


# Influence of alkyl substituents in 1,3-diethyl-2-thiobarbituric acid on the coordination environment in $M(H_2O)_2(1,3\text{-diethyl-2-thiobarbiturate})_2$ $M = Ca^{2+}, Sr^{2+}$

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## Influence of alkyl substituents in 1,3-diethyl-2-thiobarbituric acid on the coordination environment in $M(\text{H}_2\text{O})_2(\text{1,3-diethyl-2-thiobarbiturate})_2$ $M = \text{Ca}^{2+}, \text{Sr}^{2+}$

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### ABSTRACT

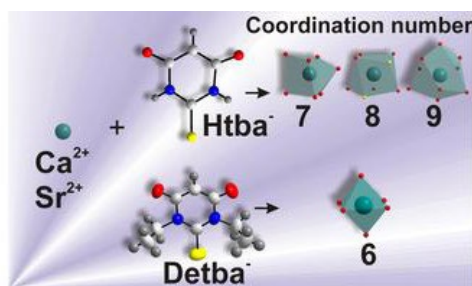
Two new isostructural complexes,  $[\text{Ca}(\text{H}_2\text{O})_2(\mu_2\text{-Detba-O,O}')_2]_n$  (**1**) and  $[\text{Sr}(\text{H}_2\text{O})_2(\mu_2\text{-Detba-O,O}')_2]_n$  (**2**) (HDetba = 1,3-diethyl-2-thiobarbituric acid), were synthesized and characterized by single-crystal and powder X-ray diffraction analysis, TG-DSC, FT-IR, and emission spectroscopy. The single-crystal X-ray diffraction data revealed that **1** and **2** are polymeric where  $M^{2+}$  ( $M = \text{Ca}, \text{Sr}$ ) is a six-coordinate octahedral binding four Detba<sup>-</sup> ions and two water molecules. The octahedra are linked through bridging Detba<sup>-</sup> ions forming a 2-D layer. Two intermolecular hydrogen bonds O–H...S in the crystal form a 3-D net. The comparison of  $M(\text{Detba})_2$  and  $M(\text{Htba})_2$  ( $\text{H}_2\text{tba} = 2\text{-thiobarbituric acid}$ ) structures showed that the coordination number of metals in  $M(\text{Detba})_2$  does not exceed six and there are no  $\pi\text{-}\pi$  interactions, unlike compounds with Htba<sup>-</sup>; Detba<sup>-</sup> ions are only bridges in HDetba coordination compounds. Thermal decomposition of **1** and **2** includes dehydration, which mainly ends at 200 °C, and organic ligand oxidation at 300–350 °C with a release of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and isocyanate. Upon excitation at 220 nm, **1** and **2** exhibit an intense emission maximum at 557 nm.

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1,3-Diethyl-2-thiobarbituric acid; alkaline earth metals; coordination compound; X-ray diffraction; thermal analysis



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## 1. Introduction

The s-block element coordination polymers have attracted attention because of their intriguing topology and promising applications in catalysis, adsorption (gas storage), and separation technologies [1–6]. The chemistry of coordination polymers based on group 2 metals with organic linkers is relatively less explored in comparison with the chemistry of d-elements. Mg(II) and Ca(II) compounds play a vital role in the human body [7], and Sr(II) reduces the risk of a bone fracture from osteoporosis [8]. These factors make the synthesis and evaluation of coordination polymer networks with alkaline earth metal cations a strategic challenge [5].

Presently, 2-thiobarbituric acid ( $H_2$ TBA) and its derivatives have important applications in pharmaceutical and analytical chemistry [9–11]. Their coordination compounds also possess potentially valuable pharmaceutical properties [12]. Previously, many  $H_2$ TBA coordination compounds with different metals and ammonium ions were synthesized and characterized [6, 13–29]. However, for 1,3-diethyl-2-thiobarbituric acid ( $C_8H_{11}N_2O_2S$ , HDetba), only compounds with alkaline metals ions ( $Li^+$ – $Cs^+$ ),  $Tl^+$ , and  $NH_4^+$  [30, 31],  $Pb^{2+}$  [32], and  $Ag^+$  [33] have been structurally characterized. Comparison of MDetba and MHTba ( $M = K, Rb, Cs, \text{ and } Tl$ ) structures indicated that incorporation of two ethyl substituents in thiobarbituric acid leads to a change of the polyhedron shape from a distorted octahedron to a trigonal prism. Detba<sup>−</sup> ligand in MDetba is always O,S-coordinated. However, the  $M^+$  ions in MHTba ( $M = Li$  and  $Na$ ) compounds are coordinated only through O [23]. In MDetba, contrary to MHTba, there are no coordinated or crystallized water molecules due to more pronounced hydrophobic nature of HDetba. A significant difference occurs in supramolecular organization of comparable coordination compounds. In MDetba structures, only weak intramolecular hydrogen bonds C–H...O and C–H...S are formed and there are no  $\pi$ – $\pi$  interactions between Detba<sup>−</sup> rings. The  $\pi$ – $\pi$  interactions, however, are typical in MHTba compounds. In the present study,  $[Ca(H_2O)_2(Detba)_2]$  and  $[Sr(H_2O)_2(Detba)_2]$  are synthesized and characterized. The crystal structures are solved and IR and emission spectra, and thermal decomposition are analyzed. The principle interest is to investigate the solid-state structure variation of 1,3-diethyl-2-thiobarbiturate compounds by changing alkali metals to alkaline earth metals. Besides, the effects of different alkaline earth metals' incorporation and a comparison with the corresponding structures of 2-thiobarbiturate compounds are topical.

## 2. Experimental

### 2.1. Reagents and synthesis

1,3-Diethyl-2-thiobarbituric acid [CAS 5217-47-0] was commercially available from Sigma–Aldrich.  $CaCO_3$  and  $SrCO_3$  (analytical grade, Acros) were used without purification. The complexes were prepared by neutralization of 1,3-diethyl-2-thiobarbituric acid with the corresponding alkaline earth metal carbonate in aqueous solution.

1,3-Diethyl-2-thiobarbituric acid (2.5 mmol) was mixed with  $CaCO_3$  at molar ratio 2 : 1 in water (10  $cm^3$ ). The mixture was stirred for 4 h at 40 °C and then filtered. Colorless crystals of  $Ca(H_2O)_2(Detba)_2$  (**1**) precipitated with evaporation of the filtrate to a small volume (0.5–1.0  $cm^3$ ) in air. Chemical analysis was carried out with an HCNS-0 EA 1112 Flash Elemental Analyser (Perkin-Elmer, Great Britain).

Anal. Calcd for  $C_{16}H_{26}CaN_4O_6S_2$  (**1**): C, 40.5; H, 5.52; N, 11.8; S, 13.5. Found: C, 41.0; H, 5.68; N, 12.1; S, 13.3 (%). Yield = 60%.

Colorless crystals of  $Sr(H_2O)_2(Detba)_2$  (**2**) were synthesized using a similar method, only  $SrCO_3$  was used instead of  $CaCO_3$ .

Anal. Calcd for  $C_{16}H_{26}SrN_4O_6S_2$  (**2**): C, 36.8; H, 5.02; N, 10.7; S, 12.3. Found: C, 37.3; H, 5.18; N, 10.5; S, 12.0 (%). Yield = 68%.

## 2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals of **1** and **2** at 25 °C using the SMART APEX II X-ray single-crystal diffractometer (Bruker AXS) equipped with a CCD-detector, graphite monochromator, and Mo  $K\alpha$  radiation. The absorption corrections were applied using SADABS. The structures were solved by direct methods using SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [34]. All hydrogens of Detba<sup>-</sup> ligands in **1** and **2** were positioned geometrically as riding on their parent atoms with  $d(\text{C}-\text{H}) = 0.93 \text{ \AA}$  for the C5–H5 bond,  $d(\text{C}-\text{H}) = 0.97 \text{ \AA}$  for all other C–H bonds, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . All hydrogens of H<sub>2</sub>O molecules were found via Fourier difference maps and refined with bond length restraints only. The structural tests for the presence of missing symmetry elements and possible voids were produced using the PLATON program [35]. DIAMOND was used for plotting the crystal structure [36].

Powder X-ray diffraction data were obtained using a D8 ADVANCE diffractometer (Bruker) equipped by a VANTEC detector with a Ni filter. The measurements were carried out using Cu  $K\alpha$  radiation. The structural parameters defined by single-crystal analysis were used as a base for the powder pattern Rietveld refinement. The refinement was performed using TOPAS 4.2 [37]. The low *R*-factors and good refinement results shown in figures 1S and 2S indicate the crystal structure of the powder samples to be representative of **1** and **2** bulk structures, respectively.

## 2.3. Physical measurements

TGA characteristics were recorded on the simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under dynamic air atmosphere at 50 ml min<sup>-1</sup> flow rate from 25 to 800 °C at 10 °C min<sup>-1</sup>. The sample weight was 7.268 mg for **1** and 6.348 mg for **2**. Platinum crucibles with perforated lids were used as the sample containers. The qualitative composition of the evolved gas was determined by FT-IR spectrometer Nicolet380 (Thermo Scientific, USA) combined with a thermal analyzer and with the TGA/FT-IR interface (homemade attachment for the gas phase analysis). This setup allows one to receive the DTA and TG data simultaneously, and the released gas phase composition. The temporal dependence of the optical density for each of the released gasses was obtained from IR spectra.

The IR absorption spectra of the compounds were recorded from 400 to 4000 cm<sup>-1</sup> at room temperature on a VECTOR 22 Fourier spectrometer (Bruker, Germany). The spectral resolution during the measurements was 5 cm<sup>-1</sup>. The photoluminescence spectra (PL) of air-dried samples were taken using a spectrofluorimeter SDL-2 (LOMO Ltd, Russia) at room temperature, under identical conditions, and the intensity of the bands can be directly compared.

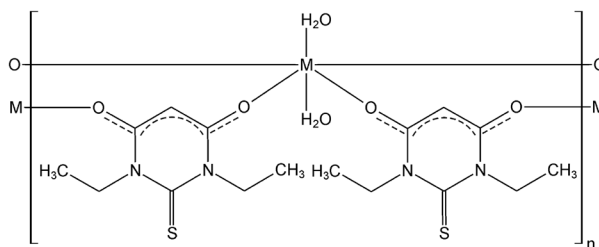
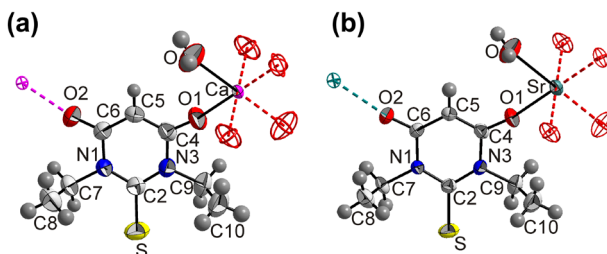
## 3. Results and discussion

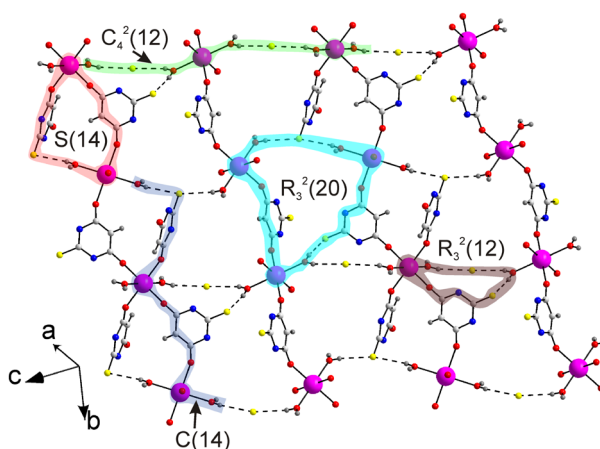
### 3.1. Crystal structures of **1** and **2**

The main structural characteristics of **1** and **2** are shown in table 1. The main defined bond lengths of only one structurally resolved enol form of HDetba [38, 39] and its coordination complexes are shown in table 1S. Satisfactory agreement of all geometrical parameters, besides torsion angle C8–C7–C9–C10, was observed for all structures. The asymmetric unit of  $M(\text{H}_2\text{O})_2(\text{Detba})_2$  ( $M = \text{Ca}, \text{Sr}$ ) unit cells contains half of the  $M^{2+}$ , one Detba<sup>-</sup>, and one H<sub>2</sub>O (figures 1, 2(a) and 2(b)). Crystals of **1** and **2** are isostructural and the structures can be presented in one scheme (figure 1).  $M^{2+}$  is coordinated by four Detba<sup>-</sup> ions through four oxygens and two *trans* H<sub>2</sub>O molecules forming a MO<sub>6</sub> octahedron. The octahedra are linked through bridging Detba<sup>-</sup> ions forming a 2-D layer. From this analysis, the chemical names for these compounds can be presented as catena-bis( $\mu_2$ -1,3-diethyl-2-thiobarbiturato–O,O′)-diaquacalcium and catena-bis( $\mu_2$ -1,3-diethyl-2-thiobarbiturato–O,O′)-diaqua-strontium. Structural analysis reveals the absence of  $\pi$ - $\pi$  interactions between the Detba<sup>-</sup> rings in **1** and **2**. However, there are two intermolecular hydrogen bonds O–H...S in this structure (table 2S). They form a 3-D net by two chains  $C_4^2(12)$ ,  $C(14)$  and other motifs:  $S(14)$ ;  $R_3^2(12)$ ;  $R_3^2(20)$  (figure 3).

**Table 1.** Crystal structure parameters for **1** and **2**.

| Single crystal                                 | Ca(H <sub>2</sub> O) <sub>2</sub> (Detba) <sub>2</sub> ( <b>1</b> )            | Sr(H <sub>2</sub> O) <sub>2</sub> (Detba) <sub>2</sub> ( <b>2</b> )             |
|--|--|---|
| Moiety formula                                 | C <sub>16</sub> H <sub>26</sub> CaN <sub>4</sub> O <sub>6</sub> S <sub>2</sub> | C <sub>16</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub> Sr |
| Dimension (mm)                                 | 0.45 × 0.45 × 0.1  | 0.45 × 0.45 × 0.1   |
| Color  | Colorless  | Colorless   |
| Molecular weight                               | 474.61   | 522.15  |
| Temperature (K)                                | 298  | 298   |
| Space group, Z                                 | <i>Pbca</i> , 4  | <i>Pbca</i> , 4   |
| <i>a</i> (Å)                                   | 9.3535(4)  | 9.529(2)  |
| <i>b</i> (Å)                                   | 13.8812(7)   | 14.161(3)   |
| <i>c</i> (Å)                                   | 16.9106(8)   | 17.094(3)   |
| <i>V</i> (Å <sup>3</sup> )                     | 2195.6(2)  | 2306.7(8)   |
| $\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )    | 1.436  | 1.504   |
| $\mu$ (mm <sup>-1</sup> )                      | 0.515  | 2.556   |
| Reflections measured                           | 19984  | 17490   |
| Reflections independent                        | 3024   | 2371  |
| Reflections with $F > 4\sigma(F)$              | 2568   | 1546  |
| $2\theta_{\text{max}}$ (°)                     | 52.62  | 52.85   |
| <i>h, k, l</i> - limits                        | -12 ≤ <i>h</i> ≤ 12<br>-19 ≤ <i>k</i> ≤ 19<br>-23 ≤ <i>l</i> ≤ 23              | -11 ≤ <i>h</i> ≤ 11<br>-17 ≤ <i>k</i> ≤ 17<br>-21 ≤ <i>l</i> ≤ 21               |
| $R_{\text{int}}$                               | 0.0238   | 0.0673  |
| The weighed refinement of $F^2$                | $w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.6233P]$                              | $w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.7736P]$                               |
| No. of refinement parameters                   | 140  | 139   |
| No. of restraints                              | 2  | 2   |
| $R1 [F_o > 4\sigma(F_o)]$                      | 0.0295   | 0.0322  |
| $wR2$  | 0.0810   | 0.0711  |
| <i>Goof</i>                                    | 1.011  | 0.996   |
| $\Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> ) | 0.240  | 0.399   |
| $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> ) | -0.236   | -0.286  |
| $(\Delta/\sigma)_{\text{max}}$                 | 0.001  | 0.001   |

**Figure 1.**  $M(\text{H}_2\text{O})_2(\mu_2\text{-Detba-O,O}')_2$  scheme,  $M = \text{Ca, Sr}$ .**Figure 2.** The asymmetric unit of the  $M(\text{H}_2\text{O})_2(\text{Detba})_2$  unit cell: (a)  $M = \text{Ca}$  (**1**); (b)  $M = \text{Sr}$  (**2**). All atoms in the asymmetric unit are labeled. 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. The ellipsoids are drawn at 50% probability level, except for the hydrogens represented by spheres.



**Figure 3.** Hydrogen bonding in **1**. The ethyl groups are deleted for clarity; H-bonds are marked by dashed lines and the H-bond motifs are marked by circles and broad lines.

**Table 2.** Structural characteristics of coordination compounds of metals with HDetba.

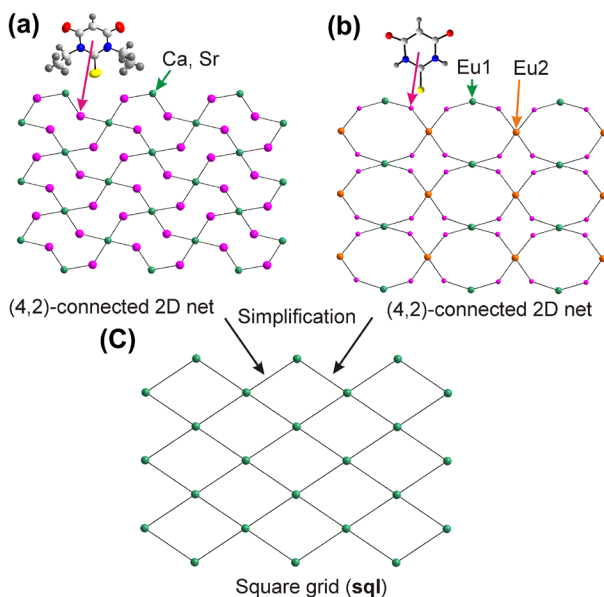
| Metal ions   | CN | Polyhedron                            | Detba <sup>-</sup> coordination | Reference    |
|--|----|---------------------------------------|---------------------------------|--------------|
| Li <sup>+</sup> and Na <sup>+</sup>                                    | 4  | Tetrahedron                           | $\mu_4$ -O,O,O',S               | [30]         |
| Ag <sup>+</sup>  | 4  | Tetrahedron                           | $\mu_4$ -O,O',S,S               | [33]         |
| K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> and Tl <sup>+</sup> | 6  | Trigonal prism                        | $\mu_6$ -O,O,O',O',S,S          | [31]         |
| Pb <sup>2+</sup>   | 6  | Pb(1) Octahedron Pb(2) Trigonal prism | $\mu_3$ -O,O',S                 | [32]         |
| Ca <sup>2+</sup> and Sr <sup>2+</sup>                                  | 6  | Octahedron                            | $\mu_2$ -O,O'                   | Present work |

The C2–S bond lengths in **1** and **2** are 1.701–1.703 Å (table 1S), which exceed the range previously observed in HDetba (1.658–1.681 Å) [38, 39], and this indirectly confirms participation of S in two hydrogen bonds. Compounds **1** and **2** have very similar bond lengths O1–C4, O2–C6 and C4–C5, C5–C6 (table 1S), indicating charge delocalization in the O=C–CH=C=O group. Earlier, such delocalization was observed in alkali and other metal compounds of 2-thiobarbiturates [9–33].

### 3.2. Topological analysis of **1** and **2**

The topological analysis of the 2-D layer in **1** and **2** was implemented using representation of Detba<sup>-</sup> ions as spheres which were located in the ions gravity center (figure 4(a)). In these compounds, the Ca<sup>2+</sup>, Sr<sup>2+</sup> ions are linked by four Detba<sup>-</sup> ligands, but each Detba<sup>-</sup> ligand bridges two Ca<sup>2+</sup> or Sr<sup>2+</sup> ions. Therefore, this net is a binodal (4,2)-connected 2-D net with the vertex symbol [40] (8<sup>4</sup>.12<sup>2</sup>)(8<sup>2</sup>)<sub>2</sub> (figure 4(a)). To the best of our knowledge, only one compound, Eu(Htba)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> [29], has a similar (4,2)-connected net with the (8<sup>4</sup>.12<sup>2</sup>)(8)<sub>3</sub> vertex symbol (figure 4(b)). In these compounds, the Htba<sup>-</sup> and Detba<sup>-</sup> ions are 2-coordinated nodes and omitting them leads to the well-known square net (**sql**) with the 4<sup>4</sup>.6<sup>2</sup> vertex symbol (figure 4(c)). Accounting for two hydrogen bonds O–H...S leads to binodal (8,4)-connected 3-D net with the point symbol (4<sup>10</sup>.6<sup>14</sup>.8<sup>4</sup>)(4<sup>5</sup>.6)<sub>2</sub> (figure 3S).

A 4-connected 2-D net with the 4<sup>2</sup>.6<sup>4</sup> vertex symbol, which is rarely observed, was found in MDetba with M<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, and Ag<sup>+</sup> [30, 31, 33]. However, MDetba with M<sup>+</sup> = Rb<sup>+</sup>, Tl<sup>+</sup>, and Cs<sup>+</sup> forms a six-connected 3-D net with the 4<sup>9</sup>.8<sup>6</sup> point symbol [40]. Pb(Detba)<sub>2</sub> shows a (6,3)-connected bimodal 2-D net with the (4<sup>6</sup>.6<sup>9</sup>)(4<sup>3</sup>)<sub>2</sub> vertex symbol [32]. The diversity of the net topology found for coordination compounds of Detba<sup>-</sup> with different metals is intriguing and can be promising in a search for exotic topological nets.



**Figure 4.** A schematic representation of the network topology of: (a)  $M(H_2O)_2(Detba)_2$  ( $M = Ca$  (**1**),  $Sr$  (**2**)), the  $Detba^-$  ligand is represented by purple spheres, the  $M^{2+}$  ions are represented by green spheres; (b)  $Eu(Htba)_3(H_2O)_3$ , the  $Htba^-$  ligand is represented by purple spheres, the  $Eu^{3+}$  ions are represented by green and orange spheres (color online); and (c) simplification of two previous nets by omitting 2-coordinated nodes which leads to a square grid (see <http://dx.doi.org/10.1080/00958972.2016.1149168> for color version).

### 3.3. Comparison of HDetba complex structures

All HDetba coordination compounds with metals are polymers, and bridging Detba<sup>-</sup> ions exhibit various coordination types (table 2). Only in **1** and **2** the ligand is coordinated exclusively through oxygen ions. There are two intermolecular H-bonds O–H...S in **1** and **2**, but other compounds show only weak intermolecular hydrogen bonds C–H...O and C–H...S. The coordination number of metal ions is 4 in MDetba ( $M = Li, Na, \text{ and } Ag$ ) or 6 in  $M(Detba)_n$  ( $n = 1, M = K, Rb, \text{ and } Cs; n = 2, M = Pb, Ca, \text{ and } Sr$ ) (table 2).

Previously, it was shown that the Detba<sup>-</sup> in coordination compounds can exist in two different conformational states: conformer (A) with a large value of torsion angle C8–C7–C9–C10 (150°); conformer (B) with a small value of this angle (0...12°) (table 15). Compounds of MDetba with big  $M^+$  ions, ion radii are equal to or bigger than  $K^+$ , tend to form conformers (B) because they can be packed closer [29, 30]. The present investigation shows that **1** and **2** have conformational state (A), in agreement with the assumption.

### 3.4. Comparison of $M(Detba)_2$ and $M(Htba)_2$ structures

The coordination number of metals in  $M(Detba)_2$  does not exceed six and there are no  $\pi$ – $\pi$  interactions between the Detba<sup>-</sup> rings unlike compounds with Htba<sup>-</sup>. Changing Htba<sup>-</sup> to the more volumetric Detba<sup>-</sup> ligand leads to a decrease of coordination number from 7 to 6 for Ca(II) and from 8 or 9 to 6 for Sr(II) [22]. Thus, the difference between the central ion size becomes less significant. Detba<sup>-</sup> in an octahedral complex polymer (**1**), similar to Htba<sup>-</sup> in  $[Ca(H_2O)_5(Htba-O)_2] \cdot 2H_2O$  and  $[Ca_2(H_2O)_8(\mu_2-Htba-O)_2(Htba-O)_2]$  [22] with monocapped trigonal prisms, are coordinated to Ca(II) only through O; Htba<sup>-</sup> in the compound with Sr(II) additionally can be linked through S. The coordination polyhedra in  $[Sr(H_2O)_4(\mu_2-Htba-O)_2]_n$  [22] and  $[Sr(\mu_2-H_2O)_2(H_2O)_2(\mu_2-Htba-O)_2(Htba-O)]_n$  [25] are a distorted square antiprism and a tri-capped trigonal prism, respectively. Known MDetba and  $M(Detba)_2$  compounds do not contain terminal Detba<sup>-</sup> ligands.



### 3.5. IR spectroscopy

The similarity of IR spectra of **1** and **2** confirms that these compounds are isostructural. The following bands were found in the IR absorption spectrum of **1**, as shown in figure 4S, curve 2 ( $\text{cm}^{-1}$ ): 3365 m, 3213 w, 2974 w, 2934 w, 2873 w, 1621 vs, 1401 vs, 1321 s, 1309 s, 1260 m, 1204 m, 1159 w, 1109 m, 1087 w, 1055 w, 965 w, 916 w, 834 w, 804 m, 773 w, 728 w, 702 w, 661 w, 638 w, 514 m, 476 m, 442 w, 421 m, and 407 m. The IR absorption spectrum of **2** (figure 3S, curve 3 ( $\text{cm}^{-1}$ )): 3360 m, 3215 w, 2975 w, 2934 w, 2874 w, 1622 vs, 1406 vs, 1319 s, 1309 s, 1260 m, 1204 m, 1158 w, 1108 m, 1086 w, 1052 w, 964 w, 913 w, 835 w, 802 m, 773 w, 728 w, 698 w, 662 w, 638 w, 511 m, 475 m, 436 m, 422 m, and 405 m.

IR spectra of **1** and **2** drastically differ from IR spectra of HDetba (figure 4S, curve 1). The broad band at  $3600\text{--}3300\text{ cm}^{-1}$  with its maximum at  $3365\text{--}3360\text{ cm}^{-1}$  in IR spectra of **1** and **2**, which is absent in the spectrum of HDetba, corresponds to  $\nu(\text{OH})$  of coordinated water. IR spectra of **1** and **2** contain two very strong bands at  $1622\text{--}1621$  and  $1406\text{--}1401\text{ cm}^{-1}$ , as shown in figure 4S, from C–O stretches. For pure Hdetba, the  $\nu(\text{CO})$  bands are located at  $1646$  and  $1521\text{ cm}^{-1}$ . The difference is consistent with ligand coordination through oxygens. The strong band at  $1158\text{ cm}^{-1}$  in the IR spectrum of HDetba, which, by analogy with  $\text{H}_2\text{tba}$  [38, 39], can be attributed to  $\nu(\text{C}=\text{S})$ , is comparatively weak in IR spectra of **1** and **2**, affected by incorporation of sulfur in intermolecular H-bonds O–H...S. Therefore, the results of IR spectroscopy are consistent with the structural data.

### 3.6. Thermal decomposition

In **1**, mass loss occurs at  $150\text{ }^\circ\text{C}$  (Figure 5S) and  $150\text{--}200\text{ }^\circ\text{C}$  with mass loss ( $\Delta m$ ) of 7.80%. This value is close to the theoretical value  $\Delta m = 7.59\%$  calculated under the supposition that two water molecules are deleted from the compound. According to IR analysis of flue gases, this compound loses water vapor. The dehydration corresponds to the endoeffect at  $197.0\text{ }^\circ\text{C}$ . The sample weight remains practically unchanged from  $200$  to  $350\text{ }^\circ\text{C}$ . Oxidation of the organic ligand from  $350$  to  $450\text{ }^\circ\text{C}$  leads to a drastic reduction in the sample mass ( $\Delta m = 56.3\%$ ) accompanied by release of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and isocyanate (Figure 6S). Strong exothermic peak is measured on the DSC curve at  $426.2\text{ }^\circ\text{C}$ . On further heating, the weight changes become constant ( $\Delta m = 83.4\%$ ) at  $750\text{ }^\circ\text{C}$ . Two endoeffects at  $547.3$  and  $712.7\text{ }^\circ\text{C}$  with a  $\text{CO}_2$  gas release are observed during transformation from  $500$  to  $750\text{ }^\circ\text{C}$ . As in the case of 2-thiobarbituric acid with  $\text{Ca}(\text{II})$  [22],  $\text{CaSO}_4$  and  $\text{CaO}$  are likely to be the final products of the thermolysis of **1**, that does not contradict to the measured value  $\Delta m$ .

In **2**, a small weight loss ( $\Delta m = 0.4\%$ ) was observed at  $100\text{ }^\circ\text{C}$ . At higher temperatures, the endoeffect is found at  $162.4\text{ }^\circ\text{C}$  (Figure 7S). The total weight loss at  $162.4\text{ }^\circ\text{C}$  was 8.80%, exceeding the theoretically calculated  $\Delta m$  for removal of two water molecules from the compound ( $\Delta m = 6.90\%$ ); water vapor is the only gaseous product released according to IR spectroscopic data (Figure 8S). Excessive weight loss during the thermal decomposition of **2** at  $162.4\text{ }^\circ\text{C}$  may be associated with the substance hygroscopicity and, also, with a possible HDetba sublimation and impurity decomposition accompanied by releasing gases which were not identified by IR spectroscopy. The sample weight decrease is only 2.4% under heating from  $200$  to  $300\text{ }^\circ\text{C}$ . The oxidation of the organic part occurred at  $300\text{--}450\text{ }^\circ\text{C}$ , and the sample weight drastically decreases ( $\Delta m = 55.3\%$ ). Two exothermic effects at  $402.8$  and  $420.7\text{ }^\circ\text{C}$  and a release of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and isocyanate gases are associated with this decomposition stage. The weakly expressed exoeffect was observed at  $450\text{--}795\text{ }^\circ\text{C}$ , and the weight decreased by 5.0% with a small amount of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  gases released. The total sample weight loss under the heating to  $795\text{ }^\circ\text{C}$  was 75%; similar to **1**, this can be explained by formation of  $\text{SrSO}_4$  and  $\text{SrO}$  mixture [22].

### 3.7. Luminescence study

The luminescence observation of HDetba, **1** and **2**, was performed in the solid state at room temperature. The highest intensity of the excitation spectrum was from  $200$  to  $220\text{ nm}$ . Free HDetba exhibits an intense emission maximum at  $557\text{ nm}$  and relatively strong bands at  $449$ ,  $448$ ,  $421$ , and  $392\text{ nm}$



upon excitation at 220 nm. The luminescence spectra of **1** and **2** excited at 220 nm are almost the same (Figure 9S). The absence of noticeable luminescence band shift on transition from HDetba to **1** and **2** is the result of electron density isolation of the ligand, which participates in the luminescence emission. The emission behavior of the ligand may be assigned as intraligand  $\pi^*-\pi$  and  $\pi^*-\pi$  charge transfer transitions [41].

## 4. Conclusion

Reaction of HDetba with calcium and strontium carbonates leads to  $M(H_2O)_2(\mu_2\text{-Detba-O,O'})_2$ ,  $M = Ca$  and  $Sr$ .  $M^{2+}$  is coordinated by four  $\text{Detba}^-$  ions and two *trans*  $H_2O$  molecules forming an octahedron linked by bridging  $\text{Detba}^-$  ions forming a 2-D layer. Comparison of the crystal structures of coordination compounds showed that all known compounds  $M(\text{Detba})_2$  and  $M\text{Detba}$  contain only bridging  $\text{Detba}^-$  which are linked with metal ions in different configurations (table 2). In **1** and **2**, coordination of  $\text{Detba}^-$  through sulfur is absent and two intermolecular H-bonds (O–H...S) appeared. Comparatively, in coordination compounds of singly charged metal ions with  $\text{Detba}^-$ , there were only weak intramolecular hydrogen bonds C–H...O and C–H...S [30–33]. The crystal structures of most of the metal complexes with  $H_2tba$  are stabilized by  $\pi-\pi$  interaction between  $Htba^-$  ions. Among all metal compounds with HDetba, only the Ag(I) compound [33] has  $\pi-\pi$  interaction with  $\text{Detba}^-$ . Regardless of the metal ion nature, coordination numbers in compounds with the larger  $\text{Detba}^-$  are 4 or 6 forming tetrahedral, octahedral, or trigonal prisms, unlike compounds like  $Htba^-$ . For other derivatives of 2-thiobarbituric acid, the molecular and supramolecular structures of metal complexes will be different. A diversity of topological nets in coordination compounds of  $\text{Detba}^-$  with different metals makes it possible to assume that some outstanding topological nets can be found in the future.

Thermal decomposition of **1** and **2** starts at a higher temperature than that in HDetba ( $T > 112^\circ\text{C}$ ) [30, 42] and comprises the dehydration and oxidation steps of the organic ligand with  $\text{CO}_2$ ,  $\text{SO}_2$  и  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and isocyanate release. Coordination of  $\text{Detba}^-$  through oxygen is proved by IR spectroscopy.

## Supplementary material

The crystallographic data for the structural analysis were deposited with the Cambridge Crystallographic Data Center (**1** – CCDC # 1433652; **2** – CCDC # 1433659). The information may be obtained free from CCDC Director: 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(1223)336-033, E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk), or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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