

Coordination effects in hydrated manganese(II) 1,3-diethyl-2-thiobarbiturates and their thermal stability

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ABSTRACT

Three new complexes of 1,3-diethyl-thiobarbituric acid (HDetba), barbiturate-bridged 2D Mn(II) polymer [Mn(H₂O)₂(Detba)₂] (**1**), trinuclear [Mn₃(H₂O)₁₀(Detba)₆] (**2**) and discrete molecular [Mn(H₂O)₄(Detba)₂·H₂O] (**3**) are synthesized and structurally characterized by the X-ray single crystal technique. In **1–3**, the Detba[−] ions are coordinated to Mn(II) only through O atoms with manganese ions in the octahedral environment. In **1**, the Mn(II) ion is coordinated by four μ₂ bridge Detba[−] ions and two terminal H₂O molecules. In **2**, the Mn1 ion is coordinated by three terminal H₂O molecules, two terminal and one μ₂ bridge Detba[−] ion, and Mn2 is connected with two μ₂-Detba[−] ions and four H₂O molecules. In **3**, the Mn(II) ion is coordinated by two terminal Detba[−] ions and four terminal H₂O molecules. There are intermolecular hydrogen bonds O–H···O, O–H···S in the structures of **1–3** which form the 3D networks. Structure **2** is stabilized by the π–π interaction. The compounds thermal decomposition comprises dehydration steps and the organic ligand oxidation.

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1. Introduction

At present, there is a rapid growth in the number of synthesized metal–organic complexes, which owes much to their unusual structures and the possibility of using them as functional materials [1]. Of particular interest are the polyfunctional ligands containing neutral and anionic binding sites. They can form complexes with metal ions that do not contain additional counter ions, which can fill potentially useful cavities and channels in structures. Such polyfunctional ligands include thiobarbituric acid (H₂tba) and its derivatives actively used in medicine and pharmacology [2]. Some of their complexes with metals have their useful pharmaceutical activity [3]. So far, the complexes with H₂tba and its 5,5'-substituted derivatives have been structurally characterized [4–6], but the metal complexes with N and N,N'-derivatives of H₂tba were

not investigated in detail. We have previously synthesized and structurally characterized the complexes of 1,3-diethyl-2-thiobarbituric acid (C₈H₁₂N₂O₂S, HDetba) with alkali metal ions, Tl(I) [7,8], Ca(II), Sr(II) [9], Ag(I) [10], Pb(II) [11], Co(II) [12] and Eu(III) [13]. In the present work, the synthesis, structure and thermal stability of polymer Mn(H₂O)₂(Detba)₂ (**1**), trinuclear Mn₃(H₂O)₁₀(Detba)₆ (**2**) and discrete Mn(H₂O)₄(Detba)₂·H₂O (**3**) were investigated.

Previously, it was shown that, depending on the crystallization conditions of alkaline earth metals thiobarbiturates [14–16] and sodium thiobarbiturate [17] from the aqueous solutions, crystalline forms containing different amounts of coordinated water molecules may be prepared. However, it is unclear how widespread this phenomenon is among H₂tba derivatives, for example, for HDetba. So far, we have been able to obtain and perform the structural characterization [7–11] of only one Detba[−] complex with a definite metal ion, and only compounds M(H₂O)₂(Detba)₂ (M = Ca, Sr) [9] containing water molecules. The principle interest of the present observation is to investigate the solid-state structure variation of manganese 1,3-diethyl-2-thiobarbiturate complexes during changing the number of coordinated water molecules.

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2. Experimental section

2.1. Reagents and synthesis

1,3-Diethyl-2-thiobarbituric acid [CAS 5217-47-0] was commercially available from Sigma–Aldrich. Manganese(II) carbonate and manganese(II) chloride tetrahydrate were obtained as a reagent analytical grade (Acros) and they were used without additional purification.

2.1.1. Synthesis of crystal **1**

1 mmol (0.2 g) of HDetba acid in 5 ml of water was neutralized by an equivalent amount of NaOH (1 mmol, 0.04 g) and, then, 0.5 mmol (0.099 g) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was added. The mixture was heated at 80 °C until the complete dissolution of HDetba. The resulted hot solution (pH = 4) was evaporated at 80 °C in a water bath to a volume of ≈ 1 ml and, then, the hot solution was immediately placed in the freezer at –3 °C for 5 min. The resulting colorless fine crystalline precipitate **1** was filtered off and dried in the air up to a constant mass. The yield was 16%. A single crystal appropriate for the X-ray diffraction analysis was obtained by evaporating the filtrate (≈ 0.5 ml) in a freezer compartment at –3 °C during a day.

The chemical analysis was carried out with an HCNS-0 EA 1112 Flash Elemental Analyser (Perkin-Elmer, England). Anal. Calc. for $\text{C}_{16}\text{H}_{26}\text{MnN}_4\text{O}_6\text{S}_2$ (**1**): C, 39.3; H, 5.35; N, 11.4; S, 13.1. Found: C, 38.7; H, 5.26; N, 11.1; S, 12.7%.

2.1.2. Synthesis of crystal **2**

The mixture of 1 mmol HDetba and 1 mmol MnCO_3 in water (10 ml) was stirred for 7 h at 50 °C and, then, it was filtered. The resulting hot filtrate (pH = 4) was evaporated at 80 °C in a water bath to a volume of ≈ 1 ml. The pink single crystal of compound **2** was selected from the total mass of the substance obtained by slow evaporation of filtrate (≈ 1 ml) at room temperature for 6 months to a volume of ≈ 0.2 ml. For slow water evaporation, the test-tube with the filtrate was covered with a paraffin film with the holes made. However, we could not get a sufficient amount of the single-phase compound $\text{Mn}_3(\text{H}_2\text{O})_{10}(\text{Detba})_6$ (**2**), which single crystal was grown.

2.1.3. Synthesis of crystal **3**

1 mmol HDetba acid was mixed with the abundance of MnCO_3 (~ 1 mmol) in water (10 ml). The mixture was stirred for 7 h at 50 °C and, then, it was filtered. The resulting filtrate was left to evaporate at room temperature. A few days later, pale pink crystals **3** were precipitated from the volume of the solution ≈ 0.5 ml, filtered off and dried in the air up to a constant mass. The yield was 34%. A single crystal for the X-ray diffraction analysis was selected directly from the total mass of the product.

Anal. Calc. for $\text{C}_{16}\text{H}_{32}\text{MnN}_4\text{O}_9\text{S}_2$ (**3**): C, 35.4; H, 5.93; N, 10.3; S, 11.8. Found: C, 35.0; H, 5.73; N, 9.97%; S, 11.4.

2.1.4. Relative stability of **1** and **3** in water

Compounds **1** and **3** are readily soluble in water and ethanol. The excess $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2 \cdot \text{H}_2\text{O}$ in a small volume of water (≈ 0.5 ml) was being kept in a closed vessel at room temperature for 30 days. After this time, the solid product was filtered off and characterized by the X-ray powder diffraction which confirmed the absence of phase transformation. In contrast, the colorless crystals of $\text{Mn}(\text{H}_2\text{O})_2(\text{Detba})_2$, which persisted in the saturated solution for 2 weeks, were gradually converted into the pale-pink crystals of $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2 \cdot \text{H}_2\text{O}$. This opens a possibility for considering compound **3** as a more thermodynamically stable phase, compared

to kinetic phase **1**. It should be noted that the solid crystals of $\text{Mn}(\text{H}_2\text{O})_2(\text{Detba})_2$ are stable at room temperature for, at least, 3 weeks.

2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals **1**, **2** and **3** at 296 K using the SMART APEX II and D8 Venture X-ray single crystal diffractometers (Bruker AXS) equipped with a CCD-detector, graphite monochromator and a Mo $K\alpha$ 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 [18]. All hydrogen atoms were found via Fourier difference maps. Further, the hydrogen atoms which are linked with C, N atoms in the Detba^- in **1–3** were positioned geometrically as riding on their parent atoms with $d(\text{C–H}) = 0.93\text{–}0.98$ Å, depending on geometry and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. All hydrogen atoms of the H_2O molecules were refined with bond length restraint $d(\text{O–H}) = 0.9$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The structure test for the presence of missing symmetry elements and possible voids was made using program PLATON [19]. The DIAMOND program is used for the crystal structure plotting [20]. The powder X-ray diffraction data of **1** and **3** were obtained using diffractometer D8 ADVANCE (Bruker) equipped by a VANTEC detector with a Ni filter. The measurements were made using Cu $K\alpha$ radiation. The structural parameters defined by the single crystal analysis were used as a base in the powder pattern Rietveld refinement. The refinement was performed using program TOPAS 4.2 [21]. The low *R*-factors and good refinement results shown in Fig. 1S indicate the crystal structures of the powder samples to be representative ones of the **1** and **3** bulk structures.

2.3. Physical measurements

TGA was carried out on the simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under the dynamic air atmosphere (50 ml/min flow rate) within 22–350 °C at the scan rate of 10 °C/min. The qualitative composition of the evolved gases was determined by an FT-IR spectrometer Nicolet380 (Thermo Scientific, USA) combined with a thermal analyzer and with the TGA/FT-IR interface (attachment for the gas phase analysis). This set up allows simultaneous accumulation of the DTA/TG data and the released gas composition. The sample weight was 10.94 mg for **1** and 9.211 mg for **3**. The platinum crucibles with perforated lids were used as containers.

3. Results and discussion

3.1. Crystal structures of (**1**)

The unit cells of $\text{Mn}(\text{H}_2\text{O})_2(\text{Detba})_2$ (**1**) correspond to the orthorhombic symmetry. Space group *Pbca* was determined from the statistical analysis of the reflection intensities. The main crystal data are summarized in Table 1. The defined main bond lengths are listed in Table 1S.

The independent part of the unit cell contains one Detba^- ion in the general position, the Mn^{2+} ion in special position 4a and one H_2O molecule in general position 8c (Fig. 1a). The Mn(II) ion is coordinated by four μ_2 bridge Detba^- ions and two terminal H_2O molecules (Fig. 2Sa) forming an octahedron. Water molecules are located opposite to each other and Detba^- ions are located along the equator of MnO_6 polyhedron. Each Detba^- is coordinated by two Mn^{2+} so that they form a 2D net (Fig. 3S). It is a simple plane

Table 1
Crystal structure parameters of $\text{Mn}(\text{H}_2\text{O})_2(\text{Detba})_2$, $\text{Mn}_3(\text{H}_2\text{O})_{10}(\text{Detba})_6$ and $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2 \cdot \text{H}_2\text{O}$.

Single crystal	$\text{Mn}(\text{H}_2\text{O})_2(\text{Detba})_2$ (1)	$\text{Mn}_3(\text{H}_2\text{O})_{10}(\text{Detba})_6$ (2)	$\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2 \cdot \text{H}_2\text{O}$ (3)
Moiety formula	$\text{C}_{16}\text{H}_{26}\text{MnN}_4\text{O}_6\text{S}_2$	$\text{C}_{48}\text{H}_{86}\text{Mn}_3\text{N}_{12}\text{O}_{22}\text{S}_6$	$\text{C}_{16}\text{H}_{32}\text{MnN}_4\text{O}_8\text{S}_2$
Dimension (mm)	$0.45 \times 0.45 \times 0.1$	$0.3 \times 0.1 \times 0.05$	$0.3 \times 0.2 \times 0.1$
Color	Colorless	Pink	Pale pink
Molecular weight	489.47	1540.47	543.51
Temperature (K)	296	296	296
Space group, Z	<i>Pbca</i> , 4	<i>P</i> $\bar{1}$	<i>Pbca</i> , 8
<i>a</i> (Å)	9.3535 (4)	9.0094 (8)	11.8868 (3)
<i>b</i> (Å)	13.8812 (7)	14.0378 (11)	13.8324 (3)
<i>c</i> (Å)	16.9106 (8)	14.5823 (12)	29.9847 (8)
α (°)	90	109.494 (3)	90
β (°)	90	92.834 (3)	90
γ (°)	90	106.941 (3)	90
<i>V</i> (Å ³)	2195.6 (2)	1640.9 (2)	4930.2 (2)
ρ_{calc} (g/cm ³)	1.481	1.559	1.464
μ (mm ⁻¹)	0.830	0.841	0.756
Reflections measured	21106	81284	23121
Reflections independent	2984	9700	5642
Reflections with $F > 4\sigma(F)$	2562	7088	4425
$2\theta_{\text{max}}$ (°)	58.67	60.39	54.95
<i>h, k, l</i> – limits	$-11 \leq h \leq 12$; $-19 \leq k \leq 16$; $-23 \leq l \leq 23$	$-12 \leq h \leq 12$; $-19 \leq k \leq 19$; $-20 \leq l \leq 20$	$-15 \leq h \leq 13$; $-17 \leq k \leq 13$; $-34 \leq l \leq 38$
R_{int}	0.0384	0.0921	0.0331
The weighed refinement of F^2	$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 1.5441P]$	$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 0.3364P]$	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 1.1261P]$
Number of refinement parameters	140	448	323
$R1 [F_o > 4\sigma(F_o)]$	0.0265	0.0464	0.0302
$wR2$	0.0589	0.1124	0.0698
<i>Goof</i>	1.024	1.034	1.012
$\Delta\rho_{\text{max}}$ (e/Å ³)	0.405	1.011	0.234
$\Delta\rho_{\text{min}}$ (e/Å ³)	-0.297	-0.774	-0.190
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001	0.001

square net with a point symbol ($4^4.6^2$). Therefore, the formula can be written as $\text{Mn}(\text{H}_2\text{O})_2(\mu_2\text{-Detba}^- \text{O}, \text{O}')_2$. Comparatively, compounds $\text{Sr}(\text{H}_2\text{O})_2(\text{Detba})_2$ and $\text{Ca}(\text{H}_2\text{O})_2(\text{Detba})_2$ [9] have absolutely the same general formula, space group, point symbol and similar cell parameters. Thus, all they are isostructural compounds and the linear cell volume per metal ion radii well agrees to that (Fig. 4S).

There are two intermolecular hydrogen bonds O–H...S in the structure (Fig. 2a, Table 2S) which form a 3D network. The topological analysis using ToposPro program [22] showed a 3-nodal net (the first node – center of Detba^- ion, the second node – center of H_2O molecule and the third node – Mn^{2+} ion) with stoichiometry $(3\text{-c})_2(4\text{-c})_2(6\text{-c})$ and with point symbol $(5^3)_2(5^4.6.7)_2(5^6.6^2.7^4.9^3)$ which is new [22]. The smallest motif in this network is $R_3^2(12)$ (Fig. 2a). There are no π - π interactions between Detba^- rings.

3.2. Crystal structures of (2)

The unit cells of $\text{Mn}_3(\text{H}_2\text{O})_{10}(\text{Detba})_6$ (**2**) correspond to the triclinic symmetry. Space group $P\bar{1}$ was determined from the statistical analysis of the reflection intensities. The main crystal data can be observed in Table 1. The main bond lengths C–O, C–N, C–C (Table 1S) and the angles in (**2**) practically coincide with those found earlier in other related compounds [7–13].

The independent part of the unit cell contains two Mn^{2+} ions (Mn1 in general position $2i$ and Mn2 in special position $1h$), five water molecules and three Detba^- ions (A, B, C) in general positions (Fig. 1b). The symmetry element $(-x, -y, -z)$, which is located in the Mn2 site multiplies all these ions forming a block $\text{Mn}_3(\text{H}_2\text{O})_{10}(\text{Detba})_6$ structure (Fig. 2Sb). These blocks are linked with each other by hydrogen bonds only.

In structure **2**, the Mn1 ion is coordinated by three terminal H_2O molecules, two terminal and one μ_2 bridge Detba^- ion forming an

octahedron. The octahedral coordination of Mn2 is formed by two $\mu_2\text{-Detba}^-$ ions and four H_2O molecules (Figs. 1b, 2Sb). The Detba^- ions with labels A and B are terminal ligands. The ion Detba^- with label C is a bridge ion and it links with two Mn^{2+} ions through two different oxygen atoms. Therefore, the formula $\text{Mn}_3(\text{H}_2\text{O})_{10}(\mu_2\text{-Detba}^- \text{O}, \text{O}')_2(\text{Detba}-\text{O})_4$ can be suggested.

Octahedron Mn2O_6 in (**2**) is less distorted in comparison with that of Mn1O_6 , because the bond lengths $\text{Mn2}-\text{O}$ (2.1447(16)–2.2026(15) Å) are characterized by a narrower interval in comparison with that of $\text{Mn1}-\text{O}$ (2.1343(15)–2.2260(17) Å). Currently, the structures of only two triple-octahedral $\text{Mn}(\text{II})$ compounds with block structures are known [5] – $[\text{Mn}_3(\text{L})_6(\text{CH}_3\text{OH})_6] \cdot 3\text{H}_2\text{O}$ (HL = 9-acridinecarboxylic acid) [23] and $[\text{Mn}_3(\text{PTMMC})_6(\text{EtOH})_6] \cdot 6\text{EtOH}$ (PTMMC – monocarboxylic polychlorinated triphenylmethyl anion radical) [24]. The ligands in these compounds are also coordinated only through O atoms. Three Mn ions, similar to (**2**), lie along a straight line, and central Mn2 is located in the inversion center. Moreover, the bond lengths also possess similar behavior: $\text{Mn2}-\text{O}$ (2.155(2) Å) and $\text{Mn1}-\text{O}$ (2.126(2) and 2.224(2) Å) [23]; $\text{Mn2}-\text{O}$ (2.154(2) Å) and $\text{Mn1}-\text{O}$ (2.146(2), and 2.233(2) Å) [24].

The crystal structure analysis showed 10 intermolecular hydrogen bonds O–H...O, O–H...S (Table 2S, Fig. 2b). There are weak hydrogen bonds C–H...S and C–H...O in **1–3**, and that is also a characteristic feature of Detba^- ions in other metal complexes [7–13]. The intermolecular H-bonds involve all H atoms of all water molecules and all three Detba^- ions. The hydrogen bonds form a 3D frame with supramolecular motifs $R_2^1(6)$, $R_2^2(8)$, $R_3^2(12)$, $R_3^3(16)$, $R_3^4(18)$ (Fig. 2b). The topological analysis of the H-bond network using ToposPro [22] showed a uninodal 3D net with the point symbol $(3^6.4^{18}.5^3.6)$ which is well known as a primitive hexagonal cell (in different notations **hex** or **sqc4**). The complex $\text{Mn}_3(\text{H}_2\text{O})_{10}(\text{Detba})_6$ is the node of this net with coordination number 8.

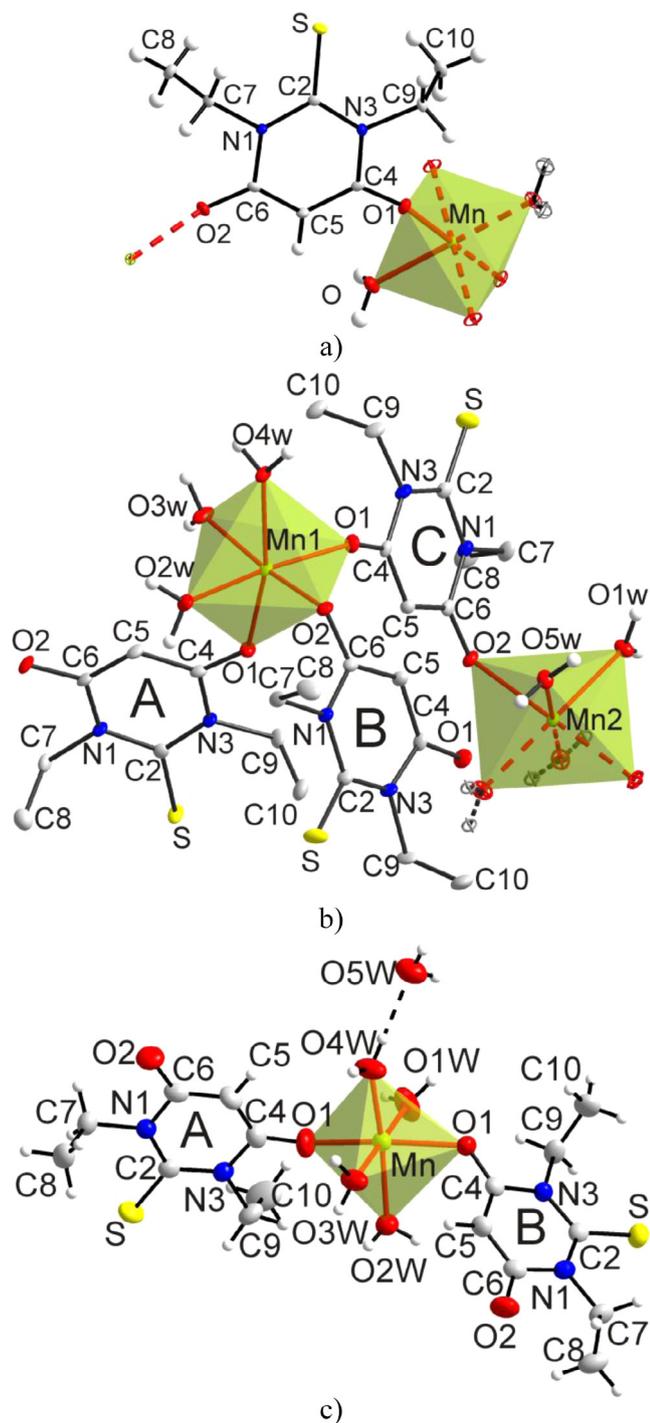


Fig. 1. The asymmetrical unit of the Mn(H₂O)₂(Detba)₂ (a), Mn₃(H₂O)₁₀(Detba)₆ (b) and Mn(H₂O)₄(Detba)₂·H₂O (c) unit cells. All atoms in the asymmetrical unit are labeled, all H atoms of Detba⁻ ions in (b) were deleted for clarity. The neighboring symmetry-generated atoms are represented by the principal ellipsoids with an individual color. The bonds linking the asymmetrical unit atoms with the symmetry-generated atoms and 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. Different Detba⁻ ions are marked by A, B, C labels. (Color online.)

The π - π interaction between the rings of Detba⁻ ions with A labels was found (Table 3S). The Detba⁻ packing type is “head-to-tail” (Fig. 5S) [25]. Previously, only AgDetba [10] showed the “head-to-tail” type π - π interaction.

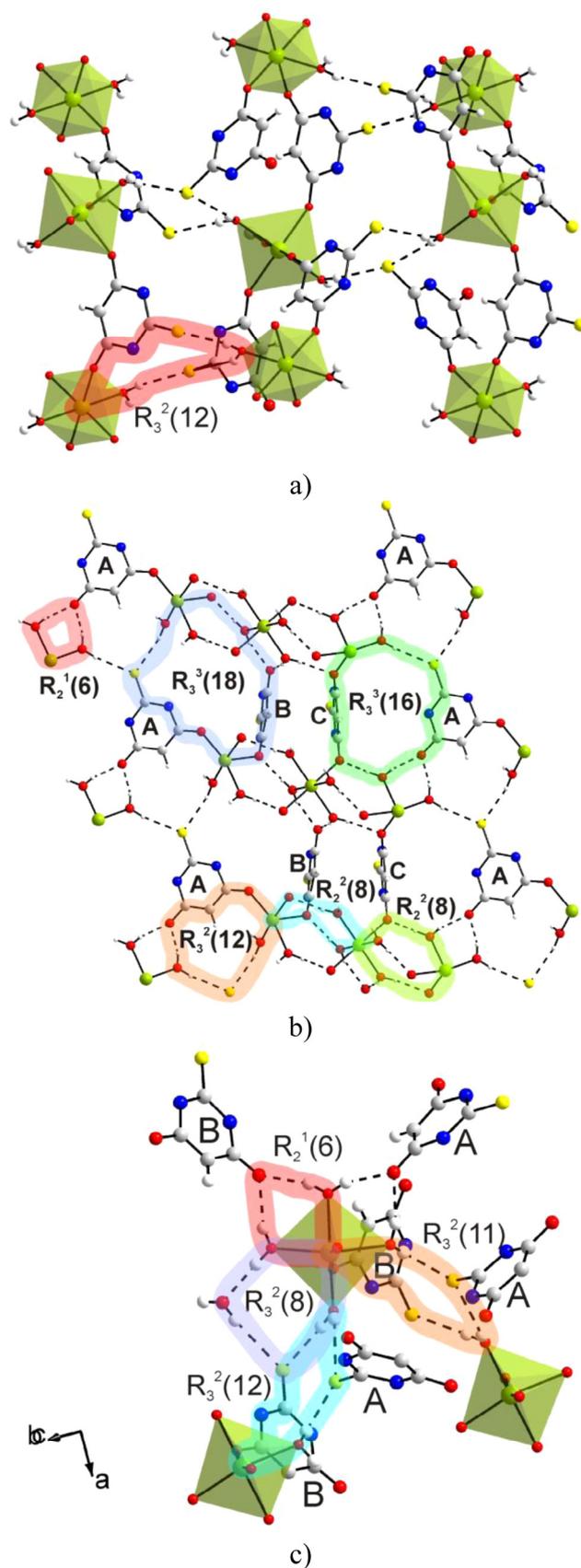


Fig. 2. Hydrogen bonding in Mn(H₂O)₂(Detba)₂ (a), Mn₃(H₂O)₁₀(Detba)₆ (b) and Mn(H₂O)₄(Detba)₂·H₂O (c). The H-bonds are marked by dashed lines, the H-bond motifs are marked by circles. Different Detba⁻ ions are marked by A, B, C labels. The CH₃-CH₂- groups were deleted for clarity.

3.3. Crystal structures of **(3)**

The unit cells of $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2 \cdot \text{H}_2\text{O}$ (**3**) correspond to the orthorhombic symmetry, and space group *Pbca* 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 listed in Table 1S.

The independent part of the unit cell contains two Detba^- ions in general positions, the Mn(II) ion in general positions 8c and five H_2O molecules in general positions (Fig. 1c). The Mn(II) ion is coordinated by two terminal Detba^- ions and four terminal H_2O molecules forming an octahedron. Contrary to (**1**), the Detba^- ions are located in the *trans*-position to each other, and water molecules are located at the equator of the MnO_6 polyhedron. However, each Detba^- is coordinated by one Mn^{2+} so that a discrete $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2$ complex is formed (Figs. 1c, 2Sc). Therefore, the formula can be written as $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba}-\text{O})_2$. There are ten intermolecular hydrogen bonds $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{S}$ in the structure (Fig. 2c, Table 2S) which form a 3D network. This is an 8-nodal net (two nodes – center of Detba^- ions, five nodes – center of H_2O molecules and one node – Mn^{2+}) with stoichiometry (3-c)(3-c)(3-c)(3-c)(3-c)(5-c)(6-c)(6-c) and with the point symbol $(4.5^2)_2(4.5^3.6^2.7^4)(4.5^4.6^2.7^3.8^4.9)(4^2.5^3.6^4.7^3.8^3)(4^2.6)(5^3)_2$ which is new [22]. Some smallest cyclic motifs in this network are $\text{R}_2^2(6)$, $\text{R}_3^2(8)$, $\text{R}_3^2(11)$, $\text{R}_3^2(12)$ (Fig. 2c). There are no π - π interactions between Detba^- rings.

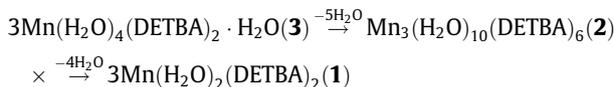
Compounds **1–3**, $\text{Sr}(\text{H}_2\text{O})_2(\text{Detba})_2$ and $\text{Ca}(\text{H}_2\text{O})_2(\text{Detba})_2$ [9] have coordinated water molecules contrary to the compounds of HDetba with alkali metals Tl(I) [7,8], Ag(I) [10], Pb(II) [11] and Eu(III) [13]. In complexes **1–3**, Ca(II), Sr(II) [9], Co(II) [12] and Eu(III) [13], Detba^- ions are coordinated to metal ions only through oxygen atoms, but, in complexes of alkaline metals (Li-Cs), Tl(I) [7,8], Ag(I) [10] and Pb(II) [11], they are linked with metal ions both through the O and S atoms. A diversity of topological nets in the coordination compounds of Detba^- makes it possible to assume that some exotic or outstanding topological nets can be found in perfect future.

3.4. Thermal decomposition of manganese(II) 1,3-2-thiobarbiturates

To corroborate the structural information about the water molecule status in **1** and **3**, as well as to know their general stability, the thermal decomposition experiments were implemented for these complexes. The STA results for the thermal decomposition/oxidation of **1** are shown in Fig. 6S. As it can be seen, the complex is thermally stable up to $\sim 70^\circ\text{C}$. Both TG and DSC curves of **1** show the two-step dehydration which is accompanied by two endo effects at 97.5°C and 161.2°C . This is confirmed by the results of IR spectroscopic analysis of evolved gases, according to which, when the sample is heated to 175°C , only the two-step dehydration takes place. The first dehydration stage proceeded in a range of ~ 70 – 110°C and showed a weight loss (Δm) equal to $\sim 1.7\%$, which is consistent with the loss of $0.5\text{H}_2\text{O}$ ($\Delta m_{\text{theor}} = 1.84\%$) in the compound. The second dehydration stage in the range of 110 – 175°C showed $\Delta m = 6.8\%$. The total weight loss (8.00%) is bigger than the weight loss calculated under the assumption of complete dehydration ($-2\text{H}_2\text{O}$, $\Delta m_{\text{theor}} = 7.36\%$). The detected difference can be explained by the hygroscopicity of $\text{Mn}(\text{H}_2\text{O})_2(\text{Detba})_2$. The intense decomposition/oxidation of 1,3-diethyl-2-thiobarbiturate moiety starts at $\sim 300^\circ\text{C}$.

The DSC and TG curves of $\text{Mn}(\text{H}_2\text{O})_4(\text{Detba})_2 \cdot \text{H}_2\text{O}$ (**3**) show one-step dehydration (Fig. 7S) which is accompanied by the endo effect at 127.5°C and it is confirmed by the results of evolved gases IR spectroscopic analysis. The dehydration of **3** starts at $\sim 65^\circ\text{C}$ and, in the range of 110 – 175°C , it showed $\Delta m = 16.4\%$. The weight loss

calculated under the assumption of the total dehydration ($-5\text{H}_2\text{O}$) is $\Delta m_{\text{theor}} = 16.6\%$. The decomposition/oxidation process starts at $\sim 270^\circ\text{C}$. When oxidizing an organic ligand in **1** and **3**, CO_2 , SO_2 and H_2O gases are released. At room temperature, the mass of the compound **3**, dried at 110°C during a day, increased by just $\sim 1\%$ and then remained unchanged for a week. Such an insignificant increase in mass is most likely due to the hygroscopicity of anhydrous $\text{Mn}(\text{Detba})_2$. It should be noted that the decomposition temperatures of the organic component in compounds **1** and **3** roughly coincide, suggesting the same anhydrous compound formation. Unfortunately, the X-ray diffraction pattern of the dehydration product proved to be unsuitable for its characterization. The stoichiometric relationships between hydrates of Mn(II) 1,3-diethyl-2-thiobarbiturate are governed by the scheme:



4. Conclusions

Three new complexes **1–3** with different water contents were obtained at different crystallization conditions by reacting 1,3-diethyl-2-thiobarbituric acid with Mn(II) salts in an aqueous solution. Their structures were solved by the single crystal X-ray diffraction analysis. The preparation of three hydrates $[\text{Mn}(\text{H}_2\text{O})_n(\text{Detba})_2]$ ($n = 2, 3.33$ and 4) suggests the existence of different hydrated 1,3-diethyl-2-thiobarbiturate complexes of other d-elements. In related saturated aqueous solutions, the solid complex **3** has the greatest stability, and solid complex **1** slowly transforms into **3**. As the number of coordinated water molecules per unit cell of $\text{Mn}(\text{Detba})_2$ decreases, in the series of compounds **3–2–1**, the type of Detba^- coordination varies from a purely terminal one in **3**, to a terminal one and a μ_2 bridge in **2**, and to a μ_2 -bridge in **1** (Fig. 2). Compounds **2**, **3** and $[\text{Co}_2(\text{BuOH})_4(\text{Detba})_4]$ (BuOH is butanol-1) [12] are the first examples of coordination compounds of the Detba^- with non-polymeric structure. Moreover, only they contain terminal Detba^- ions.

Only the intermolecular hydrogen bonds $\text{O}-\text{H} \cdots \text{S}$ are formed in isostructural compounds $\text{M}(\text{H}_2\text{O})_2(\text{Detba})_2$ ($\text{M} = \text{Mn}, \text{Sr}, \text{Ba}$). In structures **2** and **3**, additional $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds are formed (Table 2S, Fig. 2). In $[\text{Co}_2(\text{BuOH})_4(\text{Detba})_4]$ [12], there are intermolecular hydrogen bonds $\text{O}-\text{H} \cdots \text{O}$ also. In other metal complexes with Hdetba , there are no intermolecular hydrogen bonds [7,8,10,11,13]. In all structures of 1,3-diethyl-2-thiobarbiturate complexes, intramolecular H-bonds $\text{C}-\text{H} \cdots \text{S}$ and $\text{C}-\text{H} \cdots \text{O}$ are found, and that partly explains the low ability of Detba^- ions in forming intermolecular hydrogen bonds. In the air, for pure HDetba , a mass decrease at $T > 112^\circ\text{C}$ corresponds to the acid evaporation [7]. The thermal decomposition of **1** and **3** starts at higher temperatures (Figs. 6S, 7S), and it comprises the steps of dehydration and oxidation of the organic ligand with CO_2 , SO_2 , and H_2O gases release.

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Appendix A. Supplementary data

CCDC 1547014, 1507469, and 1547015 contains the supplementary crystallographic data for **1**, **2**, **3**, respectively. These data can be obtained free of charge via <http://dx.doi.org/10.1016/j.poly.2017.06.002>, 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.2017.06.002>.

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