

The *cis*–*trans* isomer transformation, spectroscopic and thermal properties of Li, Na, K 1,3-diethyl-2-thiobarbiturate complexes



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ABSTRACT

Three new complexes of 1,3-diethyl-2-thiobarbituric acid (C₈H₁₁N₂O₂S, HDETBA) with Li⁺, Na⁺, K⁺ alkali ions were synthesized. The complexes have been prepared by neutralization of 1,3-diethyl-2-thiobarbituric acid with the corresponding metal hydroxide in aqueous solution. The colorless crystals have been investigated using X-ray single crystal and powder techniques and characterized by differential scanning calorimetry, thermogravimetry and infrared spectroscopy. The compounds of MDETBA with M = Li and M = Na crystallize in the monoclinic lattice with $a = 10.678(1) \text{ \AA}$, $b = 7.2687(9) \text{ \AA}$, $c = 13.202(2) \text{ \AA}$, $\beta = 108.841(2)^\circ$, $Z = 4$, $V = 969.8(2) \text{ \AA}^3$, S.G. $P2_1/n$ and $a = 10.534(2) \text{ \AA}$, $b = 7.604(1) \text{ \AA}$, $c = 14.186(1) \text{ \AA}$, $\beta = 108.964(4)^\circ$, $Z = 4$, $V = 1074.6(3) \text{ \AA}^3$, S.G. $P2_1/n$, respectively. Compound KDETBA crystallizes in the orthorhombic lattice with $a = 4.2541(6) \text{ \AA}$, $b = 14.739(2) \text{ \AA}$, $c = 16.635(3) \text{ \AA}$, $Z = 4$, $V = 1043.1(3) \text{ \AA}^3$, S.G. $P2_12_12_1$. In Li(I) and Na(I) complexes, the DETBA[−] ion is in *cis*-configuration and, in the K(I) complex, this ion is in *trans*-configuration. The reason for the transformation from *cis*- to *trans*-configuration has been rationalized.

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1. Introduction

Alkali metal cations Li⁺, Na⁺ and K⁺ regulate the ionic equilibrium of living cells in the human body [1]. However, the coordination chemistry of group 1 metals with organic linkers in solid state is relatively less explored in comparison with transition metals. The synthesis of coordination polymer networks with these metal ions is of crucial importance for inorganic chemistry due to potentially useful properties [2,3].

The derivatives of 2-thiobarbituric acid (H₂TBA) from the general class of depressants are known as thiobarbiturates [4]. In comparison with oxybarbiturates, the specific activity of thiobarbiturates appears due to hydrophobic character of the S atom, which increases their solubility in fats, decreases the action duration, increases the hypnotic effect and leads to rapid metabolic degradation [5,6]. Thiobarbiturates are the polydentate N, O, S-donor

ligands capable of forming metal–organic framework compounds (MOFs) [7]. Their complexes with alkali metals are used in the synthesis of pharmacologically active organic thiobarbiturates [4,8] and may find application in materials science [2].

Previously, the structure and properties of 2-thiobarbituric compounds [7,9–26], including complexes with alkali metal, were studied [11,13,17,19,24]. One of the main feature of these structures is that the NH groups of 2-thiobarbituric acid are often involved in the hydrogen bonds [26], and, under deprotonation of one N atom, it forms a coordination bond M–N, where M = Au(I) [7], Co(III) [9] or Tl(I) [22]. The present study is focused on the investigation of three new complexes Li(I), Na(I) and K(I) with 1,3-diethyl-2-thiobarbituric acid (1,3-diethyl-2-sulfanylidene-1,3-diazinane-4,6-dione, HDETBA). It can be reasonably assumed that N-protected HDETBA is less prone to such interactions, and this can lead to a different ligand coordination and supermolecular organization than that in the H₂TBA complexes. A very interesting fact is that earlier only the HDETBA structure was solved [27,28], but the information about their metal

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complexes has been not reported on up to now [29]. The crystal structures solved by X-ray [27] and neutron diffraction methods [28] were the same and show only HDETBA ion *cis*-configuration. In the present experiment, there is a probability that the compounds under investigation can show *trans*-configuration due to their different structural organization.

2. Experimental

2.1. Reagents and synthesis

1,3-Diethyl-2-thiobarbituric acid [CAS 5217-47-0] was commercially available from Sigma–Aldrich. Lithium, sodium and potassium hydroxides were obtained as reagent grade materials, and they were used without further purification.

Complexes **1–3** (Table 1) were readily prepared by the neutralization of 1,3-diethyl-2-thiobarbituric acid with the corresponding metal hydroxide in the aqueous solution. The neutral complexes were prepared according to the following general procedure. The ligand (2.5 mmol) was mixed with metal hydroxide (2.5 mmol) in water (5 cm³). The mixture was being stirred for 3 h at 25 °C and then filtered. All the powders were removed by filtration, washed with acetone and dried in the air. The colorless crystals of **1–3**, suitable for single crystal X-ray diffraction analysis, were grown by a continuous filtrate evaporation at room temperature.

2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals (**1**), (**2**), (**3**) at 25 °C using the SMART APEX II X-ray single crystal diffractometer (Bruker AXS) equipped with a CCD-detector, graphite monochromator and Mo K α radiation source. The absorption corrections were applied using the SADABS program. The structures

were solved by the direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [30]. All the hydrogen atoms were refined in a constrained mode. The structure test for the presence of missing symmetry elements and possible voids was carried out using the PLATON program [31]. The DIAMOND program is used for plotting the crystal structure [32].

The powder X-ray diffraction data were obtained using diffractometer D8 ADVANCE (Bruker) equipped by a VANTEC detector with Ni filter. The measurements were made using Cu K α radiation. The structural parameters defined by single crystal analysis were used as a base in powder pattern Rietveld refinement. The refinement was produced using program TOPAS 4.2 [33]. Low *R*-factors and good refinement results shown in (Fig. 1S, a–c) indicate the crystal structure of the powder samples to be representative ones of the (**1**), (**2**) and (**3**) bulk structures, respectively.

2.3. Physical measurements

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. Simultaneous thermal analysis (STA) measurements were performed in a Netzsch STA Jupiter 449C device with Aeolos QMS 403C mass-spectrometer under dynamic argon-oxygen atmosphere (20% O₂, 50 ml min⁻¹ total flow rate). Platinum crucibles with perforated lids were used, and the sample mass prepared for STA experiments was in the range of 3–4 mg. A typical measurement procedure consisted of a temperature stabilization segment (30 min at 40 °C) and a dynamic segment at the heating rate of 10 °C min⁻¹. The qualitative composition of the gases evolved 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), 64(SO₂).

Table 1
(**1–3**) crystal structure parameters.

Single crystal	LiDETBA (1)	NaDETBA (2)	KDETBA (3)
Moiety formula	C ₈ H ₁₁ LiN ₂ O ₂ S	C ₈ H ₁₁ N ₂ NaO ₂ S	C ₈ H ₁₁ KN ₂ O ₂ S
Dimension (mm)	0.2 × 0.2 × 0.1	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.2
Color	colorless	colorless	colorless
Molecular weight	206.19	222.24	238.35
<i>T</i> (K)	298	298	298
Space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>n</i> , 4	<i>P</i> 2 ₁ / <i>n</i> , 4	<i>P</i> 2 ₁ 2 ₁ 2 ₁ , 4
<i>a</i> (Å)	10.678(1)	10.534(2)	4.2541(6)
<i>b</i> (Å)	7.2687(9)	7.604(1)	14.739(2)
<i>c</i> (Å)	13.202(2)	14.186(2)	16.635(3)
β (°)	108.841(2)	108.964(4)	90
<i>V</i> (Å ³)	969.8(2)	1074.6(3)	1043.1(3)
ρ_{calc} (g/cm ³)	1.412	1.374	1.518
μ (mm ⁻¹)	0.304	0.317	0.685
Reflections measured	7768	26323	9951
Independent reflections	2038	2119	2743
Reflections with $F > 4\sigma(F)$	1263	1145	2265
$2\theta_{\text{max}}$ (°)	53.26	52.1	59.22
<i>h, k, l</i> - limits	−13 ≤ <i>h</i> ≤ 13; −9 ≤ <i>k</i> ≤ 9; −16 ≤ <i>l</i> ≤ 16	−12 ≤ <i>h</i> ≤ 13; −9 ≤ <i>k</i> ≤ 9; −17 ≤ <i>l</i> ≤ 17	−5 ≤ <i>h</i> ≤ 5; −19 ≤ <i>k</i> ≤ 19; −22 ≤ <i>l</i> ≤ 22
<i>R</i> _{int}	0.0602	0.1147	0.0352
Refinement results			
The weighed refinement of <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.273P]$ where $P = \max(F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.968P]$	$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 0.245P]$
Number of refinement parameters	129	129	129
<i>R</i> ₁ [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.0462	0.0463	0.0321
<i>wR</i> ₂	0.0945	0.1077	0.0642
Goodness-of-fit (GOF) on <i>F</i> ²	1.015	1.024	1.030
$\Delta\rho_{\text{max}}$ (e/Å ³)	0.201	0.196	0.197
$\Delta\rho_{\text{min}}$ (e/Å ³)	−0.266	−0.167	−0.204
(Δ/σ) _{max}	0.001	0.002	0.001

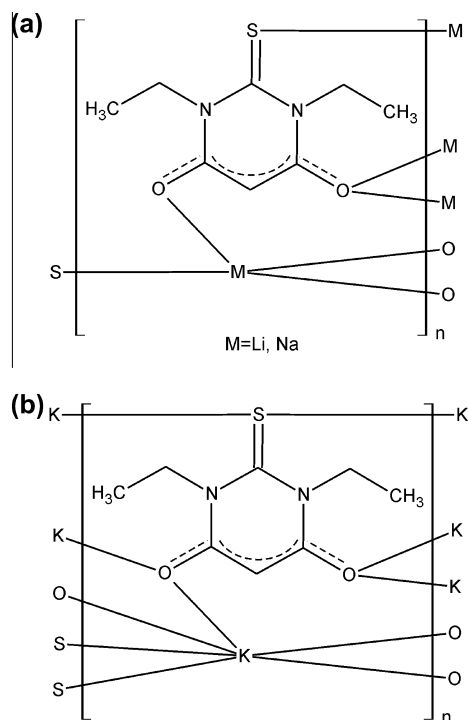


Fig. 1. MDETBA schemes: (a) $M = \text{Li, Na}$ (1–2); (b) $M = \text{K}$ (3).

3. Results and discussion

3.1. Crystal structures (1) and (2)

The unit cells of catena- $(\mu_4\text{-thiobarbiturato-O,O,O',S})$ lithium (1) and catena- $(\mu_4\text{-thiobarbiturato-O,O,O',S})$ sodium (2) correspond to monoclinic symmetry. Space group $P2_1/n$ was determined from the statistical analysis of the reflection intensities. The main crystal data are shown in Table 1. The main defined bond lengths are shown in Table 1S.

The independent part of the unit cell of polymeric complexes MDETBA ($M = \text{Li, Na}$) contains one ion M^+ and one ion DETBA^- (Figs. 1a and 2a). Ion M^+ is coordinated by four monodentate ligands DETBA^- through three O atoms and one S atom, and it forms almost an ideal tetrahedron. The tetrahedrons are pairwise linked with one common oxygen atoms edge. These tetrahedrons pairs are bridged by $\mu_4\text{-DETBA}^- \text{-O,O,O',S}$, and every $\mu_4\text{-DETBA}^- \text{-O,O,O',S}$ group is connected with three pairs of tetrahedrons. Such bridges form an infinity layer in the plane orthogonal to the a - c direction (Figs. 2S and 3S), and bridging ligands close the 14-membered [r(14)] and 18-membered cycles [r(18)] (Fig. 2S).

There are four intramolecular hydrogen bonds $\text{C-H}\cdots\text{O}$, $\text{C-H}\cdots\text{S}$ in the structure (Table 2S). According to the conventional classification such hydrogen bonds can be identified as the weak hydrogen bonds [34]. They form four 5-member cycles [structural motif S(5)] (Fig. 2a). The C_2H_5 groups in DETBA^- ion can rotate easily around the single C-C bond, but such ion form is stabilized due to the hydrogen bonds. There are no intermolecular hydrogen bonds in the structure. Also, there are no π - π interactions between DETBA^- rings, and the shortest distances are as high as 4.705(2) and 4.402(2) Å in (1) and (2), respectively. Therefore, the layers are linked by Van der Waals forces only (Fig. 3S).

3.2. Crystal structure (3) and comparison with (1–2)

The unit cell of catena- $(\mu_6\text{-thiobarbiturato-O,O,O',S,S})$ potassium (3) corresponds to orthorhombic symmetry. Space group

$P2_12_12_1$ was determined from the statistical analysis of the reflection intensities. The independent part of the KDETBA unit cell contains one K^+ ion and one DETBA^- ion (Figs. 1b and 2b). Ion K^+ is coordinated by six DETBA^- ions through four O atoms and two S atoms and forms a trigonal prism. Comparatively, the metal ions in (1–2) are coordinated by four DETBA^- ions with the tetrahedron formation. In (3), the trigonal prisms are linked by faces of their bases and form an infinite rod along axis a (Fig. 4S). The rods are bridged by DETBA^- , and there eventually forms a 3D framework in which one can find cycles r(12) and r(24) (Figs. 4S and 5S). The 12-membered r(12) cycles were previously observed and analyzed in [18].

In compound (3), similar to that in (1–2), there are four weak intramolecular hydrogen bonds $\text{C-H}\cdots\text{O}$, $\text{C-H}\cdots\text{S}$ (Table 2S and Fig. 2b), and there are no intermolecular hydrogen bonds. Like in (1–2), there are no π - π interactions, and the shortest distance between DETBA^- rings is equal to 4.254(1) Å.

Bond lengths C2-S in (1–3) are in the range of 1.684–1.693 Å (Table 1S) which exceeds the range defined for HDETBA (1.658–1.681 Å) [27,28], and this indirectly confirms the participation of the S atom in the ligand coordination. Also, bond lengths $d(\text{N1-C6})$, $d(\text{N3-C4})$ in (1–3) are in the range of 1.404–1.430 Å which exceeds the HDETBA range of 1.375–1.383 Å, supposedly, for the same reason. All three complexes have similar bond lengths O1-C4 , O2-C6 [1.240(3)–1.270(3) Å] and C4-C5 , C5-C6 [1.369(4)–1.390(3) Å], which indicates that the charge in the O=C-CH=C=O group is delocalized. Such delocalization was observed in alkali and other metal complexes of 2-thiobarbiturates [15–25]. However, HDETBA has no such delocalization since the bond length $d(\text{O1-C4})$ is nearly 0.05 Å smaller than $d(\text{O2-C6})$ (Table 1S).

The main feature that distinguishes DETBA^- ion in samples (1–2) from that ion in (3) is torsion angle C2-N1-C7-C8 (Table 1S). Compounds (1–2) have negative values $-84.9(3)^\circ$ and $-88.8(3)^\circ$, respectively, but compound (3) has positive value $89.5(2)^\circ$. Therefore, DETBA^- is found in two forms: *cis*-isomer in (1–2) (Fig. 2c) and *trans*-isomer in (3) (Fig. 2d). It should be pointed that the known HDETBA compounds [27,28,35] are presented only in the unique *cis*-isomer form. Thus, the *trans*-isomer of DETBA^- was found for the first time.

It is supposed that the M ion variation of radii in MDETBA induces the transformation between DETBA^- *cis*- and *trans*-isomers in the crystals. Actually, Li^+ and Na^+ have small ion radii and similar complex structures. However, the K^+ ion has a larger ion radius, and this leads to the structure transformation from monoclinic $P2_1/n$ to orthorhombic $P2_12_12_1$ and changes molecules packing. One can see (Table 1) that the cell volume of KDETBA decreases in reference to that of NaDETBA, and, however, ion K^+ has larger ion radii than ion Na^+ . This proves that DETBA^- ions packing in (3) becomes closer than that in (1–2). Evidently, the *cis*-isomer has fewer opportunities to make close packing due to a void between C8-S-C10 atoms (Figs. 2c and 3a). Contrary to that, the *trans*-isomer has no such void and the ions can be closer packed (Fig. 3b). Probably, the ion radii of M can influence the unit packing process, and a big value of M radii stimulates close packing with the formation of *trans*- DETBA^- . The reason for the *cis*-*trans* transformation can also be due to the kinetic features of the crystallization process. For example, the *trans*-isomer of DETBA^- in the KDETBA compound can be crystallized faster than the *cis*-isomer. In this case, the *cis*-isomer of DETBA^- can be obtained in the KDETBA compound in other conditions of synthesis and, for example, *trans*-isomer can be obtained in the (Na, Li)DETBA compounds. However, the same synthesis conditions of (1–3) compounds give a chance to assume that the increase of ion radii is the key reason for the *cis*-*trans* transformation.

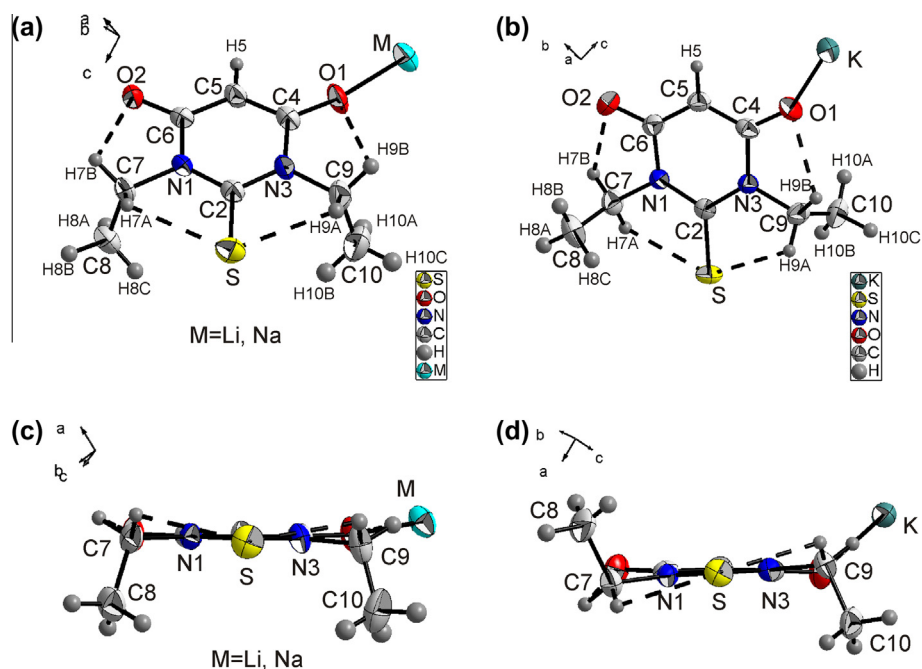


Fig. 2. The independent part of the MDETBA unit cell: (a) $M = \text{Li, Na}$ (**1–2**); (b) $M = \text{K}$ (**3**). View of MDETBA along bond C2–S: (c) $M = \text{Li, Na}$ (**1–2**), *cis*-isomer DETBA[−]; (d) $M = \text{K}$, *trans*-isomer DETBA[−]. Ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms represented by spheres. The intramolecular hydrogen bonds are shown with dashed lines.

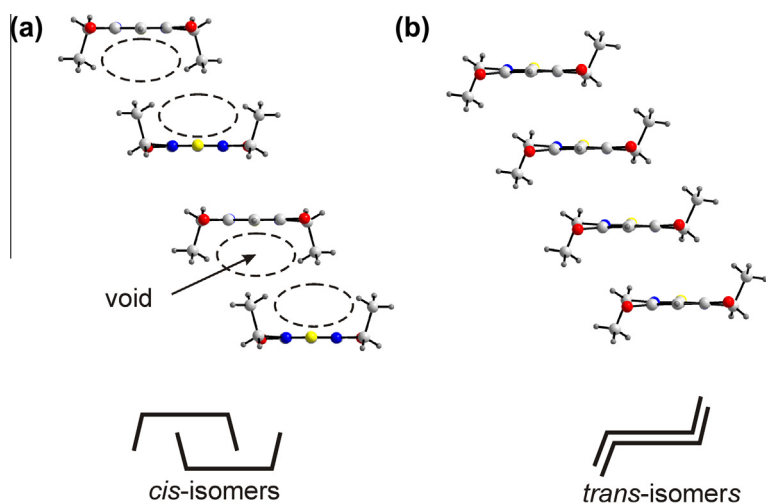


Fig. 3. The DETBA[−] packing and its transformation from *cis*-isomer in LiDETBA, NaDETBA (a) to *trans*-isomer in KDETBA (b). The void in *cis*-DETBA[−] ion is shown by arrow.

3.3. IR spectroscopy

The IR spectra of (**1–3**) and HDETBA compounds are presented in Fig. 6S. Earlier, it was shown by X-ray and neutron diffraction that the solid state of 1,3-diethyl-2-thiobarbituric acid exists in the enol form [27,28]. The spectroscopic results earlier obtained for 2-thiobarbituric acid were used for comparative analysis because the available IR data for HDETBA are incomplete [27]. Summarizing the earlier results from Refs. [36–41], the band at 1646 cm^{-1} in IR spectra was attributed to $\nu(\text{C}=\text{O})$. A similar assignment for HDETBA was performed in [24]. There are two very strong bands in IR spectra of (**1–3**) in the range of $1610\text{--}1660\text{ cm}^{-1}$ instead of one band with the mean intensity at 1646 cm^{-1} for HDETBA (Fig. 3). This indicates the ligand coordination through the oxygen atom in (**1–3**).

3.4. Thermal decomposition

The DSC and TG curves recorded for HDETBA are shown in Figs. 4 and 5. An endothermic effect at $T_{\text{max}} = 112\text{ }^{\circ}\text{C}$ corresponds to the acid melting, and $T_{\text{onset}} = 103.6\text{ }^{\circ}\text{C}$ is in agreement with the published literature data of $T_{\text{onset}} = 103.9 \pm 0.2\text{ }^{\circ}\text{C}$ [42]. HDETBA is relatively stable at melting temperature, a mass decrease at $T > 112\text{ }^{\circ}\text{C}$ corresponds to the acid evaporation because it is not accompanied by water and CO_2 evolution.

According to the TG and DSC data shown in Figs. 4 and 5, the studied substances (**1, 2, 3**) are thermally stable under oxidative conditions at least up to $200\text{ }^{\circ}\text{C}$. The decomposition/oxidation process of (**1–3**) starts at $\sim 250\text{ }^{\circ}\text{C}$ and may be divided into two major exothermic stages: a group of complex unresolved processes at $250\text{--}480\text{ }^{\circ}\text{C}$ and a subsequent transformation at $T > 500\text{ }^{\circ}\text{C}$. A slight

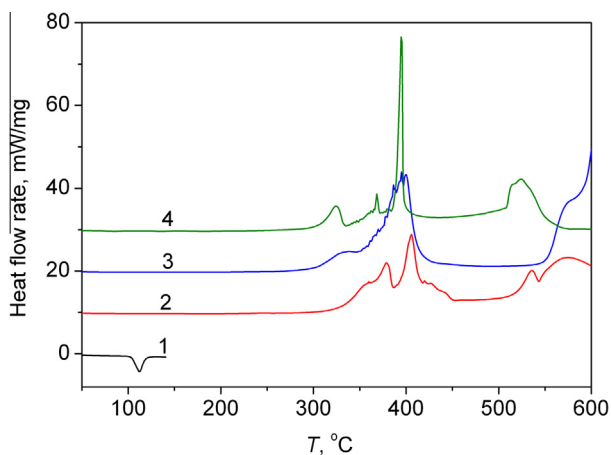


Fig. 4. DSC curves of LiDETBA (2), NaDETBA (3), KDETBA (4), in comparison with HDETBA (1). The data of (2), (3), (4) have been offset by 10, 20, 30 mW/mg, respectively, for clarity.

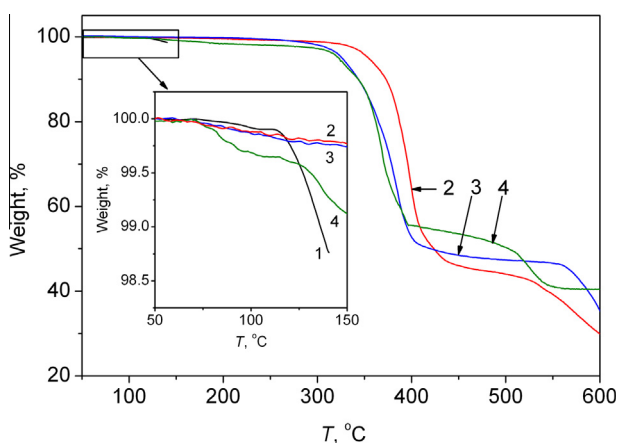


Fig. 5. TG curves of LiDETBA (2), NaDETBA (3), KDETBA (4), in comparison with HDETBA (1).

mass loss at $T > 250$ °C most probably corresponds to impurities in the complexes. On heating to 600 °C, the overall transformation was completed only for (3). As it was shown previously [18], the principle products of oxidative decomposition of Ca/Sr thiobarbiturates are Ca/Sr sulfates. Assuming the 98% purity of potassium salt, the corrected mass loss for (3) may be estimated as 60.8%. This experimental value for (3) is close to the theoretical one of 63.4% for (3) to the K_2SO_4 transformation. As to (1) and (2), no plateau was observed on TG and DSC curves on heating up to 600 °C, indicating that the transformation is not complete. Similarly to KDETBA and Ca/Sr thiobarbiturates [18], it may be assumed that sulfates could be the final products of MDETBA ($M = Li, Na$) oxidative decomposition. The theoretical values of Δm for sulfates formation are 73.3% and 68.0% for Li_2SO_4 and Na_2SO_4 , respectively. The observed mass losses at 600 °C, $\sim 70\%$ for (1) and $\sim 64\%$ for (2), do not contradict to this assumption.

4. Conclusions

Complexes 1–3 were readily prepared by the neutralization of 1,3-diethyl-2-thiobarbituric acid with the corresponding metal hydroxide in the aqueous solution. Their structures were solved by single crystal X-ray diffraction. The Rietveld refinement produced for the powder samples verifies these to be representative of the bulk structures of (1), (2) and (3). The independent part of

the unit cell of polymeric complexes MDETBA ($M = Li, Na, K$) contains one ion M^+ and one ion $DETBA^-$. The M^+ ion in Li(I) and Na(I) complexes is coordinated by four monodentate ligands $DETBA^-$ through three O atoms and one S atom, and these form almost an ideal tetrahedron. In KDETBA, ion K^+ is coordinated by six $DETBA^-$ ions through four O atoms and two S atoms, and these form a trigonal prism. In all the three complexes, the charge in group $O=C-CH-C=O$ is delocalized. In MDETBA ($M = Li, Na$) complexes, like in pure HDETBA, the ethyl groups are in *cis*-position, i.e. on one side of the plane of the heterocyclic ring. The KHDETBA compound shows a $DETBA^-$ *trans*-isomer, and the structure becomes close packed. The IR spectra indirectly confirm the coordination of $DETBA^-$ through O and S atoms. The complexes are thermally stable under the oxidative condition at least up to 200 °C. The decomposition process of MDETBA ($M = Li, Na, K$) starts at ~ 250 °C and includes two major exothermic stages at 250–480 °C and $T > 500$ °C.

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Appendix A. Supplementary data

CCDC 1003560, 1003561 and 1003562 contains the supplementary crystallographic data for compounds (1), (2) and (3), respectively. 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.2014.09.011>.

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