CRYSTAL STRUCTURE OF *CATENA*-DI(2-THIOBARBI-

TURATO-O,S)AQUALEAD(II)

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The crystal structure of *catena*-di(μ_2-2-thiobarbiturato-O,S)aqualead(II) $C_8H_8N_4O_5S_2Pb$ ($C_4H_4N_2O_2S$ is 2-thiobarbituric acid, H_2TBA) is determined. Crystallographic data for *catena*-$[Pb(H_2O)(\mu_2\text{-HTBA-O,S})_2]$ are as follows: $a = 6.5972(1)$ Å, $b = 9.8917(2)$ Å, $c = 10.0893(2)$ Å, $\alpha = 106.702(1)°$, $\beta = 93.395(2)°$, $\gamma = 107.48(1)°$, $V = 593.82(2)$ Å^3, space group $P\overline{1}$, $Z = 2$. The Pb^{2+} ion is linked with six monodentate $HTBA^-$ ligands through two O atoms and four S atoms and also connected with a water molecule. Additionally, there is a shortened Pb–S contact (3.622 Å), given which the complex polyhedron represents a distorted square antiprism. Hydrogen bonds N–H···O and O–H···O form a branched three-dimensional network. The structure is also stabilized by the π–π interaction of heterocyclic $HTBA^-$ ions.

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Compounds containing a pyrimidine ring play an important role in many biological systems, where they enter into the composition of nucleic acids, several vitamins, coenzymes, and antibiotics. One substance in this group is thiobarbituric acid (4,6-dihydroxy-2-mercaptopyrimidine, $C_4H_4N_2O_2S$, H_2TBA). It and several its derivatives have been long used due to their pharmaceutical properties [1]. Its complexes with metals can exhibit specific biological activity, e.g., anticancer action [2].

Thiobarbituric acid is a polyfunctional ligand and can exist in several tautomeric and polymorphic forms [3]. For it, we can expect the formation of complexes with different compositions and structures depending on the nature of the central metal ion and the medium acidity. This determines the scientific interest in the study of its interaction with metal ions.

The H_2TBA complexes with the ions of *d*-block elements Cu(II), Fe(II, III), Co(II), Ni(II), Zn(II), Cd(II) have been synthesized and characterized [4-6], and some of them possess antimicrobial activity [7]. For *p*-block elements, the structure of only one complex [(*n*-Bu)$_3$Sn(HTBAH)·H$_2$O] has been described [2].

In this report, the [Pb(H$_2$O)(HTBA)$_2$] complex is synthesized and using X-ray powder diffraction its structure is determined.

Experimental. Pb(NO$_3$)$_2$ (chemically pure) and H$_2$TBA (chemically pure) were used.

***Catena*-di(2-thiobarbiturato)aqualead(II),** *catena*-[Pb(H$_2$O)(μ_2-HTBA-O,S)$_2$] (**I**). A portion of Pb(NO$_3$)$_2$ was added to the suspension of 0.2 g of H$_2$TBA in 4 ml of water. The molar ratio (NO$_3$)$_2$:H$_2$TBA = 1:2 (pH 4). A light yellow residue formed in 2 days was filtered off, washed with alcohol, and dried in the air. The results of elemental analysis (found/calculated for **I**, wt.%) are as follows: C 18.37/18.79, H 1.42/1.58, N 11.24/10.95, S 12.87/12.54, Pb 40.1/40.5. Product yield was 94-96%.

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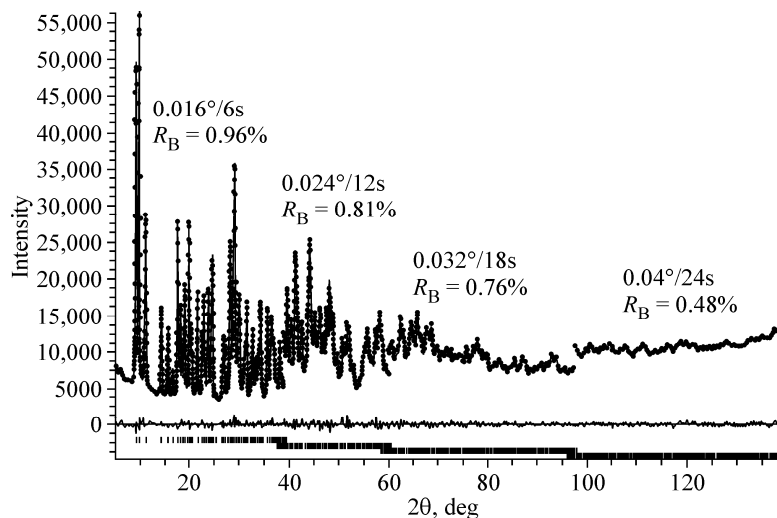
Fig. 1. Experimental (dots), theoretical (line), and differential (line below) X-ray diffraction patterns of the Rietveld refinement for the crystal of **I** and the Bragg factors R_B, step/exposure.

X-ray diffraction study. The powder X-ray diffraction pattern of **I** was recorded on a Bruker D8 ADVANCE diffractometer using a linear VANTEC detector and CuK_α radiation. In the experiment, the technique of variable cam timing (VCT) and variable scanning step (VSS) was used [8]. The experimental X-ray diffraction pattern was divided into four parts (Fig. 1) for VCT/VSS in the XRD Wizard software [9]. The total time of its measurement was about 19.5 h.

The unit cell parameters and space group were determined using the DASH 3.3 software [10]. The determination of the parameters gave the triclinic cell ($M(30) = 28.8$, $F(30) = 89.4$). The structure was solved for the centrosymmetric $P\overline{1}$ space group by its modeling in the direct space with subsequent phase annealing using the TOPAS 4.2 software [11]. The cell volume corresponded to 16-20 atoms in the asymmetric unit; therefore, two $C_4H_3N_2O_2S^-$ (HTBA$^-$) anions and one Pb^{2+} ion were generated. The phase annealing provided a structure model using which the Rietveld refinement in the TOPAS 4.2 software was performed. The coordinates of H atoms were idealized and refined along with heavy atoms in the riding model. As a result, from difference electron density maps, a peak corresponding to the oxygen atom of a water molecule was found. The hydrogen atoms belonging to a water molecule were not revealed from the difference electron density maps, thus, only one oxygen atom was refined. The VCT technique made it possible to refine the thermal parameter of Pb in the anisotropic approximation. The refinement process was stable and provided low uncertainty factors R for all four parts of the X-ray diffraction pattern (Fig. 1).

The main crystallographic characteristics of **I** and the experiment parameters are as follows: chemical formula $C_8H_8N_4O_5S_2Pb$, $M_r = 511.51$, $a = 65972(1)$ Å, $b = 9.8917(2)$ Å, $c = 10.0893(2)$ Å, $\alpha = 106.702(1)°$, $\beta = 93.395(2)°$, $\gamma = 107.48(1)°$, $V = 593.82(2)$ Å^3, space group $P\overline{1}$, $Z = 2$, $d_x = 2.850$ g/cm^3, $\mu = 31.213$ mm^{-1}, 2θ range of 5-140°, 2235 reflections, 151 refined parameters, $R_{wp} = 2.263\%$, $R_{exp} = 1.000\%$, $R_p = 1.747\%$, $GOOF(\chi) = 2.264$.

The graphical representation of all crystal structures and molecules was made using the DIAMOND software [12]. The structure was deposited with the Cambridge Structural Database (CCDC) under No. 900452. The data can be obtained from the website www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The synthesized complex compound is a chain polymer, in which the bridging HTBA$^-$ ligand via the O atom and the S atom links two Pb^{2+} ions. Its structure corresponds to the *catena*-di(μ_2-2-thiobarbiturato-O,S)aqualead(II) name and the *catena*-[Pb(H$_2$O)(HTBA-O,S)$_2$] formula.

The asymmetric unit of complex **I** contains one Pb^{2+} ion, two HTBA$^-$ ions, and one water molecule (Fig. 2*a*). The lead ion is bonded with two oxygen atoms (the bond lengths are 2.5544(6) Å and 2.736(7) Å), four sulfur atoms (for them,
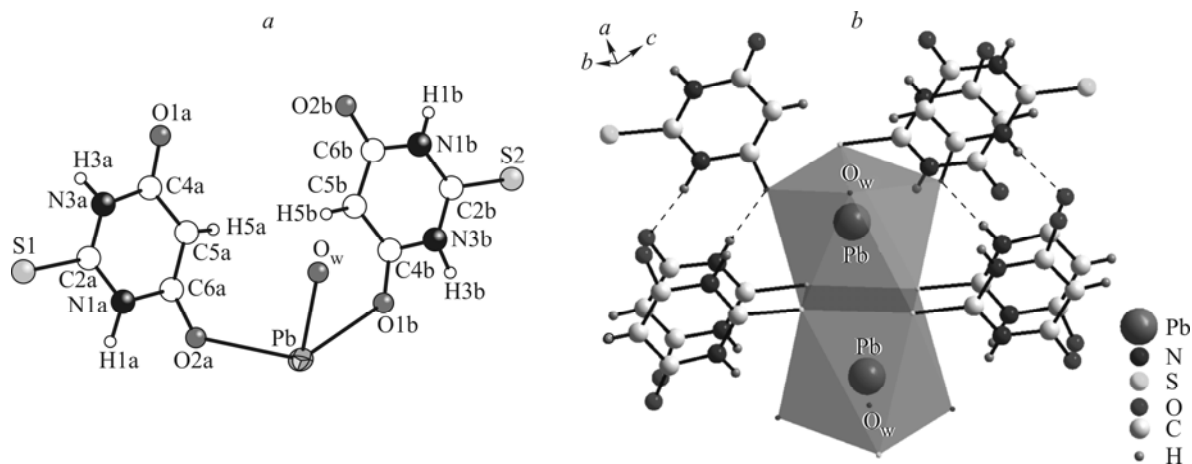
Fig. 2. Asymmetric unit of the crystal of **I** (*a*); coordination environment of Pb(II) in **I** (*b*). Intermolecular hydrogen bonds are denoted by dotted lines.

TABLE 1. Hydrogen bonds D–H⋯A (Å, deg) in the structure of **I**

D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
N1a–H1a⋯O2b[1]	1.00	1.93	2.93(1)	173
N1b–H1b⋯O2a[2]	0.78	2.15	2.92(1)	170
N3a–H3a⋯O1b[3]	0.85	2.07	2.92(1)	175
N3b–H3b⋯O1a[4]	0.94	1.94	2.81(1)	154
O–H⋯O1a[6]			2.63(1)	
O–H⋯O2b[1]			2.59(2)	

Symmetry operations: [1] *x*, 1+*y*, *z*; [2] *x*, *y*–1, *z*; [3] *x*–1, *y*, *z*–1; [4] 1+*x*, *y*, 1+*z*; [5] 1–*x*, 1–*y*, 2–*z*; [6] *x*, *y*, 1+*z*.

the bond lengths are in a range of 3.11-3.31 Å) of the HTBA⁻ ion, and one O atom of a water molecule (the bond length is 2.528(9) Å). For the fifth S atom, the Pb–S distance is 3.622(4) Å. The analysis of CCDC [13] showed that the Pb–S distance greater than 3.6 Å taken as chemical bond rarely occurs (only in two compounds with codes DISNID and RAQSAD). Therefore, it is better to treat the longest Pb–S bond as a shortened contact. Taking it into account, the Pb^{2+} ion forms a distorted square antiprism (Fig. 2*b*) and is linked with seven HTBA⁻ ions and one water molecule. Two antiprisms are connected with each other by a common face consisting of four S atoms of the HTBA⁻ ions. Each of them has a common S–S edge with another same antiprism. The edge consists of a single sulfur atom of the terminal distorted square and one of four S atoms of the face connecting the antiprisms in pairs. As a result, a stepped chain structure forms, where each step is a pair of square antiprisms connected by a common face, and the antiprisms are arranged in columns located along the *a* axis. The space between them is filled with the HTBA⁻ structural moieties.

Five intermolecular hydrogen bonds (Table 1) form a three-dimensional framework. In addition, there should be two more hydrogen bonds between a water molecule and the O1a, O2b oxygen atoms in the structure. It is between these atoms the shortened distances *d*(O–O1a) = 2.63 Å, *d*(O–O2b) = 2.59 Å were revealed using the PLATON software [14]. The O1a–O–O2b angle is 130.6(5)°, so if the H atoms of a water molecule are located near the O1a–O and O2b–O bond lines, as it should be for the normal hydrogen bond, the geometry of the H_2O molecule will not be distorted.

Using the PLATON software, the π–π interaction parameters between the HTBA⁻ anions were calculated (Table 2). The HTBA⁻ has the head-to-head type packing [15].

TABLE 2. π–π Interaction Parameters of the HTBA$^-$ Ions in the Crystal of **I**

Cg$_i$–Cg$_j$	d(Cg–Cg), Å	α, deg	β, deg	γ, deg	Cg$_i$_p, Å	Shift, Å
Cg$_1$–Cg$_2'$	3.531(4)	3.6(4)	22.75	25.59	3.184(3)	1.53

Note. Cg$_1$ is the N1a, C2a, N3a, C4a, C5a, C6a ring plane. Cg$_2$ is the N1b, C2b, N3b, C4b, C5b, C6b ring plane. Cg$_2'$ is produced from Cg$_2$ by transformation [1–x, 1–y, 1–z].

REFERENCES

1. S. Bondock, A. El-Gaber Tarhoni, and A. A. Fadda, *Phosphorus Sulfur Silicon Relat. Elem*., **182**, 1915-1936 (2007).
2. V. I. Balas, S. K. Hadjikakou, N. Hadjiliadis, et al., *Bioinorg. Chem. Appl*., Article ID 654137, 5 pages doi:10.1155/2008/654137 (2008).
3. M. R. Chierotti, L. Ferrero, N. Garino, et al., *Chem. Eur. J*., **16**, 4347-4358 (2010).
4. M. S. Masoud, A. M. Heiba, and F. M. Ashmawy, *Trans. Met. Chem*., **8**, 124-126 (1983).
5. Z. M. Zaki and G. G. Mohamed, *Spectrochim. Acta*, **A56**, 1245-1250 (2000).
6. M. S. Refat, S. A. El-Korashyb, and A. S. Ahmed, *Spectrochim. Acta*, **A71**, 1084-1094 (2008).
7. N. Nishat, Rahis-ud-din, and M. M. Haq, *Polish J. Chem*., **78**, 645-652 (2004).
8. I. C. Madsen and R. J. Hill, *J. Appl. Crystsllogr*., **27**, 385-392 (1994).
9. *Diffrac-Plus Basic XRD Wizard*, Bruker AXS GmbH, Karlsruhe, Germany (2002-2007).
10. W. I. F. David, K. Shankland, J. Streek, et al., *J. Appl. Crystallogr*., **39**, 910-915 (2006).
11. *Bruker AXS TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data*, User's Manual, Bruker AXS, Karlsruhe, Germany (2008).
12. K. Brandenburg and M. Berndt, *DIAMOND-Visual Crystal Structure Information System CRYSTAL IMPACT, Postfach 1251, D-53002*, Bonn.
13. *Cambridge Structural Database*, *Version 5.32*, Univ. Cambridge, UK (November 2010).
14. *PLATON-A Multipurpose Crystallographic Tool*, Utrecht Univ., Utrecht, The Netherlands (2008).
15. J. L. Atwood and J. W. Steed, *Supramolecular Chemistry*, Parts 1, 2, VCH Verlag GmbH, Weinheim, Germany (2000).