

COORDINATION COMPOUNDS

Crystal Structure of Hexakis-(*N*-Methylthiourea) Bismuth(III) Triperchlorate

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Abstract—A bismuth(III) complex of *N*-methylthiourea (Mtu, C₂H₆N₂S) [Bi(C₂H₆N₂S)₆](ClO₄)₃ has been synthesized, and its crystal structure has been determined. The structure is built of octahedral Bi(Mtu)₆³⁺ cations and ClO₄⁻ anions. Sulfur atoms are coordinated to bismuth(III) (at axis 2) at octahedron vertices (Bi–S, 2.7670(8), 2.8142(8), and 2.8315(8) Å); angles SBiS vary from 82.26(3)° to 96.13(2)°. The presence of amino groups and oxygen atoms in the structure results in the emergence of numerous hydrogen bonds (HBs). All H atoms of amino groups are involved in HBs; one of them is bound to the sulfur atom. One of the oxygen atoms of ClO₄⁻ anions does not participate in HBs.

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Thiourea and its derivatives belong to the group of biologically active molecules and are widely used to produce pharmaceuticals [1–3]. These compounds are universal reagents for industrial use [4, 5]. Their complexes with bismuth(III) are known to have diverse compositions and structures. This fact has

been successfully used in materials science [6], organic synthesis [7], and analytical chemistry [8].

The structure of bismuth(III) complexes with *N*-alkylthiourea derivatives has not been deposited to the Cambridge Structural Database [9].

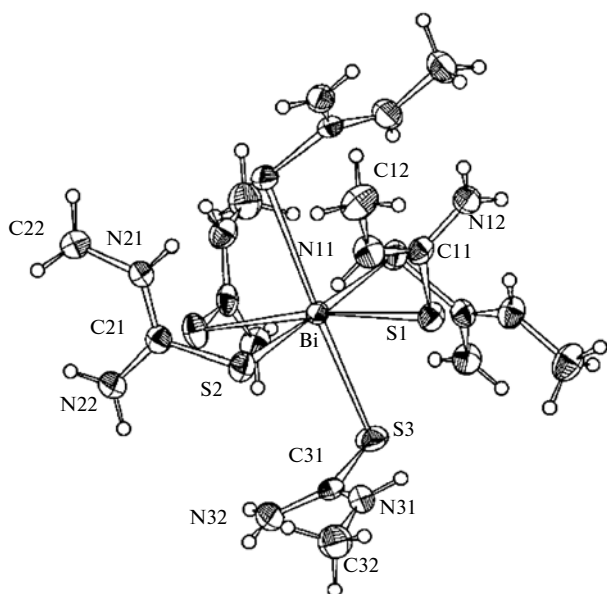


Fig. 1. Structure of Bi(Mtu)₆³⁺ ion; independent atoms are enumerated.

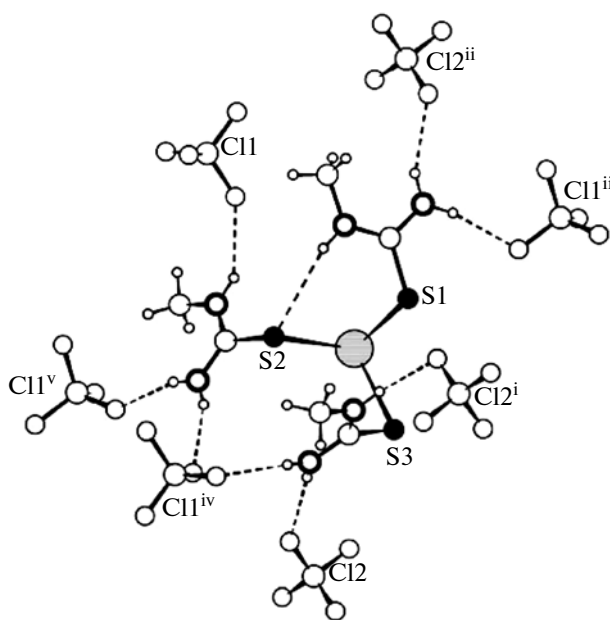
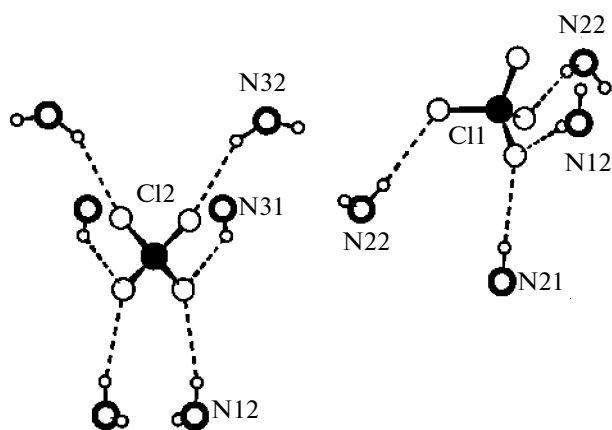


Fig. 2. Hydrogen bond system in [Bi(Mtu)₆](ClO₄)₃ (independent cation part). Symmetry operations: (i) 1 – x, 1 – y, 1 – z; (ii) x, 1 + y, z; (iii) 1 – x, y, 1.5 – z; (iv) 1.5 – x, 1.5 – y, 2 – z; (v) 1.5 – x, y – 1.5, 2.5 – z.

Table 1. Experimental details and refinement parameters for structure I

Formula weight	1048.23
Space group	<i>C2/c</i>
<i>Z</i>	4
<i>a, b, c, Å</i>	22.811(1); 14.4167(8); 13.4098(7)
β , deg	121.086(1)
<i>V, Å³</i>	3776.6(4)
ρ_{calc} , g/cm ³	1.844
μ , mm ⁻¹	5.276
$2\theta_{\text{max}}$, deg	58
Scan method	φ and ω
Total number of reflections	17806
Independent reflections	4935
Reflections with $F > 4\sigma(F)$	4354
R_{int}	0.038
Limits for <i>h, k, l</i>	$-31 \leq h \leq 31$; $-19 \leq k \leq 19$; $-18 \leq l \leq 18$
Weighting scheme for F^2	$w = 1/[\sigma^2(F_0^2) + (0.0234P)^2 + 2.2P]$; $P = (F_0^2 + 2F_c^2)/3$
Parameters refined	213
$R1 [F_0 > 4\sigma(F_0)]$	0.0275
$wR2$ (all reflections)	0.0579
Extinction parameter	0.00019(3)
$F(000)$	2000
GOOF	1.08
$\Delta\rho_{\text{max}}$, e/Å ³	1.18
$\Delta\rho_{\text{min}}$, e/Å ³	-0.63

This study is devoted to synthesizing bismuth(III) complex with *N*-methylthiourea (Mtu, C₂H₆N₂S) of composition [Bi(C₂H₆N₂S)₆](ClO₄)₃ (**I**) and determining its structure.

**Fig. 3.** Hydrogen bonds in the surrounding of ClO₄⁻ ions.

Synthesis of I. A weighed portion of 0.172 g (1.92 mmol) of Mtu (Aldrich) was dissolved in 20 mL of 1 M HClO₄; 1.29 mL of 0.249 M bismuth perchlorate solution (0.32 mmol Bi(III)) was added to the resulting solution. Red crystals precipitated from orange solution after it was left to stand for 24 h. The precipitation was filtered and dried between paper filter sheets. Product yield was 82%.

Bismuth was determined by complexometric titration; methylthiourea was determined spectrophotometrically according to the intrinsic absorption (235 nm, $\epsilon = 11540$).

For C₁₂H₃₆BiCl₃N₁₂O₁₂S₆ anal. calcd. (wt %): Bi, 19.94; Mtu, 51.6.

Found (wt %): Bi, 19.76; Mtu, 52.0.

X-ray diffraction analysis. A 0.36 × 0.33 × 0.29 mm crystal was selected for the analysis. Reflection intensity was measured using a SMART APEX II X-ray single-crystal diffractometer with a CCD detector (Bruker AXS, MoK α radiation). The crystal was cooled to 203 K to obtain the required number of reflections. Experimental absorption corrections were

Table 2. Geometric characteristics of hydrogen bonds in structure I

D–H...A*	Distance, Å		DHA angles, deg	Coordinates of atom A
	H...A	D...A		
N11–H11...S2	2.85	3.652(3)	154	1 – x, y, 1.5 – z
N12–H12A...O21	2.21	3.025(4)	155	1 – x, 1 + y, 1.5 – z
N12–H12B...O11	2.17	3.023(4)	166	
N21–H21...O11	2.22	2.986(4)	147	
N22–H22A...O12	2.24	3.087(4)	164	1.5 – x, y – 1/2, 2.5 – z
N22–H22B...O14	2.22	3.057(4)	161	1.5 – x, 1.5 – y, 2 – z
N31–H31...O21	2.30	3.063(4)	147	1 – x, 1 – y, 1 – z
N32–H32A...O12	2.57	3.434(4)	175	1.5 – x, 1.5 – y, 2 – z
N32–H32B...O22	2.21	3.022(4)	155	1 – x, y, 1.5 – z

* N–H 0.87 Å.

applied using the multiscan method and SADABS software [10]. The structure model was determined using direct methods (SHELXS) and refined by the full-matrix least-squares method using the SHELXL program package [11]. The idealized hydrogen atom positions in $\text{Bi}(\text{Mtu})_6^{3+}$ cation were determined from differential electron density synthesis. Then, the positions were refined as bound to non-hydrogen atoms. Table 1 lists the experimental details and the results of refinement for structure I.

A CIF file containing full information about structure I was deposited to the Cambridge Structural Database (no. 778958) and can be obtained upon request at www.ccdc.cam.ac.uk/data_request/cif.

The bismuth atom and one of chlorine atoms are located at the second-order axis; half of the $\text{Bi}(\text{Mtu})_6^{3+}$ ion corresponding to 1.5 ClO_4^- anions are independent. The refined interatomic distances in three independent Mtu moieties turned out to be within 3σ . Therefore, they were subsequently refined to be equal, which did not result in an increase in the divergence factor. These moieties are planar with the maximum atom departure of 0.042(2) Å. Sulfur atoms are coordinated to bismuth at octahedron vertices: Bi–S, 2.7670(8), 2.8142(8), and 2.8315(8) Å; SBiS angles, 82.26(3)°–96.13(2)° (Fig. 1). The presence of amine groups and oxygen atoms in the structure results in the emergence of numerous hydrogen bonds (HBs) (Table 2). All hydrogen atoms of amino groups are involved in HBs; one of these is bound to the sulfur atom of a neighboring Mtu ligand (Fig. 2). One of the oxygen atoms of ClO_4^- anions is not involved in HBs (Fig. 3).

N–H...S HBs are classified as weak with predominantly electrostatic interaction [12, p. 52]. The formation of these intramolecular HBs between neighboring thiourea (Tu) molecules was also found in the structure of bismuth(III) thiourea complexes. Thus, there are two HBs (H...S 2.52 Å, $\angle\text{NHS}$ 144°; H...S 2.56 Å, $\angle\text{NHS}$ = 169°) in the $[\text{Bi}(\text{Tu})_5(\text{NO}_3)](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ structure [9].

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