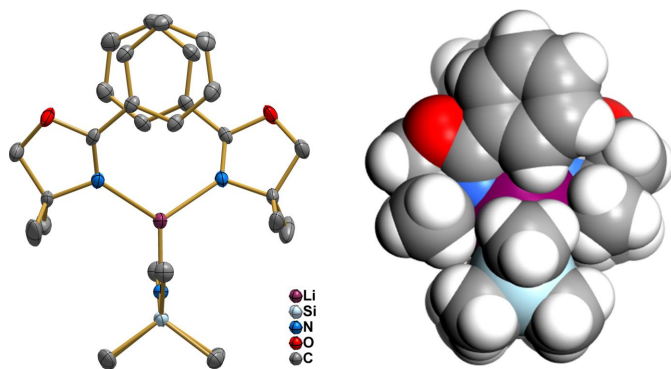


Figure 3 Left: Molecular structure of $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$, showing the eclipsed conformation of the hexamethyldisilylamide ligands. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Right: Space-filling representation of the title compound, emphasizing the efficient shielding of the lithium cation by the methyl and phenyl substituents of the HMDS⁻ and Phox ligands.

an amide ($\text{N}\{\text{SiR}_3\}_2^-$, NArH^-) and a neutral ligand such as sparteine, *N,N,N',N'*-tetramethylethylenediamine, and *N',N'',N''',N''''*-tetramethylethylenediamine (Clark *et al.*, 2009; Henderson *et al.*, 1997; Fjeldberg *et al.*, 1984). The $\text{Li}-\text{N}_{\text{oxazoline}}$ bond is longer than analogous bonds reported for dimeric lithium(I) complexes with bidentate [Jantzi *et al.*, 2006; average 2.044 (3) Å] and tridentate oxazoline ligands [Stol *et al.*, 2005; average 1.996 (3) Å]; the difference can be ascribed to distinct Li^+ coordination numbers and ligands' denticities and bulk. To our knowledge, the title compound is

the first example of a monodentate oxazoline complex of lithium(I) structurally characterized in the solid state.

In $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$, the methyl groups of the hexamethyldisilylamide moieties are nearly eclipsed (Fig. 3), with a dihedral angle of $5.80 (7)^\circ$ between the $\text{C}3-\text{Si}-\text{N}1$ and the $\text{C}3^i-\text{Si}^i-\text{N}1$ planes. Additionally, if one defines a vector connecting the symmetry-related Si and Si^i centres (Randazzo *et al.*, 2006), the relative positions of the $\text{C}3/\text{C}3^i$, $\text{C}2/\text{C}1^i$ and $\text{C}1/\text{C}2^i$ pairs across this vector produce $\text{C}-\text{Si}\cdots\text{Si}^i-\text{C}^i$ torsion angles of $-8.846 (11)$, $-2.52 (7)$ and $-2.52 (7)^\circ$, respectively (average value -4.63°). These figures are close to the 0° value attributed to the eclipsed conformation (Eliel & Wilen, 1994). Small torsion angles also appear in the amide ligand of $[\text{Cs}\{\text{N}(\text{SiMe}_3)_2\}(\text{tmeea})]$ (tmeea = tris[2-(2-methoxyethoxy)ethyl]amine), $[\text{K}\{\text{N}\{\text{SiMe}_3\}_2\}(\text{tBu-C}_6\text{H}_5)_2]$, and $[\text{K}\{\text{N}\{\text{SiMe}_3\}_2\}(\text{Me}_3\text{C}_6\text{H}_3)_2]$, with average values of $-3.81 (4)$, 4.70 and 0.75° respectively (Ojeda-Amador *et al.*, 2016; Randazzo *et al.*, 2006). A larger deviation from 0° appears in $[\text{K}(18\text{-crown-6})][\text{Li}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (mean torsion angle -11.40° ; Davison *et al.*, 2023) and in the polymeric $[\text{K}\{\text{N}\{\text{SiMe}_3\}_2\}(\text{Me}_3\text{Si})_2\text{NLi}]\{\text{Me}_3\text{Si}\}_2\text{NK}\}_\infty$ (-11.94° ; Morris *et al.*, 2007). On the other hand, the methyl groups of unsolvated $\text{K}\{\text{N}\{\text{SiMe}_3\}_2\}$ adopt an intermediate mean torsion angle of 38.29° (Tesh *et al.*, 1990), while in $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}(\text{Me}_6\text{Tren})]$ (Me_6Tren = tris[2-(dimethylamino)ethyl]amine) the average angle is 59.9° , almost exactly the ideal value of 60° for a staggered conformation (Cousins *et al.*, 2010). In the present work, eclipsing implies less repulsion between the bulky methyl groups of both the hexamethyldisilylamide and Phox ligands than in the staggered arrangement.

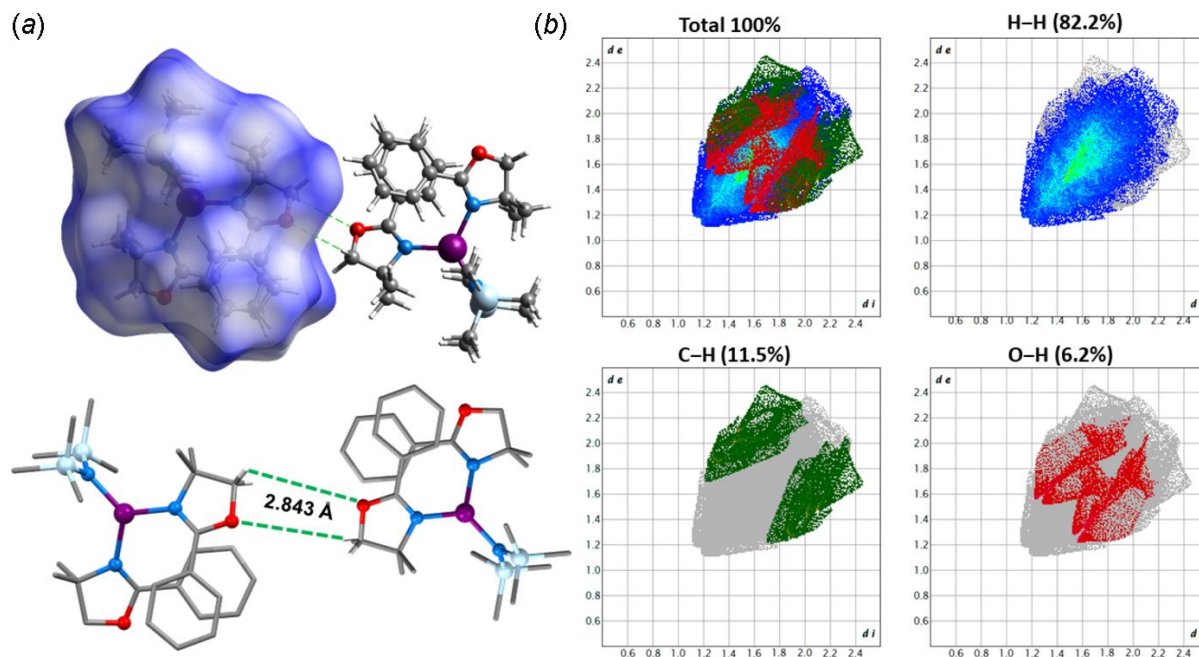


Figure 4 (a) Representation of the Hirshfeld surface for $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$, highlighting the intermolecular $\text{O}\cdots\text{H}$ contacts (green dashed lines) between the oxazoline's methylene moiety and the oxygen atom of the adjacent molecule. Grey: carbon; red: oxygen; blue: nitrogen; light blue: silicon; purple: lithium. Hydrogen atoms are omitted for clarity. (b) Two-dimensional fingerprint plots in the d_{norm} function, generated by mapping, for each d_i , the region between 0.4 and 2.6 Å from the surface to the nearest internal (d_i) and external (d_e) atoms.

3. Supramolecular features

Hirshfeld surface analysis performed with the *CrystalExplorer 21.5* software (Spackman *et al.*, 2021) allowed a comprehensive examination of the non-covalent bonds governing the solid-state structure of $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$. A pivotal aspect of this analysis involves the generation of 2D fingerprint plots (FP), which offer two-dimensional projections of the Hirshfeld surface (Hirshfeld, 1977). This enables meticulous analysis of the non-covalent forces supporting the supramolecular structure by quantifying the percentage contribution of each interaction. For $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$, the percentages of the total surface area corresponding to the $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}$, and $\text{O}\cdots\text{H}$ contacts account for 82.2%, 11.5%, and 6.2%, respectively (Fig. 4). The frail $\text{O}\cdots\text{H}$ contacts occur between the hydrogen atoms of the methylene groups in the oxazoline rings and the oxygen atom of the adjacent molecules at 2.843 Å. Besides those, there is only a weak intramolecular π - π stacking interaction between the aromatic rings of the Phox ligands, as already depicted in Fig. 2, which are 3.908 (5) Å far from one another. There is no classic intra or intermolecular hydrogen bonding in the molecule.

4. Database survey

To the best of our knowledge, this is the first example of a heteroleptic lithium(I)-oxazoline complex in which the Phox ligands are monodentate and the HMDS anion adopts a nearly eclipsed conformation of the methyl groups, giving rise to a trigonal planar coordination environment about the metal. The combination of ten methyl and two phenyl substituents in the ligands efficiently shields the central ion (Fig. 3, right) and prevents significant intermolecular contacts involving the metal.

5. Synthesis and crystallization

The reactions were carried out under dinitrogen (99.999%, Praxair or Air Liquide) using Schlenk techniques. Analytical grade 2-amino-2-methyl-1-propanol, ethyleneglycol, potassium carbonate, glycerol, benzonitrile, *n*-butyl lithium (2.5 mol L⁻¹ solution in hexanes) and hexamethyldisilazane were acquired from commercial sources (Sigma-Aldrich, Merck, Synth) and used without purification. Hexane (Honeywell) was dried by standard methods (Armarego & Perrin, 1997) and distilled under N₂(g) immediately before use. Lithium hexamethyldisilylamide, LiHMDS (Tai *et al.*, 2017), and Phox (Mulahmetovic & Hargaden, 2019) were prepared using procedures adapted from the literature; Phox was distilled twice under vacuum before use. A solution of 0.472 g (2.85 mmol) of LiHMDS in 10 mL of hexane was added slowly to a hexane solution of 0.500 g (2.85 mmol) of Phox at 273 K. The colourless reaction mixture was stirred at room temperature for about 5 h and filtered through Celite. The resulting colourless solution was cooled down to 253 K for two days, after which block-shaped colourless crystals were

Table 1

Experimental details.

Crystal data	
Chemical formula	$[\text{Li}(\text{C}_6\text{H}_{18}\text{NSi}_2)(\text{C}_{11}\text{H}_{13}\text{NO})_2]$
M_r	517.78
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	15.612 (2), 12.7649 (17), 17.180 (4)
β (°)	116.243 (5)
V (Å ³)	3070.9 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.14
Crystal size (mm)	0.50 × 0.44 × 0.28
Data collection	
Diffractometer	Bruker D8 Venture/Photon 100 CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.709, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44358, 3522, 2888
R_{int}	0.078
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.092, 1.04
No. of reflections	3522
No. of parameters	252
No. of restraints	7
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.29, -0.24

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXS2008* (Sheldrick 2008), *SHELXL2018/3* (Sheldrick, 2015), *DIAMOND* (Brandenburg & Putz, 1999), and *Mercury* (Macrae *et al.*, 2020) and *WinGX* (Farrugia, 2012).

isolated by filtration and dried under vacuum. Total yield: 0.621g (85.0%) based on the $[\text{Li}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}(\text{Phox})_2]$ formulation.

6. Refinement

Table 1 summarizes crystal data, data collection, and structure refinement details. The hydrogen atoms were located in difference-Fourier maps and were refined freely, except for the hydrogen atoms attached to C1, C6, C7, C11, C14, and C15 atoms, for which distance restraints (DFIX) were applied.

Acknowledgements

JSCN, EMI, FSS, and JFS thank the Brazilian research agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, grant 314581/2020-0) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes, Financial Code 001) for scholarships and financial support.

Funding information

Funding for this research was provided by: Conselho Nacional de Desenvolvimento Científico e Tecnológico (grant No. 314581/2020-0); Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (grant No. 0347/2021).

References

- Abu-Elfotouh, A. M. (2017). *Tetrahedron Lett.* **58**, 4750–4754.
- Armarego, W. L. F. & Perrin, D. D. (1997). *Purification of Laboratory Chemicals*, 4th ed. United Kingdom: Butterworth–Heinemann.
- Bagherzadeh, M., Latifi, R., Tahsini, L. & Amini, M. (2008). *Catal. Commun.* **10**, 196–200.
- Barclay, T. M., del Río, I., Gossage, R. A. & Jackson, S. M. (2003). *Can. J. Chem.* **81**, 1482–1491.
- Beak, P., Basu, A., Gallagher, D. J., Park, Y. S. & Thayumanavan, S. (1996). *Acc. Chem. Res.* **29**, 552–560.
- Bottini, R. C. R., Gariani, R. A., Cavalcanti, C. O., de Oliveira, F., da Rocha, N. L. G., Back, D., Lang, E. S., Hitchcock, P. B., Evans, D. J., Nunes, G. G., Simonelli, F., de Sá, E. L. & Soares, J. F. (2010). *Eur. J. Inorg. Chem.* **2010**, 2476–2487.
- Brandenburg, K. & Putz, H. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2015). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Clark, N. M., García-Álvarez, P., Kennedy, A. R., O'Hara, C. T. & Robertson, G. M. (2009). *Chem. Commun.* pp. 5835–5837.
- Connon, R., Roche, B., Rokade, B. V. & Guiry, P. J. (2021). *Chem. Rev.* **121**, 6373–6521.
- Cousins, D. M., Davidson, M. G., Frankis, C. J., García-Vivó, D. & Mahon, M. F. (2010). *Dalton Trans.* **39**, 8278–8280.
- Davison, N., Waddell, P. G. & Lu, E. (2023). *J. Am. Chem. Soc.* **145**, 17007–17012.
- Eliel, E. L. & Wilen, S. H. (1994). *Stereochemistry of Organic Compounds*, p. 1197. Hoboken, NJ: Wiley Interscience.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Fjeldberg, T., Hitchcock, P. B., Lappert, M. F. & Thorne, A. J. (1984). *J. Chem. Soc. Chem. Commun.* pp. 822–824.
- Gómez, M., Muller, G. & Rocamora, M. (1999). *Coord. Chem. Rev.* **193–195**, 769–835.
- Gregory, K. P., Schleyer, P., v. R. & Snaith, R. (1991). *Adv. Inorg. Chem.* **37**, 47–142.
- Henderson, K. W., Dorigo, A. E., Liu, Q.-L. & Williard, P. G. (1997). *J. Am. Chem. Soc.* **119**, 49, 11855–11863.
- Hirshfeld, F. L. (1977). *Theor. Chim. Acta*, **44**, 129–138.
- Huang, P., Wang, Y. X., Yu, H. F. & Lu, J. M. (2014). *Organometallics*, **33**, 1587–1593.
- Jantzi, K. L., Guzei, I. A. & Reich, H. J. (2006). *Organometallics*, **25**, 5390–5395.
- Kandasamy, K., Singh, H. B., Butcher, R. J. & Jasinski, J. P. (2004). *Inorg. Chem.* **43**, 5704–5713.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Liu, X., Chen, P. & Wu, F. (2016). *Chin. J. Org. Chem.* **36**, 1797–1804.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- McManus, H. A. & Guiry, P. J. (2004). *Chem. Rev.* **104**, 4151–4202.
- Michelin, R. A., Bertani, R., Mozzon, M., Bombieri, G., Benetollo, F. & Angelici, R. J. (1991). *Organometallics*, **10**, 1751–1757.
- Mohamed, A. H. (2010). *Coord. Chem. Rev.* **254**, 1918–1947.
- Mootz, D., Zinnius, A. & Böttcher, B. (1969). *Angew. Chem.* **81**, 398–399.
- Morris, J. J., Noll, B. C. & Henderson, K. W. (2007). *Acta Cryst.* **E63**, m2477.
- Mulahmetovic, E. & Hargaden, G. C. (2019). *Mini-Rev. Org. Chem.* **16**, 507–526.
- Neufeld, R., Michel, R., Herbst-Irmer, R., Schöne, R. & Stalke, D. (2016). *Chem. A Eur. J.* **22**, 12340–12346.
- Ojeda-Amador, A. I., Martínez-Martínez, A. J., Kennedy, A. R. & O'Hara, C. T. (2016). *Inorg. Chem.* **55**, 5719–5728.
- Power, P. P. (2004). *J. Organomet. Chem.* **689**, 3904–3919.
- Randazzo, J. B., Morris, J. J. & Henderson, K. W. (2006). *Main Group Chem.* **5**, 215–220.
- Rasappan, R., Laventine, D. & Reiser, O. (2008). *Coord. Chem. Rev.* **252**, 702–714.
- Río, I. del & Gossage, R. A. (2009). *Acta Cryst.* **E65**, m103–m104.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Stol, M., Snelders, D. J., de Pater, J. J., van Klink, G. P., Kooijman, H., Spek, A. L. & van Koten, G. (2005). *Organometallics*, **24**, 743–749.
- Tai, O., Hopson, R. & Williard, P. G. (2017). *J. Org. Chem.* **82**, 6223–6231.
- Tang, Y., Zakharov, L. N., Rheingold, A. L. & Kemp, R. A. (2005). *Polyhedron*, **24**, 1739–1748.
- Tesh, K. F., Hanusa, T. P. & Huffman, J. C. (1990). *Inorg. Chem.* **29**, 1584–1586.
- Valk, J. M., Maassarani, F., van der Sluis, P., Spek, A. L., Boersma, J. & van Koten, G. (1994). *Organometallics*, **13**, 2320–2329.
- Volpe, E. C., Manke, D. R., Bartholomew, E. R., Wolczanski, P. T. & Lobkovsky, E. B. (2010). *Organometallics*, **29**, 6642–6652.

supporting information

Acta Cryst. (2024). E80 [https://doi.org/10.1107/S2056989024004237]

Crystal structure of a three-coordinate lithium complex with monodentate phenyloxazoline and hexamethyldisilylamide ligands

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Computing details

Bis(4,4-dimethyl-2-phenyl-2-oxazoline- κ N)(hexamethyldisilylamido- κ N)lithium

Crystal data

[Li(C₆H₁₈NSi₂)(C₁₁H₁₃NO)₂]

$M_r = 517.78$

Monoclinic, *C2/c*

$a = 15.612$ (2) Å

$b = 12.7649$ (17) Å

$c = 17.180$ (4) Å

$\beta = 116.243$ (5)°

$V = 3070.9$ (9) Å³

$Z = 4$

$F(000) = 1120$

$D_x = 1.120$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9967 reflections

$\theta = 2.9$ – 27.7 °

$\mu = 0.14$ mm⁻¹

$T = 100$ K

Parallelepiped, colourless

$0.50 \times 0.44 \times 0.28$ mm

Data collection

Bruker D8 Venture/Photon 100 CMOS diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.4167 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.709$, $T_{\max} = 0.746$

44358 measured reflections

3522 independent reflections

2888 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.9$ °

$h = -20 \rightarrow 20$

$k = -16 \rightarrow 16$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.092$

$S = 1.04$

3522 reflections

252 parameters

7 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 1.6645P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.29$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Li	0.500000	0.4524 (2)	0.250000	0.0204 (6)
Si	0.57050 (2)	0.24246 (3)	0.21203 (2)	0.01863 (10)
N1	0.500000	0.30027 (11)	0.250000	0.0182 (3)
N2	0.37995 (7)	0.54071 (8)	0.16385 (7)	0.0192 (2)
O8	0.28490 (7)	0.67752 (8)	0.09434 (6)	0.0283 (2)
C1	0.50526 (11)	0.15288 (11)	0.11638 (9)	0.0283 (3)
C2	0.66991 (11)	0.15862 (12)	0.29266 (10)	0.0317 (3)
C3	0.62947 (10)	0.34286 (12)	0.17146 (10)	0.0274 (3)
C4	0.31661 (9)	0.50169 (10)	0.07406 (8)	0.0238 (3)
C5	0.37382 (13)	0.44781 (14)	0.03410 (10)	0.0391 (4)
C6	0.24248 (14)	0.43000 (18)	0.08063 (12)	0.0527 (6)
C7	0.27067 (11)	0.60331 (12)	0.02589 (9)	0.0307 (3)
C9	0.35350 (8)	0.63426 (10)	0.16790 (8)	0.0194 (3)
C10	0.38916 (9)	0.70370 (10)	0.24400 (8)	0.0198 (3)
C11	0.38259 (10)	0.81222 (10)	0.23259 (9)	0.0255 (3)
C12	0.41867 (11)	0.87807 (11)	0.30369 (10)	0.0313 (3)
C13	0.46139 (11)	0.83697 (12)	0.38667 (10)	0.0310 (3)
C14	0.46664 (10)	0.72887 (11)	0.39881 (9)	0.0280 (3)
C15	0.43035 (9)	0.66244 (11)	0.32782 (8)	0.0226 (3)
H1A	0.4564 (12)	0.1901 (13)	0.0681 (10)	0.040 (5)*
H1B	0.5497 (14)	0.1223 (15)	0.0952 (12)	0.049 (5)*
H1C	0.4750 (13)	0.0932 (15)	0.1312 (12)	0.041 (5)*
H2A	0.6467 (14)	0.0989 (15)	0.3147 (12)	0.046 (5)*
H2B	0.7134 (16)	0.1985 (18)	0.3410 (15)	0.064 (6)*
H2C	0.7052 (15)	0.1233 (16)	0.2666 (13)	0.054 (6)*
H3A	0.6706 (14)	0.3083 (15)	0.1489 (12)	0.051 (5)*
H3B	0.5826 (14)	0.3873 (15)	0.1232 (13)	0.048 (5)*
H3C	0.6702 (15)	0.3943 (16)	0.2176 (13)	0.052 (5)*
H5A	0.4240 (14)	0.4948 (15)	0.0334 (12)	0.049 (5)*
H5B	0.3314 (14)	0.4287 (16)	−0.0254 (14)	0.054 (6)*
H5C	0.4050 (15)	0.3855 (17)	0.0682 (14)	0.058 (6)*
H6A	0.2020 (15)	0.4040 (16)	0.0223 (11)	0.064 (6)*
H6B	0.2736 (14)	0.3696 (14)	0.1122 (13)	0.060 (6)*
H6C	0.204 (2)	0.465 (2)	0.110 (2)	0.101 (10)*
H7A	0.3021 (13)	0.6319 (14)	−0.0113 (12)	0.041 (5)*
H7B	0.2033 (10)	0.5970 (14)	−0.0090 (11)	0.041 (5)*
H11	0.3552 (12)	0.8399 (12)	0.1757 (9)	0.033 (4)*
H12	0.4131 (12)	0.9517 (14)	0.2954 (11)	0.038 (5)*
H13	0.4891 (13)	0.8821 (14)	0.4369 (12)	0.040 (5)*

H14	0.4949 (11)	0.7004 (12)	0.4566 (9)	0.030 (4)*
H15	0.4321 (11)	0.5886 (10)	0.3360 (10)	0.026 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li	0.0169 (14)	0.0193 (14)	0.0197 (14)	0.000	0.0033 (11)	0.000
Si	0.01801 (18)	0.01873 (17)	0.01628 (17)	0.00254 (12)	0.00498 (13)	-0.00047 (12)
N1	0.0188 (7)	0.0169 (7)	0.0171 (7)	0.000	0.0061 (6)	0.000
N2	0.0158 (5)	0.0211 (5)	0.0162 (5)	-0.0006 (4)	0.0028 (4)	0.0025 (4)
O8	0.0283 (5)	0.0300 (5)	0.0190 (4)	0.0125 (4)	0.0035 (4)	0.0056 (4)
C1	0.0322 (8)	0.0261 (7)	0.0221 (7)	0.0030 (6)	0.0079 (6)	-0.0048 (5)
C2	0.0260 (7)	0.0296 (7)	0.0302 (8)	0.0092 (6)	0.0040 (6)	0.0017 (6)
C3	0.0243 (7)	0.0325 (7)	0.0284 (7)	0.0003 (6)	0.0146 (6)	-0.0001 (6)
C4	0.0207 (6)	0.0236 (6)	0.0170 (6)	-0.0013 (5)	-0.0007 (5)	0.0030 (5)
C5	0.0380 (9)	0.0391 (9)	0.0242 (7)	0.0102 (7)	-0.0007 (7)	-0.0097 (6)
C6	0.0419 (10)	0.0597 (12)	0.0316 (9)	-0.0306 (9)	-0.0064 (8)	0.0109 (8)
C7	0.0322 (8)	0.0314 (7)	0.0196 (6)	0.0088 (6)	0.0034 (6)	0.0033 (5)
C9	0.0143 (6)	0.0238 (6)	0.0183 (6)	0.0030 (5)	0.0057 (5)	0.0061 (5)
C10	0.0168 (6)	0.0234 (6)	0.0208 (6)	0.0043 (5)	0.0096 (5)	0.0028 (5)
C11	0.0271 (7)	0.0250 (7)	0.0246 (7)	0.0072 (5)	0.0116 (6)	0.0062 (5)
C12	0.0388 (8)	0.0220 (7)	0.0345 (8)	0.0056 (6)	0.0176 (7)	0.0010 (6)
C13	0.0351 (8)	0.0325 (7)	0.0277 (7)	0.0027 (6)	0.0159 (6)	-0.0065 (6)
C14	0.0322 (7)	0.0336 (7)	0.0204 (6)	0.0070 (6)	0.0137 (6)	0.0024 (5)
C15	0.0234 (6)	0.0240 (6)	0.0219 (6)	0.0061 (5)	0.0116 (5)	0.0045 (5)

Geometric parameters (Å, °)

Li—N1	1.942 (3)	C4—C6	1.518 (2)
Li—N2	2.1263 (18)	C4—C7	1.5353 (18)
Li—N2 ⁱ	2.1264 (18)	C5—H5A	0.99 (2)
Li—Si ⁱ	3.074 (3)	C5—H5B	0.97 (2)
Si—N1	1.6782 (7)	C5—H5C	0.98 (2)
Si—C3	1.8824 (15)	C6—H6A	0.976 (15)
Si—C1	1.8881 (14)	C6—H6B	0.945 (15)
Si—C2	1.8900 (14)	C6—H6C	1.04 (3)
N2—C9	1.2756 (16)	C7—H7A	1.029 (19)
N2—C4	1.5022 (16)	C7—H7B	0.956 (14)
O8—C9	1.3610 (15)	C9—C10	1.4700 (18)
O8—C7	1.4486 (17)	C10—C15	1.3950 (18)
C1—H1A	0.968 (14)	C10—C11	1.3964 (18)
C1—H1B	1.00 (2)	C11—C12	1.381 (2)
C1—H1C	0.988 (19)	C11—H11	0.944 (13)
C2—H2A	0.99 (2)	C12—C13	1.383 (2)
C2—H2B	0.95 (2)	C12—H12	0.949 (18)
C2—H2C	0.96 (2)	C13—C14	1.392 (2)
C3—H3A	0.99 (2)	C13—H13	0.967 (18)
C3—H3B	1.00 (2)	C14—C15	1.3843 (19)

C3—H3C	1.01 (2)	C14—H14	0.963 (13)
C4—C5	1.511 (2)	C15—H15	0.952 (13)
N1—Li—N2	122.02 (7)	C5—C4—C7	111.64 (12)
N1—Li—N2 ⁱ	122.02 (7)	C6—C4—C7	111.07 (14)
N2—Li—N2 ⁱ	115.95 (14)	C4—C5—H5A	111.0 (11)
N1—Li—Si ⁱ	29.36 (3)	C4—C5—H5B	109.1 (12)
N2—Li—Si ⁱ	108.77 (5)	H5A—C5—H5B	108.4 (16)
N2 ⁱ —Li—Si ⁱ	127.05 (6)	C4—C5—H5C	109.6 (12)
N1—Si—C3	110.90 (7)	H5A—C5—H5C	108.2 (16)
N1—Si—C1	114.23 (6)	H5B—C5—H5C	110.6 (16)
C3—Si—C1	104.72 (7)	C4—C6—H6A	107.3 (13)
N1—Si—C2	115.55 (6)	C4—C6—H6B	108.6 (13)
C3—Si—C2	106.22 (7)	H6A—C6—H6B	104.3 (17)
C1—Si—C2	104.31 (7)	C4—C6—H6C	113.5 (16)
Si—N1—Si ⁱ	127.83 (9)	H6A—C6—H6C	113 (2)
Si—N1—Li	116.09 (4)	H6B—C6—H6C	109 (2)
Si ⁱ —N1—Li	116.09 (4)	O8—C7—C4	104.34 (10)
C9—N2—C4	106.52 (10)	O8—C7—H7A	109.1 (10)
C9—N2—Li	131.72 (11)	C4—C7—H7A	113.4 (10)
C4—N2—Li	121.09 (9)	O8—C7—H7B	107.2 (11)
C9—O8—C7	105.29 (10)	C4—C7—H7B	112.9 (11)
Si—C1—H1A	111.5 (11)	H7A—C7—H7B	109.6 (15)
Si—C1—H1B	111.1 (11)	N2—C9—O8	118.04 (11)
H1A—C1—H1B	107.0 (15)	N2—C9—C10	127.49 (11)
Si—C1—H1C	112.2 (10)	O8—C9—C10	114.47 (11)
H1A—C1—H1C	108.4 (15)	C15—C10—C11	119.42 (12)
H1B—C1—H1C	106.4 (15)	C15—C10—C9	120.72 (11)
Si—C2—H2A	113.3 (11)	C11—C10—C9	119.86 (11)
Si—C2—H2B	111.9 (13)	C12—C11—C10	120.24 (13)
H2A—C2—H2B	108.5 (17)	C12—C11—H11	120.5 (10)
Si—C2—H2C	112.2 (12)	C10—C11—H11	119.2 (10)
H2A—C2—H2C	101.5 (16)	C11—C12—C13	120.21 (13)
H2B—C2—H2C	108.8 (18)	C11—C12—H12	119.8 (11)
Si—C3—H3A	110.5 (11)	C13—C12—H12	120.0 (11)
Si—C3—H3B	113.2 (11)	C12—C13—C14	120.00 (14)
H3A—C3—H3B	106.9 (15)	C12—C13—H13	121.0 (11)
Si—C3—H3C	113.2 (11)	C14—C13—H13	118.9 (11)
H3A—C3—H3C	107.8 (16)	C15—C14—C13	120.07 (13)
H3B—C3—H3C	104.9 (15)	C15—C14—H14	120.0 (10)
N2—C4—C5	111.37 (11)	C13—C14—H14	119.9 (10)
N2—C4—C6	107.51 (12)	C14—C15—C10	120.03 (12)
C5—C4—C6	112.48 (16)	C14—C15—H15	120.2 (9)
N2—C4—C7	102.23 (10)	C10—C15—H15	119.8 (9)
C3—Si—N1—Si ⁱ	176.77 (5)	Li—N2—C9—O8	165.63 (9)
C1—Si—N1—Si ⁱ	58.73 (6)	C4—N2—C9—C10	175.66 (12)
C2—Si—N1—Si ⁱ	-62.30 (6)	Li—N2—C9—C10	-13.9 (2)

C3—Si—N1—Li	-3.23 (5)	C7—O8—C9—N2	-7.87 (16)
C1—Si—N1—Li	-121.27 (6)	C7—O8—C9—C10	171.71 (11)
C2—Si—N1—Li	117.70 (6)	N2—C9—C10—C15	-24.5 (2)
C9—N2—C4—C5	133.79 (13)	O8—C9—C10—C15	155.95 (12)
Li—N2—C4—C5	-37.89 (15)	N2—C9—C10—C11	154.97 (13)
C9—N2—C4—C6	-102.56 (15)	O8—C9—C10—C11	-24.56 (17)
Li—N2—C4—C6	85.76 (15)	C15—C10—C11—C12	1.6 (2)
C9—N2—C4—C7	14.45 (14)	C9—C10—C11—C12	-177.93 (13)
Li—N2—C4—C7	-157.23 (10)	C10—C11—C12—C13	-0.1 (2)
C9—O8—C7—C4	16.31 (14)	C11—C12—C13—C14	-1.1 (2)
N2—C4—C7—O8	-18.50 (14)	C12—C13—C14—C15	0.9 (2)
C5—C4—C7—O8	-137.66 (13)	C13—C14—C15—C10	0.5 (2)
C6—C4—C7—O8	95.91 (15)	C11—C10—C15—C14	-1.77 (19)
C4—N2—C9—O8	-4.81 (15)	C9—C10—C15—C14	177.72 (12)

Symmetry code: (i) $-x+1, y, -z+1/2$.