

CRYSTAL STRUCTURE OF NORFLOXACINIUM AND 2,2'-BIPYRIDYL-1'-IUM 2-THIOBARBITURATES

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Organic salts with the composition $\text{NfH}_2(\text{Htba})\cdot 6\text{H}_2\text{O}$ (**I**) and $\text{BipyH}(\text{Htba})\cdot 2\text{H}_2\text{O}$ (**II**) (H_2tba is 2-thiobarbituric acid, NfH is norfloxacin and Bipy is 2,2'-dipyridyl) are prepared. Their structures are determined by XRD (CCDC cif-file No. 1967494-1967495). Crystals **I** are triclinic: $a = 11.8821(4)$ Å, $b = 11.9959(5)$ Å, $c = 12.0038(4)$ Å, $\alpha = 119.835(1)^\circ$, $\beta = 107.691(1)^\circ$, $\gamma = 95.237(1)^\circ$, $V = 1351.80(9)$ Å³, space group $P-1$, $Z = 2$. Crystals **II** are monoclinic: $a = 7.9587(2)$ Å, $b = 19.6272(4)$ Å, $c = 10.1118(2)$ Å, $\beta = 98.118(1)^\circ$, $V = 1563.71(6)$ Å³, space group $P2_1/n$, $Z = 4$. The structures are stabilized by numerous hydrogen bonds and $\pi-\pi$ interactions involving Htba^- , NfH_2^+ , and BipyH^+ ions. Thermal decomposition of these compounds in air includes dehydration and oxidative degradation stages.

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INTRODUCTION

2-Thiobarbituric acid (H_2tba) is an ancestor of an important class of drugs referred to as thiobarbiturates [1]. The ability of H_2tba and its anion Htba^- to participate in numerous hydrogen bonds (HBs) and $\pi-\pi$ interactions enriches the supramolecular chemistry of their derivatives [2]. It is of theoretical interest to compare the structure of thiobarbituric salts containing organic base cations with 6-membered rings, in particular, norfloxacin (NfH) and 2,2'-bipyridyl (Bipy). These cations may also act as donors and acceptors in HBs and participate in $\pi-\pi$ interactions both with the Htba^- anion and with each other to form unusual supramolecular structures. Note that NfH belongs to one of the most successful classes of synthetic antibiotics referred to as quinolones (FQH) [3]. It is particularly effective against gram-negative bacteria and is used for disease prevention and treatment of various infectious diseases. One main disadvantage of NfH is its low solubility in water [4]. An effective way to improve the bioavailability of norfloxacin implies the used of its organic salts that are highly soluble in water [5]. The main goal of the present work is to prepare and establish the supramolecular structure of NfH_2^+ and BipyH^+ containing thiobarbituric salts. The synthesis, structure, and thermal stability of two novel salts with the composition $\text{NfH}_2(\text{Htba})\cdot 6\text{H}_2\text{O}$ (**I**) and $\text{BipyH}(\text{Htba})\cdot 2\text{H}_2\text{O}$ (**II**) are described.

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EXPERIMENTAL

Norfloxacin $C_{16}H_{18}FN_3O_3$ (Zhejiang Kangyu Pharmaceutical Co., Ltd, China), H_2tba (puriss.), Bipy (Sigma-Aldrich), and acetone (puriss.) were used without further purification.

Synthesis of $NfH_2(Htba)\cdot 6H_2O$ (I). A mixture of H_2tba (0.10 g, 0.69 mmol) and NfH (0.22 g, 0.69 mmol) was dissolved in 300 mL of water at 90 °C. The solution with pH 4-5 was cooled to room temperature and maintained for a week at 4 °C in a fridge. Here and below, the approximate pH values were determined using universal pH paper (0-12 pH range). As a result, several orange crystals in the form of rectangular blocks were obtained. The crystals were filtered, washed in 1 mL of acetone, and dried in air. One of them was selected for XRD analysis. For better yield, the filtrate was maintained in a fridge for 3 months at 4 °C until the mixture volume of about 10 mL. Then substance **I** was filtered, washed in 3-5 mL of acetone, and dried to constant weight in air. Yield: 58% (0.23 g). Note that both the evaporation of the solvent at room temperature and the evaporation of the solution lead to the formation of poorly crystallized precipitates containing unidentified products, apparently, resulting from partial reactant decomposition.

Synthesis of $BipyH(Htba)\cdot 2H_2O$ (II). A mixture of H_2tba (0.10 g, 0.69 mmol) and Bipy (0.11 g, 0.69 mmol) was dissolved in 2 mL of water at 90 °C. The resulting yellow-orange solution (pH \approx 4) was slowly cooled and maintained in air at room temperature. After 24 hours, yellow-orange rhombic crystals were filtered off, washed with a little amount of water, and dried to constant weight in air. Yield: 61% (0.14 g). A single crystal for XRD was selected from the total precipitate substance.

The powder XRD patterns of **I** and **II** obtained at room temperature (Bruker D8 ADVANCE diffractometer, Common Use Center of the Institute of Physics SB RAS; VANTEC linear detector; CuK_α radiation) coincided with those calculated from single crystal XRD data to confirm that the phase of polycrystalline samples is identical to that of studied single crystals.

XRD. Crystal **I** with a size of 0.4×0.35×0.25 mm and crystal **II** with a size of 0.32×0.07×0.05 mm were studied at 100 K. The reflection intensities were measured on a D8 Venture single-crystal diffractometer (Baikal Analytical Center SB RAS) with a CCD detector (Bruker AXS, MoK_α radiation). The experimental absorption corrections were introduced with the SADABS software [6] using the multiscanning method. The structures were solved by direct methods and refined using the SHELXTL program package [7]. Hydrogen positions were determined from difference electron density syntheses and then idealized and refined in the form related to the main atoms. Table 1 lists the experimental parameters and the results of structure refinements.

Structures **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (No. 1967494-1967495; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The thermal analysis of **I** and **II** was performed on a SDT-Q600 analyzer (TA Instruments, USA) under air flow (50 mL/min) in the region of 22-350 °C with a heating rate of 10 °C/min. The composition of gaseous products was determined using a Nicolet380 IR Spectrometer (Thermo Scientific, USA) combined with the thermal analyzer.

RESULTS AND DISCUSSION

The asymmetric part of the unit cell **I** contains one NfH_2^+ , one $Htba^-$, and six H_2O molecules (Fig. 1a). The geometric structure of the NfH_2^+ ion is typical of fluoroquinolones [8-12]; it consists of a flat bicyclic fragment composed of aromatic rings and a piperazine ring having the *chair* conformation. Neutral norfloxacin molecules have a bipolar structure containing a deprotonated carboxyl group ($O2B-C12B-O3B^-$), and the N1B atom of the piperazine ring connects simultaneously two protons to form a $>NH_2^+$ group. As a result of the interaction of the NfH^+ zwitterion with a H_2tba molecule in water, the proton is transferred from atom C5A of thiobarbituric acid to atom O of the deprotonated carboxyl

TABLE 1. Crystal Data and Structure Refinement Details

Parameter	NfH ₂ (Htba)·6H ₂ O (I)	BipyH(Htba)·2H ₂ O (II)
Empirical formula	C ₂₀ H ₃₄ FN ₅ O ₁₁ S	C ₁₄ H ₁₆ N ₄ O ₄ S
<i>M</i>	571.58	336.37
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	4
<i>a</i> , <i>b</i> , <i>c</i> , Å	11.8821(4), 11.9959(5), 12.0038(4)	7.9587(2), 19.6272(4), 10.1118(2)
α , β , γ , deg	119.835(1), 110.003(1), 95.237(1)	90, 98.118(1), 90
<i>V</i> , Å ³	1351.80(9)	1563.71(6)
ρ_{calc} , g/cm ³	1.402	1.429
μ , mm ⁻¹	0.191	0.233
Reflections collected	53914	38702
2 θ_{max} , deg	60.184	60.142
Unique reflections (<i>R</i> _{int}), <i>N</i> ₁	7913 (0.0297)	4589 (0.0532)
Reflections with <i>F</i> > 4 σ (<i>F</i>), <i>N</i> ₂	5970	3218
Index ranges	-16 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 16	-11 ≤ <i>h</i> ≤ 11, -27 ≤ <i>k</i> ≤ 27, -14 ≤ <i>l</i> ≤ 13
Weighting scheme for <i>F</i> ²	$w = 1 / [\sigma^2(F_0^2) + (0.1005P)^2 + 0.612P]$, $P = \max(F_0^2 + 2F_c^2) / 3$	$w = 1 / [\sigma^2(F_0^2) + (0.0651P)^2 + 0.916P]$, $P = \max(F_0^2 + 2F_c^2) / 3$
Parameters refined	382	223
<i>R</i> (<i>N</i> ₁ reflections)	0.0742	0.0843
<i>R</i> (<i>N</i> ₂ reflections)	0.0538	0.0521
<i>wR</i> (<i>F</i> ²) (<i>N</i> ₁ reflections)	0.1749	0.1471
<i>wR</i> (<i>F</i> ²) (<i>N</i> ₂ reflections)	0.1589	0.1311
<i>GOOF</i>	1.013	1.022
Extinction parameter	Not refined	Not refined
(Δ/σ) _{max}	< 0.001	< 0.001
$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$, e/Å ³	1.299 / -0.496	0.877 / -0.394

group of the zwitterion to form a Htba⁻ anion and a NfH₂⁺ cation, which are then included in the solid salt composition. After the protonation, the geometric parameters of NfH[±] remain virtually unchanged and coincide with those determined earlier for the NfH₂⁺ ion [13, 14]. The geometric parameters of the Htba⁻ ion are also virtually identical to those deposited with the CSD database [15], e.g., with the data reported in [16, 17]. These data testify electron density delocalization (characteristic of fluoroquinolones) in the O=C-CH-C=O group [10–12, 16, 17], as is indicated by O1A–C4A (1.259(2) Å), O2A–C6A (1.263(2) Å) bond lengths and the C6A–C5A–C4A (120.45(15)°) angle.

The structure analysis revealed 18 hydrogen bonds (Table 2) N–H···O, O–H···O, and C–H···F involving Htba⁻, NfH₂⁺ ions and all water molecules. The HBs form a three-dimensional framework containing a layer perpendicular to axis *b* and supramolecular motifs R₂²(8), S(6), R₃³(10), R₄⁴(14), and R₈⁶(18) (Fig. 2*a*). Two hydrogen bonds N–H···O combine each Htba⁻ and two similar neighboring ions to form an infinite zigzag chain based on the R₂²(8) supramolecular motif. Each Htba⁻ ion is connected simultaneously with two NfH₂⁺ ions via similar atomic chains formed by OW–H···O_{Htba}, OW–H···OW, and NH_{NfH2}–H···OW hydrogen bonds. The sulfur atoms in Htba⁻ are not involved in hydrogen bonding. The NfH₂⁺

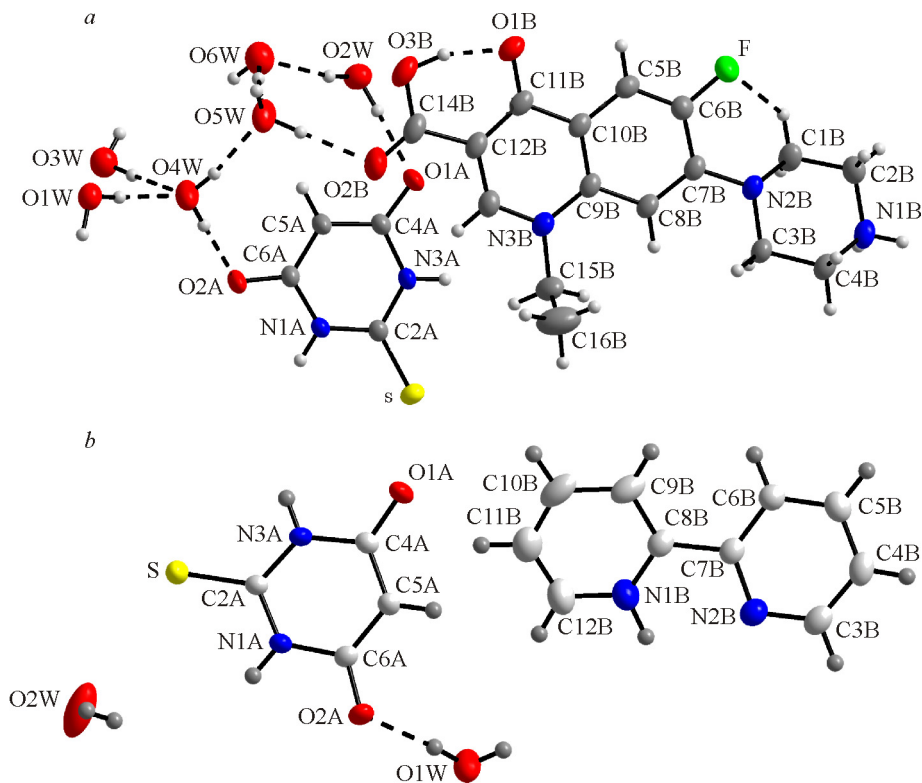


Fig. 1. Asymmetric part of the unit cell: $\text{NfH}_2(\text{Htba})\cdot 6\text{H}_2\text{O}$ (**I**) (a); $\text{BipyH}(\text{Htba})\cdot 2\text{H}_2\text{O}$ (**II**) (b). Hydrogen bonds are shown by dashed lines.

ion (Fig. 1a) contains only two potential HB donors (the O3 atom of the carboxyl group and the N1B atom of the NH_2^+ group) and seven HB acceptors (three N atoms, three O atoms, and one F atom). Similarly, the Htba^- ion has two HB donors (atoms N1A and N3A) and five HB acceptors (two O atoms, two N atoms, and one S atom). The imbalance between the numbers of HB donors and acceptors in **I** is counteracted by the participation of water molecules in numerous HBs and by the self-association of Htba^- ions via $\text{N}-\text{H}\cdots\text{O}$ bonds. Similarly to other fluoroquinolones [8-14], two intramolecular hydrogen bonds $\text{O3B}-\text{H}\cdots\text{O1B}$ and $\text{C1B}-\text{H1A}\cdots\text{F}$ in the NfH_2^+ cation form typical supramolecular motifs S(6), and the H atom of the COOH group forms a strong intramolecular hydrogen bond $\text{O2}_{\text{carboxyl}}-\text{H}\cdots\text{O1}_{\text{ketone}}$ (Fig. 2a) which reduces its ability to participate in intermolecular interactions. The NfH_2^+ ions are connected by water molecules. The topological analysis of hydrogen bonds carried out in the ToposPro program [18] revealed a new eight-sided three-dimensional network with a topological point symbol $(4.5^2.6^2.8)(4.5^2)(5.6^2.7^2.9)(5.7^2.8^2.9)(5.7^2)(5^2.6^2.7.8)(6^2.7^3.8)(6^3.7^2.8)$.

Earlier, we determined the structures of thiobarbituric salts of fluoroquinolones with the composition $\text{PefH}_2(\text{Htba})$ (**III**), $\text{PefH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$ (**IV**) [10] (PefH is pefloxacin), $\text{CfH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$ (**V**) [12] (CfH is ciprofloxacin), and $\text{LevoH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$ (**VI**) [11] (LevoH is levofloxacin). In $\text{PefH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$, the Htba^- ions are not directly connected to each other but are involved in common chains with water molecules via HBs. In anhydrous $\text{PefH}_2(\text{Htba})$, the imbalance between the number of HB donors and acceptors is counteracted by the self-association of Htba^- ions forming infinite chains. In $\text{CfH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$, two hydrogen bonds $\text{N}-\text{H}\cdots\text{O}$ form pairs of Htba^- ions ($\text{R}_2^2(8)$ motif) connected by water molecules. In **III-IV**, PefH_2^+ and Htba^- are bound by $\text{N}-\text{H}_{\text{Htba}}\cdots\text{O}_{\text{PefH}_2}$ bonds. In $\text{LevoH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$, LevoH_2^+ and Htba^- are connected by $\text{N}-\text{H}_{\text{Htba}}\cdots\text{O}_{\text{LevoH}_2}$ and $\text{O}-\text{H}_{\text{LevoH}_2}\cdots\text{O}_{\text{Htba}}$ bonds, and Htba^- are not connected to each other. In $\text{CfH}_2(\text{Htba})\cdot 3\text{H}_2\text{O}$ (**V**), similarly to **I** and **IV**, CfH_2^+ and Htba^- are connected by water molecules. Thus, the system of hydrogen bonds in the salts formed

TABLE 2. Geometric Parameters of Hydrogen Bonds in Structures **I, II**

D–H···A contact	Distance, Å			DHA angle, deg	Transformation for atom A
	D–H	H···A	D···A		
NfH₂(Htba)·6H₂O (I)					
N1A–H1···O2A	0.88	1.96	2.837(2)	174	–x+1, –y+2, –z+2
N1B–H0A···O3W	0.91	1.95	2.828(3)	161	–x+1, –y+1, –z+1
N1B–H0B···O1W	0.91	2.07	2.859(3)	144	x+1, y–1, z–1
N1B–H0B···O3W	0.91	2.59	3.062(3)	113	x+1, y–1, z–1
N3A–H3···O1A	0.88	1.93	2.810(2)	177	–x+1, –y+1, –z+1
O1W–H1A···O1B	0.93(2)	1.86(2)	2.774(3)	170(2)	x, y+1, z+1
O1W–H1BW···O4W	0.81(3)	1.89(3)	2.699(3)	178(3)	x, y, z
O2W–H2AW···O6W	0.88(3)	1.93(3)	2.793(3)	166(3)	x, y, z
O2W–H2BW···O1A	0.89(3)	1.91(3)	2.785(2)	166(4)	x, y, z
O3W–H3AW···O2W	0.82(3)	2.03(3)	2.844(3)	170(3)	–x, –y+1, –z+1
O3W–H3BW···O4W	0.83(3)	2.03(3)	2.832(3)	164(3)	x, y, z
O4W–H4AW···O2A	0.89(3)	1.83(3)	2.709(3)	172(4)	x, y, z
O4W–H4BW···O5W	0.87(2)	1.91(2)	2.767(2)	170(3)	x, y, z
O5W–H5AW···O2B	0.91(3)	1.87(3)	2.781(3)	176(4)	x, y, z
O5W–H5BW···O1W	0.94(4)	1.90(3)	2.828(3)	170(3)	–x, –y+2, –z+1
O6W–H6AW···O5W	0.93(4)	1.91(4)	2.834(4)	173(3)	x, y, z
O6W–H6BW···O2W	0.85(3)	2.17(4)	2.903(3)	145(3)	–x, –y+1, –z+1
C1B–H1A···F	0.99	2.11	2.825(3)	128	x, y, z
O3B–H3B0···O1B	0.98	1.56(4)	2.512(3)	161(3)	x, y, z
BipyH(Htba)·2H₂O (II)					
N1A–H1A···O1A	0.88	1.96	2.8332(19)	175	1/2+x, 1/2–y, 1/2+z
N1B–H1B···O1W	0.99(3)	1.89(3)	2.789(2)	150(2)	1–x, 1–y, 1–z
N3A–H3A···O2A	0.88	1.93	2.7857(19)	164	–1/2+x, 1/2–y, –1/2+z
O1W–H1WA···O2W	0.89(3)	1.87(3)	2.725(3)	160(3)	1/2–x, 1/2+y, 3/2–z
O1W–H1WB···O2A	0.90(3)	1.83(3)	2.724(2)	173(3)	x, y, z
O2W–H2WA···O1A	0.83(4)	1.98(4)	2.809(3)	173(4)	1/2+x, 1/2–y, 1/2+z
O2W–H2WB···O1W	0.80(5)	2.08(5)	2.834(4)	157(4)	–1/2+x, 1/2–y, –1/2+z
C9B–H9B···S	0.95	2.87	3.805(2)	167	–1/2–x, 1/2+y, 1/2–z

by the singly-charged fluoroquinoline cation FQH_2^+ and the Htba^- thiobarbiturate ion depends both on water content and on the fluoroquinolone nature. The NfH_2^+ ions in **I** are connected pairwise by head-to-tail π – π interactions (Table 3) [19] (Fig. 3a), and each of them also participates in a stacking interaction with one of Htba^- ions. In **III–VI**, FQH_2^+ ions also form pairs as a result of head-to-tail π – π interactions. In **III** and **V–VI**, similarly to **I**, FQH_2^+ and Htba^- ions are also connected by π – π interactions. These data show that the crystal packing in thiobarbituric salts of fluoroquinolones favors π – π interactions.

The asymmetric part of the $\text{BipyH(Htba)}\cdot 2\text{H}_2\text{O}$ (**II**) unit cell contains one BipyH^+ , one Htba^- , and two H_2O molecules (Fig. 1b). The formation of salts upon the interaction of H_2tba both with Bipy and with NfH is due to quite a large difference between $\text{p}K_a$ values of organic bases [20, 21] and H_2tba [22], in accordance with the “ $\Delta\text{p}K_a$ rule” that was proposed earlier for bicomponent crystals [23] and states that a salt rather than a cocrystal is formed if $\Delta\text{p}K_a = \text{p}K_a(\text{base}) - \text{p}K_a(\text{acid}) > 2$ or 3. The geometric parameters of Htba^- and BipyH^+ ions are virtually identical to those deposited with the CSD database [15]. BipyH^+

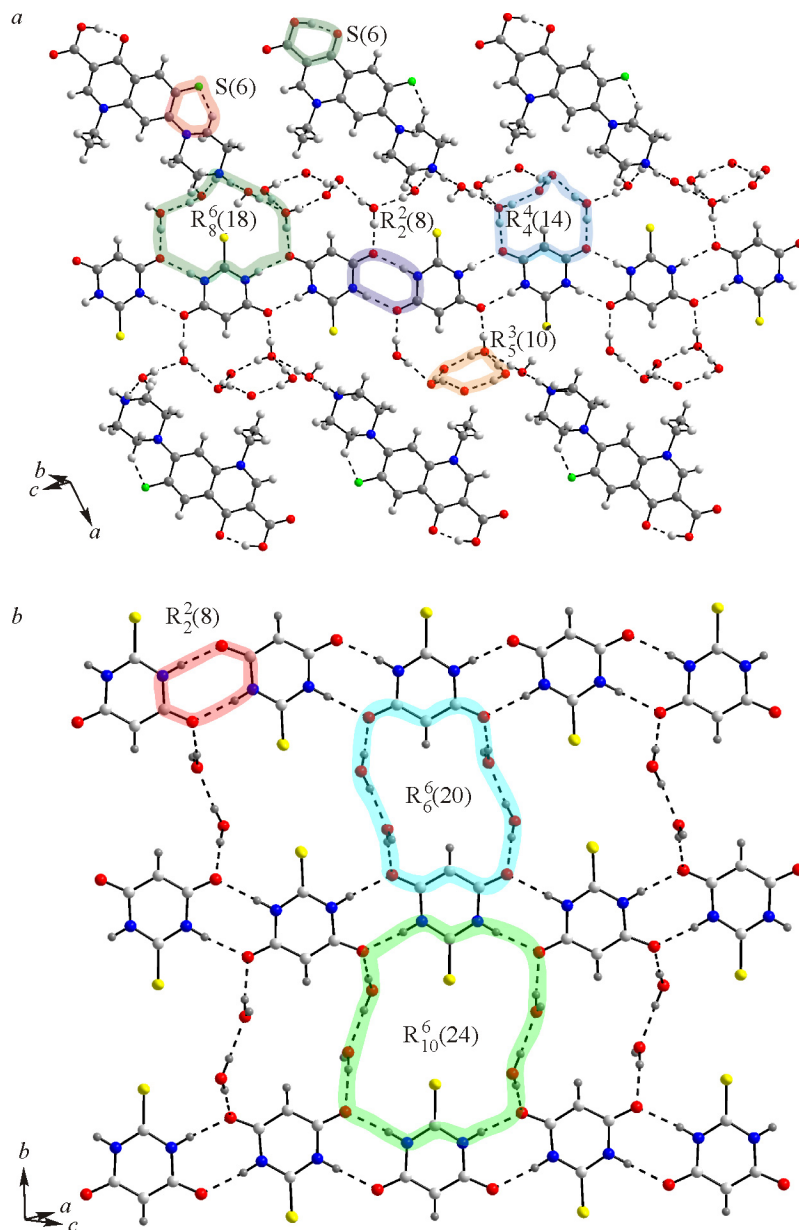


Fig. 2. Hydrogen bonds in $NfH_2(Htba) \cdot 6H_2O$ (a); layer in the plane perpendicular to axis b ; hydrogen bonds in $BipyH(Htba) \cdot 2H_2O$ (b). The supramolecular motifs (outlined by closed curves) are designated.

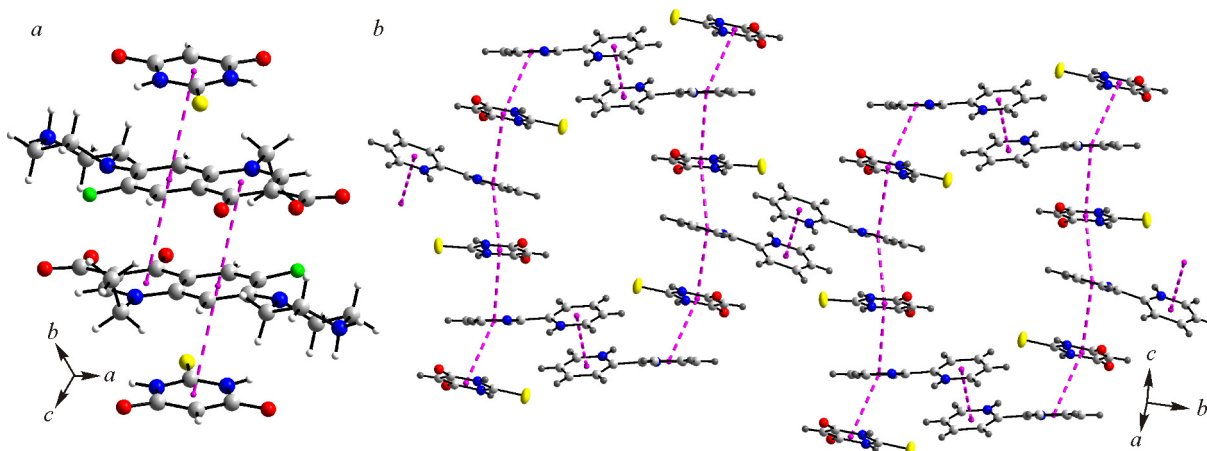
is planar, the standard deviation of atoms from this plane does not exceed 0.34 Å. Positions of nitrogen atoms corresponds to the usual *cis* conformation of the $BipyH^+$ cation [24-26] with the N–C–N torsion angle equal to $-23.0(2)^\circ$. As a result of the protonation of atom N1B, the C8B–N1B–C12B angle increased ($124.4(2)^\circ$) compared to the C3B–N2B–C7B angle ($116.61(17)^\circ$). Like in **I**, the values of geometric parameters in the $Htba^-$ ion indicate electron density delocalization in O=C–CH–C=O groups, e.g., $d(O1A–C4A) = 1.2638(19)$ Å, $d(O2A–C6A) = 1.2624(19)$ Å, and $\angle C6A–C5A–C4A$ ($120.55(15)^\circ$).

The structure analysis showed a presence of eight HBs (Table 2) (N–H \cdots O, O–H \cdots O, and C–H \cdots S) involving $Htba^-$, $BipyH^+$ ions and all water molecules. The HBs form a three-dimensional framework containing a layer in the plane of vectors $a+c$ and b . The layer contains supramolecular motifs $R_2^2(8)$, $R_6^6(20)$, $R_{10}^6(24)$ (Fig. 2b). Like in **I**, N–H \cdots O bonds combine $Htba^-$ into infinite zigzag chains due to the formation of the $R_2^2(8)$ supramolecular motif. Each of these chains is H-bonded

TABLE 3. Parameters of π - π Interactions in Crystals

Cg_i-Cg_j	$d(Cg-Cg), \text{Å}$	α, deg	β, deg	γ, deg	$Cg_i-p, \text{Å}$	Shift, Å
NfH₂(Htba)·6H₂O (I)						
$Cg_1-Cg'_2$	3.536(1)	0.8(1)	17.5	18.1	3.360(1)	1.102
Cg_2-Cg_3	3.644(1)	5.2(1)	19.8	18.1	3.4632(9)	1.134
BipyH(Htba)·2H₂O (II)						
$Cg_1-Cg'_1$	3.9832(15)	0	27.58	27.58	3.5304(10)	1.844
$Cg_2-Cg'_3$	3.6062(10)	15.62(9)	29.27	13.64	3.5044(8)	0.851
$Cg_2-Cg''_3$	3.7345(10)	10.98(9)	19.52	28.15	3.2929(8)	1.762

Notes. For **I**: Cg_1, Cg_2 are the centers of rings in NfH^+ ; Cg_3 is the center of the ring in $Htba^-$. Cg'_2 is obtained from Cg_2 by the $(1-x, 1-y, -z)$ transformation. Cg_i-p is the distance between the center of the Cg_i ring and the plane of the Cg_j ring participating in the π - π interaction. For **II**: Cg_1, Cg_2 are the centers of rings in NfH^+ ; Cg_3 is the center of the ring in $Htba^-$. Cg'_2 is obtained from Cg_2 by the $(1-x, 1-y, -z)$ transformation. Cg_i-p is the distance between the center of the Cg_i ring and the plane of the Cg_j ring participating in the π - π interaction.


Fig. 3. π - π -Interaction between $Htba^-$ ions in $NfH_2(Htba) \cdot 6H_2O$ (**I**) (a) and $BipyH(Htba) \cdot 2H_2O$ (**II**) (b).

to two similar chains due to the participation of water molecules combined pairwise by $OW-H \cdots OW$ interactions. In contrast to **I**, atom S of the thiobarbiturate ion is involved in the formation of a weak $C9B-H9B \cdots S$ hydrogen bond (Table 2). Also, the $BipyH^+$ ion is connected with a water molecule by the $N1B-H1B \cdots O1W$ hydrogen bond. Of all $BipyH^+$ containing compounds of 2-thiobarbituric acids, only the structure of the salt cocrystal [27] $BipyH(Detba) \cdot HDetba$ ($HDetba$ is 1,3-diethyl-2-thiobarbituric acid) was described [28]. In contrast to $Htba^-$ in **II**, the $Detba^-$ ion in this anhydrous substance is directly connected with one $BipyH^+$ ion by two $C-H \cdots O$ hydrogen bonds and with the other ion by one $C-H \cdots S$ hydrogen bond. Naturally, in the absence of water and insufficient number of HB donors, the structure of this compound is stabilized by weak $C-H \cdots X$ hydrogen bonds ($X = O, S$). The topological analysis of hydrogen bonds performed with the ToposPro program [18] revealed a three-sided three-dimensional network with a topological point symbol $(4.6.8)_2(6.8^4.10)$ referred to as *moa* in topological bases. Currently, there is only one known Bipy containing compound, $[Pt(Bipy)(N,S\text{-aminoethanethiolate})]Cl$ [29], that has a similar topological network of hydrogen bonding.

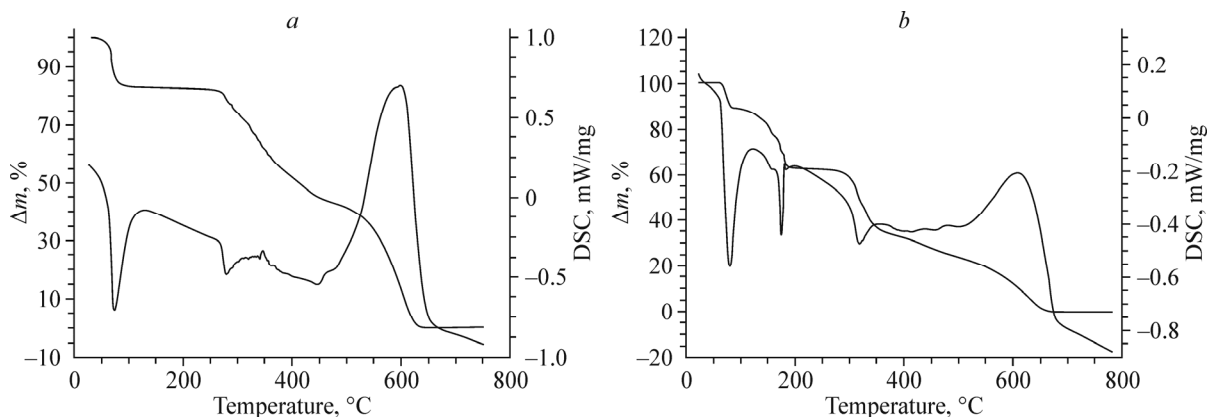


Fig. 4. TG and DSC decomposition curves for $\text{NfH}_2(\text{Htba}) \cdot 6\text{H}_2\text{O}$ (a) and $\text{BipyH}(\text{Htba}) \cdot 2\text{H}_2\text{O}$ (b).

The parameters of π - π interactions in **II** (Table 3) forming chains of alternating Htba^- and BipyH^+ ions were determined. In turn, these chains are connected by π - π interactions between two BipyH^+ ions from the neighboring chains (Fig. 3b) with the participation of the rings with protonated nitrogens which are directly not included in the chains. This interaction binds the ions into infinite ladder-shaped $\dots\text{BipyH}^+\dots\text{BipyH}^+\dots\text{Htba}^-\dots\text{BipyH}^+\dots\text{BipyH}^+\dots$ chains. As a result, a two-dimensional network is formed in the plane of vectors **a**+**c** and **b**. In $\text{BipyH}(\text{Detba}) \cdot \text{HDetba}$ [28], the structure is also stabilized by π - π interactions $\text{BipyH}^+\dots\text{BipyH}^+$, $\text{BipyH}^+\dots\text{Htba}^-$, and $\text{Htba}^-\dots\text{Htba}^- \dots$. The strategy of using relatively weak but numerous π - π interactions in crystal engineering is still poorly elaborated in scientific literature [30] and deserves more attention. Despite the fact that the energy of these interactions is only about 10 kcal/mol, they can significantly contribute to the stabilization of structures [31], like it is the case of salts **I** and **II**. Also, the structural stability of these compounds is greatly facilitated by the formation of numerous HBs involving water molecules.

The decomposition of compounds **I** and **II** begins with dehydration at ~ 50 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$ (Fig. 4) accompanied by endo-effects at 73 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$. The weight losses (Δm) at this stage are in good agreement with theoretical calculations in the assumption of complete dehydration (for **I**: $\Delta m_{\text{exp}} = 18.2\%$, $\Delta m_{\text{calc}} = 18.9\%$ ($-6\text{H}_2\text{O}$); for **II**: $\Delta m_{\text{exp}} = 11.0\%$, $\Delta m_{\text{calc}} = 10.7\%$ ($-2\text{H}_2\text{O}$)).

The oxidative degradation of **I** and **II** begins at ~ 270 $^{\circ}\text{C}$ and 100 $^{\circ}\text{C}$, respectively, and proceeds in several steps. The solid residue disappears ($\Delta m_{\text{exp}} \approx 100\%$) at 650 $^{\circ}\text{C}$ and 670 $^{\circ}\text{C}$, respectively. The products of **I** and **II** dehydration are thermally more stable than initial reagents ($T_{\text{m/dec}} = 250.6$ $^{\circ}\text{C}$ for H_2tba [32], $T_{\text{m/dec}} = 216.7$ $^{\circ}\text{C}$ for NfH [33], and $T_{\text{m}} = 69.5$ $^{\circ}\text{C}$ for Bipy). The thermal degradation of **I** is accompanied by a weak endo-effect at 278 $^{\circ}\text{C}$ and a strong exo-effect at 598 $^{\circ}\text{C}$ (Fig. 4a). The decomposition of **II** is accompanied by endo-effects at 175 $^{\circ}\text{C}$, 319 $^{\circ}\text{C}$ and a strong exo-effect at 610 $^{\circ}\text{C}$ (Fig. 4b). The revealed products of **I** and **II** thermolysis include SO_2 , CO_2 , CS_2 , and pyridine.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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