

COORDINATION COMPOUNDS

Crystal Structure of *catena*-Bis(2-thiobarbiturato-O,S)diaquacadmium

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Abstract—The crystal structure of *catena*-bis(2-thiobarbiturato-O,S)diaquacadmium ($C_8H_{10}CdN_4O_6S_2$)_n (**I**), $[Cd(H_2O)_2(HTBA)_2]_n$ ($C_4H_4N_2O_2S$ is 2-thiobarbituric acid, H_2TBA) has been determined. The crystals of compound **I** are triclinic, $a = 6.9433(3)$ Å, $b = 7.2257(3)$ Å, $c = 7.4047(3)$ Å, $\alpha = 88.559(2)^\circ$, $\beta = 75.346(2)^\circ$, $\gamma = 111.687(1)^\circ$, $V = 331.05(3)$ Å³, space group $P\bar{1}$, $Z = 1$. The Cd^{2+} ion is coordinated to the two oxygen atoms of water molecules and the two oxygen and two sulfur atoms of four $HTBA^-$ ions at the vertices of an octahedron. Octahedra are linked by bridging μ_2 - $HTBA^-$ -O,S ions into infinite chains. Intermolecular hydrogen bonds form infinite chains. The structure is also stabilized by the π - π interaction of $HTBA^-$ ions.

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Thiobarbituric acid (4,6-dihydroxy-2-mercapto-pyrimidine, $C_4H_4N_2O_2S$, H_2TBA) is a compound most derivatives of which find application in medicine [1]. Its complexes may have specific bioactivity, e.g., the H_2TBAH complex with tin(IV) has anticancer activity [2]. The possibility of the polydentate (N, O, S) coordination of this ligand to metal ions enables the synthesis of different coordination polymers with useful properties [3].

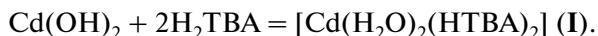
In our work, the *catena*-bis(2-thiobarbiturato-O,S)diaquacadmium complex $[Cd(H_2O)_2(HTBA)_2]_n$ (**I**) ($C_4H_4N_2O_2S$ is 2-thiobarbituric acid) was synthesized and its structure was determined by X-ray powder diffraction.

Complexes with Cd–S bonds can be considered as potential precursors for CdS films and nanomaterials [4]. The semiconducting properties of CdS make it suitable for use in solar cells and optoelectronic devices (photocells or photoresistors) [5].

EXPERIMENTAL

$Cd(OH)_2$ and H_2TBA , both of chemically pure grade, were used in the synthesis.

Synthesis of complex I. To a mixture of $Cd(OH)_2$ (0.102 g, 0.694 mmol) and H_2TBA (0.200 g, 1.39 mmol), water (10 mL) was added, and the mixture was allowed to stay on a water bath at 50–60°C for 8 h until the completion of the reaction



The formed colorless crystalline precipitate was filtered out, washed with acetone, and dried in air. The product yield was 95–98%.

For $C_8H_{10}CdN_4O_6S_2$, anal. calcd. (%): C, 22.10; H, 2.32; N, 12.89; S, 14.75.

Found (%): C, 22.37; H, 2.13; N, 12.74; S, 14.47.

The shift of $\nu(CO)$ frequencies in the IR spectrum of complex **I** from 1594 to 1621 cm^{-1} in comparison with the free ligand (1648 and 1720 cm^{-1} , respectively) indicates the coordination of $HTBA^-$ through the oxygen atom. The absence of $\nu(CS)$ bands typical for free H_2TBA in the region of 1162 and 790 cm^{-1} [6, 7] agrees with the additional coordination of the ligand through the sulfur atom. The assignment of other bands in the IR spectrum of complex **I** is difficult because of the possible existence of 10 tautomeric and polymorphous H_2TBA forms [8].

We should note that the $[Cd(H_2O)_2(HTBA)_2]$ complex (**II**) of similar composition was synthesized and characterized by various physicochemical methods earlier [7]. According to IR spectroscopy data, the $HTBA$ ligand in complex **II** is coordinated to the metal through the oxygen and sulfur atoms presumably at the vertices of a tetrahedron. The absence of an X-ray diffraction pattern for complex **II** in [7] does not allow us to state that we have obtained the same phase (moreover, complex **II** was separated from an ethanolic solution instead of an aqueous solution as in our experiment).

X-ray powder diffraction analysis. The X-ray powder diffraction pattern of complex **I** was taken on a D8 ADVANCE Bruker diffractometer (VANTEC linear

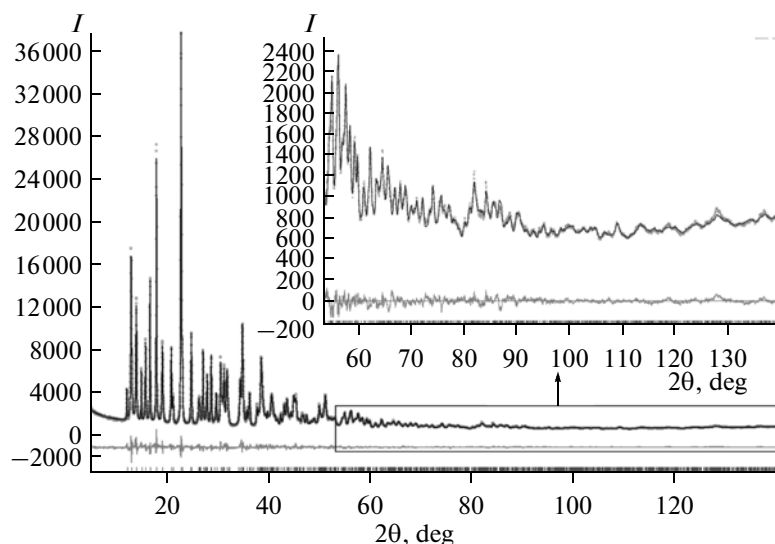


Fig. 1. Experimental (points), theoretical (upper line), and difference (lower line) X-ray diffraction patterns resulting from the Rietveld refinement of the structure of complex I.

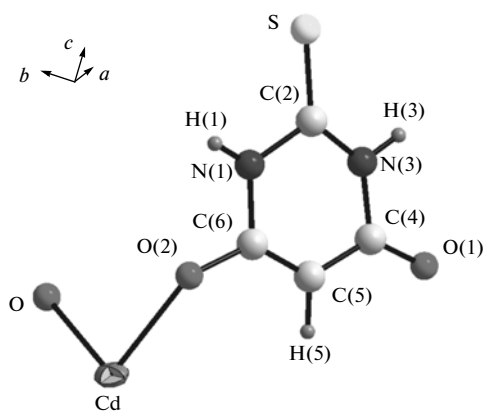


Fig. 2. Asymmetric part of the cell of complex I.

detector, $\text{CuK}\alpha$ radiation). In our experiment, the variable counting time (VCT) and variable step scanning (VSS) methods were used to make the reflections in the high-angle region of the X-ray diffraction pattern more informative [9]. The X-ray diffraction pattern of the studied powder (Fig. 1) was taken by the

Table 1. Geometric parameters of D–H···A hydrogen bonds in the structure of complex I

Hydrogen bonds	D–H, Å	H···A, Å	D···A, Å	D–H···A, deg
N1–H1···O2 ¹	0.84	1.82	2.65(1)	173
N3–H3···O1 ²	0.88	1.92	2.79(1)	178

Symmetry codes: (1) $-x, y, z - 1$; (2) $1 - x, 1 - y, 1 - z$.

VCT/VSS method and divided into the four regions: 5° – 42.3° (exposure per point: 4 s; step: 0.016°), 42.3° – 60.7° (12 s; 0.024°), 60.7° – 97.7° (20 s; 0.032°), and 97.7° – 140° (40 s; 0.040°). The total time of the experiment was ~ 24 h. The experiment was divided into parts using the XRD Wizard software [10]. 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 [11].

The structure was solved by direct space modeling and subsequent phase annealing using the TOPAS 4.2 software. The cell volume corresponded to 10–12 non-hydrogen atoms in the asymmetric part, so that one $\text{C}_4\text{H}_3\text{N}_2\text{O}_2\text{S}^-$ (HTBA⁻) ion, one Cd^{2+} ion, and one water oxygen atom were generated in the asymmetric part of a cell. The oxygen and cadmium atoms had dynamic site occupancies [11, 12], and this allowed us to consider several atoms in the same small region as a single atom. Phase annealing has given us a structure model, in which the asymmetric part of a cell contained one Cd^{2+} ion in the 1a local position, one HTBA⁻ ion with atoms in the 2i general position, and one water molecule in the 2i general position. Using this model, we performed Rietveld refinement by the TOPAS 4.2 software. No restrictions were imposed on the bond lengths and the location of atoms in the same plane except for the coordinates of HTBA⁻ hydrogen atoms, which were idealized. The thermal parameters of the Cd^{2+} ion were refined in the anisotropic approximation, and the other non-hydrogen atoms were refined isotropically. After refinement, all thermal parameters had normal values. The refinement was stable and gave low uncertainty R-factors. Only the

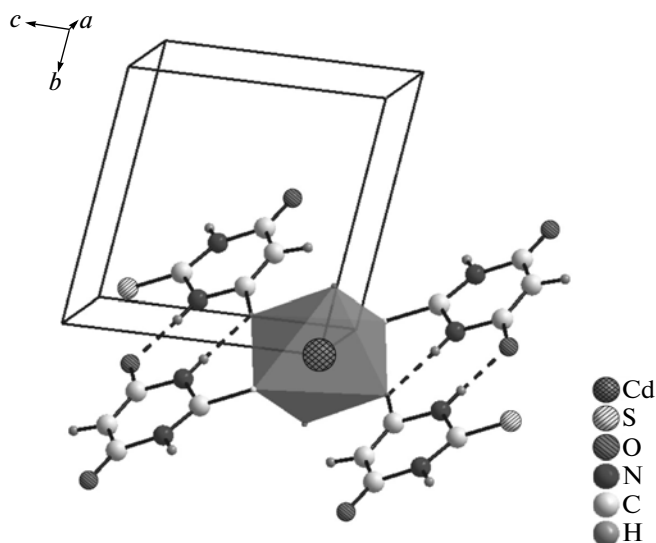


Fig. 3. Coordination surrounding of the Cd^{2+} ion. Dashed lines are intermolecular hydrogen bonds.

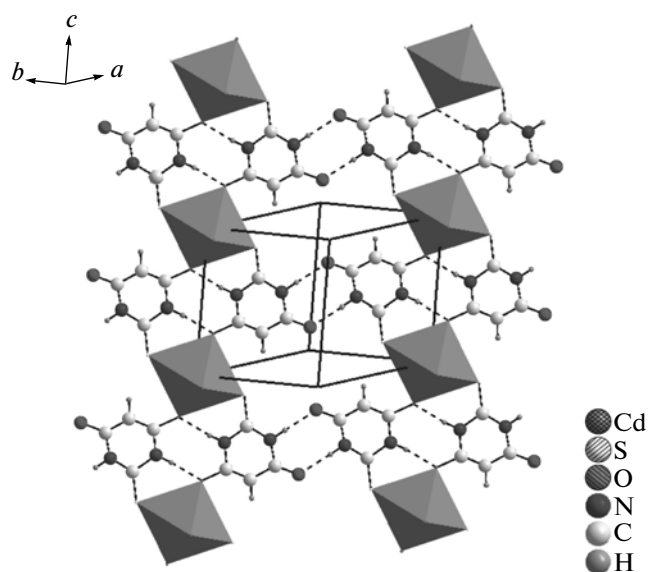


Fig. 4. Formation of chains of CdO_4S_2 octahedra along the c axis.

coordinates of the hydrogen atoms of water molecules remained undetermined. Selected crystallographic characteristics of complex **I** and the details of experiment are as follows: FW = 434.73, $a = 6.9433(3)$ Å, $b = 7.2257(3)$ Å, $c = 7.4047(3)$ Å, $\alpha = 88.559(2)^\circ$, $\beta = 75.346(2)^\circ$, $\gamma = 111.687(1)^\circ$, $V = 331.05(3)$ Å³, space group $P\bar{1}$, $Z = 1$, $\rho_{\text{calcd}} = 2.1604$ g/cm³, $\mu = 16.517$ mm⁻¹, $2\theta = 5^\circ\text{--}140^\circ$; number of reflections: 1265; number of refined parameters: 99; $R_{\text{B}} = 1.387\%$, $R_{\text{wp}} = 3.888\%$, $R_{\text{exp}} = 1.508\%$, $R_{\text{p}} = 3.591\%$, GOOF (χ) = 2.578.

The structure of complex **I** was deposited with the Cambridge Structure Database (accession no. 919796; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The asymmetric part of a cell in complex **I** contains a half of the Cd^{2+} cation, one HTBA^- anion, and one water molecule (Fig. 2). The analysis of the structure by the PLATON software [13] has not revealed any additional voids that could hold water molecules. The Cd–S and Cd–O bond lengths in complex **I** are close to the values given in the Cambridge Structure Database [14]. The Cd^{2+} ion is coordinated to four oxygen

atoms (Cd–O, 2.295 and 2.315 Å) and two sulfur atoms (Cd–S, 2.702 Å) at octahedron apices (Fig. 3). The octahedra are linked by HTBA^- ligands through the S and O(2) atoms, thus forming infinite chains along the c axis (Fig. 4). The structures of the acetone-solvated bis(thiobarbiturate) zinc(II) and manganese(II) complexes were solved in [15]. Similarly to complex **I**, these octahedral complexes contain two coordinated water molecules in *trans* position, but have no metal–sulfur bond in contrast to complex **I**. The Cd^{2+} ion is more “soft” and has a stronger affinity to the sulfur atom, and this explains the existing mode of coordination of the HTBA^- ion to it.

The structural analysis of complex **I** has shown the presence of two intermolecular hydrogen bonds (Table 1) that form infinite HTBA^- chains along the a – b axis (Fig. 4). The analysis of hydrogen bonds is incomplete, as the location of hydrogen atoms of water molecules has not succeeded. It seems likely that their participation in hydrogen bonds gives rise to layers or a framework. The discovered hydrogen bonds close eight- or six-membered rings (Figs. 3, 4), which correspond to the R_2^2 (8) or R_1^1 (6) structural motifs [16].

The analysis of shortened intermolecular contacts by the PLATON software [13] has shown the presence of π – π interaction between HTBA^- anions (Table 2).

Table 2. Geometric parameters of the π – π interaction of HTBA^- ions in the structure of complex **I**

$\text{Cg}_i\text{--Cg}_j$	$d(\text{Cg--Cg}), \text{Å}$	α, deg	β, deg	γ, deg	$\text{Cg}_i\text{--}p, \text{Å}$	Shift, Å
$\text{Cg}_1\text{--Cg}_1'$	3.514(6)	0	19.9	19.9	3.304(4)	1.196

Cg_1 is the plane of the N1–C2–N3–C4–C5–C6 ring. Cg_1' was obtained from Cg_1 by the symmetry code $[-x, 1-y, 1-z]$.

The package of HTBA⁻ ions corresponds to the head-to-tail type [16].

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