

Synthesis and Crystal Structure of a “High-temperature” Phase of Li[H₂NC(O)NH], the Missing Alkali-Metal Ureate

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The new salt-like lithium ureate, LiCN₂H₃O, **1**, was synthesized to round up the series of the recently published alkali-metal ureates. Single crystals of **1** were prepared similarly to the previously made ureates of Na–Cs in liquid ammonia. LiCN₂H₃O crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 7.5770(9), *b* = 9.059(1), *c* = 13.046(2) Å, β = 98.896(2)°, *V* = 884.8(2) Å³, and *Z* = 12. The Li⁺ ions are coordinated by four ureate anions in a distorted tetrahedral manner. As expected, the deprotonation of the urea molecules is reflected by the shape of the anions with two different C–N bond lengths.

Key words: Ureates, Lithium, X-Ray Diffraction, Alkali Metals, Liquid Ammonia

Introduction

Although urea, (H₂N)₂CO, is a well-known and commercially available chemical needed for plenty of nitrogen-containing fertilizers, cosmetics and pharmaceuticals, only few examples of salts based on deprotonated urea are known despite the existence of numerous metal-urea compounds. In the vast majority of the latter, the urea molecule just serves as a neutral ligand [1–5]. In some cases, urea acts as a base and is protonated to form salts consisting of a uronium cation [6]. Even though urea contains acidic amino protons, until recently structurally characterized binary salts based on ureate anions had not come to our attention.

The first observation of alkali-metal ureates, however, goes back to Franklin [7] who described, in 1902 (!) already, the synthesis of a phase dubbed “KCN₂H₃O” based on the reaction between potassium and urea in liquid ammonia. The analytical methods of that time, however, did not allow for a reliable characterization. The synthesis was repeated in 1936 by Jacobson for sodium ureate [8], again lacking further structural analysis. The analogous synthesis of lithium ureate as a starting material to produce several urea derivatives was mentioned in 1941 [9] but, once again,

a reliable characterization of the compound is missing up to the present day. In 2006, lithium ureate reappeared in the literature when Eames *et al.* [10] seemingly synthesized it as a reagent to deprotonate CH-acidic organic compounds, but without any structure-analytical details.

Recently, the ureates of the elements Na–Cs were successfully prepared [11] using a reaction pathway previously applied and extensively described for the alkali-metal guanidates [12–14]. To obtain single crystals of the alkali-metal ureates needed for XRD structure solution, urea and the alkali metal were dissolved in liquid ammonia in a one-step reaction to deprotonate urea by *in situ* formed alkali-metal amides. In this paper, we expand upon that reaction with respect to the remaining alkali metal, lithium. Single crystals of a “high-temperature” phase of lithium ureate were synthesized at 50 °C, and the crystal structure is presented herein.

Results and Discussion

At room temperature, there are strong indications from powder XRD for the formation of the desired lithium ureate in phase-pure form although its crystallinity does not allow for a successful structure solu-

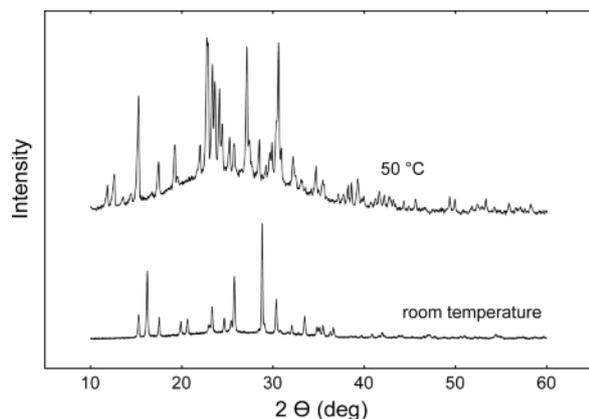


Fig. 1. Powder XRD patterns (CuK α_1 radiation) of lithium ureate synthesized at room temperature (bottom) and at 50 °C (top).

tion. No single crystals are formed. However, at a moderate temperature of 50 °C a crystallographically different (Fig. 1) and nicely crystalline phase of **1** was obtained in likewise phase-pure form. In contrast to the ureates of all other alkali metals, where a lower metal concentration always resulted in a better crystallized product, the concentration of the starting materials had to be increased to arrive at single crystals.

The single-crystal data and structure refinement details of **1** are given in Table 1. Just like for the case of sodium ureate, **1** crystallizes in the monoclinic system. A perspective view into the unit cell is shown in Fig. 2. The lithium cations form zig-zag chains along the space diagonal while the anions are arranged between and within the chains. All three symmetry-independent

Table 1. Crystal structure data for **1**.

Empirical formula	LiCN ₂ H ₃ O
Formula mass, amu	65.99
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> , Å	7.5770(9)
<i>b</i> , Å	9.059(1)
<i>c</i> , Å	13.046(2)
β , deg	98.896(2)
<i>V</i> , Å ³	884.8(2)
<i>Z</i>	12
$\rho_{\text{calcd.}}$, g cm ⁻³	1.49
<i>T</i> , K	100
Crystal dimensions, mm ³	0.23 × 0.21 × 0.09
Radiation; wavelength, Å	MoK α_1 ; 0.71073
μ (MoK α_1), mm ⁻¹	0.1
Transmission factors	0.682–0.745
θ limits, deg	2.75–26.57
Data collected	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –16 ≤ <i>l</i> ≤ 16
No. of reflections collected/unique	1846 / 1620
No. of ref. variables	164
Final <i>R</i> indices: <i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0388/0.0847
Goodness of fit	1.075
Largest difference peak/hole, e Å ⁻³	0.18/–0.20

lithium cations are coordinated by four ureate anions in distorted tetrahedra. In the case of Li1, three ureate ligands bind *via* the carbonyl oxygen atom while the fourth ureate coordinates *via* its imino N atom. In contrast, Li2 as well as Li3 are coordinated by two oxygen and two imino nitrogen atoms. The amino N atoms do not take part in any lithium coordination. The shortest distances to Li-coordinated atoms are those of the oxygen atoms. A perspective view of the environments of all the lithium cations is given in Fig. 3, while

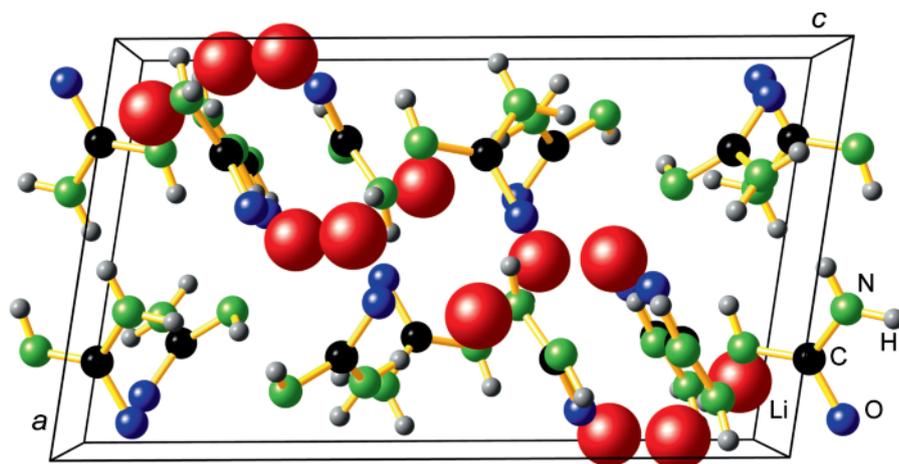


Fig. 2 (color online). View into the unit cell of lithium ureate along the crystallographic *b* axis.

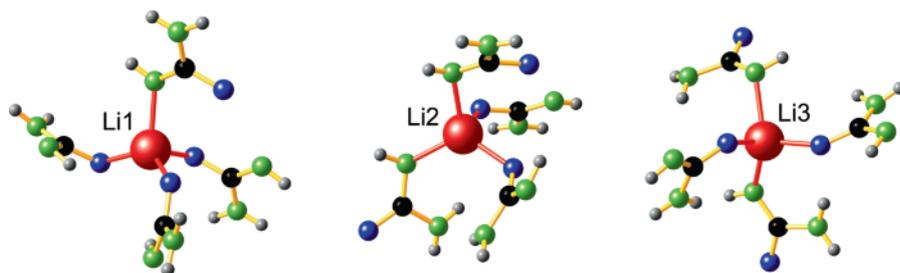


Fig. 3 (color online). Distorted tetrahedral coordination of the Li⁺ ions by ureate anions.

Table 2. Shortest interatomic distances (Å) around the lithium cations; all coordinating N atoms belong to imino groups.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Li1	O3	1.887(2)	Li2	O3	1.923(2)	Li3	O2	1.956(2)
	O1	1.952(2)		O1	1.958(2)		O1	1.966(2)
	O2	1.953(2)		N4	2.042(3)		N6	2.011(3)
	N2	2.056(3)		N2	2.102(3)		N4	2.112(3)

Table 2 summarizes their interatomic distances. Some tetrahedra are connected by edges or corners. A continuous chain of connected tetrahedra, however, does not exist.

The shapes of the three ureate anions are presented as ORTEP plots in Fig. 4. In all cases, two easily distinguishable bond lengths between the central C atom and the two N atoms are found. For the amino N atoms, their C–N bond lengths are between 1.36 and 1.38 Å, whereas the C–N bonds of the imino N atoms are shorter (1.31–1.32 Å) due to the partial C–N π bonding that sets in after deprotonation. Interestingly, and in contrast to all previously published alkali-metal

ureates, two imino H atoms point towards the carbonyl oxygen atom but not towards the amino group. Also, the anions are non-planar, very much comparable to the anions of the ureates of Na–Cs but not to pure urea.

The volume increment of the ureate anion was calculated to be 42–43 cm³ mol⁻¹ according to Biltz [15], and it is therefore comparable to that of pure urea. Nonetheless, besides structural evidence (see above) the deprotonation is mirrored in the infrared spectrum of **1** given in Fig. 5. While for urea there are three distinctive N–H stretching bands in the range of 3200–3500 cm⁻¹, the absorption bands of **1** in this area are split into a fine structure because of the formation of two different functional groups upon deprotonation. The remaining absorption bands at wavenumbers below 1600 cm⁻¹ are similar to those of urea, but shifted as the electron density and bond

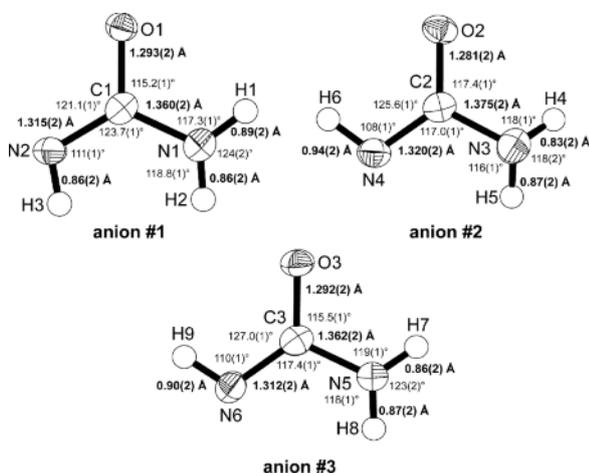


Fig. 4. ORTEP representations of the anions of lithium ureate with displacement ellipsoids drawn at the 70% probability level and H atoms as spheres of arbitrary size.

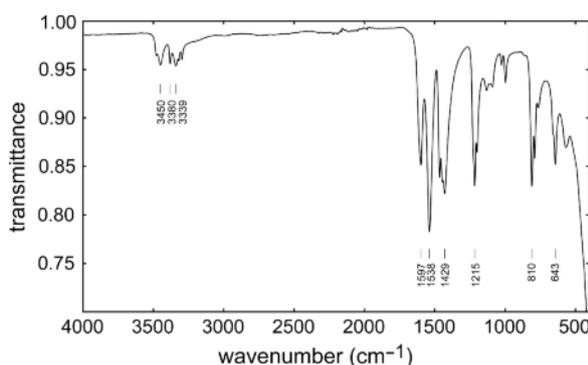


Fig. 5. Infrared spectrum of lithium ureate.

lengths change as a consequence of the deprotonation and the coordination of the lithium cations. A hydrogen bond network similar to what was previously described for the ureates of K, Rb and Cs does not exist in the structure of lithium ureate.

Conclusion

The family of structurally characterized alkali-metal ureates has been completed by the synthesis of lithium ureate. The compound crystallizes in the monoclinic space group $P2_1/n$ with three symmetry-independent lithium cations which are each tetrahedrally coordinated by four ureate anions. The shape of the anions evidences the deprotonation of urea by two distinguishable bond lengths between the C and the amino or imino N atoms.

Experimental Section

Due to the sensitivity of the product and of the starting materials towards air and moisture, the reaction was carried out under dry argon atmosphere. Urea was purified by sublimation at 90 °C. The synthesis of **1** was performed in liquid ammonia as described before for the synthesis of other guanidines [12–14]. 70 mg (10 mmol) of elemental lithium and 600 mg (10 mmol) of urea were weighed into a steel autoclave, and the vessel was evacuated. Dry ammonia (40 mL, 2 mmol, 99.999%) was subsequently condensed into the au-

toclave. The autoclave was stored at 50 °C for 16 d followed by the evaporation of ammonia to yield platelet-shaped single crystals in quantitative yield.

X-Ray structure determination

The crystal structure was solved and refined using single-crystal X-ray diffractometry. The collection of diffraction intensities was carried out under nitrogen with a Bruker APEX-1 CCD diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The temperature was controlled by an Oxford Cryostream 700 instrument. All crystal structures were solved with Direct Methods using SHELXS and refined with SHELXL based on F^2 with all measured reflections [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located from the electron density map and isotropically and freely refined.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informations-dienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-427375.

Infrared spectroscopy

An IR spectrum was measured at room temperature using a Bruker ALPHA FT-IR spectrometer equipped with an ATR Platinum Diamond sample holder. The measurement range was 400–4000 cm⁻¹. To handle the air- and moisture-sensitive product, the spectrometer was placed under argon atmosphere in a glovebox.

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- [1] I. Olovsson, *Acta Crystallogr.* **1965**, *18*, 879.
 [2] L. Lebioda, *Acta Crystallogr. B* **1977**, *33*, 1583.
 [3] D. B. Sagatys, R. C. Bott, G. Smith, K. Byriel, C. H. L. Kennard, *Polyhedron* **1992**, *11*, 49.
 [4] P. S. Gentile, J. White, S. Haddad, *Inorg. Chim. Acta* **1974**, *8*, 97.
 [5] R. Eßmann, G. Kreiner, A. Niemann, D. Rechenbach, A. Schmiedling, T. Sichla, U. Zachwieja, H. Jacobs, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1161.
 [6] J. E. Worsham, W. R. Busing, *Acta Crystallogr. B* **1969**, *25*, 572.
 [7] E. C. Franklin, O. F. Stafford, *Am. Chem. J.* **1902**, *28*, 83.
 [8] R. A. Jacobson, *J. Am. Chem. Soc.* **1936**, *58*, 1984.
 [9] K. N. Campbell, B. Knapp Campbell, *Proc. Indiana Acad. Sci.* **1941**, *51*, 161.
 [10] G. S. Coumbarides, J. Eames, M. J. Suggate, N. Weerasooriya, *J. Labelled Compd. Radiopharm.* **2006**, *49*, 641.
 [11] H. Sawinski, R. Dronskowski, *Z. Anorg. Allg. Chem.* **2014**, *640*, 846.
 [12] P. K. Sawinski, R. Dronskowski, *Inorg. Chem.* **2012**, *51*, 7425.
 [13] P. K. Sawinski, V. L. Deringer, R. Dronskowski, *Dalton Trans.* **2013**, *42*, 15080.
 [14] V. Hoepfner, P. Jacobs, P. K. Sawinski, A. Houben, J. Reim, R. Dronskowski, *Z. Anorg. Allg. Chem.* **2013**, *639*, 1232.
 [15] W. Biltz, *Raumchemie der festen Stoffe*; Verlag von Leopold Voss, Leipzig, **1934**.
 [16] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.