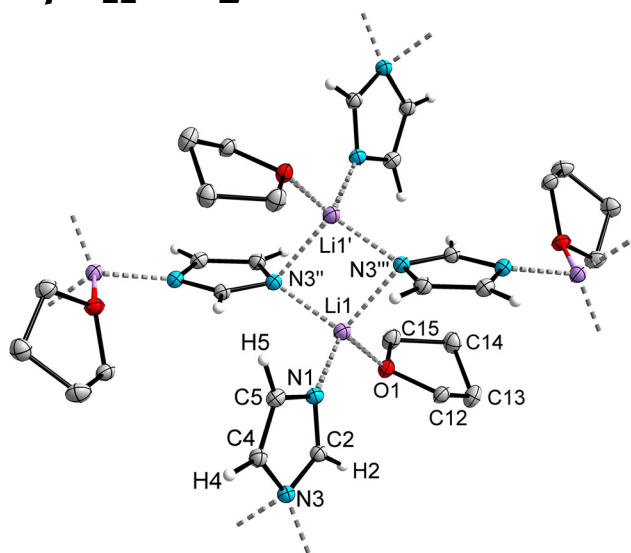


Ludwig Zapf and Maik Finze*

The crystal structure of poly[(μ_3 -imidazolato- $\kappa^3 N:N:N'$)(tetrahydrofuran- $\kappa^1 O$)lithium(I)], $C_7H_{11}LiN_2O$



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Abstract

$C_7H_{11}LiN_2O$, monoclinic, $P2_1/c$ (no. 14), $a = 8.9067(1) \text{ \AA}$, $b = 8.6975(1) \text{ \AA}$, $c = 10.2398(1) \text{ \AA}$, $\beta = 101.900(3)^\circ$, $V = 770.491(15) \text{ \AA}^3$, $Z = 4$, $R_{gt}(F) = 0.0338$, $wR_{ref}(F^2) = 0.0925$, $T = 100 \text{ K}$.

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A part of the title coordination polymer is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Maik Finze, Institut für Anorganische Chemie, Institute for Sustainable Chemistry & Catalysis with Boron (ICB), Julius–Maximilians–Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, E-mail: maik.finze@uni-wuerzburg.de. <https://orcid.org/0000-0002-6098-7148>

Ludwig Zapf, Institut für Anorganische Chemie, Institute for Sustainable Chemistry & Catalysis with Boron (ICB), Julius–Maximilians–Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.27 \times 0.19 \times 0.09 \text{ mm}$
Wavelength:	Cu $K\alpha$ radiation (1.54184 \AA)
μ :	0.67 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{\max} , completeness:	74.5° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	15814, 1581, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1466
$N(\text{param})_{\text{refined}}$:	144
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.53361 (19)	0.12825 (19)	0.44117 (16)	0.0185 (3)
C2	0.48379 (11)	0.35811 (11)	0.22531 (9)	0.0162 (2)
H2	0.5765 (14)	0.4073 (15)	0.2767 (12)	0.018 (3)*
N1	0.41746 (9)	0.24147 (9)	0.27578 (8)	0.0172 (2)
N3	0.41261 (9)	0.40236 (9)	0.09964 (7)	0.0166 (2)
C4	0.28757 (11)	0.30381 (11)	0.06743 (9)	0.0180 (2)
H4	0.2129 (14)	0.3072 (15)	-0.0192 (13)	0.020 (3)*
C5	0.29089 (11)	0.20745 (11)	0.17355 (10)	0.0180 (2)
H5	0.2164 (15)	0.1249 (16)	0.1819 (13)	0.027 (3)*
O1	0.71698 (8)	0.24863 (7)	0.52533 (7)	0.0185 (2)
C12	0.69165 (11)	0.39670 (11)	0.58265 (10)	0.0191 (2)
H12A	0.6047 (14)	0.3873 (14)	0.6266 (12)	0.019 (3)*
H12B	0.6653 (15)	0.4697 (16)	0.5065 (13)	0.027 (3)*
C13	0.84095 (12)	0.43234 (12)	0.68392 (11)	0.0246 (3)
H13A	0.8251 (16)	0.5035 (17)	0.7536 (13)	0.031 (3)*
H13B	0.9184 (16)	0.4775 (17)	0.6380 (13)	0.030 (3)*
C14	0.89286 (12)	0.27294 (13)	0.73861 (10)	0.0229 (2)
H14A	0.8352 (16)	0.2421 (16)	0.8057 (14)	0.028 (3)*
H14B	1.0050 (15)	0.2654 (15)	0.7805 (13)	0.024 (3)*
C15	0.84676 (12)	0.17319 (12)	0.61380 (10)	0.0226 (2)
H15A	0.8138 (16)	0.0663 (18)	0.6336 (14)	0.032 (3)*
H15B	0.9301 (15)	0.1673 (16)	0.5670 (13)	0.023 (3)*

Source of material

Lithium imidazolite was prepared in analogy to a literature known synthesis [5]. In a 250 mL three necked round bottom flask, equipped with a condenser and fitted with a magnetic stirring bar, imidazole (5.00 g, 73.4 mmol) was suspended in toluene (50 mL). Under vigorous stirring $n\text{BuLi}$ in hexanes (30 mL, 2.5 mol L^{-1} , 75.1 mmol) was slowly added. The

resulting pale yellow suspension was stirred at room temperature for 19 h and subsequently refluxed for 24 h, while a colorless solid precipitated. The suspension was cooled to room temperature, filtered over a glass frit, washed with toluene (3 × 20 mL), and dried in vacuum to yield 5.24 g (70.8 mmol, 96% calculated for imidazole) lithium imidazolate. Crystals of the title compound, poly[(μ₃-imidazolato-κ³N:N:N')(tetrahydrofuran-κ¹O)lithium(I)], were obtained from a saturated THF solution within 24 h.

Experimental details

All H atoms were located on a difference Fourier map and refined without any restraints.

Comment

Lithium imidazolate is a valuable starting compound for the synthesis of various imidazole-based derivatives and materials. Examples include biologically active compounds [6], ligands for coordination chemistry [7], and Li-ion conducting materials, weakly coordinating anions (WCAs), as well as components of electrolytes [5, 8–11]. Recently, we described the functionalization of both N atoms in lithium imidazolate by tricyanoborane moieties. The corresponding 1,3-bis(tricyanoborane)imidazolate anion was used for the formation of three-dimensional coordination polymers and as precursor for a new type of a ditopic dianionic N-heterocyclic carbene (NHC) [12]. Molecular lithium imidazolate was studied by theoretical methods [13–15]. Furthermore, Li–N coordination in imidazolate species is an important motif in coordination chemistry, e.g. in covalent organic frameworks [16] and zeolitic imidazolate frameworks (ZIFs) [17, 18]. Surprisingly, no crystal structure analysis on lithium imidazolate has been published, to date.

Solvent-free lithium imidazolate was synthesized by deprotonation of imidazole in toluene. Recrystallization of lithium imidazolate from THF gave the title compound, poly[(μ₃-imidazolato-κ³N:N:N')(tetrahydrofuran-κ¹O)lithium(I)], as a two-dimensional coordination polymer.

The asymmetric unit of the title compound contains one imidazolate anion [C₃N₂H₃][−], one lithium cation Li⁺, and one THF molecule. The lithium cation Li1 is tetrahedrally coordinated by the O atom of THF (*d*(Li1–O1) = 1.959(2) Å) and N atoms of three different imidazolate anions (N1, N3'', N3'''; see the Figure). The Li–N distances of the bridging N atom (*d*(Li1–N3'') = 2.088(2) Å and *d*(Li1–N3''') = 2.167(2) Å) are significantly

shorter compared to *d*(Li1–N1) = 2.019(2) Å of the terminal coordinated N atom. The Li–N coordination results in a two-dimensional coordination polymer. In contrast, for lithium-bis(DMSO) benzimidazolate a chain structure was described, in which the Li ion is coordinated by two DMSO molecules and two N atoms of different benzimidazolate ions [19].

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