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Novel 1,3-diethyl-2-thiobarbiturates of 2,2'-bipyridine and 1,10-phenanthroline:
Synthesis, crystal structure and thermal stability

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Abstract

Co-crystallization of 1,3-diethyl-2-thiobarbituric acid (HDetba) with 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) results in preparing a salt co-crystal, BipyH(Detba)(HDetba) (**1**), and the salt, PhenH(Detba)·H₂O (**2**). The compounds are characterized by single-crystal and powder X-ray diffraction and TG-DSC. The nitrogen atoms of BipyH⁺ adopt an *cis* conformation and the N—C—C—N torsion angle is −17.3(1)°. There are six intermolecular hydrogen bonds O—H···O, N—H···O, C—H···O and C—H···S in (**1**) which form a 2D plane network. One Detba[−] ion and one HDetba molecule form a pair by means of O—H···O hydrogen bonds. Detba[−] anions in (**2**) do not form dimers, they are connected by N—H···O, C—H···S and C—H···O hydrogen bonds only with PhenH⁺ cations and water molecules which form a 3D net. Different π – π interactions between the rings are found in (**1**)–(**2**).

Keywords: 1,3-diethyl-2-thiobarbituric acid; 1,10-phenanthroline; 2,2'-bipyridine; salt; salt co-crystal; X-ray diffraction; infrared spectroscopy; thermal stability

1. Introduction

Derivatives of barbituric acid have anesthetic, sedative, anticonvulsive, antimicrobial, antifungal, antiviral and anti-cancer properties [1, 2]. Moreover, the organic salts of barbituric acids and their metal complexes possess potentially useful properties, for instance, biological activities [3, 4], solvatochromism, molecular recognition, photoluminescence, catalytic activity

etc. [2]. They are promising materials for nonlinear optics (NLO) [5, 6] and organic solar cells [7]. While the structures of metal complexes with barbituric (H_2ba) and 2-thiobarbituric acids (H_2tba) and some of their derivatives have been studied [8, 9] organic salts and co-crystals of barbituric acids received less attention. For example, there are no structural data on the compounds of 1,3-diethyl-2-thiobarbituric acid ($C_8H_{12}N_2O_2S$, HDetba) (Fig. 1), although it and its compounds can be applied in various fields. For example, HDetba has been proposed as an alternative to acidic photopolymerizable dental materials [10] and for determining nicotine and twelve metabolites in human urine and animals using high-performance liquid chromatography [11]. Its compounds can be used as NLO materials [12] and for the manufacture of field-effect transistors [13]. Similar to the H_2tba , HDetba has five potential hydrogen bonding acceptors: (i) two carbonyl O atoms, (ii) one S atom and (iii) two N atoms. Each of the N atoms is linked to one $-C_2H_5$ group and therefore can only act as a weak hydrogen bonding acceptor. In the absence of strong hydrogen bonding donors in HDetba, they can be replaced by C atoms, forming weak $C-H\cdots Y$ hydrogen bonds ($Y = F, O, N$) [14]. Therefore, further exploration of organic systems of 1,3-diethyl-2-thiobarbituric acid can provide abundant supramolecular architectures.

The free bases of 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) are used as complexing agents for iron and other metal ions in chemical and biological systems. A classical use of Phen is that of the Fe(II)-complex (ferroin) as an indicator in redox titrations [15]. Bipy is an interesting ligand because of its potential application in preparing of nonlinear optical materials (NLO), sensor objects, coatings and catalysis [16], single-molecule magnets [17]. As a part of our continuing investigations in the structures and properties of 1,3-diethyl-2-thiobarbiturate compounds [18-26], a salt co-crystal 2,2'-bipyridin-1-ium 1,3-diethyl-2-thiobarbiturate 1,3-diethyl-2-thiobarbituric acid, BipyH(Detba)(HDetba) (**1**), and a salt phenanthroline-1-ium 1,3-diethyl-2-thiobarbiturate monohydrate, PhenH(Detba)· H_2O (**2**), were synthesized and characterized by single-crystal and powder X-ray diffraction methods. The thermal decomposition of compounds was also studied. To the best of our knowledge, no information on the structure of the solid and the properties of Bipy or Phen compounds with HDetba exists in literature [8]

2. Experimental section

2.1. Reagents and synthesis

1,3-diethyl-2-thiobarbituric acid, 1,10-phenanthroline chloride monohydrate and 2,2'-bipyridine were purchased from Sigma-Aldrich and used without further purification. Sodium hydroxide and ethanol (95%, CAS 64-17-5) as the reagents of analytical grade (Acros) were used without additional purification.

Compound BipyH(Detba)(HDetba) (**1**) was prepared by crystallization from ethanol. 2,2'-bipyridine (0.039 g, 2.5 mmol) and 1,3-diethyl-2-thiobarbituric acid (0.1 g, 5.0 mmol) were dissolved in ethanol (1.5 cm³) at room temperature. A light yellow transparent solution was left at a temperature of 3 °C. After 2 days, the formation of yellow rhombic single crystals was observed. The crystalline product was filtered off and dried between the sheets of filter paper in air at room temperature (yield 67%). Elemental analysis for C₂₆H₃₂N₆O₄S₂ (**1**): Calc.: C, 56.1%; H, 5.79%; N, 15.1%; S, 11.5%. Found: C, 56.7%; H, 5.58%; N, 14.9%; S, 11.2%. Single crystals suitable for the structural analysis were selected directly from the total mass of precipitate (**1**). Compound (**1**) was crystallized from the aqueous solution at pH = 3.1 (a multitest IPL-103 pH meter, Semico, Russia) with yield 40-60%. Repeated experiments showed poor reproducibility of this method.

The salt, PhenH(Detba)·H₂O (**2**), was crystallized from water. 1,10-phenanthroline hydrochloride monohydrate (0.117 g, 5.0 mmol) was dissolved in 5 ml of water and then an equimolar amount of solid NaOH was added. A white precipitate of Phen was formed. Then, 1,3-diethyl-2-thiobarbituric acid (0.1 g, 5.0 mmol) was added to this mixture. The sediment partially dissolved, changing color from white to yellow. The mixture was heated to 80 °C and kept at this temperature for one hour until the yellow precipitate completely dissolved. The light yellow solution was slowly cooled and allowed to evaporate at room temperature (pH = 3.9). A week later, a little amount of orange oil was formed in the solution, its amount increased as the water evaporated. The solid residue after complete removal of water was a mixture of orange crystals and a glassy substance. Single orange crystals of (**2**) were taken directly from the resulting mixture. Some of these crystals were used for elemental and structural analysis, as well as for thermal measurements. Elemental analysis for C₂₀H₂₂N₄O₃S (**2**): Calc.: C, 60.3%; H, 5.56%; N, 14.1%; S, 8.05%. Found: C, 59.8%; H, 5.68%; N, 14.4%; S, 7.87%. However, we could not get compound (**2**) at a volume sufficient for powder XRD measurements. The attempts to obtain other compounds of HDetba with Bipy and Phen by the crystallization from the aqueous solution were unsuccessful.

2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals (**1**) and (**2**) at 100 K using a D8 Venture X-ray single crystal diffractometer (Bruker AXS) equipped with a CCD-detector, graphite monochromator and a Mo K α radiation source. The absorption corrections were applied using the SADABS program. The structures were solved by direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [27]. All hydrogen atoms were found *via* Fourier difference maps. Further, the hydrogen atoms were linked with C, N atoms in the HDetba molecule, the Detba⁻, BipyH⁺,

PhenH⁺ ions, were positioned geometrically as riding on their parent atoms with d(C—H) = 0.93–0.98 Å, d(N—H) = 0.86–0.89 Å depending on geometry and U_{iso}(H) = 1.2U_{eq}(C, N). All hydrogen atoms of the H₂O molecules were refined with bond length restraint d(O—H) = 0.9 Å and U_{iso}(H) = 1.2U_{eq}(O). The structure test for the presence of missing symmetry elements and possible voids was produced using the PLATON program [28]. The DIAMOND program was used for crystal structure plotting [29].

Powder X-ray diffraction data of (1) was obtained using a D8 ADVANCE diffractometer (Bruker) equipped with a VANTEC detector with a Ni filter. The measurements were made using Cu Kα radiation. The structural parameters defined by a single crystal analysis were used as base in the powder pattern Rietveld refinement. The refinement was produced using the TOPAS 4.2 program [30]. Low *R*-factor and good refinement results (Table 1S, Fig. 1S) indicate the phase purity of the powder sample (1).

2.3. Physical measurements

The chemical analysis was carried out with an HCNS-0 EA 1112 Flash Elemental Analyser. TGA was carried out on a simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under dynamic air atmosphere (50 ml/min flow rate) within 25–350 °C at the scan rate of 10 °C/min. The compound weight was 4.516 mg for (1) and 4.590 mg for (2). Platinum crucibles with perforated lids were used as containers.

3. Results and discussion

3.1. Theoretical consideration

2,2'-bipyridine and 1,10-phenanthroline behave as weak bases, often forming monoprotonated species of BipyH⁺ and PhenH⁺, respectively, as a result of protonation of one N atom. In the aqueous solution, stepwise acidity constants are pK_{a1} = 1.51, pK_{a2} = 4.48 for the BipyH₂²⁺, and pK_{a1} = 1.92, pK_{a2} = 5.01 for the PhenH₂²⁺ (30 °C, 0.1M KNO₃) [31]. The acidity constant is pK_{a1} = 2.78 for HDetba (25 °C, 0.25M KCl) [32]. The HDetba speciation (Fig. 2) shows the predominance of an anionic species at pH > 4 (α₁ ≈ 1), and a neutral species at pH < 1.5 (α₂ ≈ 1) in the aqueous solution. A neutral molecule Bipy species (Fig. 2) is dominated at pH > 6 (α₀ ≈ 1), a cationic species BipyH⁺ between pH 2 and pH 4 (α₁ ≈ 0.7–0.8). A diprotonated cationic species BipyH₂²⁺ (α₂) forms at pH < 3, and it is dominated at pH < 1. The speciation of Phen – HDetba system (Fig. 2S) shows the predominance of a neutral Phen species at pH > 6.5, a cationic species PhenH⁺ between pH 2.5 and pH 4.5, and a cationic species PhenH₂²⁺ at pH < 1.

According to the species distribution diagrams, pH values of the aqueous solution were chosen for the synthesis of (1) [pH \approx 3] and (2) [pH \approx 4].

It is generally accepted that the reaction of an acid with base is expected to form a salt if $\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid}) > 2$ or 3 [33]. Indeed, when the equimolar amounts of HDetba interact with Phen ($\Delta pK_a = 2.23$), salt (2) was obtained. The difference in the values of K_a of BipyH⁺ и HDetba is less ($\Delta pK_a = 1.70$), which promoted the formation of (1) salt co-crystals at pH 3.

3.1. Crystal structures of (1)

The unit cells of (1) correspond to triclinic symmetry. Space group *P*-1 was determined from the statistical analysis of reflection intensities. The main crystal data are enumerated in Table 1. Compound (1) is a salt co-crystal [34]. The asymmetric unit contains one BipyH⁺ ion, one Detba[−] ion and one HDetba molecule (Fig. 3a). The main bond lengths C—N, C—C and valence angles (Table 2S) practically coincide with those found earlier in other related compounds of HDetba [18–26], but C—S and O1—C4 bonds are slightly (0.01–0.02 Å) shorter. However, the O2A—C6A bond is noticeably (0.03–0.04 Å) longer than the others (Table 2S), since the O2A atom in the HDetba molecule is bonded to the hydrogen atom, that is, the HDetba acid is in the enol form. The conformations of Bipy and its protonated species constitute an important aspect in understanding the properties of this popular ligand in coordination chemistry. Bipy exists in a *trans* conformation in solid state [35]. The *cis* conformer of the cation is by far more stable than *trans*, according to *ab initio* self consistent-field (SCF) calculation [36]. As expected, 2,2'-bipyridine offers interesting motifs by virtue of the predominantly *cis* dispositions of the pairs of nitrogen atoms in its monoprotinated salts [8]. The monoprotinated *cis* species of BipyH⁺ could be stabilized by cationic hydrogen bond N—H \cdots N, as in numerous proton sponges [14]. However, there are also compounds in which BipyH⁺ is in the form of a *trans* conformer [8, 37]. In (1), the bipyridinium cation has a *cis* conformation and the N—C—C—N torsion angle is $-17.3(1)^\circ$. It clearly indicates that BipyH⁺ does not behave as a proton sponge. As expected [38], a weak intramolecular hydrogen bond is found in the BipyH⁺ cation with an N2 \cdots N1 distance of 2.654(1) Å and N2—H \cdots N1 angle of 106.52(7)°. The main bond lengths C—N, C—C and the angles in BipyH⁺ practically coincide with those found earlier in other related compounds [8]. For instance, the bond lengths C7C—C8C (1.4790(16) Å), N1C—C8C 1.3470(15) Å and N2C—C7C (1.3514(16) Å) coincide with those found in [BipyH]ClO₄ [C7C—C8C (1.481 Å), N1C—C8C 1.347 Å and N2C—C7C (1.352 Å)] (CSD refcode PYPYPC02) [39]. In (1), the BipyH⁺ ion is planar, the standard deviation of atoms from this plane is 0.183 Å. As expected [40], the effect of protonation at N2 site in BipyH⁺ is manifested in the C—N—C angles being much wider than those at an unprotonated N1 atom [$123.4(1)^\circ$ versus $117.2(1)^\circ$]. Six

intermolecular hydrogen bonds O—H \cdots O, N—H \cdots O, C—H \cdots O and C—H \cdots S in the structure (Table 2) form a 2D plane network with supramolecular motifs $R_2^1(6)$, $R_2^1(7)$ and $R_8^8(39)$ (Figure 4a). One Detba $^-$ ion and one HDetba molecule join to form pairs by means of O2A—H1A \cdots O2B and C5A—H5A \cdots O2B hydrogen bonds. In the salt co-crystal (**1**), a strong hydrogen bond O2A—H1A \cdots O2B is characterized by a small distance $d(\text{O}\cdots\text{O}) = 2.440(1) \text{ \AA}$, a large value of the angle O2A—H1A \cdots O2B ($178(2)^\circ$) and a long bond O2A—H1A ($d(\text{O2A—H1A}) = 1.32(2) \text{ \AA}$). Close geometric parameters of the O—H \cdots O hydrogen bond were previously established in the salt co-crystal of the piperidine (Pipe) with 2-thiobarbituric acid, PipeH(Htba)(H₂tba) (**3**) [41]. In the formation of strong hydrogen bonds, an increase in the distance $d(\text{O—H})$ reaches 0.2 \AA [42] as in compound (**1**). In (**3**), the Htba $^-$ ion and the H₂tba molecule also form a pair, but this happens due to two hydrogen bonds N—H \cdots O. These pairs are combined into infinite chains by the intermolecular hydrogen bonds O—H \cdots O and N—H \cdots O. Replacing the hydrogen atoms of the NH groups in H₂tba by the C₂H₅ groups leads to weakening of N atoms donor capacity. In this case, weak C—H \cdots O hydrogen-bonds in (**1**) play an important role in the formation of the supramolecular structure. The C—H \cdots O hydrogen-bond distances in (**1**) are of the same order of magnitude as those reported previously [37].

Topological analysis of the net, using simplification and excluding all 0-, 1- and 2-coordinated nodes revealed that this is a uninodal 4-c net with point symbol ($4^3.6^3$) which is known as **SP (6,3)Ia** [30]. It should be noted that H-bond net of NH₄Detba [18] forms a relative 2D net with point symbol ($4^4.6^2$) named **sql**. Compounds LiDetba and NaDetba [19] have relative 2D nets ($4^2.6^4$) named **SP (6,3)Id**. Compounds M(Detba)₂(H₂O)₂ (M = Ca, Sr, Mn) [23, 26] also have 2D nets ($4^4.6^2$) **sql**, compound Eu(Detba)₃ [24] has 2D net (6^3) **hcb**, and Pb(Detba)₂ [21] has 2D net (4^3)₂($4^4.6^6.8^3$) **kgd**. A common property of all these nets is that they form only 2D nets and this can be associated with a small amount of hydrogen bond donors in HDetba ligands. Further analysis of interactions in (**1**) reveals π – π interactions between HDetba, Detba $^-$ and BipyH $^+$ rings (Table 3S, Fig. 3Sa).

3.2. Crystal structures of (**2**)

The unit cell of (**2**) also corresponds to triclinic symmetry. The main crystal data are shown in Table 1. The asymmetric unit contains two Detba $^-$ ions, two PhenH $^+$ ions and two water molecules. (Fig. 3b). The structure test for the presence of missing symmetry elements revealed nonspacegroup translation A (0, 1/2, 1/2). As groups of atoms (O1C, O1D); (C9C, C9D), (O1W, O2W) violated this translation, the crystal has pseudosymmetry and no obvious spacegroup change was needed. The main bond lengths C—N, C—C (Table 2S) and the valence angles in HDetba $^-$ ion coincide with those found earlier in other related compounds [18–26]. Similar to (**1**) C—S and O1—C4 bonds are slightly (0.01 – 0.02 \AA) shorter. In PhenH $^+$, the C1A—C2A

(1.434(2) Å), C1B—C2B 1.436(2) Å), N1A—C2A (1.363(2) Å), N1B—C2B (1.363(2) Å), N2A—C1A (1.357(2) Å), and N2B—C1B (1.359(2) Å) distances coincided with those found earlier (CSD refcode CUZDIK) [43]. PhenH⁺ ions are practically flat, so the standard deviation of atoms from planes for ions A and B is only 0.048 and 0.052 Å, respectively. As in compound (1), the effect of protonation at the N2A and N2B sites in A and B respectively, is manifested in the C—N—C angles being much wider than those for the unprotonated nitrogen atoms [123.1(1), 123.0(1)° *versus* 116.5(1), 116.4(1)°]. Similar to (1), a weak intramolecular hydrogen bond is found in A and B of PhenH⁺ cation with an N2...N1 distance of 2.7476(2) Å and 2.7517(2) Å, and N—H...N angle of 104.121(9)°, 104.31(1)°, respectively. The torsion angle C8—C7—C9—C10 of Detba[−] ions in (1)–(2) is small (<4 deg) therefore the Detba[−] ions are present in conformational state (A) [18].

Nine N—H...O, O—H...O, C—H...O and C—H...S intermolecular hydrogen bonds in the structure (Table 2) form a 3D net. Some 2D nets can be marked (Fig. 4b) and the shortest ring motifs in them are R₄⁴(18), R₄⁴(20), R₆⁶(20). Water molecules participate in moderately strong O—H...O interaction with anions (d(O...O) = 2.809 and 2.876 Å). There are also π – π interactions between Detba[−] and PhenH⁺ rings (Table 3S, Fig. 3Sb). The self-assembly and crystal structure for 1,10-phenanthroline barbiturate monohydrate, PhenH(Hba)·H₂O (CSD refcode MUYVET), and 1,10-phenanthroline 2-thiobarbiturate, PhenH(Htba) (CSD refcode MUYVET) have been reported earlier [5]. The study demonstrated how two barbiturate or thiobarbiturate moieties join to form dimers by means of N—H...O hydrogen bonds (d(N...O) = 2.805 and 2.823 Å). These dimers were stabilized by the cation–anion interactions of N—H...O and N—H...N types. As in (2), the water molecules in PhenH(Hba)·H₂O participate in the formation of moderately strong hydrogen bonds with Hba[−] anions. Similar to (1)–(2), in PhenH(Hba)·H₂O and PhenH(Htba) the C—N—C angles for protonated N atoms were larger than for the unprotonated N atoms, and the charge in O1=C4—C5—C6=O2 group of Hba[−] and Htba[−] was delocalized.

Topological analysis of (2) using ToposPro program [30] showed that this 3D net is a 6-nodal (3-c)(4-c)(4-c)(5-c)(5-c)(5-c) net with the point symbol (3.4.5.6³)(3.4.6⁵.7².8)(3.4².5.6²)(4.6.8)(4².6⁵.7².8)(4³.6⁶.7), which is our novel contribution.

3.4. Thermal decomposition

The TG-DSC curves of BipyH(Detba) (1) and PhenH(Detba)·H₂O (2) in the range of 25–300 °C are shown in Fig. 4S and Fig. 5S, respectively. The TG curve clearly indicates that thermal decomposition/oxidation of (1) occurs in one step (Fig. 4S). An endothermic effect for (1) at 110.3 °C corresponds to the compound melting. This value of melting point is higher than that

for Bipy (70.5 °C) and less than that for HDetba (112 °C, [19]), which confirms the individuality of the compound (**1**). The decrease in the mass of the substance at $T > 112$ °C corresponds to the oxidation of compound and evaporation of HDetba and Bipy. In the range of 150–230 °C, the mass of the sample decreased rapidly in accordance to the mean TG curve (Fig. 4S). The transformations at 150–230 °C are accompanied by the exo effect at ~160 °C and endo effect at 216 °C. The appearance of a weak endothermic peak at 216 °C can be explained by the thermal effects superposition of oxidative decomposition and evaporation of thermolysis products. In the temperature range of 150–230 °C, almost all the bipyridine is removed, which is confirmed by the absence of an endothermic effect at the boiling point of Bipy (273 °C). At 250 °C, the total mass loss reaches ~95%, and then the mass decreases only by ~1% when heated to 300 °C. The carbonaceous residue (~5%) is probably formed as a result of incomplete oxidation of the HDetba molecules and Detba^- ions with the release of CO_2 . As seen from the TG curve (Fig. 5S), the thermal decomposition process for the (**2**) can be divided into three stages. The first stage starts in the range of 70–135 °C with mass loss of 4.60%, which corresponds to the loss of H_2O molecule with the theoretical mass loss of 4.52%. The Phen and HDetba have their melting points of 117 °C and 112 °C [19], respectively, these data confirm the individuality of compound (**2**). The dehydration of (**2**) is accompanied by endo effect at 93.6 °C. In the second stage of transformation at 140–250 °C, evaporation and oxidation of 1,3-diethyl-2-thiobarbituric acid and phenanthroline occur simultaneously. With the temperature over 250 °C, the endothermic evaporation processes of HDetba and Phen are likely to become increasingly important, as evidenced by the endothermic peak at 275 °C on the DSC curve. The carbonaceous residue of thermolysis (**2**) at 310 °C was an oily black substance.

4. Conclusions

For the first time, the organic salt co-crystal (**1**) and salt (**2**) of 1,3-dialkyl-2-thiobarbituric acid were prepared and structurally characterized. The compounds were obtained by the reaction in the aqueous medium of an acid with the Bipy and Phen. At Bipy : HDetba = 1 : 2 molar ratio, an anhydrous salt co-crystal (**1**) was formed, containing BipyH^+ ion, Detba^- ion, and HDetba molecule. The salt (**2**) was obtained by the reaction of an acid with the 1,10-phenanthroline at a Phen : HDetba = 1 : 1 molar ratio. It contains one PhenH^+ cation, one Detba^- anion and one water molecule. The formation of the salt co-crystal (**1**) and the salt (**2**) is consistent with the " ΔpK_a rule" proposed earlier for two-component organic crystals [33].

The protonation of the N atom in (**1**) and (**2**) resulted in a slight deformation of the ring and consequently a slightly larger C—N—C bond angle ($>120^\circ$). In (**1**), the O—H \cdots O and C—H \cdots O

intermolecular hydrogen bonds connect the anion and neutral acid in a pair. The O—H \cdots O hydrogen bond between an acid (HDetba) and its conjugate base (Detba $^-$) is very strong, with $d(\text{O}\cdots\text{O}) = 2.440(1)$ Å. The Detba $^-$ anion is bound to one BipyH $^+$ ion by two N—H \cdots O and C—H \cdots O intermolecular hydrogen bonds (Fig. 4a). HDetba is bound by two C—H \cdots O intermolecular hydrogen bonds with one BipyH $^+$ cation and C—H \cdots S intermolecular hydrogen bond with another cation. BipyH $^+$ cations in (1), and PhenH $^+$ in (2), are not directly connected to each other (Fig. 2). The Detba $^-$ anions in (2) do not form dimers, unlike barbiturate and thiobarbiturate ions in corresponding phenanthroline salts [5]. Each chain of two water molecules is bound by the OW—HW \cdots O hydrogen bonds with three Detba $^-$ anions, which in turn are connected with to the PhenH $^+$ cations by the N—H \cdots O, C—H \cdots S hydrogen bonds. The C—H \cdots X (X = O, S) weak hydrogen bonds exert a significant influence on the supramolecular architecture of the compounds. The compound (2) has a new topology of a 3D net. Several types of π – π interactions between the rings were found in the (1)-(2) (Fig. 2S). Co-crystal of (1) melts at 110.3 °C and salt (2) is dehydrated in the range of 70-135 °C, a further increase in temperature leads to their oxidative decomposition.

Supplementary data

The crystallographic data (excluding structure factors) for the structural analysis have been deposited with Cambridge Crystallographic Data Centre ((1) - CCDC # 1826542; (2) - CCDC # 1826544). The information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk).

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Graphical Abstract

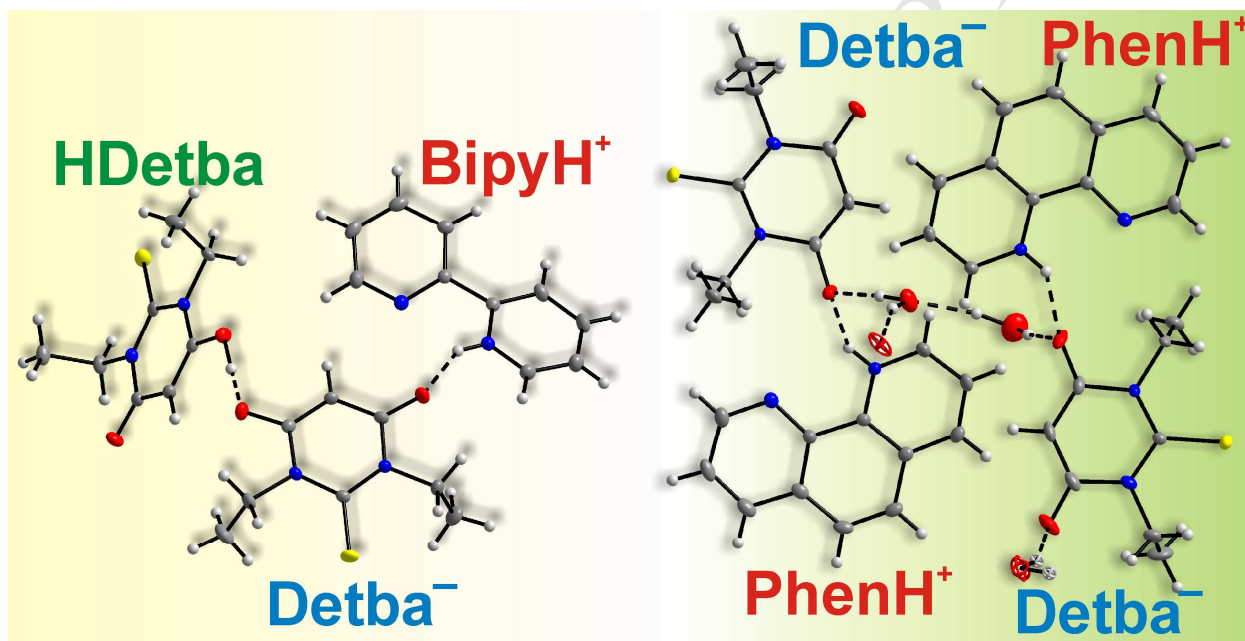


Table 1. Crystal structure parameters of (1) and (2)

Single crystal	BipyH(Detba)(HDetba) (1)	PhenH(Detba)·H ₂ O (2)
Moiety formula	C ₂₆ H ₃₂ N ₆ O ₄ S ₂	C ₂₀ H ₂₂ N ₄ O ₃ S
Dimension (mm)	0.40×0.31×0.18	0.34×0.31×0.15
Color	Yellow	Yellow
Molecular weight	556.69	398.48
Temperature (K)	100	100
Space group, Z	<i>P</i> -1, 2	<i>P</i> -1, 4
<i>a</i> (Å)	10.1936 (6)	10.9194 (9)
<i>b</i> (Å)	11.0122 (6)	13.351 (1)
<i>c</i> (Å)	13.4505 (8)	13.8901 (11)
α (°)	68.875 (2)	104.723 (3)
β (°)	87.388 (2)	101.020 (3)
γ (°)	72.767 (2)	99.626 (3)
<i>V</i> (Å ³)	1342.00 (14)	1872.1 (3)
ρ_{calc} (g/cm ³)	1.378	1.414
μ (mm ⁻¹)	0.243	0.203
Reflections measured	57298	90030
Reflections independent	7863	10998
Reflections with <i>F</i> > 4 σ (<i>F</i>)	6564	7730
2 θ_{max} (°)	60.15	60.16
<i>h, k, l</i> - limits	-14 ≤ <i>h</i> ≤ 14; -15 ≤ <i>k</i> ≤ 15; -18 ≤ <i>l</i> ≤ 18	-15 ≤ <i>h</i> ≤ 15; -18 ≤ <i>k</i> ≤ 19; -19 ≤ <i>l</i> ≤ 19
<i>R</i> _{int}	0.0381	0.0775
The weighed refinement of <i>F</i> ²	$w=1/[\sigma^2(F_o^2)+(0.0385P)^2+0.6513P]$	$w=1/[\sigma^2(F_o^2)+(0.056P)^2+0.744P]$
Number of refinement parameters	350	521
<i>R</i> 1 [<i>F</i> _o > 4 σ (<i>F</i> _o)]	0.0344	0.0493
<i>wR</i> 2	0.0891	0.1241
<i>Goof</i>	1.017	1.036
$\Delta\rho_{\text{max}}$ (e/Å ³)	0.382	0.893
$\Delta\rho_{\text{min}}$ (e/Å ³)	-0.359	-0.406
(Δ/σ) _{max}	0.001	0.404

Table 2. Hydrogen-bond geometry in (1) and (2) structures (Å, °).

D—H	d(D—H)	d(H...A)	\angle D— H...A	D...A	A	Transformation for A atom
BipyH(Detba)(HDetba) (1)						
N2C—H2C	0.86	1.91	142	2.6395 (14)	O1B	x, y, z
C6C—H6C	0.93	2.39	163	3.2923 (17)	O1A	x, y, 1+z
C9C—H9B	0.93	2.53	168	3.4411 (15)	O1A	x, y, 1+z
C4C—H4C	0.93	2.76	171	3.6822 (14)	S1	1+x, -1+y, 1+z
C5A—H5A	0.93	2.6486(7)	121.47 (8)	3.233 (1)	O2B	x, y, z
O2A—H1A	1.12(2)	1.32 (2)	178 (2)	2.440 (1)	O2B	x, y, z
PhenH(Detba)·H ₂ O (2)						
N1A—H1A	0.86	1.94	142	2.671 (2)	O2D	x, y, z
N1B—H1B	0.86	1.96	139	2.674 (2)	O2C	x, y, z
O1W—H1WA	0.90 (2)	1.94 (2)	163 (2)	2.809 (2)	O2C	x, y, z
O1W—H1WB	0.83 (2)	2.11 (2)	154 (2)	2.876 (2)	O1D	1-x, 1-y, 1-z
O2W—H2WA	1.05 (2)	1.82 (2)	168 (2)	2.854 (2)	O1W	x, y, z
O2W—H2WB	1.05 (2)	1.79 (2)	170 (2)	2.827 (2)	O2D	x, y, z
C12B—H12B	0.93	2.20	142	2.992 (2)	O1C	1-x, 2-y, 2-z
C10A—H10A	0.93	2.84	145	3.639 (2)	S2	x, 1+y, z
C12A—H12A	0.93	2.39	126	3.030 (2)	O1D	1-x, 1-y, 1-z

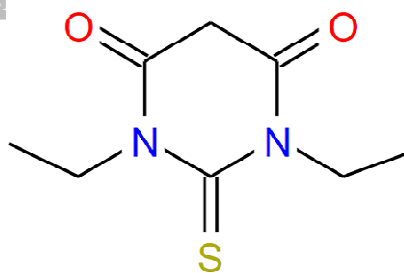


Fig. 1. Graphic formulas of 1,3-Diethyl-2-thiobarbituric acid (HDetba)

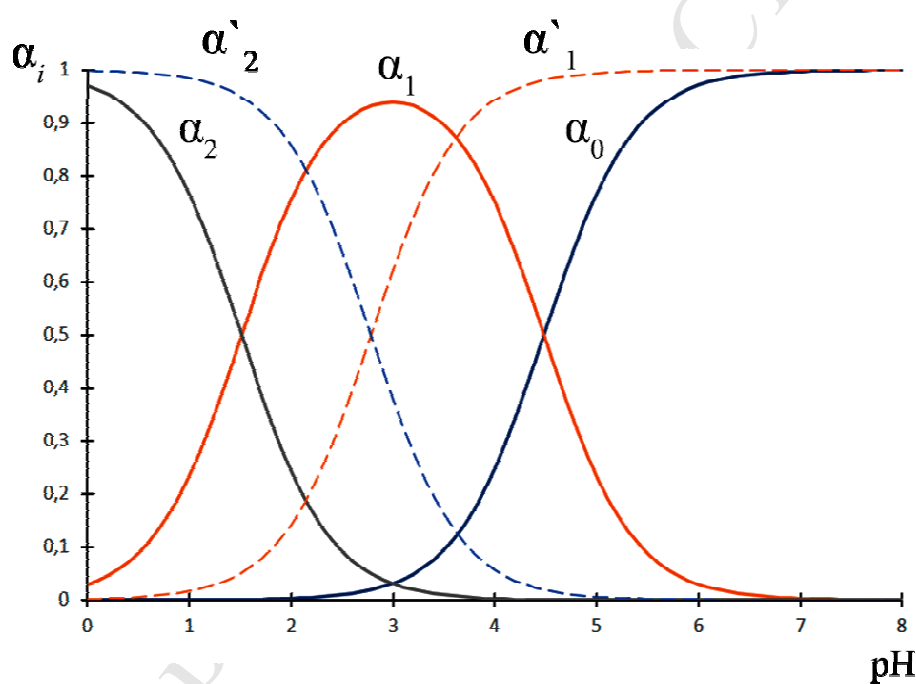


Fig. 2. Bipy and HDetba species distribution diagram as a function of solution pH: α_0 – Bipy, α_1 – BipyH⁺, α_2 – BipyH₂²⁺; α'_2 – HDetba, α'_1 – Detba[−]. Here α_i , α'_i are the molar fractions of corresponding species.

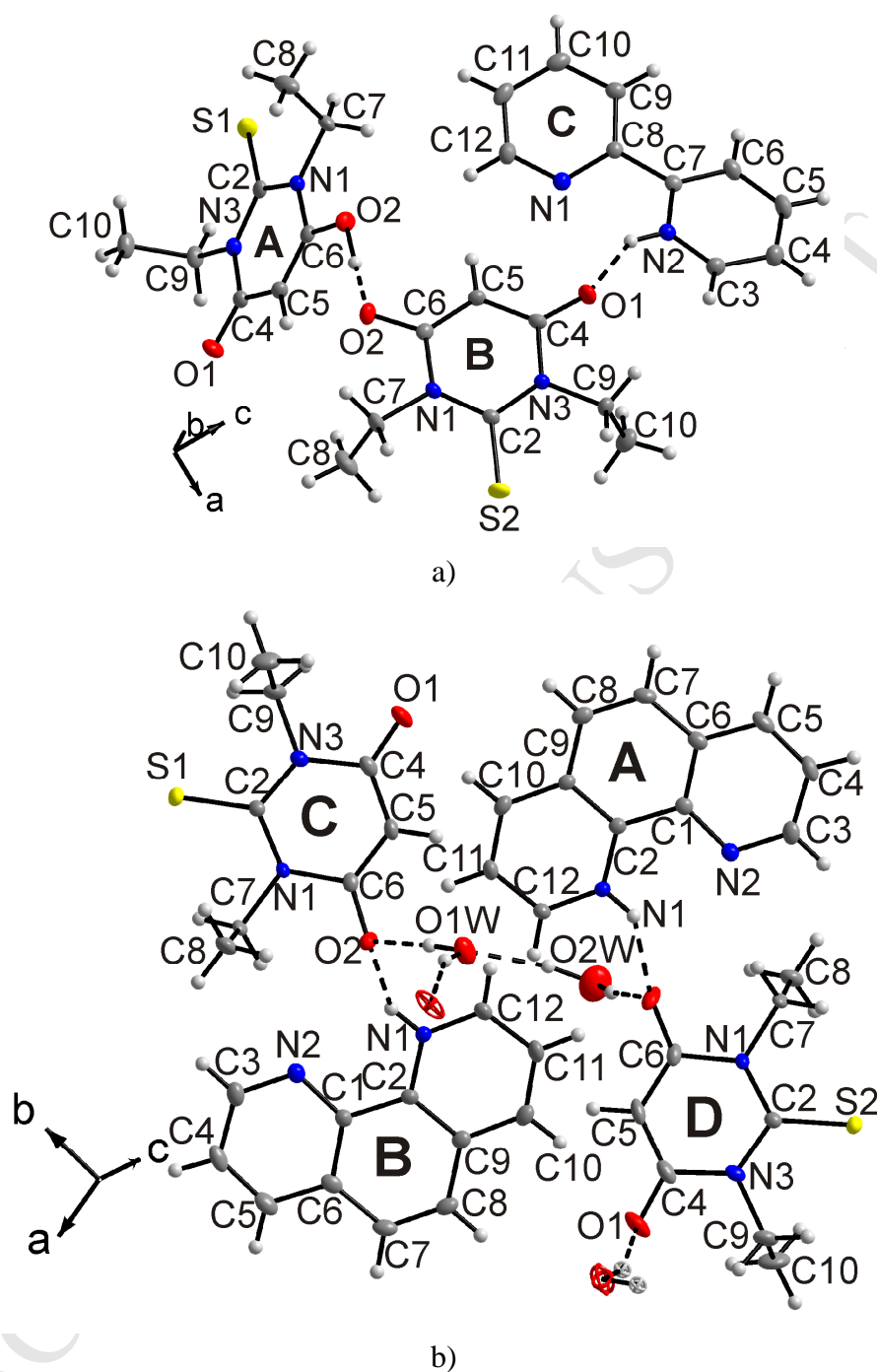


Fig. 3. The asymmetric unit of the (1) (a), (2) (b) unit cell. Symmetry independent, different molecules are marked by A, B, C, D labels. All atoms in the asymmetric unit are labeled. The neighboring symmetry-generated atoms are represented by principal ellipsoids with an individual color. The intermolecular hydrogen bonds are represented by dashed lines. The ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms represented by spheres.

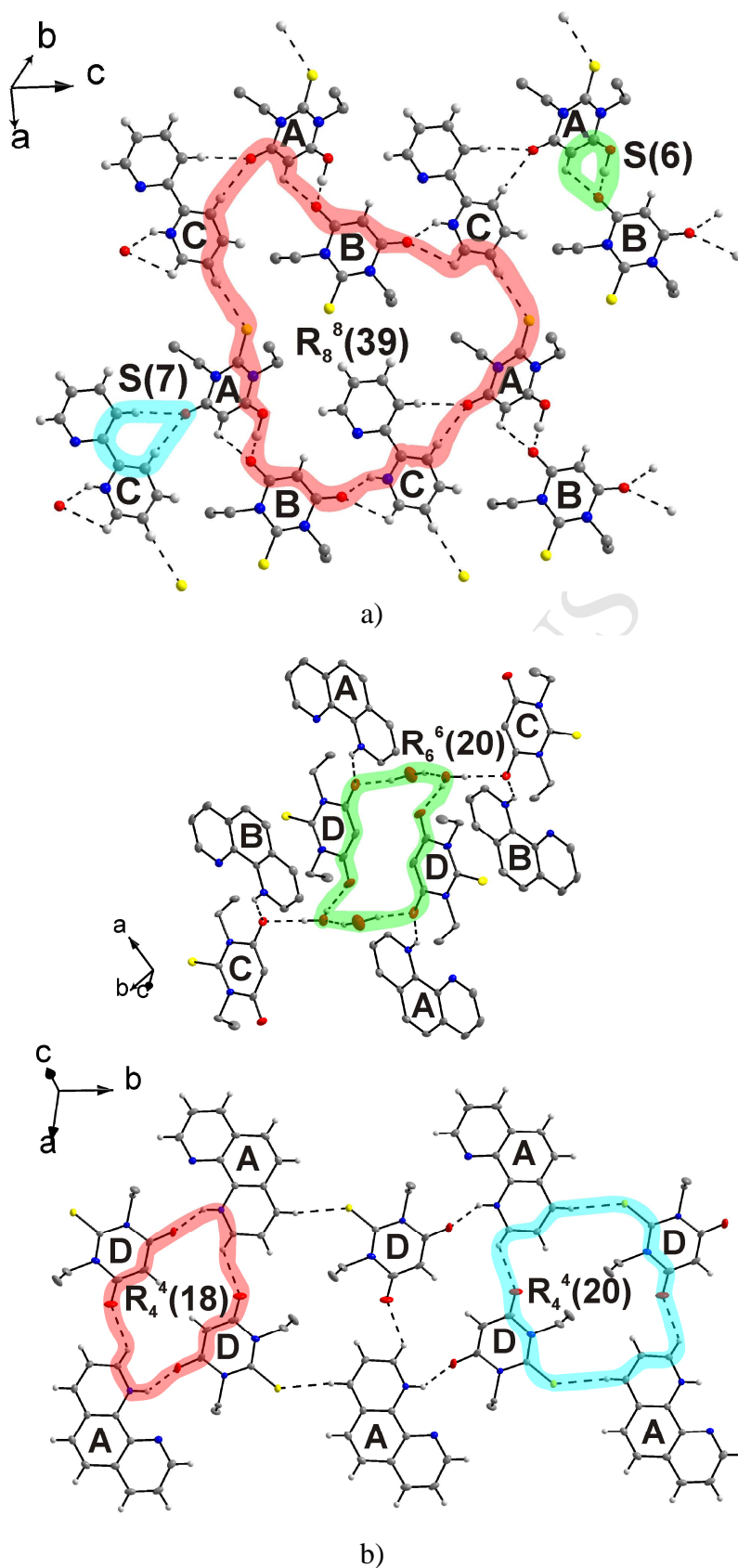


Fig. 4. Hydrogen bonding in (1) (a) and (2) (b). The H-bonds are marked by dashed lines, the H-bond motifs are marked by circles. Different ions/molecules are marked by A, B, C, D labels. Some H atoms were deleted to simplify the figure.

- The Bipy and the Phen with HDetba form salt co-crystal (1) and salt (2), respectively
- In (1), H-bonds connect Detba⁻ and HDetba in a pair, in (2) the Detba⁻ ions do not
- The O—H...O hydrogen bond between an acid HDetba and Detba⁻ is very strong
- The compound PhenH(Detba)·H₂O has a new topology of a 3D net
- Co-crystal of (1) melts at 110.3 °C and salt (2) starts to dehydrate at 70 °C