

Structure of Barbituratobis(2,2'-Dipyridyl)copper(II) Heptahydrate

N. N. Golovnev^{a,*}, M. S. Molokeev^{a,b,c}, I. V. Sterkhova^d, and M. K. Lesnikov^a

^aSiberian Federal University, Krasnoyarsk, Russia

^bKirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia

^cFar East State Transport University, Khabarovsk, Russia

^dFavorskii Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia

*e-mail: ngolovnev@sfu-kras.ru

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Abstract—The structure of the complex $[\text{Cu}(\text{Bipy})_2(\text{BA})] \cdot 7\text{H}_2\text{O}$ (**I**), where Bipy is 2,2'-dipyridyl, and BA^{2-} is the barbituric acid anion (H_2BA), is determined (CIF file CCDC no. 1887338). The thermal decomposition and IR spectrum of complex **I** are studied. The crystals are orthorhombic: $a = 26.118(3)$, $b = 27.685(3)$, $c = 15.683(2)$ Å, $V = 11370(2)$ Å³, space group $Fdd2$, $Z = 16$. The discrete structure of the polar crystal consists of neutral $[\text{Cu}(\text{Bipy})_2(\text{BA})]$ particles and molecules of crystallisation water. The Cu^{2+} ion is bound to the N atoms of two bidentate Bipy molecules and the N atom of the BA^{2-} ion at the vertices of the trigonal bipyramid CuN_5 . Compound **I** is the first example of the metal complex only with the N-coordinated anions of barbituric acid (BA^{2-} , HBA^-). The structure is stabilized by hydrogen bonds $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ to form a three-dimensional network with the $\pi-\pi$ interaction between the Bipy molecules. The compound begins to lose water at $\sim 50^\circ\text{C}$ and is completely dehydrated above 200°C .

Keywords: copper(II), barbituric acid, 2,2'-dipyridyl, complex, structure, properties

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INTRODUCTION

Barbituric acid ($\text{C}_4\text{H}_4\text{N}_2\text{O}_3$, H_2BA) is the key compound of the important class of depressants and hypnotic drugs named barbiturates. Complex formation and noncovalent interactions, such as hydrogen bonds and $\pi-\pi$ interaction, are significant in the chemistry of barbiturates [1]. In all structurally characterized complexes, the HBA^- anion is coordinated to the metal ions through the O atoms [2–13]. In compound $[\text{Pd}(\text{En}-\text{N},\text{N}')(\mu_2-\text{BA}-\text{C},\text{N})_2] \cdot 4\text{H}_2\text{O}$ (En is ethylenediamine) [14], the BA^{2-} ion acts as the $\mu_2-\text{C},\text{N}$ bridging ligand. Other metal complexes with BA^{2-} ions are unknown, although they can have unusual structures and potentially useful properties. We synthesized barbituratobis(2,2'-dipyridyl)copper(II) heptahydrate, $[\text{Cu}(\text{Bipy})_2(\text{BA})] \cdot 7\text{H}_2\text{O}$ (**I**) (where Bipy is 2,2'-dipyridyl), and studied its structure, IR spectrum, and thermal decomposition. The characterization of compound **I** can be of practical interest, since Cu^{2+} ions can affect the drug activity of barbiturates [2, 15] and the dipyridyl complexes of Cu(II) are catalytically active [16].

EXPERIMENTAL

Synthesis of complex I. Water (5 mL), freshly prepared $\text{Cu}(\text{OH})_2$ (0.038 g, 0.39 mmol), and Bipy

(Aldrich, 98%) (0.122 g, 0.78 mmol) were added to H_2BA (reagent grade) (0.10 g, 0.78 mmol). The mixture was heated with continuous stirring and kept at 80°C to the complete dissolution of the reagents. The obtained dark green solution was cooled down to room temperature, brought to pH 10–11 with 0.1 M NaOH, and left to stay in air for 5 days. The formed dark green crystalline precipitate was filtered off and dried in air. The yield of compound **I** was 0.082 g (33% based on copper). A single crystal suitable for X-ray diffraction analysis was selected directly from the overall mass of the precipitate. The compound is stable in air for at least 2 months.

For $\text{C}_{24}\text{H}_{32}\text{N}_6\text{O}_{10}\text{Cu}$

Anal. calcd., %	C, 45.9	H, 5.14	N, 13.4
Found, %	C, 45.4	H, 5.23	N, 13.1

IR for **I** (ν , cm^{-1}): 1680, 1579 $\nu(\text{CO})$ BA^{2-} , 1597 $\nu(\text{CC})/\nu(\text{CN})$ Bipy, 3026, 3054, 3094, 2923 $\nu(\text{NH})$ and $\nu(\text{CH})$, 3373 $\nu(\text{OH})$. The bands were assigned according to published data [17, 18].

X-ray diffraction analysis. Intensities of X-ray reflections from a dark green crystal $0.40 \times 0.35 \times 0.25$ mm in size were measured at 100 K on a D8 Venture single-crystal diffractometer with a CCD detector (Bruker AXS, MoK_α radiation). Absorption correc-

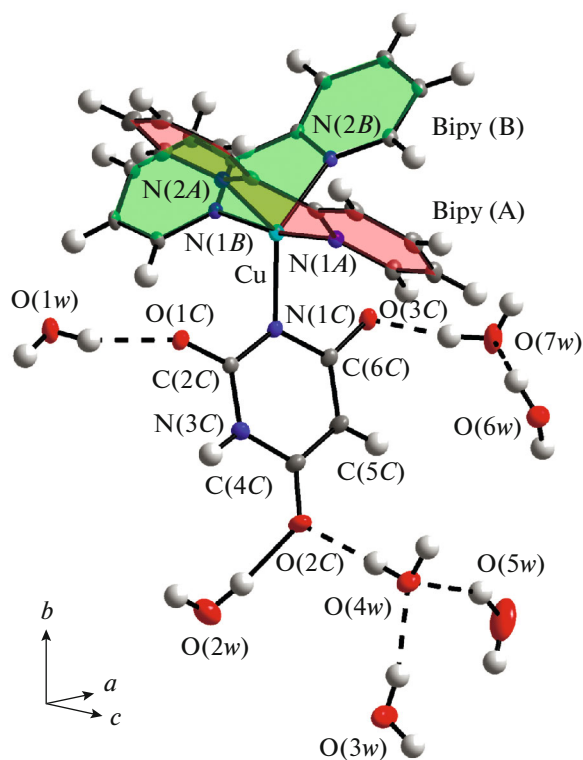


Fig. 1. Independent part of the cell of compound I. Two independent 2,2'-dipyridyl molecules are designated as Bipy (A) and Bipy (B).

tions were applied using the SADABS program. The structure was solved by direct methods (SHELXS) [19] and refined using the SHELXL program taking into account anisotropy of thermal parameters of all non-hydrogen atoms. All hydrogen atoms were localized on the difference electron density map. Further the H atoms bound to the C and N atoms in the BA^{2-} ions and Bipy molecules were localized geometrically in the riding model with restraints to the C–H (0.93–0.98 Å) and N–H (0.86–0.89 Å) bond lengths depending on the geometry with the thermal parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. All coordinates of the hydrogen atoms in the H_2O molecules and OH^- ions were refined with mild restraints to the O–H bond lengths (0.9 Å) and with the thermal parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The structure was checked to the missed symmetry elements and possible cavities using the PLATON program [20]. The main crystallographic data and experimental parameters were the following: $FW = 628.09$, $a = 26.118(3)$, $b = 27.685(3)$, $c = 15.683(2)$ Å, $V = 11370(2)$ Å³, space group $Fdd2$, $Z = 16$, $\rho_{\text{calcd}} = 1.468$ g/cm³, $\mu = 0.833$ mm⁻¹, $2\theta_{\text{max}} = 60.15^\circ$, number of measured parameters 36971, number of independent reflections 8323, $R_{\text{int}} = 0.0587$, Flack parameter 0.04(1), $R_1 = 4.08\%$, $wR(F^2) = 8.58\%$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.304/-0.391$ e/Å³.

The powder X-ray pattern of the polycrystalline sample of complex I at room temperature (D8 ADVANCE diffractometer (Bruker, Center for Collective Use of the Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences), VANTEC linear detector, $\text{CuK}\alpha$ radiation) coincided with that calculated from the single-crystal data, which confirmed that the polycrystals and the studied single crystal of compound I were identical.

The graphical representations of the crystal structure and molecules were constructed using the DIAMOND program [21].

The structure was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1887338; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

In complex I, the doubly-charged BA^{2-} anion is coordinated to copper(II) through the deprotonated N atom. When H_2BA is ionized via the first step ($\text{p}K_{a1} = 3.89$), the proton is detached from the $-\text{C}(5)\text{H}_2$ group, whereas ionization via the second step of the imine group of the HBA^- ion occurs only in highly alkaline media ($\text{p}K_{a2} = 11.9$) [15]. This explains the crystallization of compound I from an aqueous solution at pH 10–11.

The independent part of the cell of compound I contains the Cu^{2+} ion, the BA^{2-} ion, two Bipy molecules, and seven H_2O molecules (Fig. 1). The Cu^{2+} cation is bound to two N,N' -bidentate Bipy molecules (Cu–N 1.997(3)–2.199(3) Å) and one BA^{2-} ion through the N(1) atom (Cu–N 1.990(3) Å) to form the trigonal bipyramid CuN_5 . The bipyramids are connected to each other only by hydrogen bonds (Fig. 2). The BA^{2-} ions and Bipy molecules are nearly planar.

The coordination of HBA^- , BA^{2-} , and thiobarbiturate ions (HTBA^- , TBA^{2-}) through the nitrogen atom only has not earlier been found in any compound [22]. In dimeric complex $[\text{Pd}(\text{En}-N,N')(\mu_2\text{-BA}-\text{C}, \text{N})]_2 \cdot 4\text{H}_2\text{O}$ (II) [14], the μ_2 -bridging BA^{2-} ion is coordinated to one Pd(II) through the nitrogen atom and through the carbon atom (C(5)) to another metal. The C–O distances in compound I (1.252(4)–1.263(5) Å) are by ~ 0.02 Å longer than those in compound II and by 0.04 Å longer than those in the ketoisomer H_2BA [23]. This can be attributed to a higher electron density delocalization in the cyclic structure of the BA^{2-} ligand for complex I. In the atomic group $\text{O}(2)\text{C}=\text{C}(4)\text{C}-\text{C}(5)\text{C}(\text{H})-\text{C}(6)\text{C}=\text{O}(3)\text{C}$ (Fig. 1) of the BA^{2-} ion in compound I and ligands HBA^- [2–13] and HTBA^- [24], the alignment of the electron density is observed, which is manifested as an elongation of the C–O bonds and shorten-

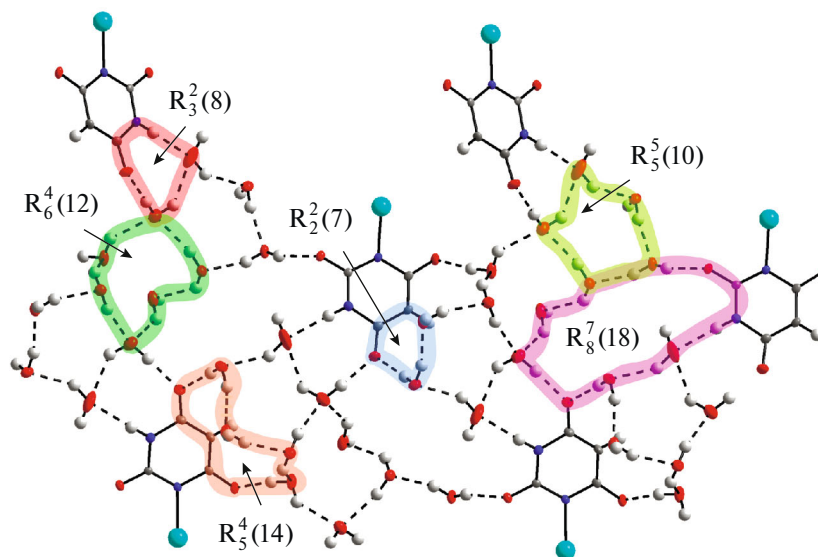


Fig. 2. Layer formed by the hydrogen bonds in compound I.

ing of the C(4)–C(5) and C(5)–C(6) bonds. The coordination of BA^{2-} to Pd(II) through the C(5) carbon atom results in another electron density distribution in the cyclic ligand. For example, the C(4)C–C(5)C (1.45 Å) and C(5)C–C(6)C (1.47 Å) bond lengths in the Pd(II) complex considerably exceed the corresponding values in compound I, which are equal to 1.38 and 1.39 Å, respectively, and in the complexes with the HBA^- [2–13] and HTBA^- [24] ligands. The C(4)C(5)C(6) angle in complex I ($121.7(4)^\circ$) is noticeably larger than those in the palladium complex ($116.7(2)^\circ$) and ketone form H_2BA [23]. This angle is closer to the value obtained for the coordinated HBA^- ion [2–13]. Thus, the coordination of BA^{2-} through the C(5) atom additionally to the N atom changes the geometric parameters in the atomic group $\text{O}(2)=\text{C}(4)-\text{C}(5)\text{H}-\text{C}(6)=\text{O}(3)$, but the C(2)C–N(1)C–C(6)C angle ($121.2(3)^\circ$) in complex I coincides with a similar angle in $[\text{Pd}(\text{En}-\text{N},\text{N}')(\mu_2-\text{HBA}-\text{C},\text{N})_2 \cdot 4\text{H}_2\text{O}]$ ($121.6(2)^\circ$). Other examples of the coordination of barbituric acid anions to metal ions through the nitrogen atom are unknown [22].

Thirteen intermolecular hydrogen bonds $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ in the structure of compound I (Table 1) form a three-dimensional network in which the 2D layer and supramolecular motifs can be distinguished [25]: $\text{R}_2^2(7)$, $\text{R}_3^2(8)$, $\text{R}_5^5(10)$, $\text{R}_6^4(12)$, $\text{R}_5^4(14)$, and $\text{R}_8^7(18)$ (Fig. 2). Among specific features of the behavior of the coordinated BA^{2-} ion compared to HBA^- and HTBA^- is the absence of its self-association by the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. Only Bipy molecules are involved in the $\pi-\pi$ interaction with the distances between the centers of the rings equal to 3.47–3.68 Å.

The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves for compound I are shown in Fig. 3. According to the IR spectroscopic analysis of the leaving gases, only water is removed below 200°C . At 200°C the mass loss ($\Delta m_{\text{exp}} = 20.3\%$) satisfactorily coincides with the theoretical value calculated under the assumption of the complete dehydration of the compound ($-7\text{H}_2\text{O}$, $\Delta m_{\text{calcd}} = 20.1\%$). The dehydration is accompanied by an endothermic effect at 107°C . Three stages of the oxidative decomposition of the coordinated Bipy molecules and HBA^- ion can be distinguished in a temperature range of $200-450^\circ\text{C}$. A strong exothermic effect at 422°C corresponds to the last stage. The final thermolysis product at the temperatures above 470°C is CuO ($\Delta m_{\text{exp}} = 12.4\%$, $\Delta m_{\text{calcd}} = 12.7\%$).

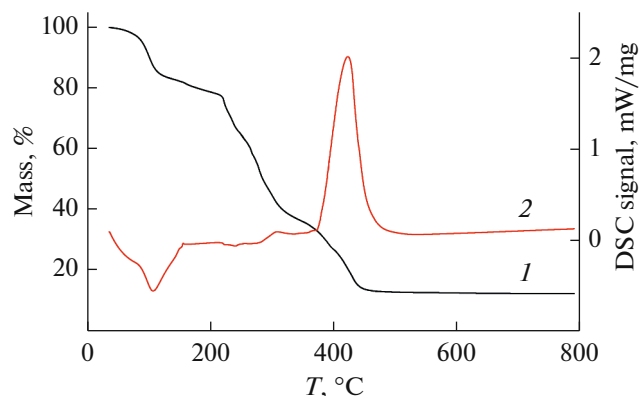


Fig. 3. (1) TG and (2) DSC curves for the decomposition of compound I.

Table 1. Geometric parameters of hydrogen bonds in the structure of compound I

D–H···A	Distance, Å			Angle D–H···A, deg	Transformations for atom A
	D–H	H···A	D···A		
O(1w)–H(1wA)···O(1C)	0.89(3)	1.90(3)	2.750(4)	159(4)	x, y, z
O(1w)–H(1wB)···O(6w)	0.89(3)	1.95(3)	2.815(5)	164(4)	$1 - x, 3/2 - y, z - 1/2$
O(2w)–H(2wA)···O(5w)	0.93(4)	2.02(5)	2.795(7)	140(3)	$x - 1/4, y - 5/4, z - 1/4$
N(3C)–H(3C)···O(5w)	0.88	1.98	2.857(6)	177	$x - 1/4, y - 5/4, z - 1/4$
O(2w)–H(2wB)···O(2C)	0.91(5)	1.73(5)	2.638(5)	172(5)	x, y, z
O(3w)–H(3wB)···O(4w)	0.88(3)	1.94(3)	2.806(5)	168(6)	x, y, z
O(4w)–H(4wA)···O(2C)	0.90(3)	1.80(4)	2.672(5)	163(5)	x, y, z
O(4w)–H(4wB)···O(1w)	0.91(4)	1.91(4)	2.798(5)	165(5)	$1 - x, 3/2 - y, 1/2 + z$
O(5w)–H(5wA)···O(4w)	0.92(5)	1.98(5)	2.801(6)	148(5)	x, y, z
O(6w)–H(6wA)···O(7w)	0.89(3)	2.06(4)	2.757(5)	135(4)	x, y, z
O(6w)–H(6wB)···O(2w)	0.89(3)	1.94(4)	2.814(5)	167(4)	$1/4 + x, 5/4 - y, 1/4 + z$
O(7w)–H(7wA)···O(2w)	0.90(4)	1.99(5)	2.697(6)	134(4)	$5/4 - x, 1/4 + y, 1/4 + z$
O(7w)–H(7wB)···O(3C)	0.90(4)	1.71(4)	2.606(4)	171(4)	x, y, z

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