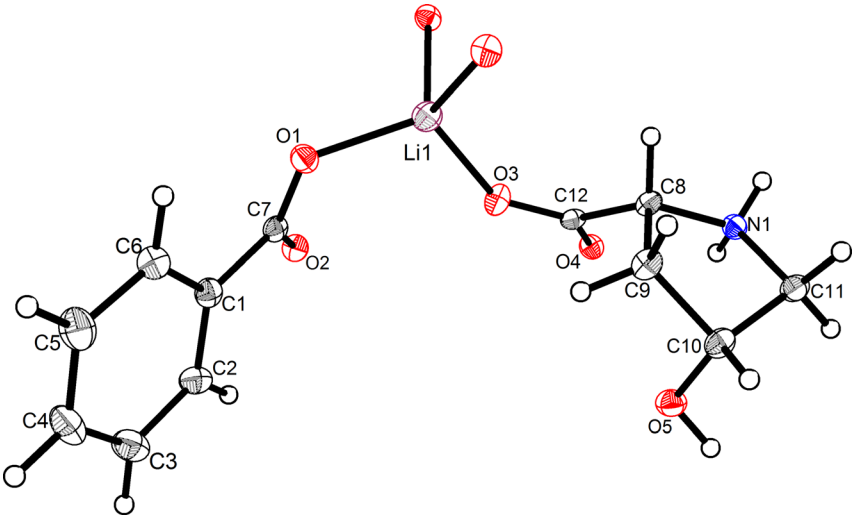
Dejing Yin, Lingling Wang and Zhenbo Yuan*

Crystal structure of poly[(μ-benzoato)-(μ-cis-4–hydroxy-D-proline)lithium], $C_{12}H_{14}LiNO_5$



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Abstract

$(C_{12}H_{14}LiNO_5)_n$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.1481(4) Å, b = 8.9342(7) Å, c = 25.733(2) Å, Z = 4, V = 1183.57(16) Å^3, $R_{gt}(F)$ = 0.0539, $wR_{ref}(F^2)$ = 0.1478, T = 100 K.

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The molecular structure 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.

Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.20 × 0.04 × 0.02 mm
Wavelength:	Cu *K*α radiation (1.54178 Å)
μ:	0.94 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	68.3°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8,285, 2157, 0.100
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1855
$N(param)_{refined}$:	182
Programs:	Bruker [1], SHELX [2, 3], DIAMOND [4]

1 Source of material

Lithium hydroxide monohydrate (0.0419 g, 1 mmol), benzoic acid (0.1220 g, 1 mmol) and cis-4-hydroxy-D-proline (0.1311 g, 1 mmol) were dissolved in 2 mL of hot deionized water and then left to stand on a hot plate (70–80 °C) to allow slow evaporation of solvent until needle colorless crystals had emerged from solution.

2 Experimental details

The structure was solved and refined using the Bruker Shelxtl software package [2, 3]. All hydrogen atoms were placed in the calculated positions and constrained to ride on

***Corresponding author: Zhenbo Yuan**, Key Laboratory of Carbohydrate Chemistry and Biotechnology, Ministry of Education, School of Biotechnology, Jiangnan University, Wuxi 214122, P.R. China, E-mail: zhenboyuan1992@jiangnan.edu.cn. https://orcid.org/0000-0002-2435-0318
Dejing Yin and Lingling Wang, Key Laboratory of Carbohydrate Chemistry and Biotechnology, Ministry of Education, School of Biotechnology, Jiangnan University, Wuxi 214122, P.R. China, E-mail: ydjszlg@jiangnan.edu.cn (D. Yin), wanglingling@jiangnan.edu.cn (L. Wang)

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0220 (9)	0.0208 (5)	0.57642 (15)	0.0213 (9)
C2	−0.1896 (9)	0.1001 (5)	0.55701 (17)	0.0255 (10)
H2	−0.285184	0.164557	0.579295	0.031*
C3	−0.2616 (10)	0.0855 (6)	0.50550 (18)	0.0314 (11)
H3	−0.404115	0.141536	0.492396	0.038*
C5	0.0808 (11)	−0.0916 (6)	0.49202 (18)	0.0326 (11)
H5	0.170596	−0.159697	0.470086	0.039*
C4	−0.1263 (10)	−0.0110 (6)	0.47272 (17)	0.0327 (11)
H4	−0.176232	−0.021155	0.437359	0.039*
C7	0.1048 (8)	0.0369 (4)	0.63252 (16)	0.0186 (8)
C6	0.1595 (10)	−0.0737 (5)	0.54361 (17)	0.0263 (10)
H6	0.307055	−0.126285	0.55623	0.032*
C8	0.8006 (9)	0.4659 (4)	0.70540 (16)	0.0209 (9)
H8	0.928761	0.389686	0.717759	0.025*
C9	0.8433 (9)	0.4931 (4)	0.64694 (15)	0.0220 (9)
H9A	1.014035	0.453763	0.635675	0.026*
H9AB	0.70511	0.444642	0.626136	0.026*
C10	0.8326 (9)	0.6631 (4)	0.64121 (16)	0.0223 (9)
H10	0.923825	0.697883	0.609091	0.027*
C11	0.9694 (9)	0.7163 (5)	0.69026 (16)	0.0220 (9)
H11A	1.160143	0.705126	0.68731	0.026*
H11B	0.927141	0.822008	0.698058	0.026*
C12	0.5276 (8)	0.4148 (4)	0.72028 (15)	0.0187 (8)
Li1	0.5867 (16)	0.0985 (8)	0.6827 (3)	0.0249 (15)
N1	0.8595 (7)	0.6126 (4)	0.73080 (13)	0.0187 (8)
H7	0.712 (6)	0.645 (6)	0.7435 (19)	0.027 (14)*
H1	0.953 (7)	0.604 (5)	0.7591 (11)	0.010 (10)*
O1	0.3316 (6)	−0.0048 (3)	0.64441 (11)	0.0227 (7)
O2	−0.0584 (6)	0.0897 (3)	0.66424 (10)	0.0216 (7)
O3	0.4585 (6)	0.2899 (3)	0.70252 (11)	0.0254 (7)
O4	0.3930 (6)	0.4975 (3)	0.74887 (10)	0.0203 (6)
O5	0.5652 (6)	0.7033 (3)	0.64091 (11)	0.0244 (7)
H5A	0.5500 (12)	0.806 (7)	0.638 (2)	0.037*

their parent atoms. The absolute structure determination succeeded as the derived Flack parameter is found to be near zero [0.0 (3) from 636 selected quotients] using Parsons' method [5].

3 Comment

Lithium compounds play an important role in reducing manic episodes and suicidality for patients with bipolar disorder [6–8]. Compared to FDA approved lithium pharmaceuticals (lithium carbonate and lithium citrate), organic lithium salts are expected to improve the pharmacokinetic properties [9]. Therefore, organic lithium salts have been widely investigated for their good values of new drug development and market prospects [10]. Herein, we report a new salt-type cocrystal which contains three components, including lithium ion, the benzoate anion, and cis-4-hydroxy-D-proline as amino acid. In the structure of the title compound, each lithium ion was linked with four adjacent carboxylate moieties, two from benzoate and two from cis-4-hydroxy-D-proline molecules (Li–O distance: 1.884, 1.902, 1.890, 1.980 Å). The benzoato ligand is almost flat which is in agreement with the literature [11]. The hydroxyl group and protonated nitrogen atoms of cis-4-hydroxy-D-proline formed hydrogen bonds with carboxylate moieties, respectively (O–H···O$^-$: 2.873 Å, N^+–H···O $^-$: 2.852, 2.896 Å).

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References

1. Bruker. SAINT (Version 8.38A); Bruker AXS Inc: Madison, Wisconsin, USA, 2017.
2. Sheldrick G. M. *SHELXTL* – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Ver. 3.2*; Crystal Impact: Bonn, Germany, 2012.
5. Parsons S., Flack H. D., Wagner T. Use of intensity quotients and differences in absolute structure refinement. *Acta Crystallogr.* 2013, *B69*, 249–259.
6. Thies-Flechtner K., Müller-Oerlinghausen B., Seibert W., Walther A., Greil W. Effect of prophylactic treatment on suicide risk in patients with major affective disorders-data from a randomized prospective trial. *Pharmacopsychiatry* 1996, *29*, 103–107.
7. Goodwin F. K., Fireman B., Simon G. E., Hunkeler E. M., Lee J., Revicki D. Suicide risk in bipolar disorder during treatment with lithium and divalproex. *JAMA* 2003, *290*, 1467–1473.
8. Cipriani A., Hawton K., Stockton S., Geddes J. R. Lithium in the prevention of suicide in mood disorders: updated systematic review and meta-analysis. *BMJ* 2013, *346*, f3646.
9. Smith A. J., Kim S.-H., Duggirala N. K., Jin J., Wojtas L., Ehrhart J., Giunta B., Tan J., Zaworotko M. J., Shytle R. D. Improving lithium therapeutics by crystal engineering of novel ionic cocrystals. *Mol. Pharm.* 2013, *10*, 4728–4738.
10. Sanii R., Andaloussi Y. H., Patyk-Kaźmierczak E., Zaworotko M. J. Polymorphism in ionic cocrystals comprising lithium salts and l-proline. *Cryst. Growth Des.* 2022, *22*, 3786–3794.
11. Fei Y., Pengju L., Libing G., Dong X. The crystal structure of bis(benzoato-κ2 O,O′)-(2,9-dimethyl-1,10-phenanthroline-κ2 N,N′)-copper(II), $C_{28}H_{22}CuN_2O_4$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1219–1221.