COORDINATION COMPOUNDS

Crystal Structures of Cesium and Rubidium 2-Thiobarbiturates

N. N. Golovnev[a] and M. S. Molokeev[b]

[a] *Siberian Federal University, Svobodnyi pr. 79, Krasnoyarsk, 660041 Russia*
[b] *Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok 50/38, Krasnoyarsk, 660036 Russia*
e-mail: ngolovnev@sfu-kras.ru
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Abstract—The crystal structures of cesium 2-thiobarbiturate $C_4H_3CsN_2O_2S$ (**I**) and rubidium 2-thiobarbiturate $C_4H_3N_2O_2RbS$ (**II**) ($C_4H_4N_2O_2S$ is 2-thiobarbituric acid, H_2TBA) have been determined. Isostructural crystals are monoclinic; $a = 7.9609(3)$ Å, $b = 11.8474(3)$ Å, $c = 7.7317(2)$ Å, $\beta = 101.285(3)°$, $V = 715.13(4)$ Å^3, space group $C2/m$, $Z = 4$ for **I** and $a = 7.6369(2)$ Å, $b = 11.7690(3)$ Å, $c = 7.5568(2)$ Å, $\beta = 100.212(1)°$, $V = 668.44(3)$ Å^3, space group $C2/m$, $Z = 4$ for **II**. Each metal ion in complexes **I** and **II** is bonded to four oxygen atoms and two sulfur atoms at the vertices of a six-vertex polyhedron. N−H···O hydrogen bonds link HTBA$^-$ ions into chains. The structure is also stabilized by the "head-to-tail" $\pi-\pi$ interaction of HTBA$^-$ ions.

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Thiobarbituric acid ($C_4H_4N_2O_2S$, H_2TBA) is the key compound among the heterocyclic compounds; many of its derivatives find increasingly wide application as medicines. Examples are sodium thiopental (an analgesic) and metalatal (an antiemetic agent) [1]. In view of a broad spectrum of useful properties of many H_2TBA derivatives, the preparation of new compounds of the basis of thiobarbituric acid and the study of their structural features is a topical problem.

In this work, cesium 2-thiobarbiturate $C_4H_3CsN_2O_2S$ (**I**) and rubidium 2-thiobarbiturate $C_4H_3N_2O_2SRb$ (**II**) were synthesized and their crystal structure was determined by X-ray diffraction.

EXPERIMENTAL

Synthesis of complexes I and II. To chemically pure H_2TBA (0.20 g, 1.39 mmol), distilled water (5 mL) was poured, thereupon chemically pure Cs_2CO_3 or Rb_2CO_3 (2.78 mmol) were added in double excess. The slow release of gaseous CO_2 from the obtained mixtures was observed. In order for the reaction to be completed, the mixtures were allowed to stand for 24 h. Colorless precipitates were then filtered out, washed with alcohol, and dried in air. The yield of the products was 90–95%. We have not managed to obtain any crystals of the complexes that would be suitable for structure determination by single-crystal X-ray diffraction.

The IR spectra of complexes **I** and **II** recorded in KBr pellets nearly coincide and contain most of the bands typical for the H_2TBA thione enol tautomer (Fig. 1) [2], thus confirming that the thiobarbiturate ion in these three compounds has a similar structure.

The most considerable distinction between the spectra of the complexes and H_2TBA is observed in the region of 1100–1720 cm^{-1}. Thus the band at 1720 cm^{-1} assigned to $\nu(C=O)$ in the H_2TBA spectrum [2] is absent in the spectrum of complexes **I** and **II**, but strong bands appear in them at 1610 and 1630 cm^{-1}. This confirms the coordination of the ligand to the Rb^+ and Cs^+ ions via oxygen atoms. The intensity of the H_2TBA absorption band at 1159 cm^{-1}, which is assigned to $\nu(C=S)$ [3, 4], considerably decreases in the IR spectra of the complexes due to the coordination of the ligand via the sulfur atom.

The X-ray powder diffraction patterns of complexes **I** and **II** were recorded on a Bruker D8 ADVANCE diffractometer (VANTEC linear detector, CuK_α radiation) by the VCT/VSS method [5]. They were divided into the three regions: 5°−40° (exposure per point: 6 s; step: 0.016°), 40°−65° (exposure per point: 18 s; step: 0.024°), 65°−97.5° (exposure per point: 30 s; step: 0.032°), and 97.5°−140° (exposure per point: 48 s; step: 0.040°). The X-ray powder diffraction patterns of complexes **I** and **II** only slightly differ from each other, so only the X-ray powder dif-
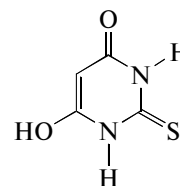
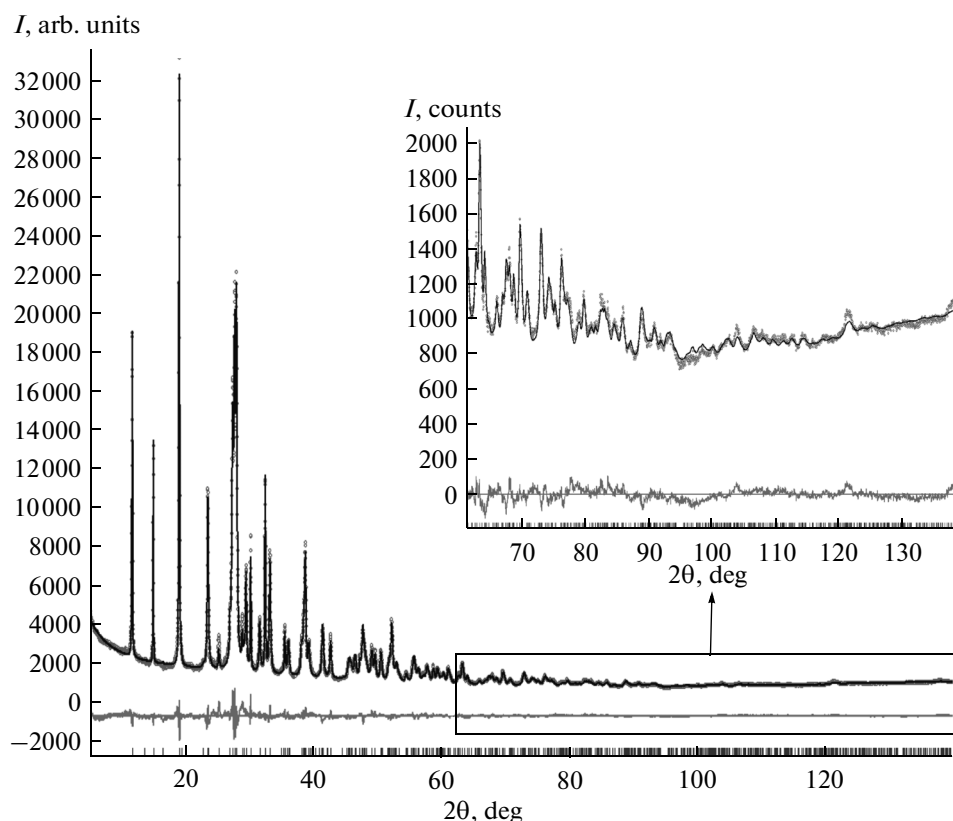**Fig. 1.** Graphic formula of the thione enol tautomer of H_2TBA.

Fig. 2. Experimental (points), theoretical (upper line), and difference (lower line) X-ray diffraction patterns of complex **I** and magnified X-ray diffraction pattern fragment obtained in a high angle range (embedding).

fraction pattern of complex **I** is shown in Fig. 2. The experiment was divided into parts using the XRD Wizard software [6]. Peak positions were determined using the EVA software (2004 release) from the DIFFRAC-PLUS software suite (Bruker). The unit cell parameters and space group were determined by the TOPAS 4.2 software [7]. The structure was solved by direct space modeling and subsequent annealing method using the TOPAS 4.2 software. For the selected groups, the unit cell volume in the asymmetric part corresponded to ~10 or 11 atoms, so one $C_4H_3N_2O_2S^-$ (HTBA$^-$) ion and two M$^+$ (Cs$^+$ or Rb$^+$) ions were generated in the asymmetric part of a cell. The solution was found in terms of space group $C2/m$. A soft restriction that the atoms in HTBA$^-$ tend to be in the same plane was imposed in the process of refinement. The coordinates of hydrogen atoms were idealized. The VCT method allowed us to refine the thermal parameters of Cs$^+$ and Rb$^+$ in the anisotropic approximation. The thermal parameters of all non-hydrogen atoms had normal values. The refinement was stable and gave low R values. The main crystallographic characteristics and parameters of X-ray diffraction experiment for complex **I** are as follows: bulk formula: $C_4H_3CsN_2O_2S$; FW = 276.051, $a = 7.9609(3)$ Å, $b = 11.8474(3)$ Å, $c = 7.7317(2)$ Å, $\beta = 101.285(3)°$, $V = 715.13(4)$ Å^3, space group $C2/m$, $Z = 4$, $\rho_{calcd} = 2.564$ g/cm^3, $\mu = $

42.669 mm^{-1}; 2θ range, 5°–140°, 728 reflections, 64 refined parameters, $R_{wp} = 3.974\%$, $R_{exp} = 1.449\%$, $R_p = 3.596\%$, GOOF(χ) = 2.742; and for complex **II**: bulk formula: $C_4H_3N_2O_2RbS$, FW = 228.614, $a = 7.6369(2)°$, $b = 11.7690(3)°$, $c = 7.5568(2)$ Å, $\beta = 100.212(1)°$, $V = 668.44(3)$ Å^3, space group $C2/m$, $Z = 4$, $\rho_{calcd} = 2.272$ g/cm^3, $\mu = 12.618$ mm^{-1}; 2θ range, 5°–140°, 675 reflections, 90 refined parameters, $R_{Bragg} = 1.775\%$, $R_{wp} = 3.503\%$, $R_{exp} = 1.299\%$, $R_p = 3.182\%$, GOOF(χ) = 2.697. The structures of complexes **I** and **II** were deposited with the Cambridge Structure Database (accession nos. 908570 and 918662, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Crystals of complexes **I** and **II** are isostructural to each other. The asymmetric part of their unit cells contains the M$^+$ ion in the 4h local position and half a HTBA$^-$ ion; in total, the cell contains four M$^+$ ions and four HTBA$^-$ ions (Fig. 3a). The M$^+$ ion is bonded to four oxygen and two sulfur atoms. The pairs of Cs–O bond lengths in complex **I** are equal to 3.106(6) and 3.163(6) Å. In complex **II**, two Rb–O bonds have lengths of 2.942(4) Å, and another two Rb–O bonds have lengths of 3.002(4) Å. For comparison, similar
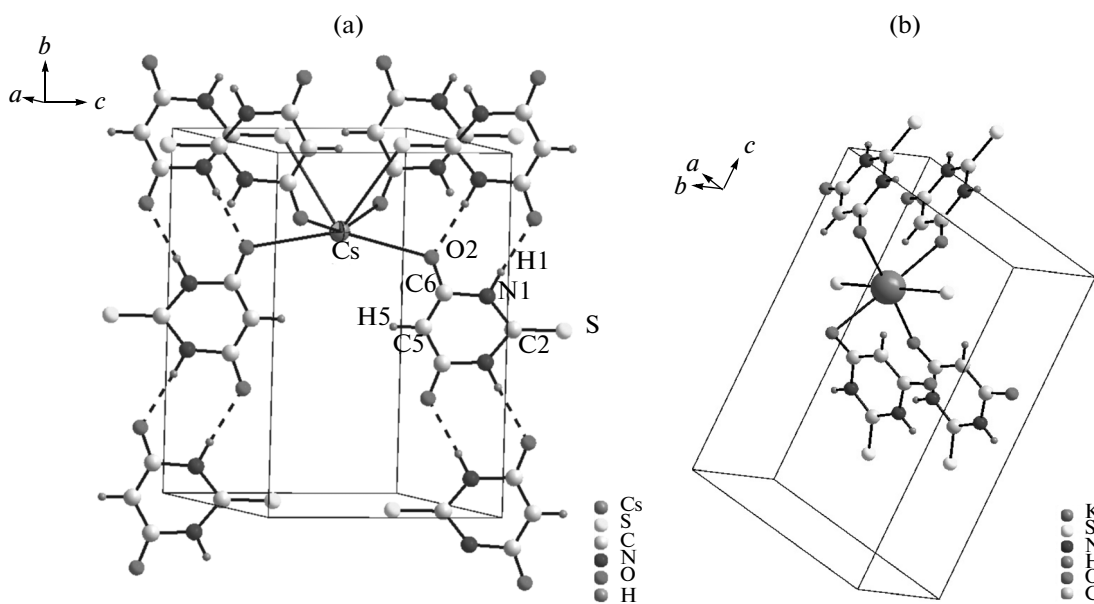
Fig. 3. Coordination surrounding of (a) the Cs^+ ion in the structure of CsHTBA and (b) the K^+ ion in the structure of KHTBA.

Cs–O distances (3.1–3.2 Å) were determined in the complexes of Cs^+ with related barbiturate acid, and the Rb–O bond lengths in the complexes of Rb^+ were 2.9–3.2 Å [8]. Taking into account the two Cs–S bonds (3.6766 and 3.9343 Å) in complex **I** and the two equal Rb–S bonds (3.586 Å) in complex **II**, the corresponding tetrahedra form six-vertex polyhedra (Fig. 4). It should be noted that the Cs–S distances close to 3.68 Å are encountered in many compounds among 17 structures with the Cs–S bond from the Cambridge Structure Database, and the Cs–S distances close to 3.93 Å are present only in three compounds. The Rb–S bond length is longer than 3.586 Å and rarely encountered. The S–C2 distance of 1.63(2) Å in **I** and 1.72(1) Å in **II** is close to the distance obtained for free H_2TBA [8], being in agreement with the predominantly electrostatic interaction between the sulfur atom and the Cs^+ and Rb^+ ions. For this reason, the M–S bonds in these compounds may be considered as shortened contacts. The linkage of MO_4S_2 polyhedra by edge sharing into layers lying normal to the *c* axis is shown in Fig. 4 for complex **II**, which was used as an example. A set of six linked polyhedra forms an inner hexagonal cavity, which is partially filled with ligand structure moieties. They are linked by sharing six edges, four of which are formed by two oxygen atoms, and the other two are formed by sulfur atoms. For comparison, the K^+ ion in the KHTBA crystal structure is also bonded to four oxygen and two sulfur atoms (Fig. 3b) [9, 10], but the mutual orientation of the ligands in these compounds is different. The KO_4 moiety in KHTBA is a nearly planar square, and CsO_4 in CsHTBA and RbO_4 in RbHTBA are distorted tetrahedra. The geometries of the

six-vertex KHTBA and MHTBA polyhedra (M = Cs or Rb) are also different.

The structural analysis of complexes **I** and **II** shows the presence of intermolecular hydrogen bond (Table 1), which forms chains of $HTBA^-$ ions along the *b* axis (Fig. 3a). The parameters of "head-to-tail" π–π interaction between the centers of $HTBA^-$ ion rings [12] were determined by the PLATON software [11] (Table 2). The package of $HTBA^-$ in KHTBA corresponds to the "head-to-head" type [10].
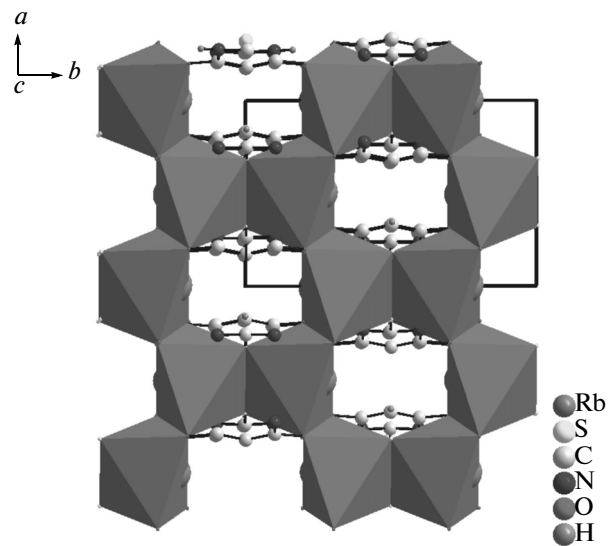

Fig. 4. Bonding of RbO_4S_2 polyhedra by edge sharing into layers perpendicular to the *c* axis in the structure of complex **II**.

Table 1. D−H···A hydrogen bond (Å, deg) in the structures of complexes **I** and **II***

Complex	D−H···A	D−H	H···A	D···A	D−H···A
I	N1−H1···O2^1	0.90	2.05	2.95(1)	176
II	N1−H1···O2^1	0.81	1.99	2.795(7)	171

* 1—Symmetry codes: $1/2 - x$, $1/2 - y$, $-z$.

Table 2. Parameters of the π−π interaction between HTBA$^−$ in the complexes (Å, deg)*

MHTBA	$Cg_i - Cg_j$	$d(Cg - Cg)$	α	β	γ	Cg_i_p	Shift, Å
I	$Cg_1 - Cg_1''$	3.543(5)	0	12.47	12.47	3.459(4)	0.765
II	$Cg_1 - Cg_1''$	3.414(4)	0	12.47	12.47	3.333(4)	0.737

* Cg_1 is the plane of the N1−C2−N1'−C6'−C5−C6 ring; the N1' and C6' atoms were obtained from the N1 and C6 atoms by the symmetry codes x, $-y$, z. Cg_1'' was obtained from Cg_1 by the symmetry codes $-x$, $-y$, $-z$.

Hence, alkali metal ions have the same coordination number (CN) despite their different ionic radii (r) (at CN = 6 r(K$^+$) = 1.52 Å, r(Rb$^+$) = 1.66 Å, and r(Cs$^+$) = 1.81 Å (see [13], page 67) and are homotypically bonded to the donor atoms of HTBA$^−$. The distinction of the K$^+$ coordination polyhedron from the Rb$^+$ and Cs$^+$ polyhedra is manifested in their geometry, and also in the mutual arrangement of HTBA$^−$ ions and the type of π−π interactions between ligands.

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