BRIEF COMMUNICATIONS

CRYSTAL STRUCTURE OF *CATENA*-(2-THIO-BARBITURATO)DITHALLIUM(I)
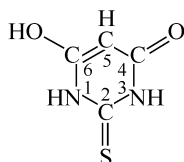
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By powder X-ray diffraction the crystal structure of *catena*-(2-thiobarbiturato)dithallium(I) $C_4H_2N_2O_2STl_2$ ($C_4H_4N_2O_2S$ is 2-thiobarbituric acid, H_2TBA), Tl_2TBA, is determined. Crystallographic data for Tl_2TBA are as follows: $a = 15.1039(3)$ Å, $b = 12.0818(2)$ Å, $c = 3.86455(6)$ Å, $\beta = 97.203(1)°$, $V = 741.34(2)$ Å^3, space group $P2_1/n$, $Z = 4$. There are two non-equivalent thallium atoms in the structure. The Tl1 polyhedron is a distorted trigonal prism due to the shortened Tl–S contact (3.634 Å), and the Tl2 polyhedron is a distorted square antiprism.

Thiobarbituric acid (4.6-dihydroxy-2-mercaptopyrimidine, $C_4H_4N_2O_2S$, H_2TBA), its derivatives, and complexes with metals are biologically active substances [1, 2]. Thiobarbituric acid used as a reagent exists in the thione-enol form. It is formed by passing the most acidic proton of the CH_2 group to the oxygen atom of the neighboring carbonyl group. The ≡C6–OH group is the most probable electron donor center of the ligand.

Nitrogen atoms of the NH group and S can be other ligand centers linking the metals. Complexing of metal ions, for example, cobalt(III) [3] having a high chemical affinity for a nitrogen atom, leads to the proton abstraction from the NH group and N,S-coordination of ligand with the formation of a four-membered chelate ring. The formation of a metal– sulphur bond should be expected, in the first instance, for soft Lewis acids, e.g., the Tl^+ ion.

This communication describes the synthesis of polycrystalline 2-(thiobarbiturato)dithallium(I) $C_4H_2N_2O_2STl_2$, Tl_2TBA and its structure determined using powder X-ray diffraction.

Experimental. CH_3COOTl (analytical grade), H_2TBA (chemically pure), and LiOH (chemically pure) were used.

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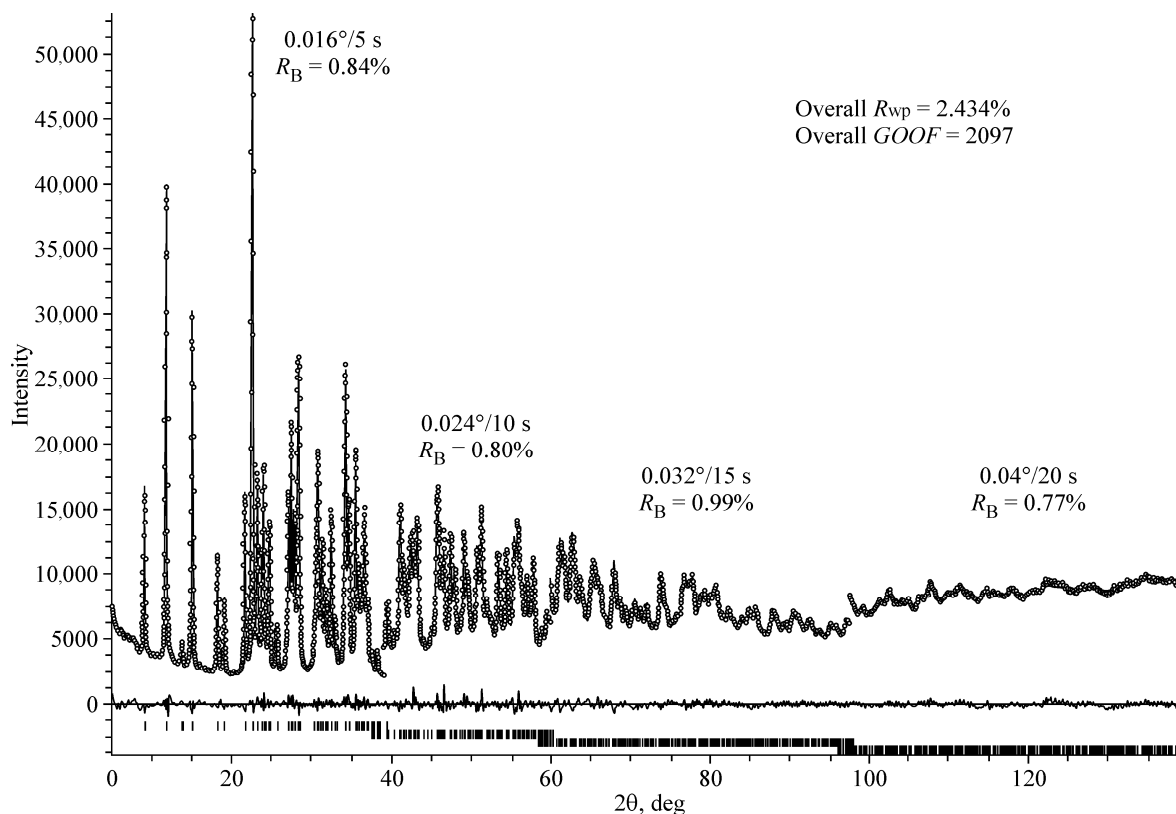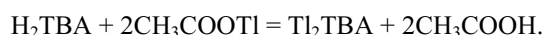
Fig. 1. Experimental (points), theoretical (line), and differential (line below) X-ray diffraction patterns of the Rietveld refinement result for the crystal of **I** and the Bragg factors R_B, step/exposure for each part of the X-ray diffraction pattern and overall for all X-ray diffraction patterns profile factors R_{wp} together with $GOOF$ (χ).

Catena-**2-(thiobarbiturato)dithallium(I)**, *catena*-Tl_2TBA **(I)**. 0.10 g (4.2 mmol) of LiOH were dissolved in 4 ml of water, and then 0.20 g (1.4 mmol) of H_2TBA were added. After its complete dissolution, 0.74 g (2.8 mmol) of CH_3COOTl were introduced according to the reaction

$$H_2TBA + 2CH_3COOTl = Tl_2TBA + 2CH_3COOH.$$

A light yellow precipitate formed was filtered off, washed with alcohol, and dried in the air. The results of elemental analysis for **I** (found/calculated, wt.%) are as follows: C 8.31/8.72, H 0.42/0.36, N 4.83/5.08, S 6.15/5.82, Tl 72.94/74.20.

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. The technique of variable scan timing (VST) and variable scanning step (VSS) was used. The exposure time increased with an increase in the 2θ angle significantly improving the quality of the recorded X-ray diffraction pattern [4]. As a rule, the full width at a half maximum (FWHM) contains 5-8 experimental points. However, with an increase in the θ angle, the peaks become much broader, so in the 2θ large angle regions, the step size can be increased in order to shorten the experimental time [5].

The experimental X-ray diffraction pattern was divided into four parts (Fig. 1). The total experimental time was about 16.2 h, and without using the variable step scanning method it would exceed 31 h. The experiment was decomposed into parts for VCT/VSS using the XRD Wizard software [5]. The peak positions were determined using the EVA program (2004 release) from the Bruker DIFFRAC-PLUS software.

The unit cell parameters and the space group were determined using the DASH 3.3 software [6]. The determination of the parameters gave the monoclinic cell: $a = 15.1097$ Å, $b = 12.8038$ Å, $c = 3.8667$ Å, $\beta = 97.258°$ (M(24) = 29.1; F(24) = 58.8). Using the DASH 3.3 software, a list of the most probable space groups in the decreasing order of probability was obtained: $P2_1/n$ (log-probability score 20.99); $P2_1/a$ (15.14); Pn (11.78); $P2_1$ (9.22). Hence, $P2_1/n$ was selected as the
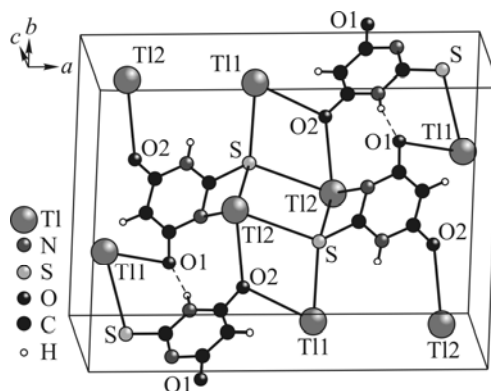
Fig. 2. Structure of Tl₂TBA. Hydrogen bonds are denoted by dotted lines.

most appropriate of all space groups. The structure was solved by its modeling in the direct space with subsequent phase annealing using the TOPAS 4.2 software [7]. The cell volume corresponded to 9–12 atoms in the asymmetric unit; therefore, one $C_4H_2N_2O_2S$ (TBA^{2-}) ion and two Tl$^+$ ions in the asymmetric unit of the cell were generated. The phase annealing provided a structural model with which the Rietveld refinement in the TOPAS 4.2 software was performed. In order to decrease the number of refined parameters, a soft constraint on the bond lengths in the TBA^{2-} ion was used. To this end, the average bond lengths were taken from the single crystal experiment on the KHTBA ($C_4H_3KN_2O_2S$) crystal [8]. In addition, we have imposed a soft constraint for the atoms to be in one plane in TBA^{2-}. The coordinates of hydrogen atoms were idealized and refined along with heavy atoms in the riding model. The VCT technique made it possible to refine the thermal parameters of both Tl$^+$ ions in the anisotropic approximation, which improved the refinement result. After the refinement, the thermal parameters of all non-hydrogen atoms had the normal values. Since the N3 nitrogen atom had a short contact with the Tl2 atom d(N3–Tl2) = 2.817(6) Å, it was decided to remove the hydrogen ion at N3. The refinement process was stable and provided low uncertainty factors R for all four parts of the X-ray diffraction pattern (Fig. 1). Since the structure was successfully solved in space group $P2_1/n$, it was decided not to test the other space groups. The main crystallographic characteristics of **I** and the experiment parameters are as follows: chemical formula $C_4H_2N_2O_2STl_2$, M_r = 550.91, a = 15.1039(3) Å, b = 12.0818(2) Å, c = 3.86455(6) Å, β = 97.203(1)°, V = 741.34(2) Å^3, space group $P2_1/n$, Z = 4, d_x = 4.936 g/cm^3, μ = 84.787 mm^{-1}, 2θ range of 5-140°, 1396 reflections, 107 refined parameters, R_{wp} = 2.434%, R_{exp} = 1.161%, R_p = 1.855%, $GOOF(\chi)$ = 2.097.

The graphical representation of all crystal structures and molecules was made using the DIAMOND software [9]. The structure was deposited with the Cambridge Structural Database under number 904109. The data can be obtained from the website www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The structure of the Tl₂TBA complex is shown in Fig. 2. The asymmetric unit of the cell contains two Tl$^+$ ions and one TBA^{2-} anion. Heterocyclic H₂TBA can be treated as substituted thiourea, malonyl thiourea, because it has a thionic C=S group in its composition. The S atom, together with two O atoms and one N atom, link the ligand with Tl$^+$ ions. There are two non-equivalent thallium atoms in the structure of **I**. With respect to Tl1, the TBA^{2-} ion is a monodentate ligand coordinated by O or S, and with respect to Tl2 it is both O- or S-monodentate and N,S-bidentate ligands. All ligands are bridging ones. Each sulphur atom is linked at the same time with three Tl$^+$ ions, and the oxygen atom is linked with two Tl$^+$ ions (Fig. 2). Each TBA^{2-} ion connects 7 Tl$^+$ ions (4 Tl1 and 3 Tl2) by bridging bonds.

The Tl1 atom is coordinated by four oxygen atoms (a bond length range 2.79-3.29 Å) and two sulphur atoms (3.068(4) Å and 3.215(4) Å). Packing features lead to the formation of a relatively rare form of the Tl1 polyhedron (a trigonal prism), in which the Tl1 atom is linked with six TBA^{2-} ions. The Tl2 atom is coordinated by three O atoms (2.52-3.22 Å), two N atoms (2.817(6) Å and 3.009(7) Å), and two S atoms (3.219(7) Å and 3.404(7) Å) (Fig. 3). Given the shortened Tl2–S contact (3.63 Å), the Tl2 polyhedron is a distorted square antiprism (Archimedean antiprism).
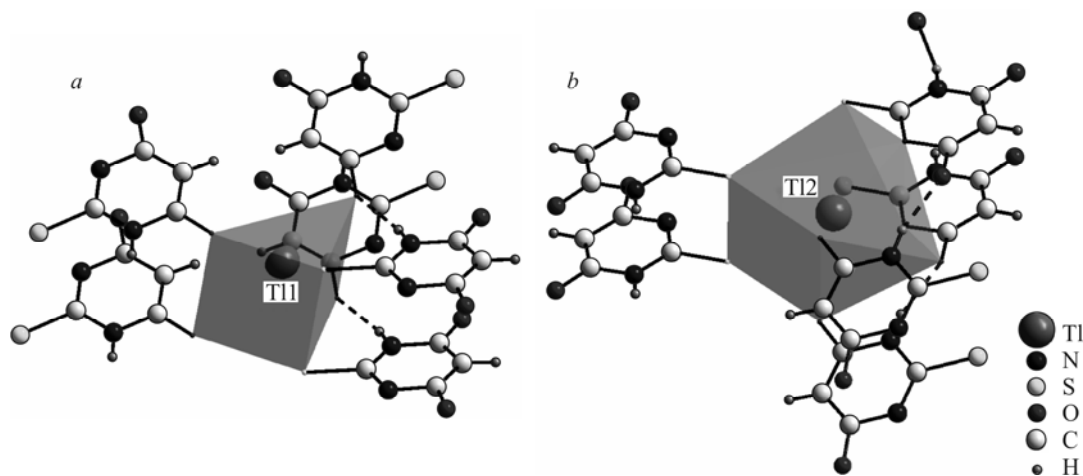
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Fig. 3. Coordination environment of ions: Tl1 (*a*); Tl2 (*b*). Intermolecular hydrogen bonds are denoted by dotted.

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
N1–H1···O1[1]	0.86	2.00	2.840(8)	166

[1]Symmetry operation: 1/2–*x*, 1/2+*y*, 1/2–*z*.

TABLE 2. Parameters of the π–π Interaction of the TBA^{2-} 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$_1'$	3.865(5)	0	17.59	17.59	3.684(3)	1.168

Cg$_1$ is the N1, C2, N3, C4, C5, C6 ring plane. Cg$_1'$ is produced from Cg$_1$ by transformation [*x*, *y*, 1–*z*].

The Tl1 and Tl2 polyhedra are linked in three different ways: by a common vertex (S or O1); a common face formed of the pairs of S and O2 atoms. The distorted square antiprisms with central Tl2 atoms share the S–S edge. Two Tl1 polyhedra are linked by a triangle face formed of S, O1, and O2 atoms. The space between the polyhedra along the *c* axis is filled with ligands.

The N3–Tl2–S angle for the bidentate ligand is only 51.92°. This, together with the presence of different donor atoms (N, O, S) in the nearest environment, leads to a structural distortion of the Tl2 polyhedron. A distorted trigonal prismatic structure of the Tl1 polyhedron can also be associated with the participation of different donor atoms (S and O) of TBA^{2-} in complexing. In addition, the distorted form of the polyhedra can be associated with the effect of the 6s^2 lone pair of the Tl$^+$ ion on the structure.

The structural analysis showed the presence of one intermolecular hydrogen bond (Table 1) forming linear chains of TBA^{2-} ions along the *b* axis, which, together with the Tl$^+$ ions, form a three-dimensional framework. The N1–H1···O1 hydrogen bond closes an 8-membered ring (Fig. 2), to which the R_1^1 (8) structural motif corresponds, and a 6-membered ring, to which the R_1^1 (6) structural motif corresponds. The analysis of shortened intermolecular contacts using the PLATON software [10] revealed the presence of π–π interaction between the centers of the TBA^{2-} anion rings; its parameters are summarized in Table 2. The TBA^{2-} ions have the head-to-head type packing [11].

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