

COORDINATION
COMPOUNDS

Polymeric Lithium(I) Diaquabarbiturate: Crystal Structure

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Abstract—The lithium(I) *catena*-diaquabarbiturate complex $[\text{Li}(\text{H}_2\text{O})_2(\text{HBA}-\text{O}, \text{O}')]_n$ (**I**), where H_2BA is barbituric acid, has been structurally characterized by X-ray diffraction (CIF file CCDC no. 1447689), and its thermal decomposition and IR spectrum have been studied. Crystals of complex **I** are monoclinic, $a = 6.4306(7)$ Å, $b = 16.720(1)$ Å, $c = 7.1732(8)$ Å, $\beta = 108.253(4)^\circ$, $V = 732.5(1)$ Å³, space group $P2_1/c$, and $Z = 4$. One independent μ_2 -bridging HBA^- ligand is coordinated to two Li(I) ions via the two oxygen atoms of $\text{C}_{4(6)}=\text{O}$ carbonyl groups. Each Li^+ ion is linked with two μ_2 - HBA^- ions and two terminal water molecules at tetrahedron vertices. μ_2 - HBA^- ions link tetrahedra into a chain. The structure is stabilized by multiple hydrogen bonds and π - π -interaction between HBA^- . The shift of $\nu(\text{C}=\text{O})$ vibration bands in the IR spectrum of complex **I** in comparison with H_2BA towards lower frequencies agrees with the coordination of HBA^- via oxygen atoms. The dehydration of complex **I** occurs in two stages in the regions of 100–150 and 150–240°C.

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The chemistry of coordination polymers of alkali metals with organic ligands in a solid state is poorly studied in comparison with transition metals, although they may have various useful properties [1, 2]. Interest in the coordination chemistry of lithium is associated with its application in scientific studies [3], medicine [4], and lithium batteries [5]. Lithium salts are successfully used in the therapy of manic depression and different nervous and mental diseases [4]. An important problem is the synthesis of compounds that would slowly release Li^+ ions in an organism [6].

Barbituric acid (H_2BA) is the parent of a great class of depressants (barbiturates), which have a positive effect on the central nervous system and exhibit some other useful pharmaceutical properties. H_2BA is applied in the production of plastics and pharmaceutical preparations [7]. It represents a multidentate ligand able to form metal ion complexes characterized by potential bioactivity, solvatochromism, photoluminescence, catalytic activity, etc. [8]. It is interesting that lithium(I) and barbituric acids may have a synergistic effect in a human organism. Thus, the simultaneous administration of LiCl and H_2BA derivatives leads to more long-term aversion to saccharine than the same dose of LiCl [9].

In this work, the crystal structure, thermal stability, and IR spectrum of a new polymeric Li(I) complex with barbituric acid have been studied.

EXPERIMENTAL

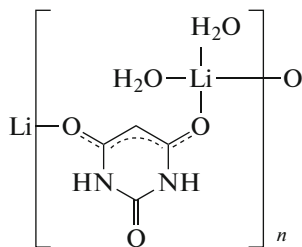
Synthesis of $[\text{Li}(\text{H}_2\text{O})_2(\text{HBA})]_n$ (I**).** To a mixture of H_2BA (0.10 g, 0.78 mmol) (Aldrich, >99%) and water (2 mL), solid LiOH of chemically pure grade (0.030 g, 1.25 mmol) was added, and the mixture was stirred for 30 min until the complete dissolution of H_2BA . Further, pH of this mixture was brought to 7 using a 0.1 M solution of HCl (chemically pure grade). The light pink crystals formed in a week were filtered out, washed with acetone, and dried in air. The yield was 30%. A single crystal of complex **I** was selected from the total mass of the synthesized compound.

IR spectrum of complex **I** (ν , cm^{-1}): 3366 $\nu(\text{O}-\text{H})$, 1682 $\nu(\text{C}=\text{O})$, 1616 $\nu(\text{C}=\text{O})$.

Single-crystal X-ray diffraction analysis. A transparent colorless $0.48 \times 0.32 \times 0.26$ -mm crystal of complex **I** was studied at 150 K. Reflection intensities were measured on a Bruker AXS SMART APEX II single-crystal diffractometer (MoK_α radiation) with a CCD detector. A crystal represented a twin consisting of two domains. The reflection intensities of two

Table 1. Some parameters of X-ray diffraction experiment and refinement details for the structure of complex I

Parameter	Value
Bulk formula	C ₄ H ₇ LiN ₂ O ₅
Formula weight	170.06
Space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>c</i> , 4
<i>a</i> , Å	6.4306(7)
<i>b</i> , Å	16.720(1)
<i>c</i> , Å	7.1732(8)
β, deg	108.253(4)
<i>V</i> , Å ³	732.5(1)
ρ _{calcd} , g/cm ³	1.542
μ, mm ⁻¹	0.139
2θ _{max} , deg	55.13
Reflections in total	6236
Independent reflections, <i>N</i> ₁	6236
Number of reflections with <i>F</i> > 4σ(<i>F</i>), <i>N</i> ₂	5492
<i>h</i> , <i>k</i> , <i>l</i> index ranges	-8 ≤ <i>h</i> ≤ 5, -21 ≤ <i>k</i> ≤ 19, -8 ≤ <i>l</i> ≤ 9
Weighting pattern for <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.1448P]$, $P = \max(F_o^2 + 2F_c^2)/3$
Number of refined parameters	121
<i>R</i> (for <i>N</i> ₁)	0.0417
<i>R</i> (for <i>N</i> ₂)	0.0363
<i>wR</i> (<i>F</i> ²) (for <i>N</i> ₁)	0.0974
<i>wR</i> (<i>F</i> ²) (for <i>N</i> ₂)	0.0935
GOOF	1.027
Extinction coefficients	Not refined
(Δ/σ) _{max}	<0.001
Δρ _{max} /Δρ _{min} , e/Å ³	0.290/-0.309

**Fig. 1.** Structure of [Li(H₂O)₂(HBA-O,O')]_n.

domains were divided into two groups in the process of integration by the APEX II software. Experimental corrections for absorption were applied using the TWINABS software by multiscanning. The structural model was solved by direct methods and refined using the SHELXTL software suite [10]. All hydrogen atoms were located from difference electron density syntheses. The hydrogen atoms of the HBA⁻ ion were further idealized and refined as bonded with major atoms. Some parameters of X-ray diffraction experiment and refinement results for the structure of complex I are given in Table 1.

The structure of complex I was deposited with the Cambridge Structure Database (no. 1447689; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

IR spectra of complex I and H₂BA in KBr were recorded on a Nicolet 6700 FT-IR spectrometer in the region of 4000–400 cm⁻¹.

Simultaneous thermal analysis of complex I was performed on a Netzsch STA Jupiter 449C thermal analyzer connected with an Aeolos QMS 403C mass spectral analyzer in a 20% O₂–Ar mixture flow in a platinum crucible with a perforated cover (sample weight, 4.00 mg; heating rate, 10 K/min).

RESULTS AND DISCUSSION

The independent part of a unit cell of complex I contains one Li(I) atom, one HBA⁻ ion, and two water molecules in general positions (Figs. 1 and 2). Each Li(I) atom is linked with two bridging HBA⁻ ions and two terminal water molecules at the LiO₄ tetrahedron apices. The Li–O bond lengths in complex I (1.912(3)–1.956(3) Å) are typical for Li(I) complexes [11]. The other interatomic distances in complex I (C4–O2, 1.2602 Å; C6–O3, 1.266(2) Å, C2–O1, 1.248(2) Å, C4–C5, 1.396(2) Å, C5–C6, 1.388(1) Å) are closer to the values obtained for the enol H₂BA tautomer (form IV) [12] in comparison with its ketone tautomer [13]. All the C–O distances in complex I have intermediate values between those typical for double and ordinary bonds, thus indicating the delocalization of electron density over the entire ring. However, the shortest C2–O1 bond is still in the carbonyl group, which does not participate in the coordination of the HBA⁻ ligand to lithium. Hence, the most pronounced delocalization of electron density in the O₂=C₄–C₅H–C₆=O₂ atomic moieties (Fig. 1). In the ketone form of a H₂BA molecule, the C–O bond lengths in all carbonyl groups are 1.21–1.22(1) Å, and the C5–C4(6) distances are ≈1.49 Å [13]. The same ratios between the bond lengths in H₂BA and HBA⁻ were also established in ionic cocrystals formed by barbituric acid and barbiturates of Na(I), K(I) [14], Rb(I) [15], and Ca(II) [16, 17].

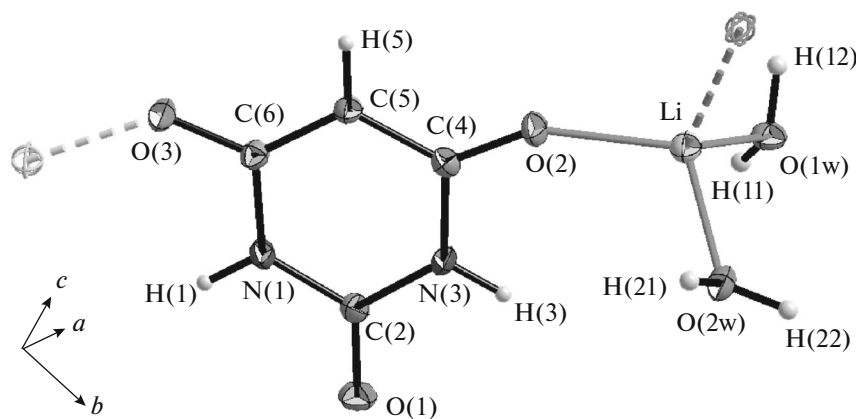


Fig. 2. Independent part of a unit cell of complex I.

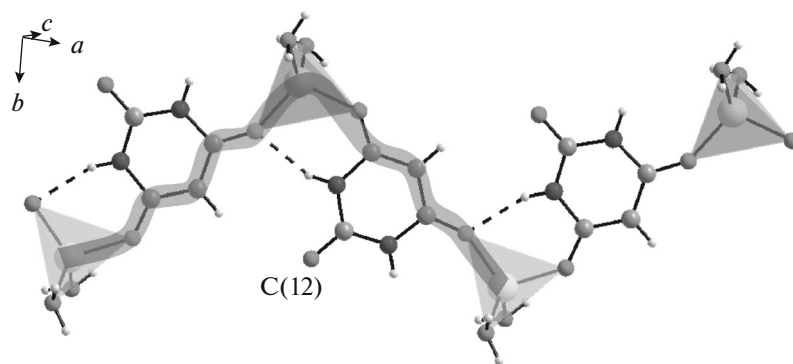


Fig. 3. Structure of a chain of tetrahedra running along direction $a + c$. The translation moiety of the C(12) structure is marked with a band.

The LiO_4 tetrahedra in the structure of complex **I** are linked via bridging μ_2 -HBA⁻ ligands to form polymeric chains running along direction $a + c$ (Fig. 3). The lithium atoms in the barbituric complexes $\text{Li}_4(\mu_2\text{-H}_2\text{O})(\text{H}_2\text{O})_8(\mu_2\text{-HTBA-O,O})(\text{HTBA-O})$ (**II**) [18] and $\text{Li}(\mu_4\text{-DETBA-O,O,O',S})$ (**III**) [19] (H_2TBA is 2-thiobarbituric acid, and HDETBA is 1,3-diethyl-2-thiobarbituric acid) also have a tetrahedral coordina-

tion. However, as follows from the above formulas and Fig. 1, the geometric surroundings of Li(I) atoms in complexes **I–III** are different.

The structural analysis of complex **I** showed the existence of six $\text{N-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{O}$ hydrogen bonds in which all HBA⁻ ions and all water molecules participate (Table 2). Hydrogen bonds form a three-dimensional network, in which a layer in the plane

Table 2. Geometric parameters of hydrogen bonds in the structure of complex **I**

D–H \cdots A contact	Distance, Å			DHA angle, deg	Symmetry codes of atom A
	D–H	H \cdots A	D \cdots A		
N(1)–H(1) \cdots O(2)	0.86	2.02	2.839(2)	160	$x - 1, 1/2 - y, z - 1/2$
N(3)–H(3) \cdots O(1w)	0.86	2.06	2.916(2)	176	$1 - x, 1 - y, 1 - z$
O(1w)–H(11) \cdots O(2w)	0.89(2)	1.82(2)	2.704(2)	172(2)	$1 - x, 1 - y, 1 - z$
O(1w)–H(12) \cdots O(1)	0.90(2)	1.83(2)	2.723(2)	170(2)	$1 + x, y, 1 + z$
O(2w)–H(21) \cdots O(1)	0.84(2)	1.89(2)	2.726(2)	172(2)	$1 + x, y, z$
O(2w)–H(22) \cdots O(1)	0.91(2)	1.75(2)	2.658(2)	174(2)	$1 - x, 1/2 + y, 1/2 - z$

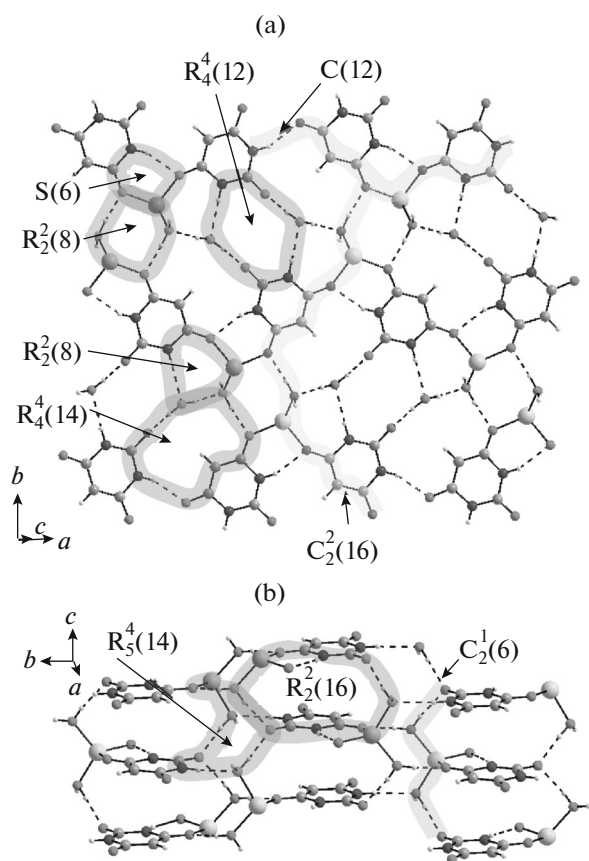
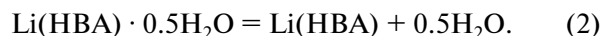


Fig. 4. Layer formed by hydrogen bonds in the plane perpendicular to direction $a + c$; supramolecular motifs are highlighted and labelled (a, b).

perpendicular to direction $a + c$ and $R_2^2(8)$, $S(6)$, $R_4^4(12)$, $R_2^2(16)$, $R_4^4(14)$, $R_5^4(14)$, $C_2^1(6)$, $C(12)$, and $C_2^2(16)$ supramolecular motifs can be distinguished (Fig. 4) [20]. The structure of complex **II** is also stabilized by hydrogen bonds, but no intermolecular hydrogen bonds are formed in complex **III**, though weak intramolecular hydrogen bonds exist. The center-to-center distance [21] between HBA^- rings (3.70 Å) points to π - π -interaction. Such interaction also exists in complex **II**, but is absent in complex **III**.

The assignment of bands in the IR spectrum of H_2BA (ν , cm^{-1}) [22]: 1752 $\nu(\text{C}_2=\text{O})$, 1710 $\nu_{\text{as}}(\text{C}_{4(6)}=\text{O})$, 1695 $\nu_{\text{s}}(\text{C}_{4(6)}=\text{O})$. Instead of these bands, the IR spectrum of complex **I** contains $\nu(\text{C}_2=\text{O})$ bands at lower frequencies of 1682 and 1616 cm^{-1} , which agree with the coordination of HBA^- via O atoms. The broad band with a maximum at 3366 cm^{-1} belongs to the $\nu(\text{O}-\text{H})$ vibration of coordinated water molecules.

Two well-resolvable endothermic stages are observed in the TG and DSC curves below 250°C within the temperature ranges of 100–150°C ($T_{\text{max}} = 127^\circ\text{C}$) and 150–240°C ($T_{\text{max}} = 215^\circ\text{C}$) (Fig. 5) and may be explained by the elimination of water molecules in the following order:



The mass losses at stages (1) and (2) (Fig. 5) coincide with the theoretically calculated values for complex **I** (15.88 and 21.17%, respectively). It is possible to hypothesize that $\text{Li}_2(\mu_2\text{-H}_2\text{O})(\text{HBA})_2$ is formed at

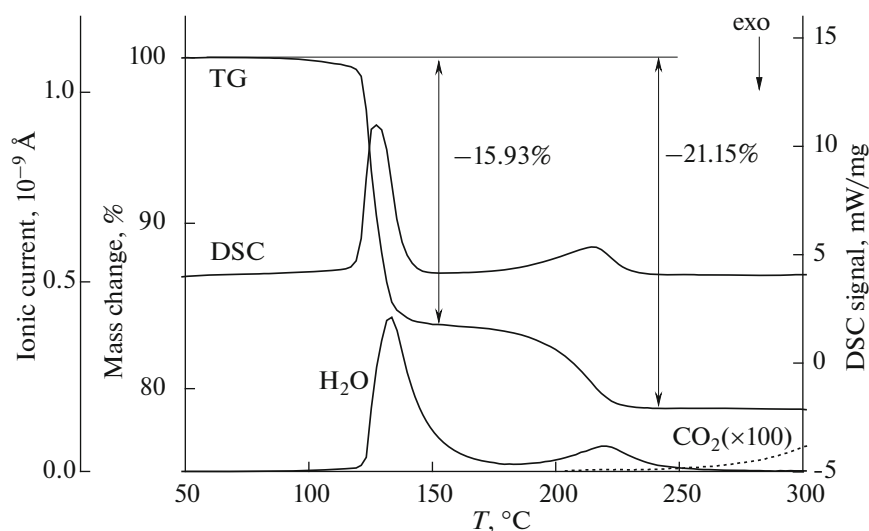


Fig. 5. TG and DSC curves and intensities in the mass spectrum of the ionic current of water ($m/z = 18$) and CO_2 ($m/z = 44$) ions in the oxidative decomposition of complex **I**.

stage (1). The anhydrous complex formed at stage (2) is more stable under heating than H₂BA. Thus, the oxidation of HBA⁻ in complex **I** with the formation of CO₂ and water begins at ~300°C, and the oxidation of H₂BA is started at 253.2°C [23].

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