## COORDINATION COMPOUNDS

# Crystal Structure of [Bi(*N*-Ethylthiourea)$_4$(ClO$_4$)$_2$]ClO$_4$

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**Abstract**—The structure of the bismuth(III) complex with *N*-ethylthiourea (Ettu) has been determined for the first time. We found that the crystal structure of [Bi(Ettu)$_4$(ClO$_4$)$_2$]ClO$_4$ is built of distorted octahedral cations [Bi(Ettu–S)$_4$(ClO$_4$–O)$_2$]$^+$ and anions ClO$_4^-$. The deviation of one of the two independent Ettu molecules from the plane structure is explained by the mutual repulsion of the ligands and the formation features of hydrogen bonds. The C$_2$H$_5$(Ettu) group is in the *cis* position relative to the thiocarbonyl group.

In medicine, bismuth(III) compounds have been used for over two hundred years in the treatment of various diseases [1, 2]. In general, their anti-ulcer activity is of particular interest [3]. It is assumed [4] that thiolate complexes inhibiting urease activity, which is essential for the vital activity of Helicobacter pylori bacteria, are formed in the body. Bismuth(III) compounds are relatively nontoxic. They can induce the synthesis of thiol-enriched proteins, which reduces side effects from platinum anticancer drugs [5].

Substituted thioureas and their metal complexes are used in materials science, analytical chemistry, and medicine [6, 7]; for example, they are potential precursors for semiconductor materials Bi$_2$S$_3$ [8] and Bi$_9$O$_{7.5}$S [9].

Here, we study the synthesis and structure of a new bismuth(III) complex with *N*-ethylthiourea (Ettu).

## EXPERIMENTAL

**Synthesis of [Bi(Ettu)$_4$(ClO$_4$)$_2$]ClO$_4$ (I).** Chemically pure Bi$_2$O$_3$ was dissolved in an excess of chemically pure 1 M HClO$_4$ to obtain a 0.3 M solution of Bi(ClO$_4$)$_3$. The resulting solution (5 mL) was added to solid Ettu (Fluka, 98%) in the Bi(III) : Ettu molar ratio equal to 1 : 6. The resulting orange crystalline precipitate was filtered off and dried in air. Yield, 60%. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of the filtrate in air at room temperature.

**X-ray diffraction analysis.** The sets of intensities of diffraction reflections for a crystal of compound **I** (orange, 0.24 × 0.27 × 0.35 mm) were obtained on a Bruker SMART APEX II automated diffractometer equipped with a CCD detector (Mo$K_\alpha$-radiation) at 203 K. The adsorption correction was applied using the multiscan program SADABS [10]. The structure was solved by a direct method (SHELXTL) [11]. Non-hydrogen atoms were refined in the anisotropic approximation. The hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms.

Trigonal space group $P3_121$ of the structure of **I** and the lowered dispersion value in the distribution of normalized structural amplitudes $\langle|E^2 - 1|\rangle = 0.645$ required us to verify space groups with lower symmetry combined with merohedric twinning. However, all variations of twinning rules with the corresponding refinement of the structure resulted in space group $P3_121$, for which the absolute structure of **I** was unambiguously determined after the refinement procedure.

The crystallographic data for compound **I** have been deposited with the Cambridge Structural Database (CCDC No. 1408478; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The crystal structure of **I** is built of octahedral cations [Bi(Ettu)$_4$(ClO$_4$)$_2$]$^+$ and tetrahedral anions ClO$_4^-$. The Bi atoms and the Cl atoms of the coordinated ClO$_4^-$ anions are located on the two-fold axis with the coordinates *x*, *x*, 0.5. The outer-sphere ClO$_4^-$ anion is disordered (Fig. 1).

The Bi–O distance in the cation is elongated to 2.844(9) Å (according to related literature, the average Bi$^{3+}$–O$^{2-}$ distance is 2.27(5) Å [12]). In compound **I**, the S1–C11 and S2–C21 distances equal to 1.727(11) Å
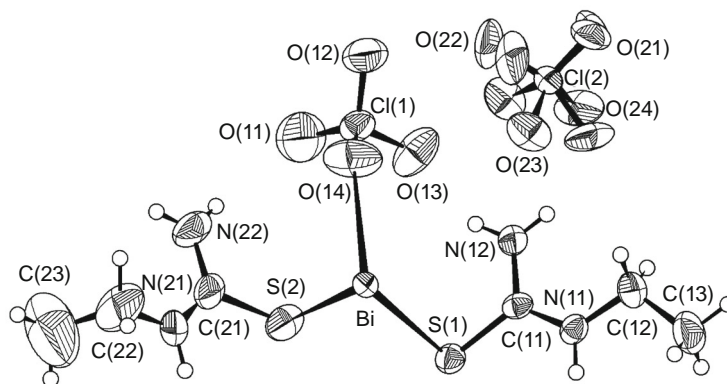
**Fig. 1.** Independent part of $[Bi(Ettu)_4(ClO_4)_2]^+$ and atomic numeration in compound **I**. Thermal ellipsoids are shown at the 50% probability level.

Crystallographic data, details of data collection, and characteristics of data refinement of the structure of **I**

| Molecular formula | $C_{12}H_{32}BiCl_3N_8O_{12}S_4$ |
|---|---|
| FW | 924.04 |
| Space group; $Z$; crystal system | $P3_121$; 3; trigonal |
| $a$, Å | 11.866(2) |
| $c$, Å | 19.480(5) |
| $V$, Å$^3$ | 2375.4(8) |
| $F(000)$ | 1362 |
| $\rho_{calc}$, g/cm$^3$ | 1.804 |
| $\mu$, mm$^{-1}$ | 6.146 |
| $2\theta_{max}$, deg | 51 |
| $T$, K | 203 |
| Number of reflections: collected | 17947 |
| unique ($R_{int}$) | 2945 (0.065) |
| with $F > 4\sigma(F)$ | 2683 |
| Reflection index intervals | $-14 \leqslant h \leqslant 14$; $-14 \leqslant k \leqslant 14$; $-23 \leqslant l \leqslant 23$ |
| Number of parameters refined | 201 |
| Extinction parameter | 0.0014(3) |
| Flack parameter | $-0.007(6)$ |
| $R1$ [$F_o > 4\sigma(F_o)$] | 0.0334 |
| $wR2$ | 0.0764 |
| GOOF | 1.022 |
| $(\Delta\rho)_{max}/(\Delta\rho)_{min}$, e/Å$^3$ | 0.84/−0.74 |

and 1.756(15) Å, respectively, are longer than those in thiourea (Tu) and its *N*-derivatives (the average C—S distance is 1.705 Å; there is no information for Ettu [13]), which is explained by the delocalization of the electron density in the Ettu molecule coordinating Bi(III) through the S atom. The distortion of the BiS$_4$O$_2$ octahedron results from the long Bi—O distances. Thus, the SBiS angles fall in the range of 78.27(10)°−99.40(10)°, while the OBiS angles range from 77.6(2)° to 104.4(2)° and the O14BiO14a angle is 111.6(5)°. Interestingly, the Ettu molecule containing the S2 atom is non-planar, the torsion angle C21−N21−C22−C23 is 105(2)°; it is equal to 180(1)° for the molecule containing the S1 atom. The deviation from the planar structure can be attributed to the mutual repulsion of the ligands and the formation of the hydrogen bonds C23−H8C···O22 and C22−H7A···O12 (Table 2). Other hydrogen bonds are also present in the structure (Fig. 2).

*N*-alkylthiourea can exist in two conformations, in which the alkyl radical C$_2$H$_5$ is located in either the *cis* or *trans* position with respect to the thiocarbonyl group [14]. The *trans*-position of the ethyl groups relative to the CS group in **I** as well as nine of ten Ettu complexes of platinum(II), cadmium(II), mercury(II), silver(I), rhenium(III), and copper(I) [13] can be due to the decrease of mutual repulsion of the ligands with this configuration. Only in the Cu(II) complex with Ettu the latter is in the form of the *trans* conformer [15].

As in **I**, in all structurally characterized complexes mentioned above, too, Ettu is a terminal ligand coordinated to the metal atom by the S atom [13]. The bridging S,S-coordination of Tu to Bi(III) is observed in [Bi$_2$(Tu)$_3$(CH$_3$COO)$_6$] · H$_2$O [16]; its presence was suggested in concentrated aqueous solutions based on the EXAFS data [17].

The uncoordinated ClO$_4^-$ ion in structure **I** is disordered over two orientations; the coordinated one is ordered. The Cl1−O distances in the inner-sphere

**Table 2.** Geometrical parameters of hydrogen bonds in the structure I

| D–H $\cdots$ A | Distances, Å | | | DHA, deg | Symmetry transformation of the A atom |
|---|---|---|---|---|---|
| | D–H | H$\cdots$A | D$\cdots$A | | |
| N11–H1$\cdots$O13 | 0.87 | 2.19 | 3.021(12) | 161 | $1 - y, x - y, z + 1/3$ |
| N12–2A$\cdots$O24 | 0.87 | 2.36 | 3.11(2) | 144 | $x, y, z$ |
| N12–2B$\cdots$O13 | 0.87 | 2.26 | 3.065(12) | 153 | $x, y, z$ |
| N21–H5$\cdots$O21 | 0.87 | 2.16 | 2.97(2) | 156 | $x - 1, y - 1, z$ |
| N21–H5$\cdots$O21 | 0.87 | 2.23 | 3.07(2) | 164 | $y - 1, x - 1, 1 - z$ |
| N22–6A$\cdots$O12 | 0.87 | 2.24 | 3.106(15) | 172 | $x - y, 1 - y, 2/3 - z$ |
| N22–6B$\cdots$O11 | 0.87 | 2.52 | 3.384(19) | 170 | $x, y, z$ |
| C12–3A$\cdots$O22 | 0.98 | 2.50 | 3.39(2) | 152 | $y, x, 1 - z$ |
| C23–8C$\cdots$O22 | 0.97 | 2.41 | 3.31(3) | 153 | $x - 1, y - 1, z$ |
| C22–7A$\cdots$O12 | 0.98 | 2.32 | 3.20(2) | 149 | $x - y, 1 - y, 2/3 - z$ |

$ClO_4^-$ ion are in the range of 1.387(11)–1.432(9) Å, the OCl1O angles fall in the range from 106.5(6) to 112.3(8)°. In the disordered tetrahedron of the uncoordinated $ClO_4^-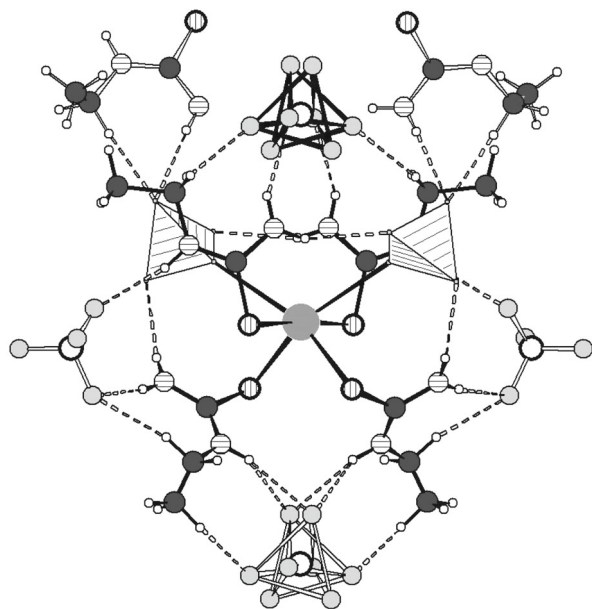$ ion, the Cl2–O distances are in the range of 1.300(15)–1.503(16) Å, the OCl2O angles vary from 101.9(9) to 117.8(12)°. In aqueous perchlorate solutions of bismuth(III) complexes with Tu [18] and $N$-methylthiourea (Mtu) [19], an unusual ratio of stepwise stability constants ($K_i$) was found ($K_{n+1} > K_n$).

This may result from coordination of $ClO_4^-$ to Bi, which agrees with the O-coordination of $ClO_4^-$ ions in compound **I**. Furthermore, the coordinated (terminal and O,O'-bridging) $ClO_4^-$ ions are present in $[Bi_2(Tu)_6(ClO_4)_4](ClO_4)_2$ [20]. Thus, coordination of $ClO_4^-$ to $Bi^{3+}$ in aqueous solutions cannot be excluded.

On the other hand, there are no inner-sphere $ClO_4^-$ ions in complex $[Bi(Mtu)_6](ClO_4)_3$ [21]. The combination of these facts can be due to the influence of the nature of thiourea ligand and synthesis conditions on the bismuth(III) coordination environment.



**Fig. 2.** Hydrogen bonds (dashed lines) in the structure of compound **I**. Carbon, nitrogen, and sulfur atoms are depicted with black and horizontally and vertically dashed circles, respectively. Inner-sphere $ClO_4^-$ ions are presented as tetrahedrons.

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