

COORDINATION
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Crystal Structure of Thallium(I) 2-Thiobarbiturate

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Abstract—The crystal and molecular structures of thallium(I) thiobarbiturate $C_4H_3N_2O_2STl$ ($C_4H_4N_2O_2S$ is 2-thiobarbituric acid, H_2TBA) have been determined. Crystallographic data for $Tl(HTBA)$ are $a = 11.2414(7)$ Å, $b = 3.8444(3)$ Å, $c = 14.8381(9)$ Å, $\beta = 99.452(2)^\circ$, $V = 649.00(7)$ Å³, space group $P2/c$, $Z = 4$. Each of the two independent thallium ions is bonded to four oxygen and two sulfur atoms to form a distorted tetrahedron. $N-H\cdots O$ and $C-H\cdots S$ hydrogen bonds form a branched three-dimensional network. The structure is also stabilized by $\pi-\pi$ interaction between heterocyclic $HTBA^-$ ions. The IR spectra of $Tl(HTBA)$ agree with X-ray powder diffraction data. The compound is also stable below 280°C, and Tl_2SO_4 is one of the thermolysis products in an oxidative medium in the region of 500–650°C.

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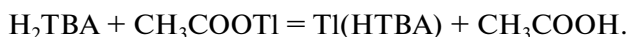
The role of thallium ions in biosystems has not been established yet, but these ions are known to destroy the nervous system. They easily pass through the channels of cell membranes due to the closeness of their radii to those of K^+ ions. Toxic effect is likely to be due to a higher chemical affinity of Tl^+ ions to S- and N-donating ligands in comparison with K^+ ions [1]. Increasingly high attention is currently paid to the behavior and propagation of thallium in the environment [2, 3]. Thallium compounds are relatively poorly studied, though they can find practical application. Thus, some thermoelectrical materials have been synthesized from them [4], and ²⁰¹Tl isotope atoms are suitable for use as γ -radiation sources in radiodiagnostics [1].

Thiobarbituric acids are one of the most important classes of bioligands applied in medicine. Thiobarbiturates have anesthetic, sedating, anticonvulsant [5], antibacterial [6], antimycotic [7], antiviral [8], and anticancer [9] properties. Their complexes with metals can exhibit specific antibacterial [10] and anticancer [11] activities.

The thallium(I) 2-thiobarbiturate complex was synthesized within the systematic study of the synthesis, structure, and properties of metal thiobarbiturate complexes [12]. Its structure was studied by X-ray powder diffraction, and some IR spectroscopic and thermal studies were performed.

EXPERIMENTAL

CH_3COOTl (chemically pure) and H_2TBA (chemically pure) were used in the synthesis. Thallium 2-thiobarbiturate ($C_4H_3N_2O_2STl$) (hereinafter, $Tl(HTBA)$) was synthesized by the reaction



CH_3COOTl (0.37 g, 1.4 mmol) was dissolved in water (50 mL), and H_2TBA (0.20 g, 1.4 mmol) was added to the resulting solution. The formed grey precipitate was allowed to stand at room temperature for several days and then filtered out, washed with an alcohol, and dried in air.

For $C_4H_3N_2O_2STl$, anal. calcd. (%): C, 13.82; H, 0.87; N, 8.06; S, 9.23. Found (%): C, 13.6; H, 0.96; N, 7.84; S, 9.47.

The X-ray powder diffraction pattern of $Tl(HTBA)$ was recorded on a Bruker D8 ADVANCE diffractometer at room temperature using a VANTEC linear detector (CuK_α radiation). All the reflections in the X-ray diffraction pattern were indexed in a monoclinic unit cell (space group $P2/c$) with parameters close to the values for $K(HTBA)$ [13, 14]. The Reitveld refinement was performed by the TOPAS 4.2 software [15]. The refinement was stable and gave low unreliability factors (Fig. 1). Selected crystallographic characteristics and parameters of X-ray diffraction experiment for $Tl(HTBA)$ are $M_r = 347.529$, $a = 11.2414(7)$ Å, $b = 3.8444(3)$ Å, $c = 14.8381(9)$ Å, $\beta = 99.452(2)^\circ$, $V = 649.00(7)$ Å³, space group $P2/c$, $Z = 4$, $\rho_{calcd} = 3.557$ g/cm³,

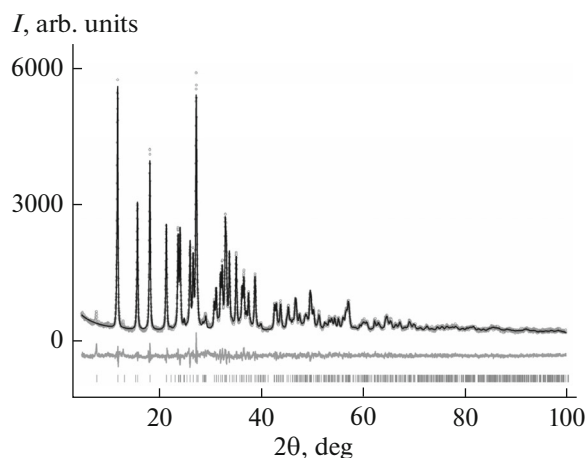


Fig. 1. Difference X-ray diffraction pattern of Tl(HTBA).

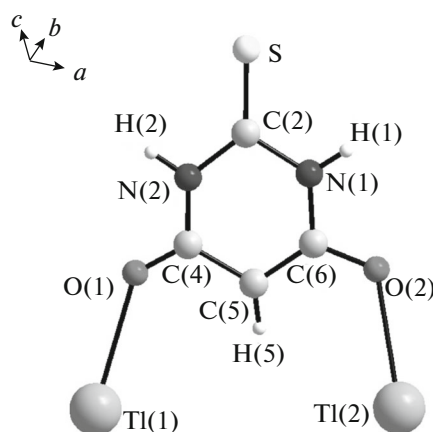


Fig. 2. Asymmetric Tl(HTBA) unit cell part.

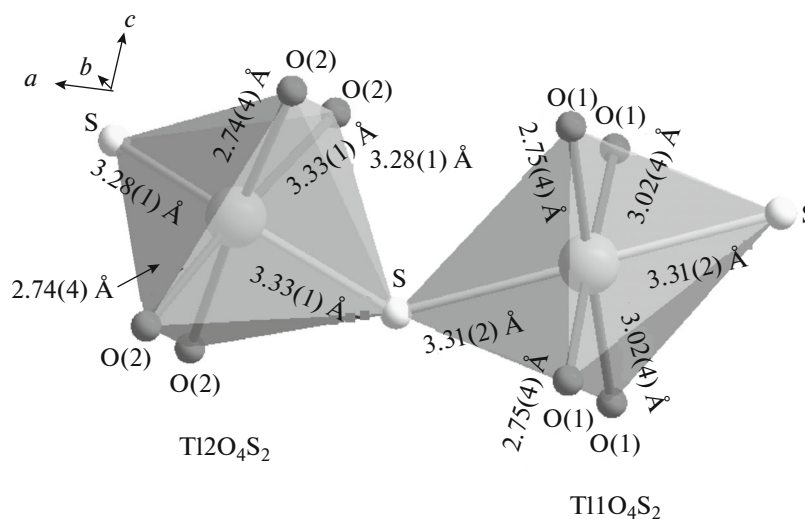


Fig. 3. Tl₁O₄S₂ and Tl₂O₄S₂ octahedra linked via a shared sulfur atom vertex.

$\mu = 50.345 \text{ mm}^{-1}$; 2θ range, 5° – 100° ; 671 reflections, 78 refined parameters, $R_{wp} = 6.49\%$, $R_{exp} = 4.47\%$, $R_p = 4.90\%$, $\chi^2 = 1.45$. The structure was deposited with the Cambridge Structure Database (no. 1058717);

deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

Geometric parameters of D–H \cdots A hydrogen bonds in the structure of Tl(HTBA)

D–H \cdots A	D–H, Å	H \cdots A, Å	D \cdots A, Å	D–H \cdots A, deg
N1–H1 \cdots O2 ²	0.87	1.95	2.82 (7)	178
N3–H3 \cdots O1 ³	0.86	2.03	2.88 (7)	172
C5–H5 \cdots S ¹	0.89	2.88	3.44 (5)	123

Symmetry codes: (1) $x, -y + 2, z - 1/2$; (2) $-x + 2, -y + 2, -z + 1$; (3) $-x + 1, -y + 1, -z + 1$.

RESULTS AND DISCUSSION

The asymmetric part of a Tl(HTBA) unit cell (Fig. 2) contains one HTBA[–] ion and two independent Tl¹⁺ and Tl²⁺ ions in the $2f$ and $2e$ local positions, respectively, on second-order axes. Each thallium ion is bonded to four oxygen and two sulfur atoms to form a distorted octahedron (Fig. 3). The Tl–O and Tl–S bond lengths agree with the distances given in the Cambridge Structure Database [16]. The octahedra are linked to each other via sulfur and oxygen atoms to form an infinite layer in plane ab (Fig. 4).

Structural analysis has shown the presence of three intermolecular N–H \cdots O and C–H \cdots S hydrogen

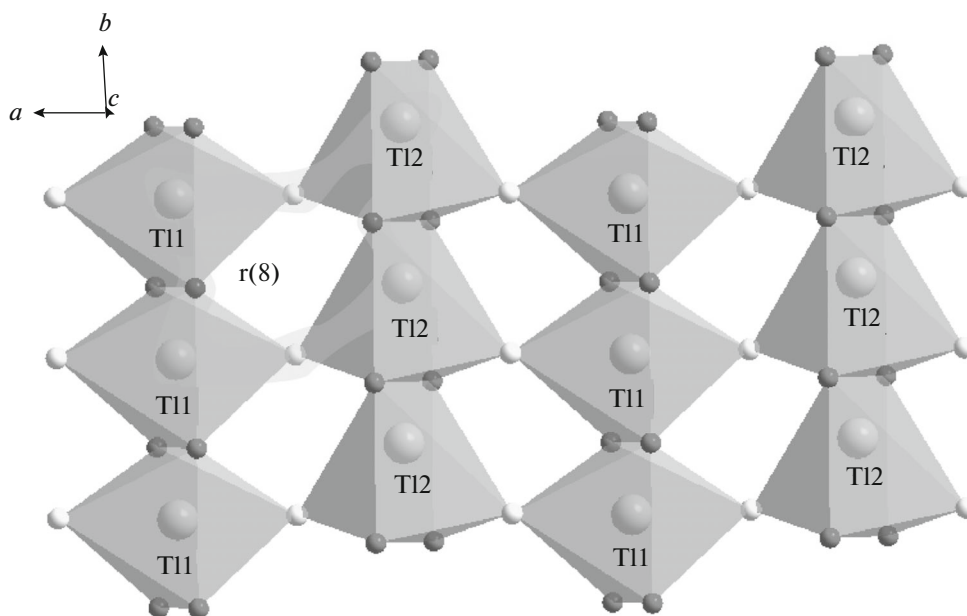


Fig. 4. Layer built of (Tl1,Tl2)O₄S₂ octahedra in plane *ab*. A typical cyclic moiety denoted as *r*(8) is shown.

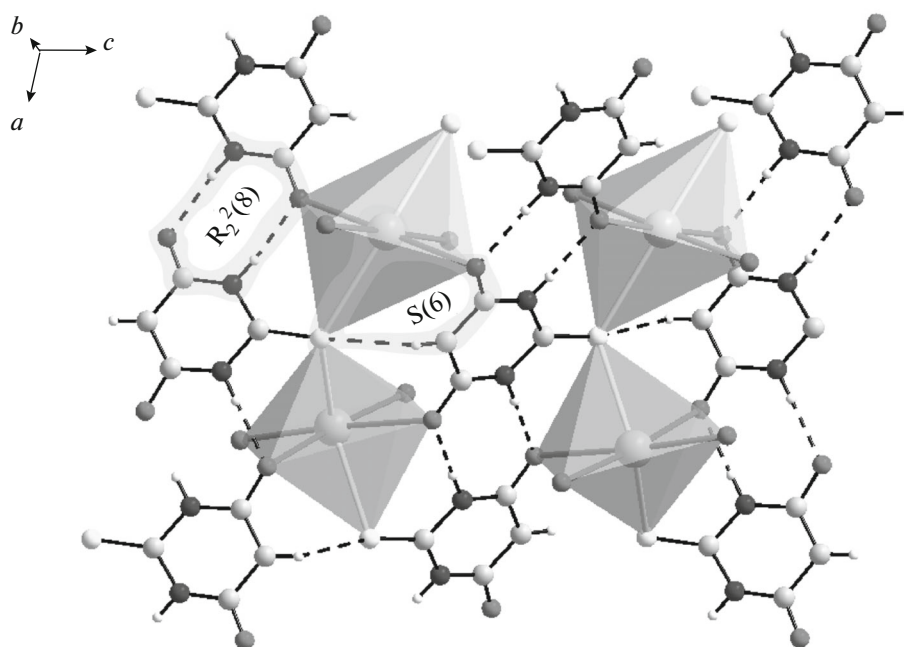


Fig. 5. Hydrogen bonds in Tl(HTBA). Typical supramolecular motifs are shown.

bonds (Fig. 5, table), which form a three-dimensional network. Using the PLATON software [17], “head-to-head” π - π interaction [18] between two neighboring N1, C2, N3, C4, C5 rings in Tl(HTBA) with a center-to-center distance of 3.94(3) Å and a shift of 1.38 Å was established.

The complex Tl₂(TBA) was precipitated from a strongly alkaline solution and structurally characterized in the earlier work [19]. It also contained two non-equivalent thallium atoms, and its polymeric structure was rather complicated (Fig. 6). An important distinctive feature of the Tl₂(TBA) structure from

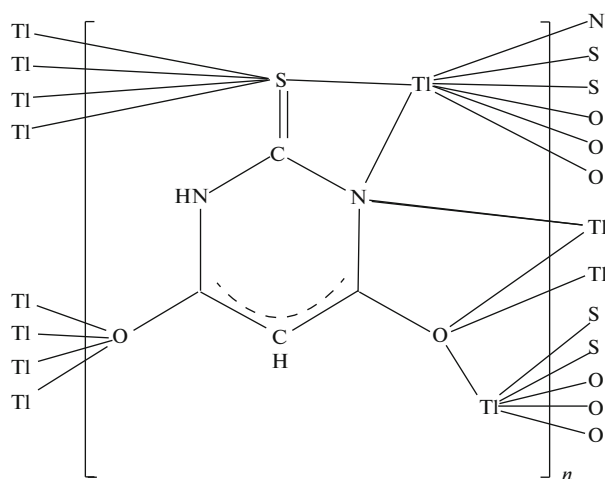


Fig. 6. Chemical bonds in the polymeric $Tl_2(TBA)$ complex.

$Tl(HTBA)$ is that the ligand is coordinated via a nitrogen atom to form a four-membered chelate ring.

Anhydrous thiobarbituric acid can exist in the form of six polymorphs [20]. Using the results of studying the IR spectra of its different polymorphs [21–23], it has been concluded in the monography [12] that the most high-frequency $\nu(C-O)$ band lies in the region of $1705-1750\text{ cm}^{-1}$, and the $\nu(C-S)$ frequency changes from 1145 to 1165 cm^{-1} . The IR spectrum of $Tl(HTBA)$ in KBr (FTIR Nicolet 6700) is observed to contain a band with a lower frequency (1651 cm^{-1}) in the region of $\nu(C-O)$ vibrations, thus being in agreement with the coordination of $HTBA^-$ to the thallium ion via oxygen atoms. The expected range of $\nu(C-S)$ frequencies does not contain any bands, thus confirming S-coordination of the ligand. Hence, IR spectroscopy results agree with X-ray diffraction data.

The thermal decomposition of $Tl(HTBA)$ was studied on a NETZH 409 analyzer in an air flow (50 mL/min) at a heating rate of 10 K/min and a sample weight of 6.63 mg .

According to the TG curve (Fig. 7), the sample mass loss of $\sim 3\%$, which most likely corresponds to the removal of hygroscopic water and, probably, to the oxidative decomposition of an admixture, is observed below 280°C . In the region of $280-510^\circ\text{C}$, it is possible to distinguish three $Tl(HTBA)$ mass loss stages accompanied by corresponding exotherms with peaks at 301 , 362 , and 451°C . They are produced by the oxidation of the organic $HTBA^-$ ion with the liberation of gaseous H_2O , CO_2 , SO_2 , and NO [24]. One of the final thermolysis products is Tl_2SO_4 . This is confirmed by the presence of a weak endotherm corresponding to the transition of the monoclinic α phase to the orthorhombic β phase in the DSC curve at 500°C , and an endotherm associated with Tl_2SO_4 melting at 632°C [25]. The total mass loss at 650°C is $\sim 35\%$ and must be

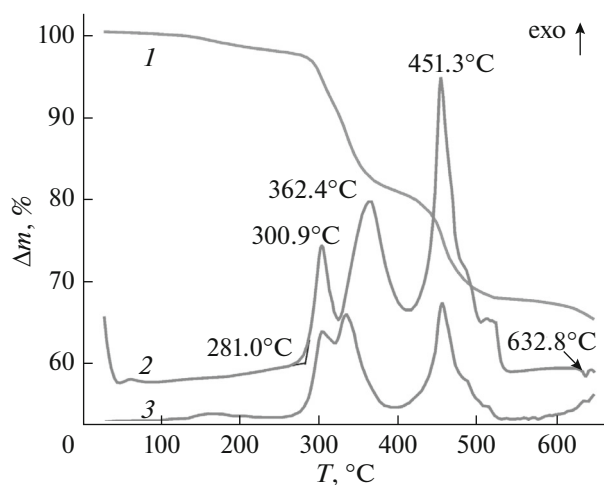


Fig. 7. (1) TG, (2) DTA, and (3) DTG curves for the $Tl(HTBA)$ complex.

27.4% on Tl_2SO_4 basis. After subtraction of the weight loss at a temperature below $\sim 220-250^\circ\text{C}$, the experimental weight loss will be $\sim 30\%$, which is closer to the theoretically expected value. The observed difference can be explained by the formation of a mixture of products and/or admixtures in $Tl(HTBA)$.

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