

COORDINATION COMPOUNDS

# Structures of Bis(2-thiobarbiturato-*O*)tetraaquamagnesium and *catena*-[( $\mu_2$ -2-Thiobarbiturato-*O,O*)(2-thiobarbiturato-*O*)bis( $\mu_2$ -aqua)diaquastrontium] Monohydrate

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**Abstract**—The crystal structures of bis(2-thiobarbiturato-*O*)tetraaquamagnesium  $\text{Mg}(\text{H}_2\text{O})_4(\text{HTBA-O})_2$  **I** and *catena*-[( $\mu_2$ -2-thiobarbiturato-*O,O*)(2-thiobarbiturato-*O*)bis( $\mu_2$ -aqua)diaquastrontium] monohydrate *catena*-[ $\text{Sr}(\mu_2\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2(\mu_2\text{-HTBA-O,O})(\text{HTBA-O})]_n \cdot n\text{H}_2\text{O}$  (**II**), where  $\text{H}_2\text{TBA}$  is 2-thiobarbituric acid  $\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$ , have been determined. Crystal data for **I**:  $a = 6.7598(2)$  Å,  $b = 7.6060(2)$  Å,  $c = 8.5797(2)$  Å,  $\alpha = 79.822(2)^\circ$ ,  $\beta = 76.622(1)^\circ$ ,  $\gamma = 69.124(1)^\circ$ ,  $V = 398.82(2)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,  $Z = 1$ ; for **II**:  $a = 20.8499(4)$  Å,  $b = 19.2649(5)$  Å,  $c = 4.14007(9)$  Å,  $\beta = 92.023(2)^\circ$ ,  $V = 1661.91(7)$  Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4$ . The  $\text{Mg}^{2+}$  ion in **I** is bonded to six O atoms of two  $\text{HTBA}^-$  ions and four water molecules that form a nearly regular octahedron. Each  $\text{Sr}^{2+}$  ion in **II** is coordinated to three oxygen atoms of three  $\text{HTBA}^-$  ions and six water molecules that form an almost ideal tricapped trigonal prism. These polyhedra share edges to form infinite chains. Intermolecular hydrogen bonds create layered structures of **I** and **II**.

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Thiobarbituric acid ( $\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$ ,  $\text{H}_2\text{TBA}$ ) and its derivatives are of pharmaceutical importance [1]. Despite this fact, little data are available on the synthesis and especially structure of even simple compounds [2], for example, their salts with Group II metal ions. One of the important biometal ions is  $\text{Mg}^{2+}$ . It is present in chlorophyll and is necessary for the enzymatic activity of  $\text{Na}^+/\text{K}^+$ -ATPase responsible for maintaining of nonequilibrium  $\text{Na}^+$  and  $\text{K}^+$  concentrations in living cell and intercellular fluid [3]. In the last years, it has been recognized that strontium(II) has a positive effect on bone tissue growth. The medicinal product strontium ranelate, registered in Russia under the name Bivalos, reduces the risk of bone fracture in osteoporosis, significantly increases mineral density and strength of bone, and aids de novo bone formation [4]. Its successful application stimulates further studies dealing with synthesis and structure of strontium(II) salts.

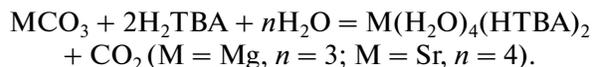
In this work, we synthesized  $\text{Mg}(\text{H}_2\text{O})_4(\text{HTBA-O})_2$  (**I**) and *catena*- $\text{Sr}(\mu_2\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2(\mu_2\text{-HTBA-O,O})(\text{HTBA-O})]_n \cdot n\text{H}_2\text{O}$  monohydrate (**II**) and determined their crystal structures by X-ray powder diffraction.

## EXPERIMENTAL

Chemically pure grade  $\text{MgCO}_3$  and  $\text{H}_2\text{TBA}$  were used.  $\text{SrCO}_3$  was precipitated by the reaction of chem-

ically pure  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  with ammonium carbonate in an aqueous solution. The precipitate was washed with water and dried in air to constant weight.

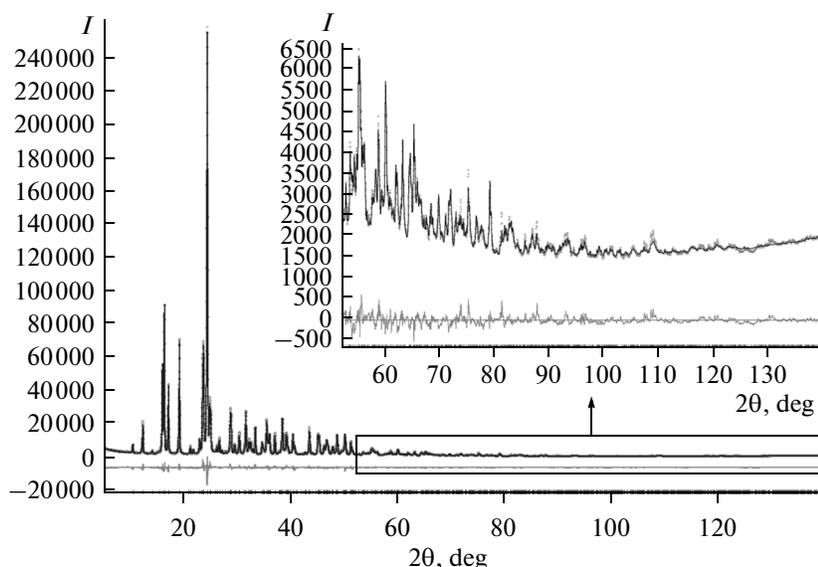
**Synthesis of I and II.** To a mixture of 0.694 mmol of  $\text{MCO}_3$  and 1.39 mmol of  $\text{H}_2\text{TBA}$ , 3–5 mL of water was added, and the reaction mixture was heated in a water bath at 50–60°C for 3–4 h until the reaction completion (crystal water was omitted for simplicity):



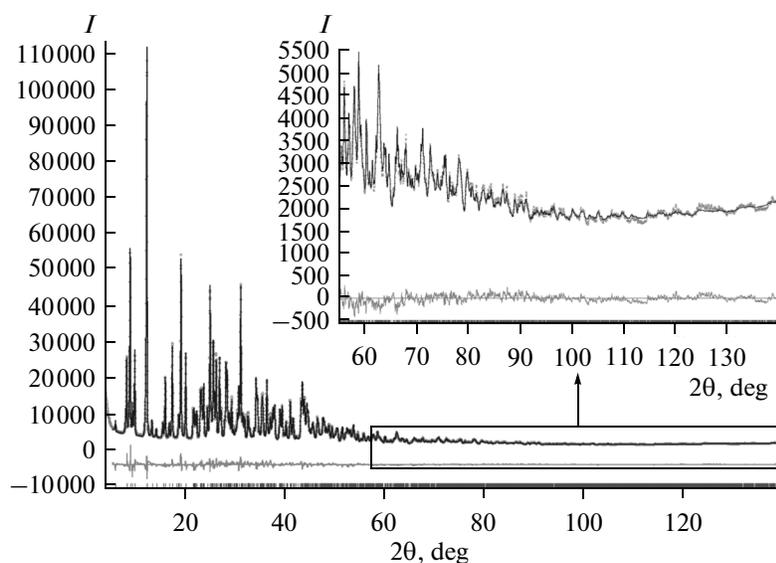
The resulting pale pink crystalline precipitates were filtered off, washed with acetone, and dried in air.

**X-ray crystallography.** The X-ray powder diffraction patterns of **I** and **II** were recorded on a Bruker D8 ADVANCE diffractometer (VANTEC linear detector,  $\text{CuK}_\alpha$  radiation). The variable time counting (VCT) and variable step scanning (VSS) method was used. The counting time was increased with an increase in the  $2\theta$  angle to improve the X-ray diffraction pattern quality in the high-angle region [5]. Then, the experimental data were converted into one XYE file containing  $2\theta_i$  coordinates, intensity  $I_i$ , and standard deviation  $\sigma(I_i)$  for each experimental time.

The X-ray powder diffraction patterns of **I** (Fig. 1) and **II** (Fig. 2) were recorded at 300 K and divided into four segments: 5°–42° (counting time, 4 s per point;



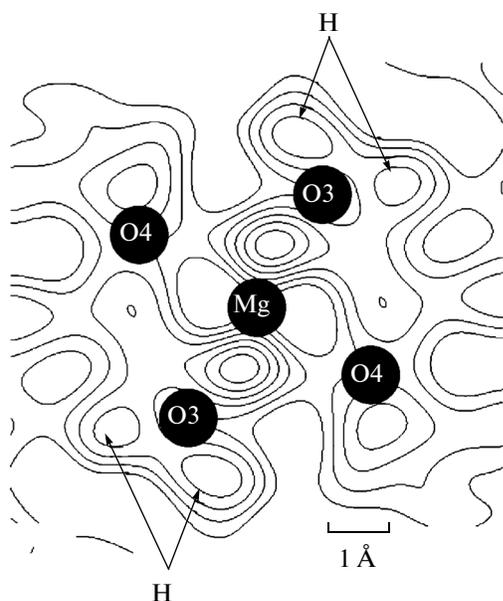
**Fig. 1.** Experimental (symbols), theoretical (line), and difference (lower line) X-ray diffraction pattern resulting from the Rietveld refinement of the crystal structure of **I**.



**Fig. 2.** Experimental (symbols), theoretical (line), and difference (lower line) X-ray diffraction pattern resulting from the Rietveld refinement of the crystal structure of **II**.

step,  $0.016^\circ$ ),  $42^\circ$ – $62^\circ$  (counting time, 12 s per point; step,  $0.024^\circ$ ),  $62^\circ$ – $97^\circ$  (counting time, 20 s per point; step,  $0.032^\circ$ ), and  $97^\circ$ – $140^\circ$  (counting time, 40 s per point; step,  $0.040^\circ$ ). The total time of each experiment was  $\sim 24$  h; the division of the pattern into intervals was performed with the XRD Wizard software [6]. The peak positions were determined with the EVA program (20004 release) from the DIFFRAC-PLUS software suit (Bruker).

For **I**, a triclinic unit cell was found by the ITO program [7]:  $a = 7.604 \text{ \AA}$ ,  $b = 8.579 \text{ \AA}$ ,  $c = 6.764 \text{ \AA}$ ,  $\alpha = 103.359^\circ$ ,  $\beta = 110.909^\circ$ ,  $\gamma = 79.759^\circ$  ( $F(20) = 36$ ). These parameters were transformed to the standard form with the PLATON program [8]. No unindexed reflections were found. The structure determination was performed in centrosymmetric space group  $P\bar{1}$ . The structure was solved by the direct space method with simulated annealing by means of the TOPAS 4.2 program [9]. The asymmetric unit volume corre-



**Fig. 3.** Cross-section of the difference electron density synthesis through the Mg, O3, and O4 atoms. The arrows show the maxima corresponding to the hydrogen atoms of water molecules.

sponded to 12 or non-hydrogen atoms; therefore, one  $C_4H_3N_2O_2S^-$  ion (HTBA<sup>-</sup>), one  $Mg^{2+}$  ion, and two O atoms of water molecules were generated in the asymmetric unit. A structure was obtained in which the  $Mg^{2+}$  ion was located at the origin, and all atoms of the HTBA<sup>-</sup> ion were in general position. The Rietveld refinement was performed with the TOPAS 4.2 software. No restraints were imposed on bond lengths or angles, except the coordinates of the H atoms in the HTBA<sup>-</sup> ion, which were idealized. The thermal parameters of all non-hydrogen atoms after the refinement had normal values. Difference electron density synthesis revealed two maxima near the O3 atom of the water molecule corresponding to H atoms (Fig. 3). These atoms were included in the refinement, which led to a noticeable decrease in residual factors. The key crystallographic data and experimental details are as follows:  $C_8H_{14}MgN_4O_8S_2$ , FW = 382.68,  $a = 6.7598(2)$  Å,  $b = 7.6060(2)$  Å,  $c = 8.5797(2)$  Å,  $\alpha = 79.822(2)^\circ$ ,  $\beta = 76.622(1)^\circ$ ,  $\gamma = 69.124(1)^\circ$ ,  $V = 398.82(2)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,  $Z = 1$ ,  $\rho_{calc} = 1.576$  g/cm<sup>3</sup>,  $\mu = 3.861$  mm<sup>-1</sup>,  $2\theta$  range  $5^\circ$ – $140^\circ$ , number of reflections 1524, number of refined parameters 97,  $R_B = 1.989\%$ ,  $R_{wp} = 4.689\%$ ,  $R_{exp} = 0.915\%$ ,  $R_p = 4.125\%$ , GOOF ( $\chi$ ) = 5.123.

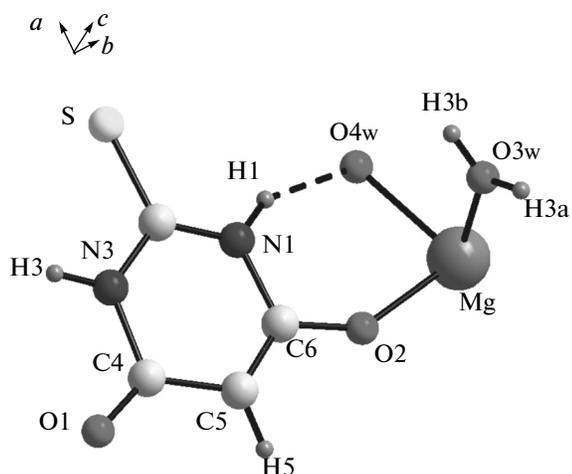
The unit cell parameters and space group for **II** were determined with the DASH 3.3 program [10]. The search for the parameters gave a monoclinic unit cell with  $a = 20.861$  Å,  $b = 19.2908$  Å,  $c = 4.0071$  Å,

$\beta = 91.059^\circ$  ( $M(23) = 15.5$ ;  $F(23) = 42.8$ ). No unindexed reflections were found. Analysis of the results of profile refinement with the use of the TOPAS 4.2 program showed that space group  $P2_1/n$  was most probable. The structure was solved by the direct space method with simulated annealing by means of the TOPAS 4.2 program. The asymmetric unit volume corresponded to 24–29 non-hydrogen atoms; therefore, two  $C_4H_3N_2O_2S^-$  ions (HTBA<sup>-</sup>), one  $Sr^{2+}$  ion, and several (more than five) O atoms of water molecules were generated in the asymmetric unit. The O atoms had dynamic site occupancy [9, 11], which made it possible to consider several atoms in the same small region as a single atom. For the structure model in which the asymmetric unit contained one  $Sr^{2+}$  ion, two HTBA<sup>-</sup> ions, and five water molecules, the Rietveld refinement was performed [9]. To decrease the number of refined parameters, soft restraints were imposed on the bond lengths in the HTBA<sup>-</sup> ion. To do this, the average bond lengths were taken from the single-crystal experiment for potassium thiobarbiturate  $C_4H_3KN_2O_2$  [12]. In addition, a soft restraint was added on the location of the atoms in each HTBA<sup>-</sup> ion in the same plane. The coordinates of H atoms were idealized. The thermal parameter of  $Sr^{2+}$  was refined in the anisotropic approximation and the other non-hydrogen atoms, in the isotropic approximation. Crystals of **II**  $C_8H_{16}N_4O_9S_2Sr$  are monoclinic, FW = 463.99,  $a = 20.8499(4)$  Å,  $b = 19.2649(5)$  Å,  $c = 4.14007(9)$  Å,  $\beta = 92.023(2)^\circ$ ,  $V = 1661.91(7)$  Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4$ ,  $\rho_{calc} = 1.814$  g/cm<sup>3</sup>,  $\mu = 7.363$  mm<sup>-1</sup>,  $2\theta$  range  $4^\circ$ – $140^\circ$ , number of reflections 3151, number of refined parameters 107,  $R_B = 2.087\%$ ,  $R_{wp} = 4.145\%$ ,  $R_{exp} = 0.863\%$ ,  $R_p = 3.850\%$ , GOOF ( $\chi$ ) = 4.806.

Structures **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (nos. 910777 and 912071, respectively). Full data can be obtained on request from the CCDC ([www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

## RESULTS AND DISCUSSION

The C–O, C–N, and C–C bond lengths and the corresponding bond angles in the HTBA<sup>-</sup> ions in **I** and **II** are close to those found for other compounds, for example, in [12, 13]. The asymmetric unit of **I** contains a  $Mg^{2+}$  cation, a HTBA<sup>-</sup> anion, and two water molecules (Fig. 4). The  $Mg^{2+}$  ion is bonded to six O atoms (Mg–O, 2.063–2.190 Å) of two HTBA<sup>-</sup> ions and four water molecules, forming an almost regular octahedron. The HTBA<sup>-</sup> ions in the complex are *trans* to each other, which can be explained by mutual repulsion of relatively bulky HTBA<sup>-</sup> ligands. The island structure of **I** (Fig. 5) corresponds to the name



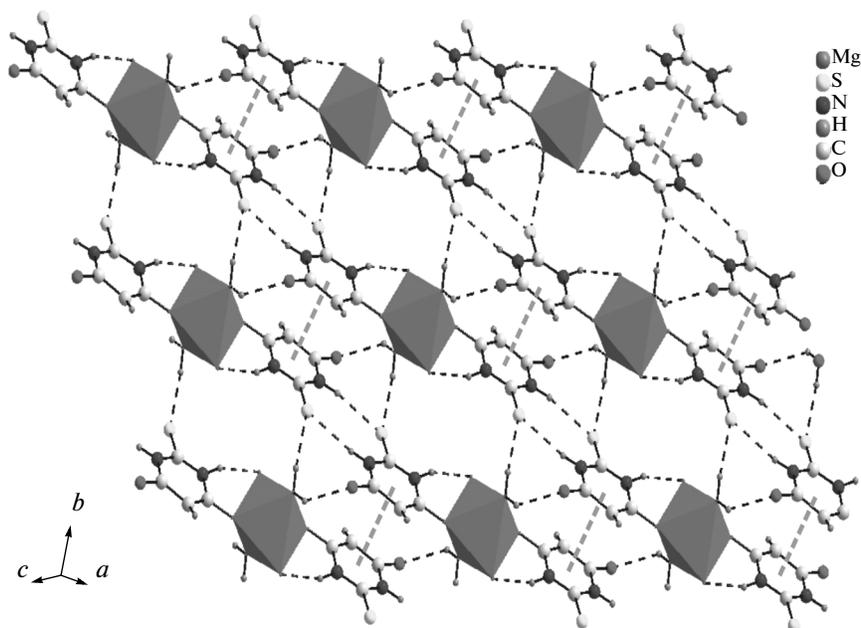
**Fig. 4.** Asymmetric unit of **I**. Hereinafter, the dashed line denotes a hydrogen bond.

bis(2-thiothiobarbiturato-*O*)tetraaquamagnesium and to the formula  $\text{Mg}(\text{H}_2\text{O})_4(\text{HTBA-}O)_2$ .

The asymmetric unit of **II** contains a  $\text{Sr}^{2+}$  ion, two  $\text{HTBA}^-$  anions, and five water molecules (Fig. 6). The Sr–O bond lengths (2.575–2.8256 Å) are consistent with literature data. In salts, the Sr(II) atoms are usually surrounded by 8–10 oxygen atoms with the Sr–O distance from 2.4 to 3.0 Å [2, 14]. The C6–O2 and

C4–O1 bonds (1.274 and 1.266 Å, respectively) in **II** are longer than in the carbonyl groups C=O of thiobarbituric acid (1.21–1.24 Å) [15], which confirms the coordination of  $\text{HTBA}^-$  to Sr(II) through the O atoms. In **II**, the  $\text{Sr}^{2+}$  ion is surrounded by nine O atoms that form a nearly ideal tricapped trigonal prism (Fig. 7). The  $\text{Sr}^{2+}$  ion is coordinated through oxygen atoms to three  $\text{HTBA}^-$  ions and six water molecules. The coordination sphere of each  $\text{Sr}^{2+}$  ion contains, in addition to four bridging  $\mu_2\text{-H}_2\text{O}$  molecules, two terminal water molecules. One  $\text{H}_2\text{O}$  molecule is a molecule of crystallization. Three O atoms of the coordinated  $\text{H}_2\text{O}$  ions form one of the polyhedron faces. One of the two independent  $\text{HTBA}^-$  ions as  $\mu_2\text{-O, O}$  bridging (type B), and the other is a terminal (type A) ligand. Tricapped trigonal prisms share trigonal faces in their base; each of them is formed by one O atom of the  $\text{HTBA}^-$  ion (B) and two O atoms of bridging water molecules. This leads to formation of infinite chains of face-sharing coordination polyhedra running along the *c* axis. The structure of the complex corresponds to the name *catena*-[ $(\mu_2\text{-}2\text{-thiothiobarbiturato-}O,O)(2\text{-thiothiobarbiturato-}O)\text{bis}(\mu_2\text{-aqua})\text{diaquastrontium}]$ monohydrate and to the formula *catena*-[ $\text{Sr}(\mu_2\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2(\mu_2\text{-HTBA-}O,O)(\text{HTBA-}O)]_n \cdot n\text{H}_2\text{O}$ .

Analysis of structure **I** (Fig. 5) shows that intermolecular hydrogen bonds (Table 1) combine isolated coordination octahedra into chains composed of  $\text{HTBA}^-$  ions,  $\text{Mg}^{2+}$ , and  $\text{H}_2\text{O}$  molecules. They are



**Fig. 5.** Formation of a layer in **I** through intermolecular hydrogen bonds. The plane of the paper is perpendicular to the *c* axis. Bold dashed lined denote  $\pi\text{-}\pi$  stacking interactions. The water oxygen atoms are not shown.

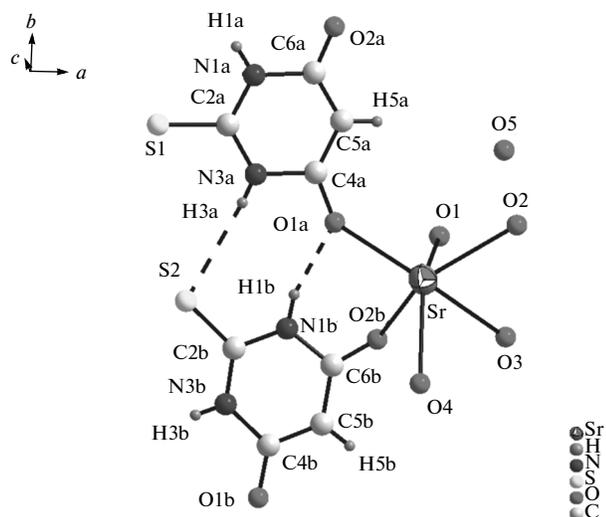


Fig. 6. Asymmetric unit of II.

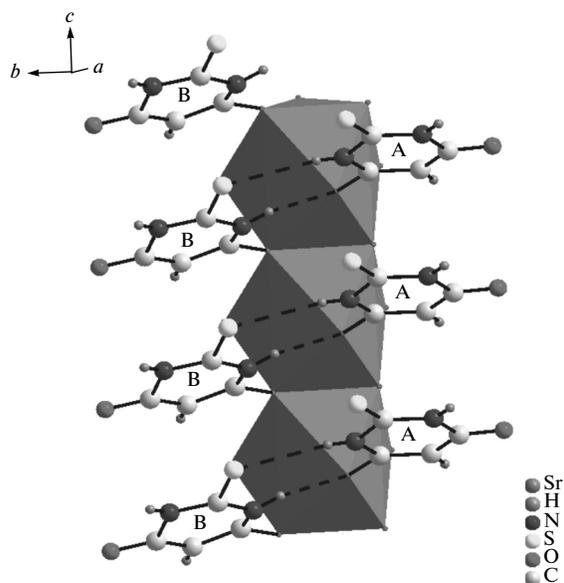


Fig. 7. Combination of Sr(II) coordination polyhedra into a chain running along the *c* axis in structure II.

combined by O–H...O and O–H...S intermolecular H-bonds into layers perpendicular to the body diagonal of the unit cell. The layers are not bound to each other, but the involvement of nonlocalized H atoms at the water O4 atom in hydrogen bonding can lead to a framework structure. Intermolecular hydrogen bonds in I form six-, eight-, and sixteen-membered rings

(Fig. 5). They correspond to structural motifs  $R_1^1(6)$ ,  $R_2^2(8)$ , and  $R_4^4(16)$  [3, p. 501]. Intermolecular H-bonds in structure II (Table 1) form infinite chains

Table 1. Geometry of hydrogen bonds in structures I and II

D–H...A	Distance, Å			DHA angle, deg	Symmetry codes for atom A
	D–H	H...A	D...A		
<b>I</b>					
N1–H1...O4	1.00	1.87	2.807(6)	153	$x, y, z$
O3–H3b...O1	0.83	2.23	2.644(7)	111	$1 - x, -y, -z - 1$
N3–H3...S	0.93	2.48	3.382(4)	165	$2 - x, -y - 1, -z - 1$
O3–H3a...S	0.88	2.72	3.480(5)	145	$x - 1, 1 + y, z$
<b>II</b>					
N1b–H1b...O1a	0.85	1.99	2.80(1)	160	$x, y, z$
N3b–H3b...O1b	0.78	1.98	2.76(1)	175	$-x, -y, 1 - z$
N1a–H1a...S1	0.81	2.53	3.322(8)	164	$-x, 1 - y, 3 - z$
N3a–H3a...S2	0.77	2.71	3.472(7)	170	$x, y, z$

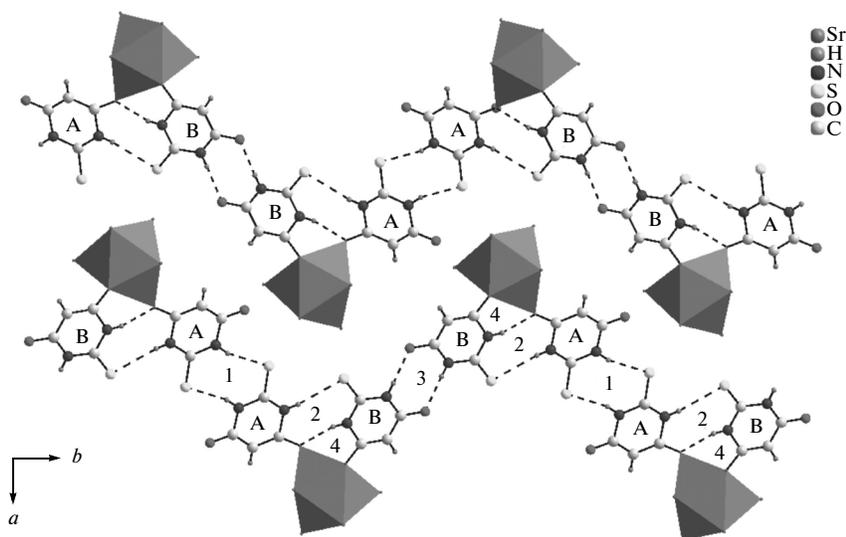


Fig. 8. Formation of zigzag layers perpendicular to the *a* axis in structure **II**.

of HTBA<sup>-</sup> ions running along the *b* axis (Fig. 8). The N–H...O and N–H...S interactions combine the chains of coordination polyhedra into zigzag layers perpendicular to the *a* axis. We failed to localize the H atoms of all five water molecules, but the probability of their participation in formation of a framework structures is rather high. The alternation pattern of the independent HTBA<sup>-</sup> ions in the chain is AABBA... The donors of the intermolecular H-bonds are only N atoms. When eight-membered rings ( $R_2^2(8)$ ) are formed, the acceptors can be either two S atoms or O and S atoms, or two O atoms (Fig. 8). If the resulting rings are designated by 1, 2, and 3, respectively, their alternation pattern in the chain is 12321232... ((1232) period). In addition, the N1b–H1b...O1a intermolecular H-bond (Fig. 6) closes six-membered ring 4 [( $R_1^1(6)$ ] involving Sr(II).

Analysis of shortened intermolecular contacts in **I** with the PLATON program [8] points to  $\pi$ – $\pi$  stacking interaction between the HTBA<sup>-</sup> anions of the head–tail type [3]. (Table 2). In the structure of KHTBA

[12], another HTBA<sup>-</sup> packing—of the head–head type—is realized. In **II**,  $\pi$ – $\pi$  ring stacking is lacking: the centroid–centroid distance is 4.141(6) Å, and the shift of the rings with respect to each other is 2.0941 Å.

Thus, in Mg(II) and Sr(II) 2-thioarbiturate complexes, the ligands are coordinated only through the O atoms, which is consistent with the fact that they are classified with hard acids according to Pearson's principle [3]. As distinct from the island structure of **I**, structure **II** is a chain one owing to the fact that it contains bridging ligands in addition of the terminal one. The increase in ionic radius in going from Mg(II) to Sr(II) is manifested as the increase in coordination number from 6 to 9. Common features in the supramolecular organization of compounds **I** and **II** are the formation of layered structures and similar six- and eight-membered rings and participation of S atoms in intermolecular hydrogen bonding. The difference is in the self-association of HTBA<sup>-</sup> ions in **II** and their combination into a chain through water mol-

Table 2. Parameters of  $\pi$ – $\pi$  stacking interaction of HTBA<sup>-</sup> ions in crystal of **I**

$Cg_i-Cg_j$	$d(Cg-Cg)$ , Å	$\alpha$ , deg	$\beta$ , deg	$\gamma$ , deg	$Cg_i-p$ , Å	Shift, Å
$Cg_1-Cg_1^*$	3.567(3)	0	15.64	15.64	3.435(2)	0.962

\*  $Cg_1$  is the plane of the N1C2N3C4C5C6 ring.  $Cg_1^*$  was generated from  $Cg_1$  by symmetry code  $1-x, -y, -z-1$ .

ecules in **I**, as well as in the formation of some different rings.

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