

# Crystal Structure of Hexakis(thiourea)-Bis(( $\mu$ -Perchlorato-O,O')-(Perchlorato-O)-Bismuth) Diperchlorate

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Received May 30, 2012

**Abstract**—The complex  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4](\text{ClO}_4)_2$  (**I**) (Tu is thiourea) was synthesized and studied by X-ray diffraction. The crystallographic data of **I** are:  $a = 14.205(1)$  Å,  $b = 13.083(1)$  Å,  $c = 22.078(2)$  Å,  $\beta = 96.182(1)^\circ$ ,  $V = 4079.1(7)$  Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 4$ . The molecule is located on a twofold axis and consists of the binuclear cation  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4]^{2+}$  and two outer-sphere anions  $\text{ClO}_4^-$ . The Bi–S bond lengths are 2.61–2.62 Å. For each terminal and bridging  $\text{ClO}_4^-$  ion, one Bi–O distance varies from 2.744 to 3.048 Å and the other distance is longer (3.167 or 3.269 Å) and is considered as a shortened contact. The structure contains a hydrogen bond network involving all hydrogen atoms. The IR and Raman spectroscopy data confirm the thiourea coordination by the sulfur atom.

DOI: 10.1134/S1070328413020097

The coordination chemistry of bismuth, like that of other post-transition methods, is less studied than the coordination chemistry of transition elements. The use of bismuth compounds to treat gastritis and gastric ulcer and the potential use of the <sup>212</sup>Bi isotope in the therapy of cancer stimulates further research in this area [1].

Thiourea (Tu, CH<sub>4</sub>N<sub>2</sub>S) is a biologically active molecule widely used to prepare pharmaceutical products [2] and is a versatile reagent for industry [3]. The complexation of thiourea with Bi(III) is used in material science [4] and in analytical chemistry [5]. The observed unusual sequence of stepwise stability constants of  $\text{Bi}(\text{Tu})_n^{3+}$  and  $\text{Bi}(\text{Mtu})_n^{3+}$  complexes (Mtu = N-methylthiourea) in perchloric acid solutions [6, 7] can be a consequence of coordination of  $\text{ClO}_4^-$  ions to  $\text{Bi}^{3+}$  ions as indicated by EXAFS and LAXS [8].

In this study, we prepared the complex  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4](\text{ClO}_4)_2$  (**I**) and determined its structure by X-ray diffraction analysis.

## EXPERIMENTAL

Reagent grade chemicals Tu, HClO<sub>4</sub>, and Bi<sub>2</sub>O<sub>3</sub> were used. The solution of Bi(ClO<sub>4</sub>)<sub>3</sub> was prepared by dissolving Bi<sub>2</sub>O<sub>3</sub> in an excess of 9 M HClO<sub>4</sub>.

**Synthesis of I.** An excessive amount of crystalline thiourea was added to a 0.5 M solution of bismuth perchlorate in 1 M HClO<sub>4</sub>; after 24 h, the insoluble precipitate was filtered off. On storage of the filtrate for

2–5 days, a yellow finely crystalline solid formed, which was filtered off and washed with acetone. The product yield relative to bismuth was 70–82%.

For C<sub>6</sub>H<sub>24</sub>Bi<sub>2</sub>N<sub>12</sub>O<sub>24</sub>S<sub>6</sub>Cl<sub>6</sub>

anal. calcd. (%): C, 4.60; H, 1.74; N, 11.62; S, 13.08.

Found (%): C, 4.37; H, 2.03; N, 12.04; S, 12.67.

IR ( $\nu$ , cm<sup>-1</sup>): 464  $\delta_2(\text{ClO}_4)$ , 627  $\delta_1(\text{ClO}_4)$ , and  $\beta(\text{SCN})$ , 707  $\nu(\text{C}=\text{S})$ , 1094  $\nu(\text{N}-\text{C}-\text{N}) + \delta(\text{NH}_2) + \nu(\text{C}=\text{S})$ , 1120  $\nu_1(\text{ClO}_4)$ , 1618  $\delta(\text{N}-\text{H})$ , 2926, 3192, 3280, and 3388  $\nu(\text{NH})$ . The bands were assigned according to published data [9, 10]. The decrease in thiourea  $\nu(\text{C}=\text{S})$  from 733 to 707 cm<sup>-1</sup> attests to Tu coordination by the S atom [9, 10]. The Raman spectrum of **I** exhibited four bands due to the non-coordinated  $\text{ClO}_4^-$  ions (466, 627, 928, and 1111 cm<sup>-1</sup>) and a band at 239 cm<sup>-1</sup>, which was earlier assigned to  $\nu(\text{Bi}-\text{S})$  [11].

Analysis for C, H, N, S was performed on a Flash EA 1112 elemental analyzer.

**X-ray diffraction.** A yellow-colored crystal of **I** with dimensions 0.33 × 0.19 × 0.18 mm was studied. The reflection intensities were measured by a SMART APEX II single-crystal X-ray diffractometer with the CCD detector (Bruker AXS, MoK $\alpha$  radiation). The experimental absorption corrections were applied using the SADABS program [12] by the multi-scan method. The model of the structure was determined by the direct method and refined using the SHELXTL

**Table 1.** X-ray experimental parameters and structure refinement details for **I**

Parameter	Value
Temperature, K	298
Space group	<i>C2/c</i>
<i>Z</i>	4
$2\theta_{\max}$ , deg	57
<i>a</i> , Å	14.205(1)
<i>b</i> , Å	13.083(1)
<i>c</i> , Å	22.078(2)
$\beta$ , deg	96.182(1)
<i>V</i> , Å <sup>3</sup>	4079.1(7)
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	2.396
$\mu$ , mm <sup>-1</sup>	9.41
The total number of measured reflections	18979
The number of independent reflections ( $R_{\text{int}}$ )	5148 (0.069)
The number of reflections with $F > 4\sigma(F)$	3476
Range of indices <i>h, k, l</i>	$-19 \leq h \leq 18,$ $-17 \leq k \leq 17,$ $-29 \leq l \leq 29$
Weighing scheme (on $F^2$ )	$w = [\sigma^2 + (0.0469P)^2]^{-1},$ $P = (F_o^2 + 2F_c^2)/3$
The number of refined parameters	254
$R_1$ ( $F_o > 4\sigma(F_o)$ )	0.043
$wR_2$	0.1036
Extinction coefficient	0.00041(4)
GOOF	0.989
$\Delta\rho_{\max}/\Delta\rho_{\min}$ , e/Å <sup>3</sup>	1.163/−1.335

**Table 2.** Selected interatomic distances and bond angles in the structure of **I**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Bi–S(1)	2.620(2)	Bi–O(13)	2.916(6)
Bi–S(2)	2.610(2)	Bi–O(21)	3.048(7)
Bi–S(3)	2.610(2)	Bi–O(22)	3.167(6)
Bi–O(11a)	2.744(7)	Bi–O(11)	3.269(8)
S(1)–C(1)	1.741(8)	C(2)–N(21)	1.307(10)
S(2)–C(2)	1.726(8)	C(2)–N(22)	1.304(10)
S(3)–C(3)	1.752(8)	C(3)–N(31)	1.296(9)
C(1)–N(11)	1.298(9)	C(3)–N(32)	1.307(9)
C(1)–N(12)	1.308(9)		
Angle	$\omega$ , deg	Angle	$\omega$ , deg
S(1)BiS(2)	90.93(7)	O(13)BiS(3)	81.6(2)
S(1)BiS(3)	91.40(6)	O(13)BiO(11)	100.4(2)
S(2)BiS(3)	91.78(7)	O(21)BiS(1)	77.7(1)
O(11)BiS(1)	83.3(2)	O(21)BiS(2)	102.4(1)
O(11)BiS(2)	171.1(2)	O(21)BiS(3)	162.2(1)
O(11)BiS(3)	81.6(2)	O(21)BiO(11)	83.1(2)
O(13)BiS(1)	83.3(2)	O(21)BiO(13)	113.4(2)
O(13)BiS(2)	171.1(2)		

program package [13]. The hydrogen atom positions were found from difference electron density maps, then idealized, and refined in the form bound to the main atoms. Table 1 summarizes the experimental parameters and structure refinement details.

The structure of **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 878996; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data\_request/cif).

## RESULTS AND DISCUSSION

The  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4](\text{ClO}_4)_2$  molecule is located on a twofold axis. Each  $\text{Bi}^{3+}$  ion is at the center of the  $\text{BiO}_3\text{S}_3$  octahedron (Fig. 1). The octahedra are connected through the  $\text{ClO}_4^-$  and its symmetric analog. The third vertex of the symmetrically independent octahedron is the oxygen atom of the second  $\text{ClO}_4^-$  tetrahedron. The three remaining vertices of the octahedron are formed by the thiourea S atoms. The structure has one more  $\text{ClO}_4^-$  ion, which is located in the outer-sphere position. Figure 2 shows a  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4]^{2+}$  cation and independent  $\text{ClO}_4^-$  anion.

Two Bi–O(13) and Bi–O(21) bonds, 2.916(6) and 3.048(7) Å, are rather weak. Without considering these bonds, it is impossible to present a reasonable structure of the polyhedron. According to CCDC [14], in

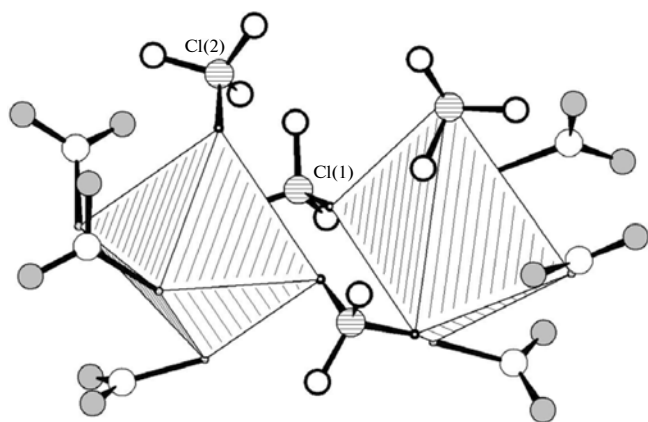


Fig. 1. Polyhedral structure of the cation  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4]^{2+}$ . Dark circles are N atoms.

three of the 38 structures containing a  $\text{S}_3\text{Bi}-\text{O}$  group, the Bi–O bond lengths are close to the found values and are 3.071 Å (code HOZVATO1), 2.937 Å (CELJOS), and 2.990 Å (ATIYEH). These facts are consistent with the assumption of octahedral environment of Bi(III) in I.

The geometric parameters of the structure of I are summarized in Table 2. Apart from the above-noted Bi–O bonds, there are shortened Bi–O(22) contacts (3.167 Å) and Bi–O(11) (3.269 Å), which are designated by dashed lines in Fig. 2. Other Bi–O distances are longer than 4 Å. The Cl–O distances are in the range of 1.384(7)–1.433(6) Å. The Cl(2)–O(24) distance (1.309(8) Å) stands out of this trend, and this is due to calculation error caused by great vibration amplitude of this oxygen atom. The Tu molecules have a usual planar conformation.

Owing to the presence of  $\text{ClO}_4^-$  groups, the structure contains a hydrogen bond (HB) network involving all hydrogen atoms. The spatial positions of HB are shown in Fig. 3, and their parameters are summarized in Table 3.

The existence of inner-sphere perchlorate Bi(III) complexes was established by EXAFS and LAXS methods [8]. In a 0.80 M solution of bismuth perchlorate containing 1.87 mol/L of perchloric acid,  $\text{Bi}(\text{ClO}_4)_2^+$  is formed, while at  $\text{ClO}_4^-$  concentration of 3.86 mol/L and Bi(III) concentration of 0.66 mol/L,  $\text{Bi}(\text{ClO}_4)_3$  is formed. These data are confirmed by X-ray diffraction. The complex  $[\text{Bi}(\text{Cyclen})(\text{H}_2\text{O})(\text{ClO}_4)_3]$  (Cyclen = 1,4,7,10-tetraazacyclododecane) [15] (RIPXUJ in CCDC) contains three monodentate perchlorate ions (Bi–O, 2.69–2.81 Å). To our knowledge, there are no other structurally characterized bismuth compounds with coordinated  $\text{ClO}_4^-$ .

The structure of a Bi(III) complex with bridging perchlorate ions was established for the first time. In

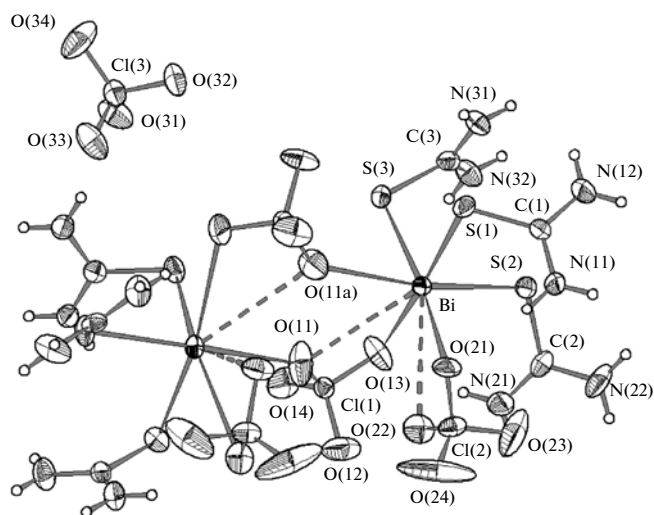


Fig. 2.  $[\text{Bi}_2(\text{Tu})_6(\text{ClO}_4)_4]^{2+}$  and  $\text{ClO}_4^-$  ions with atom numbering. The Bi...O contacts with  $>3.1$  Å distance are marked by dashed lines. The O(11a) atom is related to O(11) by  $(1-x; y; 0.5-z)$ . The thermal vibration ellipsoids are shown with confidence probability of 25%.

the complexes formed by  $\text{Pb}^{2+}$ , which is isoelectronic to  $\text{Bi}^{3+}$ , with azathioesters, the Pb–O bond lengths for the coordinated  $\text{ClO}_4^-$  ions vary over broad limits (3.06–3.36 Å), like those in I. When determining the

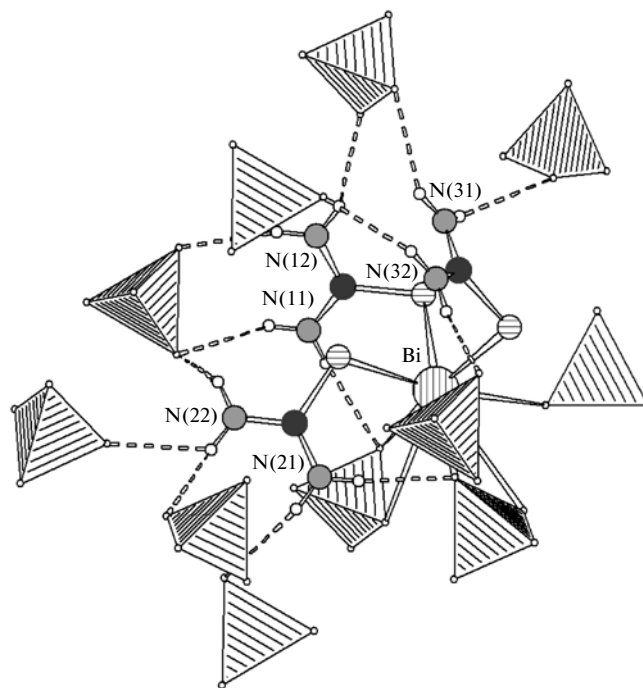


Fig. 3. Hydrogen bonds in structure I. The tetrahedra show the  $\text{ClO}_4^-$  ions.

**Table 3.** Geometric parameters of hydrogen bonds in the structure of **I**

D–H distance	Distance, Å				Transformations for atom A, deg
	D–H	H...A	D...A	DHA angle, deg	
N(11)–H(11A)···O(32)	0.86	2.36	3.077(9)	142	0.5 – x; 0.5 + y; 0.5 – z
N(11)–H(11B)···O(21)	0.86	2.17	2.992(8)	160	
N(12)–H(12A)···O(31)	0.86	2.13	2.974(10)	165	0.5 – x; 0.5 + y; 0.5 – z
N(12)–H(12B)···O(24)	0.86	2.09	2.900(10)	156	x – 0.5; y – 0.5; z
N(21)–H(21A)···O(32)	0.86	2.43	3.149(10)	142	x; 1 – y; z – 0.5
N(21)–H(21B)···O(13)	0.86	2.08	2.929(11)	172	
N(22)–H(22A)···O(23)	0.86	2.25	2.796(11)	121	0.5 – x; 1.5 – y; –z
N(22)–H(22A)···O(14)	0.86	2.58	3.286(10)	140	1 – x; 1 – y; –z
N(22)–H(22B)···O(32)	0.86	2.58	3.139(10)	123	0.5 – x; 0.5 + y; 0.5 – z
N(31)–H(31A)···O(22)	0.86	2.33	3.040(8)	140	x – 0.5; y – 0.5; z
N(31)–H(31A)···O(12)	0.86	2.60	3.033(10)	112	x – 0.5; y – 0.5; z
N(31)–H(31B)···O(21)	0.86	2.32	2.980(9)	134	0.5 – x; y – 0.5; 0.5 – z
N(32)–H(32A)···O(33)	0.86	2.23	3.012(10)	151	x – 0.5; 0.5 – y; z – 0.5
N(32)–H(32B)···O(31)	0.86	2.06	2.903(8)	166	1 – x; y; 0.5 – z

shape of the Pb(II) coordination polyhedron, the authors [16] took into account even the longest Pb–O bonds. The same  $\mu$ -O,O,O'-coordination mode of  $\text{ClO}_4^-$  was reported for Pb(II), Ag(I), and Hg(II) complexes [14]. However, analogous account for the shortened Bi–O(22) and Bi–O(11) contacts designated by dashed lines in Fig. 1 in the determination of the C.N. of bismuth is little substantiated. The C.N. of  $\text{Bi}^{3+}$  is 6 (the coordination polyhedron is a distorted octahedron). This may be due to binding of  $\text{Bi}^{3+}$  to different sorts of ligands with different types of coordination of  $\text{ClO}_4^-$  (O- and  $\mu$ -O,O') and the possible stereochemical activity of the lone pair  $6s^2$ .

#### ACKNOWLEDGMENTS

This work was supported by the grant of RF President for Leading Scientific Schools of the RF (NSh-4828.2012.2) and the Federal Target Program "Scientific and Scientific-Pedagogical Cadres of Innovative Russia for 2009–2013" (State Contract no. 02.740.11.0629).

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