

COORDINATION  
COMPOUNDS

Crystal Structure  
of *catena*-( $\mu_4$ -1,3-Diethyl-2-thiobarbiturato-O,O',S,S)silver(I)

N. N. Golovnev<sup>a</sup>, M. S. Molokeev<sup>b, c</sup>, and M. A. Lutoshkin<sup>a</sup>

<sup>a</sup> Siberian Federal University, Svobodnyi pr. 79, Krasnoyarsk, 660041 Russia

<sup>b</sup> Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences,  
Akademgorodok 50/38, Krasnoyarsk, 660036 Russia

<sup>c</sup> Far-Eastern State University for Railway Research, Khabarovsk, ul. Serysheva 47, 680021 Russia

e-mail: ngolovnev@sfu-kras.ru

Received October 27, 2014

**Abstract**—The crystal structure of *catena*-( $\mu_4$ -1,3-diethyl-2-thiobarbiturato-O,O',S,S)silver(I) [Ag( $\mu_4$ -DETBA-O,O',S,S)] (**1**), where HDETBA is 1,3-diethyl-2-thiobarbituric acid C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S, has been solved by X-ray powder diffraction. Crystals of complex **1** are monoclinic,  $a = 7.8339(2)$  Å,  $b = 15.4970(4)$  Å,  $c = 8.7502(2)$  Å,  $\beta = 111.916(2)^\circ$ ,  $V = 985.53(5)$  Å<sup>3</sup>, space group  $P2_1/c$ ,  $Z = 4$ . The Ag<sup>+</sup> ion is coordinated by two oxygen atoms and two sulfur atoms to form a distorted tetrahedron. Tetrahedra share sulfur atom vertices to form infinite chains linked via bridging DETBA<sup>−</sup> ions into a three-dimensional framework. No hydrogen bonds have been found in the structure, but  $\pi$ – $\pi$  interaction is observed between DETBA<sup>−</sup> ions.

DOI: 10.1134/S0036023615050071

2-Thiobarbituric acid and its derivatives are depressants and belong to the class of medicines referred to as thiobarbiturates [1]. Some of them, e.g., sodium thiopental [2], thiobarbital (5,5-diethyl)-2-thiobarbituric acid), and thiobutabarbital (5-(2-butyl)-5-ethyl-2-thiobarbituric acid) [3], are of great therapeutic importance. Thiobarbiturates contain donating nitrogen, oxygen, and sulfur atoms, which can form metal–organic frameworks, including frameworks with a porous structure [4]. The structure and properties of complexes with 2-thiobarbituric acid were studied earlier [5–15]. Unlike 2-thiobarbituric acid, its derivatives remain almost unstudied; for example, there is little information about their structures, tautomerism, acid–base equilibria, and complexation with metals. Crystal structures were described only for 5-(isopropylidene)-2-thiobarbituric acid [16] and 1,3-diethyl-2-thiobarbituric acid (C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S, HDETBA) [17, 18]. There is the only known work [19] in which HDETBA metal complexes have been studied. In that work, the ionic radius was found to produce an effect on the conformation of the coordinated DETBA<sup>−</sup> ion, in particular, on the mutual arrangement of ethyl radicals, which can be situated either on the same side of the heterocyclic ring plane (*cis*-isomer) or on its opposite sides (*trans*-isomer). The DETBA<sup>−</sup> complexes with Li<sup>+</sup> and Na<sup>+</sup> ions [19] and HDETBA [17, 18] were found to be *cis*-isomers, whereas the complex with the K<sup>+</sup> ion has a *trans*-configuration.

This paper describes the synthesis, structure, and IR spectrum of the new 1,3-diethyl-2-thiobarbituric

complex of silver(I) [Ag( $\mu_4$ -DETBA)] (**1**). Silver and some of its compounds are of great medicobiological importance, but the mechanism of the action of silver ions in biological media is not clear until now [20]. The silver(I) complexes with thiobarbituric acids may be expected to have a specific bioactivity. Thus, the tin(IV) complex with 2-thiobarbituric acid has an anticancer activity [21]. The structure of the studied complex is also of theoretical interest, as the Ag<sup>+</sup> ion has a radius of  $\sim 1$  Å, which is nearly equal to the Na<sup>+</sup> ion radius (0.99 Å), so the DETBA<sup>−</sup> ion in the studied complex must be in a *cis*-configuration according to the earlier proposed hypothesis [19].

## EXPERIMENTAL

**Synthesis.** AgNO<sub>3</sub> (chemically pure), HDETBA (Sigma-Aldrich, 99%), and NaOH (chemically pure) were used. The Ag(DETBA) crystalline complex (**1**) was synthesized by stirring an equimolar mixture of AgNO<sub>3</sub>, HDETBA, and NaOH (1.39 mmol each) in water (5 mL) for 3–4 h until the termination of the reaction



The formed nearly colorless fine-crystalline precipitate was filtered out, washed with alcohol, and dried in air until a constant weight was attained. The product yield was 90–95%. We have not managed to obtain crystals suitable for single-crystal X-ray diffrac-

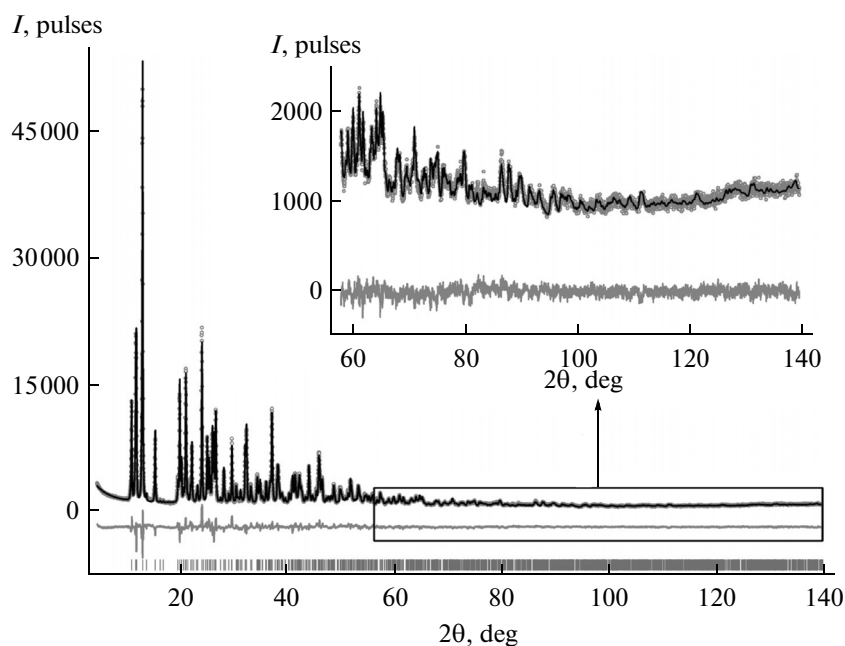


Fig. 1. Difference X-ray diffraction pattern of complex **1**.

tion structural characterization, so X-ray powder diffraction was used for this purpose.

**X-ray diffraction analysis.** The X-ray powder diffraction pattern of complex **1** (Fig. 1) was taken on a Bruker D8 ADVANCE diffractometer (VANTEC linear detector,  $\text{CuK}\alpha$  radiation). Peak positions were determined by the EVA 2004 software from the Bruker DIFFRAC-PLUS software suite. The unit cell parameters and space group ( $P2_1/c$ ) were found by the TOPAS 4.2 software [22]. The structure was solved by direct space modeling (TOPAS 4.2). The unit cell volume corresponded to 14 atoms in the asymmetric unit cell portion. Hence, one  $\text{DETBA}^-$  ( $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2\text{S}^-$ ) ion and one  $\text{Ag}^+$  ion have been generated in the process of structure solution. The structure of complex **1** was successfully solved and refined by the Rietveld method, as confirmed by low  $R$ -factors of uncertainty (Table 1). The structure was deposited with the Cambridge Structure Database (deposit@ccdc.cam.ac.uk or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), accession no. 1028301).

## RESULTS AND DISCUSSION

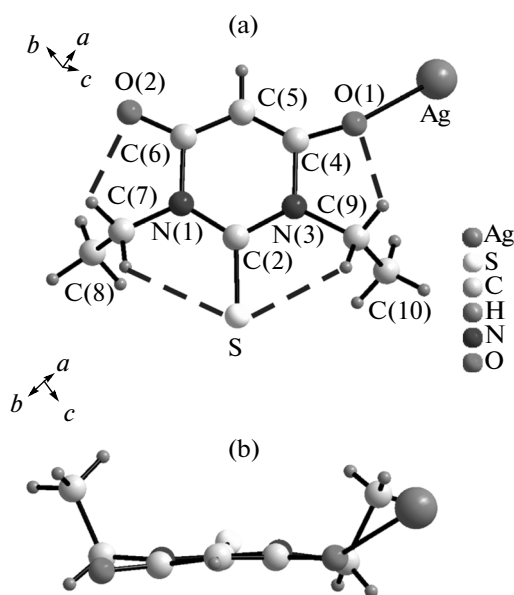
The asymmetric unit cell portion in complex **1** contains one  $\text{DETBA}^-$  ion and one  $\text{Ag}^+$  ion (Fig. 2). As expected, the  $\text{DETBA}^-$  ion has a *cis*-configuration, in agreement with the hypothesis about the effect of the radius of an ion on its isomerism. On the other hand, complex **1** is not isostructural to  $\text{Li}(\text{DETBA})$  and  $\text{Na}(\text{DETBA})$  [19] and has radically different unit cell parameters and  $\text{DETBA}^-$  ligand coordination modes.

The bond lengths in complex **1** ( $\text{Ag}-\text{O}$ , 2.461(8), 2.551(8) Å;  $\text{Ag}-\text{S}$ , 2.558(6), 2.540(6) Å) are ordinary

for silver(I) complexes [23]. The values of angles ( $\text{SAgS}$ , 127.3(2)°;  $\text{OAgO}$ , 109.4(1)°;  $\text{OAgS}$ , 102.5(3)–110.3(3)°) indicate that the tetrahedron is distorted. The  $\text{C}(2)-\text{S}$  bond (1.702(19) Å) is longer than the value obtained by X-ray diffraction (1.658(2) Å) [17] and neutron diffraction (1.681(9) Å) [18] for  $\text{HDETBA}$ . This confirms the participation of the sulfur atom in the coordination of  $\text{DETBA}^-$ . According to the literature data, an  $\text{HDETBA}$  crystal exists in the form of a thionemonocarbonyl tautomer, in which the  $\text{C}(4)-\text{O}(1)$  and  $\text{C}(6)-\text{O}(2)$  bond lengths (1.265(3) Å [17], 1.261(5) Å [18], and 1.312(3) Å [17], 1.309(3) Å [18], respectively) considerably differ from each other. The lengths of these bonds in complex **1** have close

Table 1. Selected crystallographic characteristics and X-ray diffraction experiment details for complex **1**

Space group	$P2_1/c$
$a$ , Å	7.8339(2)
$b$ , Å	15.4970(4)
$c$ , Å	8.7502(2)
$\beta$ , deg	111.916(2)
$V$ , Å <sup>3</sup>	985.53(5)
$Z$	4
$2\theta$ range, deg	5–140
Number of reflections	1880
Number of refined parameters	78
$R_{\text{wp}}$ , %	5.93
$R_p$ , %	4.62
$R_{\text{exp}}$ , %	2.31
$\chi^2$	2.57
$R_B$ , %	3.69



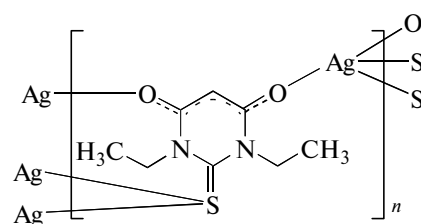
**Fig. 2.** Asymmetric unit cell portion in complex **1**: (a) labelling of atoms and (b) view along the C(2)–S bond. Hydrogen bonds are shown in dashes.

values within errors: C(4)–O(1) is 1.29(2) Å and C(6)–O(2) is 1.25(2) Å. The other geometric characteristics of the coordinated DETBA<sup>−</sup> ion are close to the values found for crystalline HDETBA [17, 18].

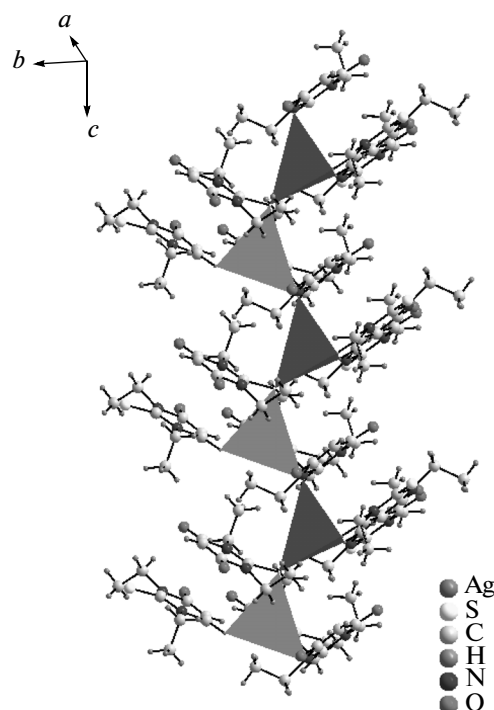
The DETBA<sup>−</sup> ligand in the polymeric complex is  $\mu_4$ -O,O',S,S-coordinated and linked to four silver atoms: each of the two oxygen atoms is linked to one silver atom, and the sulfur atom is bonded to two silver atoms (Fig. 3).

The tetrahedral surrounding of the Ag<sup>+</sup> ion is built of two oxygen atoms and two sulfur atoms. The metal ions in the Li(DETBA) and Na(DETBA) complexes immediately interact with three oxygen atoms and one sulfur atom [19], i.e., their coordination surrounding differs from the coordination surrounding of silver(I) in complex **1**. The AgO<sub>2</sub>S<sub>2</sub> tetrahedra in complex **1** are bonded by sharing vertices (sulfur atoms) to form infinite chains running along the *c* axis (Fig. 4). The latter are linked to each other by bridging DETBA<sup>−</sup> ions to form a three dimensional framework (Fig. 5).

The framework can be distinguished to contain 12- and 14-membered rings denoted by us as r(12) and r(14). Similar rings were observed earlier in calcium(II) and strontium(II) 2-thiobarbiturates [6]. No



**Fig. 3.** Chemical bonds in the structure of [Ag( $\mu_4$ -DETBA-O,O',S,S)].



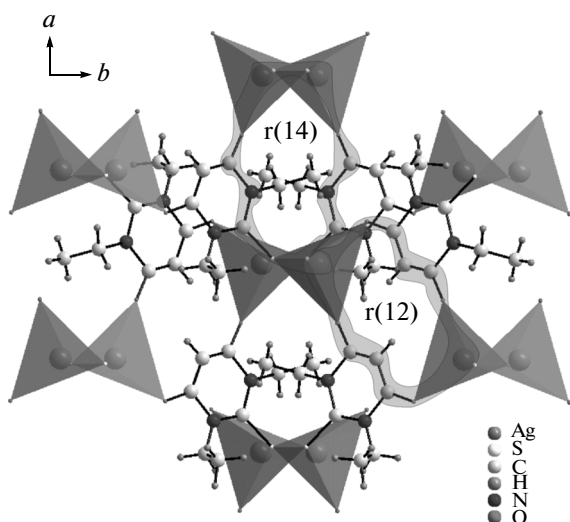
**Fig. 4.** Chains of AgO<sub>2</sub>S<sub>2</sub> tetrahedra running along the *c* axis in the structure of complex **1**.

intermolecular hydrogen bonds have been found in the structure of complex **1** in common with the M(DETBA) complexes (M = Li, Na, K) [19], but weak intramolecular hydrogen bonds C(9)–H(9B)⋯O1 and C(7)–H(7B)⋯O2 with interatomic C⋯O distances of 2.62(2) Å and C(9)–H(9A)⋯S and C(7)–H(7A)⋯S with interatomic C⋯S distances of 3.02(2) and 3.05(5) Å, respectively, are formed. D–H⋯A angles range within 97(1)°–110(1)°. Unlike M(DETBA), there exists  $\pi$ – $\pi$  interaction with the

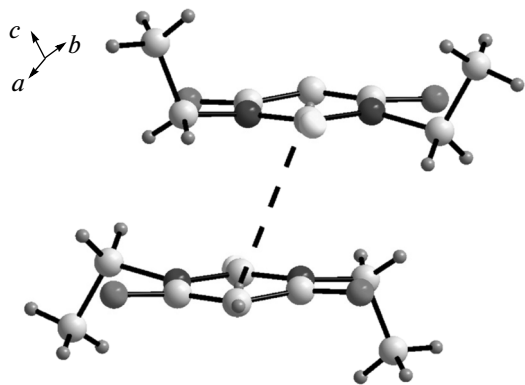
**Table 2.** Geometric parameters of the  $\pi$ – $\pi$  interaction in the structure of complex **1**

Cg <sub><i>i</i></sub> –Cg <sub><i>j</i></sub> *	Cg–Cg, Å	$\alpha$	$\beta$	$\gamma$	Cg <sub><i>i-p</i></sub> , Å	Shift, Å
		deg				
Cg <sub>1</sub> –Cg <sub>1</sub> '	3.749(13)	0	23.59	23.59	3.435(9)	1.501

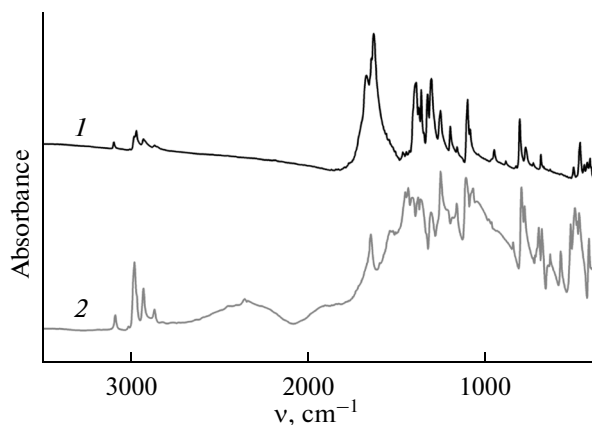
\* Cg<sub>1</sub>' is the plane of the N(1)–C(2)–N(3)–C(4)–C(5)–C(6) ring. Cg<sub>1</sub>' was obtained from Cg<sub>1</sub> by the symmetry code  $-x, 1-y, 1-z$ .



**Fig. 5.** View of the structure of complex **1** along the *c* axis. Cyclic moieties are additionally shaded.



**Fig. 6.**  $\pi$ - $\pi$  interaction between DETBA<sup>-</sup> ions.



**Fig. 7.** IR spectra of (1) AgDETBA and (2) HDETBA.

“head-to-tail” type packing of DETBA<sup>-</sup> ions in complex **1** (Table 2, Fig. 6).

The IR absorption spectra of HDETBA and complex **1** in KBr were recorded on a Nicolet 6700 spectrometer (Fig. 7).

There is no complete assignment of bands in the IR spectrum of crystalline HDETBA in the literature [17]. Two new bands, namely, a very intense band at 1630 cm<sup>-1</sup> and an intense band at 1671 cm<sup>-1</sup>, appear in the IR spectrum of complex **1** instead of the band at 1646 cm<sup>-1</sup> assigned to  $\nu(\text{C}=\text{O})$  in the IR spectrum of HDETBA [17]. This distinction between the spectra points to the coordination of the DETBA<sup>-</sup> ligand in complex **1** via an oxygen atom. By analogy with 2-thiobarbituric acid [24, 25], the strong band at 1160 cm<sup>-1</sup> in the IR spectrum of HDETBA can be assigned to  $\nu(\text{C}=\text{S})$  vibrations. The intensity of this band is considerably lower in the IR spectrum of complex **1** and, moreover, an additional band appears at 1197 cm<sup>-1</sup> near it. Hence, IR spectroscopic results for complex **1** agree with the coordination of the DETBA<sup>-</sup> ligand via oxygen and sulfur atoms.

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*Translated by E. Glushachenkova*