

Crystal structure, spectroscopic and thermal properties of the coordination compounds $M(1,3\text{-diethyl-2-thiobarbiturate})$ $M = \text{Rb}^+, \text{Cs}^+, \text{Tl}^+$ and NH_4^+



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ABSTRACT

Four new compounds of 1,3-diethyl-2-thiobarbituric acid ($\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2\text{S}$, Hdetba) with Rb^+ , Cs^+ , Tl^+ and NH_4^+ ions were prepared by Hdetba neutralization with the metal carbonates or ammonium hydroxide in aqueous solution. The colorless crystals have been investigated using X-ray diffraction techniques, differential scanning calorimetry, thermogravimetry and infrared spectroscopy. The coordination compounds of MDetba with $M = \text{Rb}$, Cs and Tl crystallize in the orthorhombic space group $P2_12_12_1$, but compound NH_4Detba crystallizes in the triclinic space group $P\bar{1}$. The MDetba structures were compared at the molecular and supramolecular levels. The Detba^- ion in the NH_4^+ compound forms conformer (A) with two diethyl groups on one side of the ion ring, whereas the Detba^- ion in the $\text{Rb}(\text{I})$, $\text{Cs}(\text{I})$ and $\text{Tl}(\text{I})$ compounds forms conformer (B) with two diethyl groups on different sides of the ring. The results of IR spectroscopy and thermal analysis are consistent with the X-ray data.

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1. Introduction

2-Thiobarbituric acid (H_2Tba) and its derivatives from the general class of barbiturates are known as thiobarbiturates [1]. They have long been used as efficient depressants because of their pharmaceutical properties [2]. The most famous of them are thiobarbital (5,5-diethyl-2-thiobarbituric acid) and thiobutabarbital (5-(2-butyl)-5-ethyl-2-thiobarbituric acid) [3], which are used as antihypertensive and anesthetic agents, respectively. As compared to oxybarbiturates, the specific activity of thiobarbiturates is largely due to a higher pronounced hydrophobic nature of the sulfur atom, as compared to the oxygen atom. The presence of a sulfur atom in thiobarbiturate results in higher fat solubility, short duration of action, increased hypnotic potency and accelerated metabolic degradation [4–6].

Due to the presence of several potential donors, such as two amine nitrogens, two carbonyl oxygens and a thione sulfur atom, thiobarbiturates are very interesting polyfunctional ligands in coordination chemistry [7–25]. Thiobarbiturate coordination compounds of alkali ions are used in the synthesis of pharmacologically active organic thiobarbiturates [1,2] and may find application in materials science [16,26]. However, up to now, they have been poorly investigated [9,11,12,17,18,25]. According to structural studies of alkali ion coordination compounds with 2-thiobarbituric acid [9,12,17], the following rules are observed when progressing down group I of the periodic system from light to heavier elements: (1) a more active trend for metal-sulfur bond formation; (2) an increase of the alkali ion coordination number; (3) a decrease in number of coordinated water molecules; (4) an increase in the number of chemical bonds formed by the ligand Htba^- with metal ions. The structures of the compounds are stabilized by numerous hydrogen bonds, $\text{N}\cdots\text{O}$, $\text{N}\cdots\text{S}$, $\text{O}\cdots\text{O}$ and $\text{O}\cdots\text{S}$, and $\pi\cdots\pi$ interactions. The coordination compounds of Li^+ , Na^+ , K^+ with 1,3-diethyl-2-thiobarbituric acid ($\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2\text{S}$, HDetba) [25] appreciably differ from the corresponding 2-thiobarbiturate coordination compounds. The presence of ethyl substituents

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near two nitrogen atoms affects both the coordination environment of the metal ions and the supramolecular interactions.

In the present study, four new compounds, MDetba (M = Rb, Cs, Tl and NH₄), are considered their crystal structures are solved, and their IR and thermal decomposition are analyzed. The principle interest of the observation is to investigate the solid-state structure variation of 1,3-diethyl-2-thiobarbiturate compounds on alkali-metal (or NH₄, Tl) substitution, and to give a comparison with the corresponding structures of the 2-thiobarbiturate compounds.

2. Experimental

2.1. Reagents and synthesis

1,3-Diethyl-2-thiobarbituric acid [CAS 5217-47-0] was commercially available from Sigma–Aldrich. Rubidium and cesium carbonates, thallium(I) nitrate and ammonium hydroxide (analytical grade, Acros) were used without further purification. Initially, the thallium(I) carbonate was prepared by precipitation on addition of excess Na₂CO₃ to an aqueous solution of TlNO₃.

Compounds **1–4** (Table 1) were prepared by the neutralization of 1,3-diethyl-2-thiobarbituric acid with the corresponding metal carbonate or ammonium hydroxide in aqueous solution. The crystallization of **1** and **2** was carried out from small volumes of concentrated aqueous solutions (pH 4–5) obtained by neutralization of 1,3-diethyl-2-thiobarbituric acid with the corresponding metal carbonate. For the synthesis of **3** and **4**, the ligand (5.0 mmol) was mixed with thallium(I) carbonate (2.5 mmol) or ammonium hydroxide (5 mmol) in water (5 cm³). The mixtures were stirred for 5 h at 22 °C to complete the reaction and precipitate the products. All the powders were removed by filtration, washed with

acetone and dried in the air. The colorless crystals of **1–4**, suitable for single crystal X-ray diffraction analysis, were grown by continuous filtrate evaporation at room temperature.

2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals of **1–4** at 25 °C using a SMART APEX II X-ray single crystal diffractometer (Bruker AXS) equipped with a CCD-detector, graphite monochromator and Mo K α radiation source. Absorption corrections were applied using the SADABS program. The structures were solved by direct methods using the package SHELXS and refined with an anisotropic approach for non-hydrogen atoms using the SHELXL program [27]. All the hydrogen atoms of the Detba[−] ligands in **1–3** were positioned geometrically as riding on their parent atoms, with d(C–H) = 0.93 Å for the C5–H5 bond, d(C–H) = 0.97 Å for all other C–H bonds and U_{iso}(H) = 1.2U_{eq}(C). All hydrogen atoms of the NH₄⁺ ion in NH₄Detba compound **4** were found via Fourier difference maps and refined without any constraints. The structural tests for the presence of missing symmetry elements and possible voids were produced using the PLATON program [28]. The DIAMOND program was used for the crystal structure plotting [29].

The powder X-ray diffraction data were obtained using a D8 ADVANCE (Bruker) diffractometer coupled with a VANTEC detector and a Ni filter. The measurements were made using Cu K α radiation. The structural parameters obtained by single crystal analysis were used as a base in the powder pattern Rietveld refinement. The refinement was performed using the program TOPAS 4.2 [30]. The low R-factors and good refinement results shown in Figs. 1S–4S indicate the crystal structures of the powder samples to be representative of the bulk structures of **1–4**, respectively.

Table 1
Crystal structure parameters for **1–4**.

Single crystal	RbDetba (1)	CsDetba (2)	TlDetba (3)	NH ₄ Detba (4)
Moiety formula	C ₈ H ₁₁ N ₂ O ₂ RbS	C ₈ H ₁₁ CsN ₂ O ₂ S	C ₈ H ₁₁ N ₂ O ₂ STl	C ₈ H ₁₅ N ₃ O ₂ S
Dimension (mm)	0.4 × 0.07 × 0.07	0.4 × 0.07 × 0.07	0.3 × 0.1 × 0.1	0.45 × 0.45 × 0.1
Color	Colorless	Colorless	Colorless	Colorless
Molecular weight	284.72	332.16	403.62	217.29
Temperature (K)	298	298	298	298
Space group, Z	P2 ₁ 2 ₁ 2 ₁ , 4	P2 ₁ 2 ₁ 2 ₁ , 4	P2 ₁ 2 ₁ 2 ₁ , 4	P-1, 2
a (Å)	4.3730(9)	4.5236(9)	4.3767(4)	8.472(2)
b (Å)	14.789(3)	14.739(3)	14.7003(14)	8.853(4)
c (Å)	16.923(3)	16.937(4)	16.6064(16)	8.964(2)
α (°)	90	90	90	98.436(4)
β (°)	90	90	90	116.059(3)
γ (°)	90	90	90	109.916(4)
V (Å ³)	1094.5(4)	1129.3(4)	1068.44(17)	531.8(3)
ρ_{calc} (g/cm ³)	1.728	1.954	2.509	1.357
μ (mm ^{−1})	4.691	3.441	15.288	0.285
Reflections measured	8922	10638	10410	4901
Reflections independent	2265	2951	2880	2598
Reflections with $F > 4\sigma(F)$	1853	2572	2530	2112
$2\theta_{\text{max}}$ (°)	52.92	59.32	59.74	56.94
h, k, l - limits	−5 ≤ h ≤ 5 −18 ≤ k ≤ 17 −21 ≤ l ≤ 21	−6 ≤ h ≤ 6 −19 ≤ k ≤ 20 −23 ≤ l ≤ 23	−6 ≤ h ≤ 6 −19 ≤ k ≤ 20 −23 ≤ l ≤ 22	−11 ≤ h ≤ 11 −11 ≤ k ≤ 11 −11 ≤ l ≤ 11
R_{int}	0.0586	0.0303	0.0353	0.0206
Refinement results				
The weighed refinement of F^2	$w = 1 / [\sigma^2(F_o^2) + (0.006P)^2 + 0.0P]$ where $P = \max(F_o^2 + 2F_c^2) / 3$	$w = 1 / [\sigma^2(F_o^2) + (0.0185P)^2 + 0.0P]$	$w = 1 / [\sigma^2(F_o^2) + (0.0P)^2 + 0.0P]$	$w = 1 / [\sigma^2(F_o^2) + (0.0642P)^2 + 0.089P]$
Number of refinement parameters	129	129	130	142
$R_1 [F_o > 4\sigma(F_o)]$	0.0343	0.0233	0.0263	0.0390
wR ₂	0.0588	0.0428	0.0436	0.1071
Goof	1.001	1.008	0.999	1.045
$\Delta\rho_{\text{max}}$ (e/Å ³)	0.423	0.369	0.724	0.383
$\Delta\rho_{\text{min}}$ (e/Å ³)	−0.285	−0.492	−0.806	−0.235
(Δ/σ) _{max}	0.001	0.003	0.002	0.001

2.3. Physical measurements

Simultaneous thermal analysis (STA) measurements were performed on a Netzsch STA Jupiter 449C device with an Aeolos QMS 403C mass-spectrometer under a dynamic argon-oxygen atmosphere (20% O₂, 50 ml min⁻¹ total flow rate). Platinum crucibles with perforated lids were used and the sample masses taken for the STA experiments were 3.9–4.1 mg for (Rb, Cs, Tl)Detba and 5.2 mg for NH₄Detba. The measurement procedure consisted of a temperature stabilization segment (30 min at 40 °C) and a dynamic segment at a heating rate of 10 °C min⁻¹. The qualitative composition of the evolved gases was determined by on-line QMS in the Multiple Ion Detection mode. The following predefined ions were scanned: *m/z* = 18 (H₂O), 28 (N₂, CO), 30 (NO), 32 (O₂), 44 (CO₂) and 64 (SO₂). The IR absorption spectra of the compounds were recorded over the range of 400–4000 cm⁻¹ at room temperature on a VECTOR 22 Fourier spectrometer. The spectral resolution during the measurements was 5 cm⁻¹.

3. Results and discussion

3.1. Crystal structures of 1–3

The asymmetric unit of the MDetba (M = Rb, Cs, Tl) unit cells contains one M⁺ ion and one Detba⁻ ion (Figs. 1a, 2a–c). The crystal structures are isostructural to that of KDetba reported earlier [25]. The M⁺ ion is coordinated by six Detba⁻ ions through four O atoms and two S atoms, forming a trigonal prism. The trigonal prisms are linked by the base facets and form an infinite rod along the *a* axis. From this analysis, the chemical names for these compounds can be presented as catena-(μ₆-1,3-diethyl-2-thiobarbiturato-O,O,O',O',S,S)-rubidium, cesium and thallium. There are no intermolecular hydrogen bonds and π–π interactions.

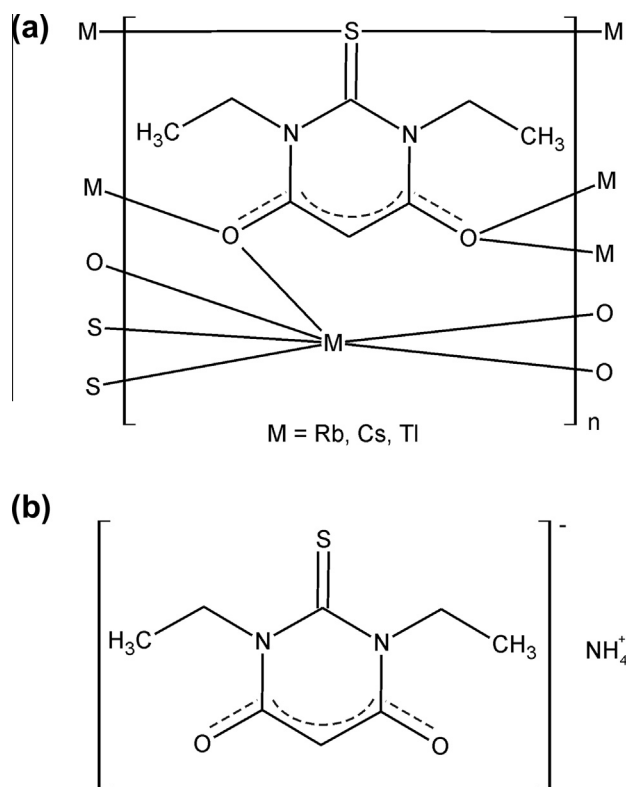


Fig. 1. MDetba schemes: (a) M = Rb, Cs, Tl (1–3); (b) M = NH₄ (4).

The C2–S bond lengths in 1–3 are in the range of 1.687–1.694 Å (Table 1S), which exceeds the range previously found for HDetba (1.658–1.681 Å) [31,32], and this indirectly confirms the participation of the S atom in the ligand coordination. All three compounds have similar O1–C4, O2–C6 and C4–C5, C5–C6 bond lengths (Table 1S), which indicates charge delocalization in the O=C–CH–C=O group. Such delocalization was observed in alkali and other metal compounds of 2-thiobarbiturates [9–25].

3.2. Comparison of the structures 4, 1–3 and MDetba (M = Na, Li, K)

The main structural characteristics of 4 are shown in Table 1. The main obtained bond lengths are shown in Table 1S. The asymmetric unit of the unit cell of NH₄Detba contains one NH₄⁺ ion and one Detba⁻ ion (Figs. 1b and 2d). The NH₄⁺ ion is connected to four Detba⁻ ions by three intermolecular N–H...O hydrogen bonds and one N–H...S bond (Table 2S, Fig. 2d). They form 2D-layers through two C₂²(8) chains along the *a* and *b* axes and the rings R₂²(8) and R₄⁴(16) (Fig. 3). The pattern consists of chains whose links contain R₂²(8) rings. Therefore, the extended notation for this pattern is C₂²(8)[R₂²(8)] [33]. These layers lie in the *ab* plane (Figs. 3, 5S) and there are only Van-der-Waal forces between the layers. The structural analysis reveals π–π interactions between the Detba rings (Table 3S, Fig. 6S). The Detba⁻ ions adopt the “head-to-tail” mode in the crystal packing [34]. The main feature that distinguishes the Detba⁻ ion in samples 1–3 from that in 4 is the absolute value of the torsion angle C8–C7–C9–C10 (Table 1S). Coordination compounds 1–3 have large values of ~150°, but compound 4 has a small value of ~4°. Previously, such a difference was found between the LiDetba, NaDetba and KDetba compounds (Table 1S) [26]. The Detba⁻ ions were found in two different conformational states: conformer (A) in LiDetba and NaDetba, with two diethyl groups on one side of the ion ring, and conformer (B) in KDetba, with the diethyl groups on different sides of the ring. However, Hdetba compounds [31,32] exist only as conformer (A). One can find that compounds 4 and 1–3 present the Detba⁻ ion in conformational states (A) and (B), respectively.

Earlier, it was supposed that the MDetba compounds with large M⁺ ions (radii equal or bigger than that of the K⁺ ion) tend to form conformer (B) because they can be closer packed [25]. The present investigation shows that compounds 1–3 also adopt conformational state (B) and this fact well agrees with the above assumption (Fig. 7S). Compound 4 cannot be used for this purpose because the NH₄⁺ and Detba⁻ ions only interact through intermolecular hydrogen bonding. The crystal structure of NH₄Detba is different from those of MDetba (M = Li, Na) due to the absence of a coordination bond in 4 and differences in the hydrogen bonding. The packing of the Detba⁻ ions is, however, very similar for both of them (Fig. 8S). The crystal structure of Hdetba [31,32] displays conformer (A) of Detba⁻, but the packing of these ions is different from that in MDetba (M = Li, Na, NH₄).

3.3. Comparison of the structures of MDetba and MHtba

The structures of M⁺ metal cation coordination compounds with Htba⁻ and Detba⁻ correspond to the generalized formula [M(μ₆-L–O,O,O',O',S,S)]_n (L = Htba⁻, M = K, Rb, Cs; L = Detba⁻, M = K, Rb, Cs, Tl), i.e. the ligand coordination is the same in all these compounds. The difference is in the coordination polyhedron structure. So, in the compounds with Htba⁻ it is a distorted octahedron, and in the compounds with a Detba⁻ it is a trigonal prism. If, similarly to KHtba [12], the relatively large distances of Rb–S [3.898(1) Å] and Cs–S [3.934(3) Å] are considered in MHtba (M = Rb, Cs) [17] as chemical bonds, then the corresponding polyhedra take the square antiprism form (Fig. 8S), like that in KHtba [12]. However, such long interatomic distances, apparently, should be considered

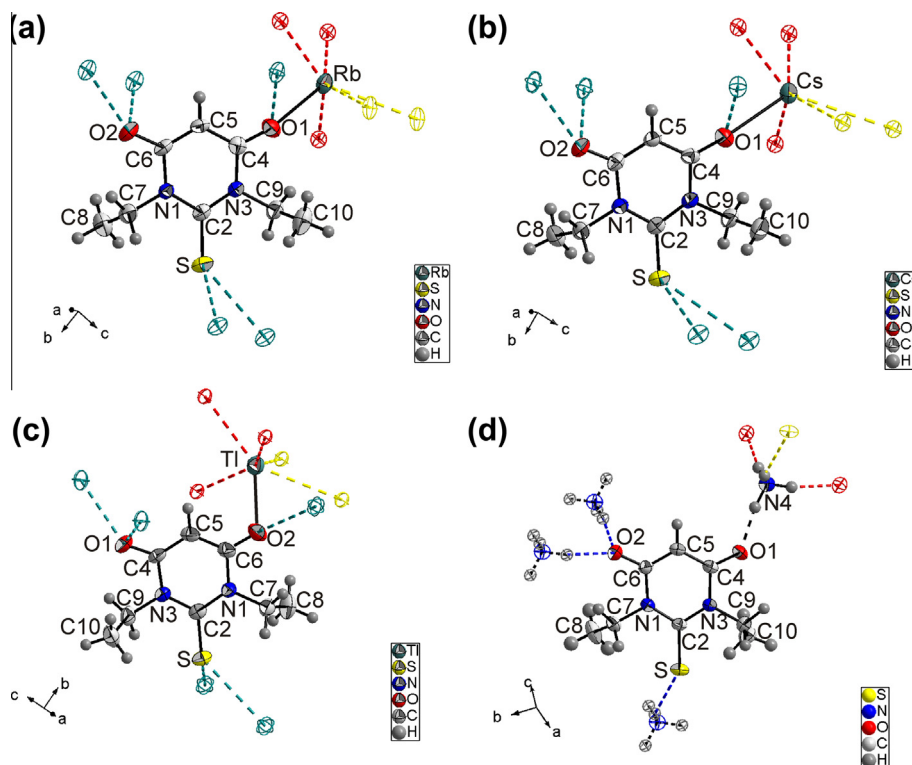


Fig. 2. The asymmetric unit of the MDetba unit cell: (a) $M = \text{Rb}$ (1); (b) $M = \text{Cs}$ (2); (c) $M = \text{Tl}$ (3); (d) $M = \text{NH}_4$ (4). All atoms in the asymmetric unit are labeled. The directly neighboring symmetry-generated atoms are represented by principal ellipsoids with an individual color. The bonds linking asymmetric unit atoms with the symmetry-generated atoms are represented by dashed lines, except for the intermolecular hydrogen bond in 4, which is shown with dashed lines also. The ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms which are represented by arbitrary spheres. (Color online.)

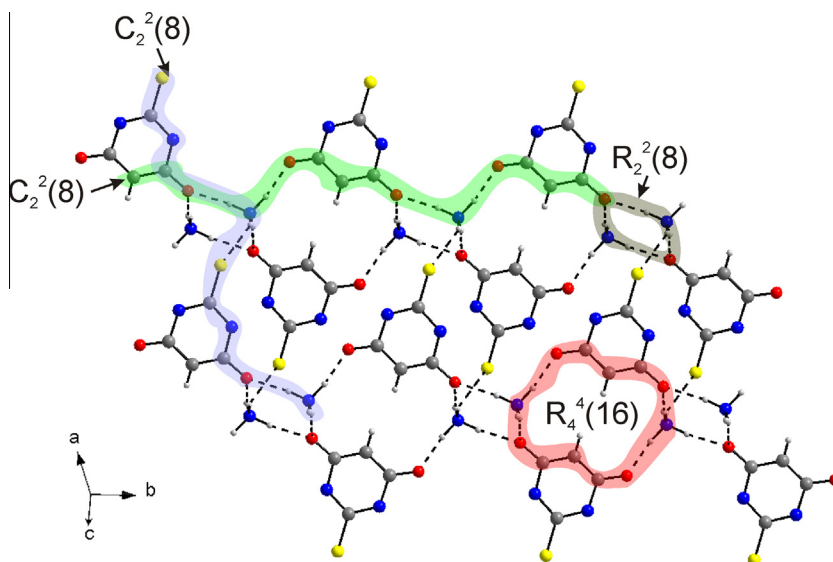


Fig. 3. Hydrogen bonding in 4. The $\text{CH}_2\text{--CH}_3$ groups are deleted for clarity, the H-bonds are marked by dashed lines, the H-bond motifs are marked by circles and broad lines.

as shortened contacts. The S--C2 bond lengths in the compounds under investigation coincide with the bond lengths in H_2tba [35,36] and Hdetba [31,32] within the esd. That is consistent with the predominantly electrostatic interactions of an S atom with Cs^+ and Rb^+ ions, [17] as well as with other alkali ions [9,11,12]. The C4--O1 and C6--O2 bond lengths are approximately the same, which indicates electron density delocalization within the $\text{C4(O1)--C5(H)--C6(O2)}$ structural fragment. In the single known crystalline form of Hdetba , where the molecule exists in the

thionedicarbonyl structure, the C4--O1 bond length is shorter than the C6--O2(H) bond length by 0.045 \AA [31,32]. Comparatively, in the thionedicarbonyl form of H_2tba , the difference is as high as $\sim 0.07 \text{ \AA}$ [36].

In MDetba ($M = \text{Rb}, \text{Cs}, \text{Tl}$), there are no intermolecular hydrogen bonds. Comparatively, in Mhtba ($M = \text{Rb}, \text{Cs}$), there are two $\text{N--H} \cdots \text{O}$ H-bonds which combine Htba^- ions into pairs with the formation of an 8-membered cycle (motif $\text{R}_2^2(8)$). In NH_4Htba [37] and NH_4Detba , all the hydrogen atoms of the NH_4^+ ions are involved

in hydrogen bond formation. In NH_4Detba , there are two $\text{N-H}\dots\text{O}$ and two $\text{N-H}\dots\text{S}$ hydrogen bonds, but in the NH_4Htba , three $\text{N-H}\dots\text{O}$ and one $\text{N-H}\dots\text{S}$ hydrogen bonds exist. In both compounds, the $\text{N-H}\dots\text{O}$ hydrogen bonds form 8-membered cycles (motif $\text{R}_2^2(8)$), which exist as isolated elements in NH_4Detba or generate infinite chains from Htba^- ions in NH_4Htba .

3.4. Topological analysis

One of the most powerful techniques in crystal engineering is the reduction of crystal structures to networks (nets), and then topological analysis can be used to understand the nature of framework [38]. To simplify the analysis and net representation, in the present analysis all the molecules were considered as spheres which were located at the molecules' center of gravity. As compounds **1–3** are isostructural, one net can represent all these compounds. In these compounds, the Cs^+ , Rb^+ , Tl^+ ions are linked by six Detba^- ligands and each Detba^- ligand bridges six Cs, Rb or Tl ions. Therefore, from a topological point of view, the Detba^- ligand acts as a six connecting node and the Cs^+ , Rb^+ and Tl^+ ions act as a six-connected node. Although the two nodes are chemically different, in our case the two nodes are topologically equivalent, and thus, the Schläfli symbol for this uninodal six-connected 3D network

is $(4^9.8^6)$ (Fig. 4a). To the best of our knowledge, there is no literary information about polymeric compounds with such a Schläfli symbol. The 6-connected 3D net $(4^9.6^6)$, known as the “acs” net, which was observed for the ammonium 1,3-dimethylbarbiturate compound, [39] is the most similar to the net observed for MDetba ($\text{M} = \text{Cs}, \text{Rb}, \text{Tl}$) (Fig. 4b). However, it should be noted that the 3D-net in the 1,3-dimethylbarbiturate compound is formed by H-bonds instead of bonds between a metal ion and an anion. Similarly, the net of compound **4** can be plotted using the H-bonding (Figs. 3 and 4c). The Detba^- and NH_4^+ ions act as 4-connected nodes and topologically they are equivalent. The Schläfli symbol of this uninodal four-connected 2D net is $(4^3.6^3)$ (Fig. 4c). Such a 2D bilayer honeycomb topological network “hcb” was also found for the compounds $\text{Zn}(\text{Ata})_2$ [40] ($\text{Hata} = 5\text{-amino-1H-tetrazole}$) and $\text{Zn}_2(\text{Atz})_3(\text{N}_3)\cdot\text{H}_2\text{O}$ compound [41] ($\text{Atz} = 5\text{-amino-tetrazolate}$), and the authors wrote that such a 2D arrangement with mixed polygons had rarely been observed [41]. It is worth mentioning that a 4-connected 2D net with the $(4^2.6^4)$ Schläfli symbol, which is also rarely observed and close to $(4^3.6^3)$, was found for MDetba ($\text{M} = \text{Li}, \text{Na}$) (Fig. 4d). Therefore, the compounds under investigation are significant from a topological point of view, and coordination compounds of Detba with different metals could be promising in the search for exotic topological nets.

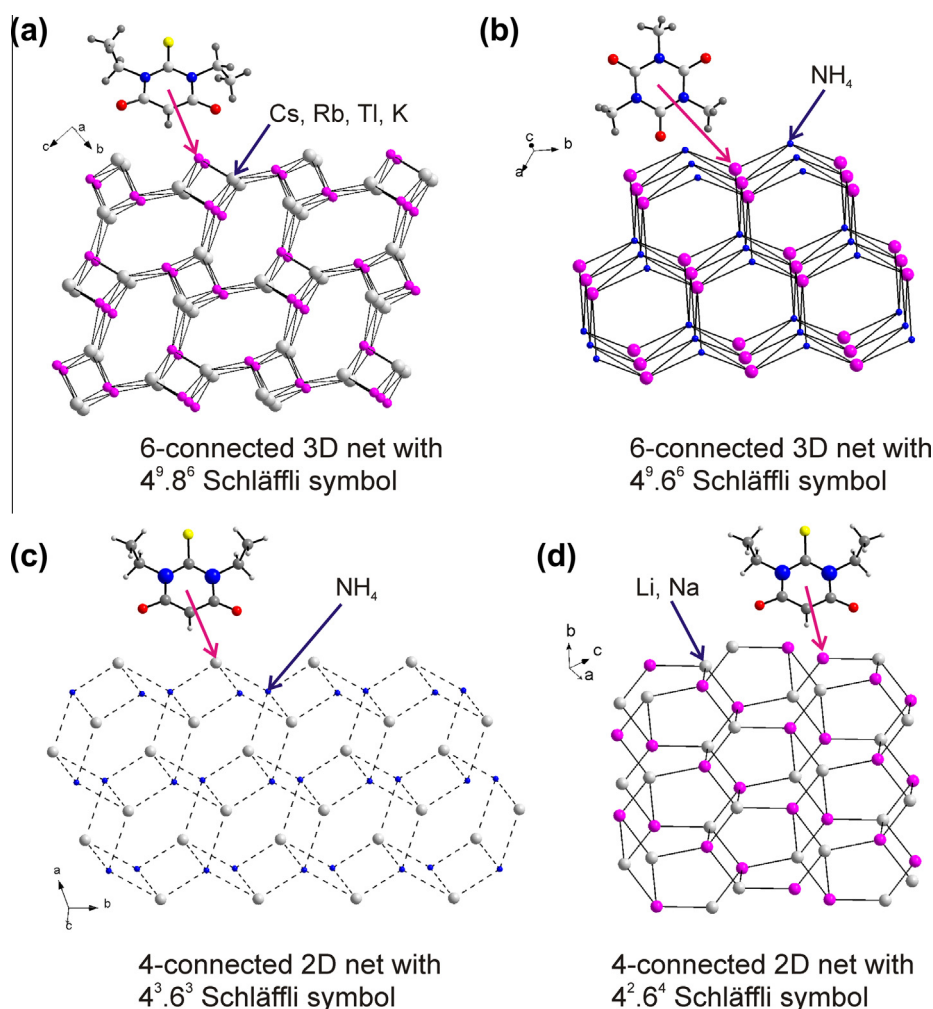


Fig. 4. The schematic representation of the network topology of: (a) MDetba ($\text{M} = \text{K}, \text{Rb}$ (**1**), Cs (**2**), Tl (**3**)); the Detba^- ligand is represented by purple spheres, the M ions are represented by gray spheres; (b) the ammonium 1,3-dimethylbarbiturate compound, the 1,3-dimethylbarbiturate ligand is represented by purple spheres and NH_4^+ ions are represented by blue spheres; (c) NH_4Detba (**4**): the Detba^- ligand is represented by gray spheres and NH_4^+ ions are represented by blue spheres; (d) MDetba ($\text{M} = \text{Li}, \text{Na}$): the Detba^- ligand is represented by purple spheres, the M ions are represented by gray spheres. (Color online.)

3.5. IR spectroscopy

The IR spectra of **1–3** contain two very strong bands in the narrow ranges of 1611–1614 and 1655–1658 cm^{-1} , in the region for C–O stretching vibrations, as shown in Fig. 9S. For pure Hdetba, the $\nu(\text{CO})$ bands are located at 1646 and 1521 cm^{-1} . The difference is consistent with ligand coordination through the oxygen atoms. The positions of strong $\nu(\text{CO})$ bands at 1621 and 1596 cm^{-1} in the IR spectrum of **4** are also different from those observed for Hdetba; but this is due to their participation in N–H...O hydrogen bonds (Fig. 3). The similarity of the IR spectra of compounds **1–3**, particularly in the range of 1700–470 cm^{-1} , confirms that these compounds are isostructural. Some differences in the $\nu(\text{NH})$ oscillations of compounds **1–4** can be attributed to the different strengths of the formed hydrogen bonds. The strong band at 1155 cm^{-1} in the IR spectrum of Hdetba, which by analogy with H₂tba [42,43] can be attributed to the $\nu(\text{C}=\text{S})$ vibration, is very weak in the IR spectra of the compounds, in accordance with ligand coordination through the donor sulfur atom in **1–3**. The attenuation of this band intensity in the IR spectrum of compound **4** is probably due to the participation of the S atom in the N–H...S hydrogen bond (Fig. 3), which is absent in Hdetba [31,32]. Therefore, the results of the IR spectroscopy are consistent with the X-ray data.

3.6. Thermal decomposition of 1–4

Two different decomposition/oxidation patterns were observed for compounds **1–4**.

3.6.1. Thermal decomposition of (Rb, Cs, Tl)Detba

The TG and DSC thermal decomposition curves of **1** and **2** resemble those reported earlier for the K-containing compound [25] and four main conversion regions located at $T > 250^\circ\text{C}$ are revealed, as shown in Figs. 5a, b, 10S and Table 4S. An additional slightly endothermic process occurs for **2** at 120–240 $^\circ\text{C}$; no ion appearance was observed by means of mass-spectroscopy. Most probably, this accounts for elimination of unreacted Detba, which is present in the synthesized sample as an impurity at a level of ~ 2.92 wt.%. The total experimental mass loss was found to be 41.36% (including -2.92 wt.% Hdetba) for the sample heated at 600 $^\circ\text{C}$. To estimate the pure **2** decomposition stoichiometry, the thermal data were corrected assuming a 97.08% purity of compound **2** (Fig. 5b).

As for TlDetba (**3**), for safety reasons, the temperature ramp for TlDetba was restricted to prevent a thallium carry-over and the experiment was stopped just after the beginning of the decomposition/oxidation at 252 $^\circ\text{C}$ (Fig. 11S).

The temperature of the beginning of thermal conversion decreases in the sequence **1–3**; the first two stages are low-exothermic (Table 4S, stages 1 and 2). These stages proceed as the thermal decomposition of organic moiety without pronounced oxidation. Comparatively, the following stages include deep hydrocarbonaceous and carbonaceous residue oxidation (Table 4S, stages 3 and 4). It should be noted that the carbonaceous matter, which is oxidized at stage 4, contains an amount of nitrogen and sulfur, but not hydrogen. The total mass losses for RbDetba and CsDetba can be estimated as -50.73% and -39.6% , respectively (Fig. 5a and b). As was shown earlier, the principle oxidative decomposition products of Ca/Sr thiobarbiturates [15] and KDetba [25] are the corresponding metal sulfates. Similar to these results, XRD analysis of the bulk CsDetba calcination (600 $^\circ\text{C}$, 1 h, air) residue indicates the formation of Cs_2SO_4 as a single crystalline product (Fig. 12S). However, the experimental values of $\Delta m = -50.73\%$ and -39.60% obtained from the TG curve are lower than the calculated mass losses -53.12% and -45.5% for the

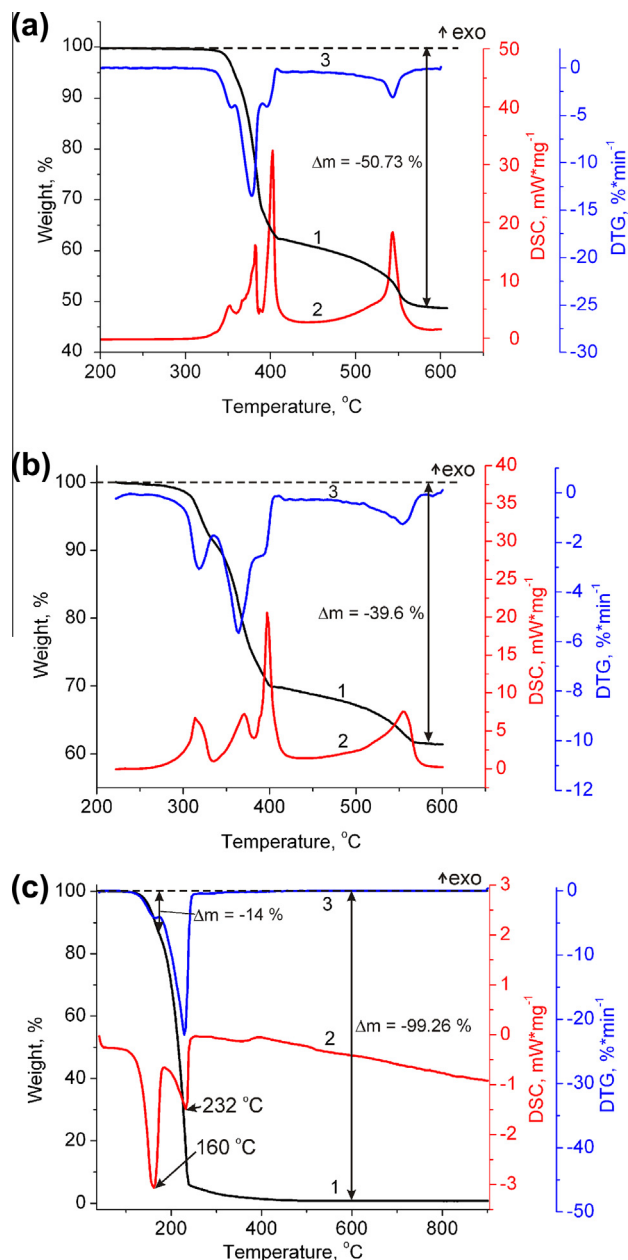


Fig. 5. TG (1), DSC (2) and DTG (3) curves of the thermal decomposition of RbDetba (a), CsDetba (b) and NH_4Detba (c) in a dynamic argon-oxygen atmosphere (20% O_2), $\beta = 10^\circ\text{C min}^{-1}$.

transformation of **1** and **2** to the corresponding Rb_2SO_4 and Cs_2SO_4 sulfates. This mass unbalance can be provisionally explained by differences in the thermal treatment conditions for the bulk and DSC runs and the incomplete transformation in the case of DSC.

3.6.2. Thermal decomposition of NH_4Detba

The thermal decomposition process of **4** may be divided into two stages. The first endothermic mass loss is situated at 100–175 $^\circ\text{C}$ ($T_m = 160^\circ\text{C}$, Δm is $\sim -14\%$), as evident from Fig. 5c. The mass decrease is accompanied by an enhancement of the intensity of ions with $m/z = 17$ (Fig. 13S), which is specific for the ammonium mass-spectrum. Therefore, it may be concluded that the first conversion step is decomposition of **4** to NH_3 and free Hdetba, which partly vaporizes at $T > 120^\circ\text{C}$, as we have demonstrated earlier [25]. The overlap of these two processes is the reason for a

substantial excess of the experimental value $\Delta m \sim -14\%$ in reference to the theoretical value $\Delta m = -7.8\%$, calculated for the reaction of NH_3 elimination from **4** on heating.

The second transformation step is most probably the endothermic vaporization of the formed acid, accompanied by decomposition of the organic moiety at high temperatures, as shown in Figs. 5c and 13S. The endothermic process of the mass loss (about 90%) is observed at 175–240 °C, and the exothermic carbonaceous residue oxidation to CO_2 occurs at 350–600 °C. The total Δm is 99.26%, and this value indicates a high initial salt **4** purity.

4. Conclusions

The coordination compounds of heavy alkali ions (K, Rb, Cs) with Detba^- and Htba^- correspond to the general formula $[\text{M}(\mu_6\text{-L-O,O,O',O',S,S})_n]$ (L = Htba^- or Detba^-). The coordination polyhedron in the compounds with Detba^- is a trigonal prism. In the compounds with Htba^- , however, the coordination polyhedron is a distorted octahedron. Thus, the incorporation of two ethyl radicals in thiobarbituric acid leads to an increase of its volume and, consequently, induces steric barriers which change the polyhedron shape from a distorted octahedron to the trigonal prism. Besides, the elongation of M–(O,S) bond lengths appear in MDetba in comparison to those in MHtba . Moreover, in MDetba the ligand is always O,S-coordinated and this could be a common steric feature for all other yet uninvestigated Detba^- compounds with alkali ions. In the coordination compounds MHtba , the O,S-coordination is also found, except for the compounds $[\text{Li}_4(\text{H}_2\text{O})_9(\text{Htba})_4] \cdot 2\text{H}_2\text{O}$ and $[\text{Na}_2(\text{H}_2\text{O})_2(\text{Htba})\text{Cl}]_n$, where only coordination through the O atoms is observed. This can be explained by the more hydrophilic nature of H_2tba in comparison to that of Hdetba and, consequently, by coordination of water molecules to the metal ions. Also, the absence of crystallized water in the MDetba compounds can be explained for this reason.

Coordination compounds **1–3** and **4** represent the Detba^- ion in different conformational states, (B) and (A), respectively, which is consistent with the previously proposed hypothesis about the influence of the alkali cation ionic radius on Detba^- ion conformers in compounds. A similar regularity may appear in other coordination compounds, for example in 1,3-substituted barbituric and thiobarbituric acids.

The thermal decomposition processes of MDetba (M = K, Rb, Cs) are similar and they possess four main conversion regions. The compounds are thermally stable under oxidative conditions at least up to 240 °C. NH_4Detba is unstable at $T > 100$ °C and decomposes to NH_3 and free Hdetba , which partly vaporizes at $T > 120$ °C. The main gaseous products generated by the thermal decomposition of **1**, **2** and **4** are H_2O , CO_2 , SO_2 and NO .

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Appendix A. Supplementary data

CCDC **1**, **2**, **3**, **4** contain the supplementary crystallographic data for 1043911, 1043909, 1043912, 1043910. These data can be

obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2015.05.048>.

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