



Research paper

First outer-sphere 1,3-diethyl-2-thiobarbituric compounds $[M(H_2O)_6(1,3\text{-diethyl-2-thiobarbiturate})_2 \cdot 2H_2O]$ ($M = Co^{2+}, Ni^{2+}$): Crystal structure, spectroscopic and thermal properties



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ABSTRACT

Two new *d*-element compounds, $[Co(H_2O)_6](Detba)_2 \cdot 2H_2O$ (**1**) and $[Ni(H_2O)_6](Detba)_2 \cdot 2H_2O$ (**2**) (HDetba – 1,3-diethyl-2-thiobarbituric acid) were synthesized and characterized by single-crystal and powder X-ray diffraction analysis, TG–DSC and FT-IR. Structural analysis revealed that (**1**) and (**2**) are discrete structures, in which M^{2+} ion ($M = Co, Ni$) is six-coordinated by water molecules and it forms an octahedron. The outer-sphere Detba[−] ions and H₂O molecules participate in O–H... (O/S) intermolecular hydrogen bonds which form the 2D layer. Thermal decomposition includes the stage of dehydration and the following stage of oxidation of Detba[−] with a release of CO₂, SO₂, H₂O, NH₃ and isocyanate gases.

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1. Introduction

2-Thiobarbituric acid (H₂tba) and its derivatives have important applications mainly in pharmaceuticals [1–4]. They form coordination compounds with metal ions, primarily with *d*-elements, and the crystals possess different composition and structure due to the presence of donor N, O and S atoms [5–21]. These coordination compounds may have potentially valuable pharmaceutical properties [17,18]. The donor atoms of thiobarbituric acid can form a large number of different hydrogen bonds, and cyclic molecules or their anions can participate in the π – π interactions. Such broad interaction opportunities cause a rich supramolecular chemistry of compounds with thiobarbituric acids and rich prospects for their application [22]. For example, the self-assembled monolayers (SAMs) of 2-thiobarbituric acids on the surface of metallic gold,

as formed by intermolecular hydrogen bonds, can be used as the protein sensors or as the artificial chemical sensor of barbituric acid in the presence of diethylbarbituric acid [23,24].

Whereas the series of coordination compounds of 2-thiobarbituric acid with *d*-elements are synthesized and characterized [5–21], the data about their derivatives are scarce. For example, only the structure of coordination compounds $M = Li, Na, K, Tl, Rb, Cs, Ag(I), Pb(II), Eu(III)$ with 1,3-diethyl-2-thiobarbituric acid (C₈H₁₁N₂O₂S, HDetba) [21,25–28] were solved from all compounds with N,N-substituted thiobarbituric acids. It was shown earlier that HDetba exhibits *n*-channel organic thin film transistor properties [29]. Besides, on the basis of this acid, the compounds exhibiting high nonlinear properties were obtained [30], and its derivatives play an important role in medicinal and pharmaceutical chemistry [3]. The present study is aimed at the synthesis, investigation of crystal and supramolecular structure, and evaluation of spectroscopic and thermal properties of two isostructural compounds of *d*-elements Co(II) and Ni(II) which contain 1,3-diethyl-2-thiobarbiturate anions (Detba[−]) in the outer-sphere.

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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. Basic cobalt carbonate and basic nickel carbonate were obtained as a reagent analytical grade (Acros) and they were used without additional purification.

The 0.005 mole HDetba acid was mixed with the abundance of basic cobalt carbonate or basic nickel carbonate (~0.005 mole) in water (20 cm³). The mixtures were stirred for 7 h at 50 °C and, then, they were filtered. The pale pink crystals of [Co(H₂O)₆](Detba)₂·2H₂O (**1**) and the green crystals of [Ni(H₂O)₆](Detba)₂·2H₂O (**2**) were grown in small volume 0.2–0.4 cm³ by continuous evaporation of the filtrate at room temperature. The crystalline precipitates were separated and dried between filter paper sheets. The crystalline product yield was as high as 60–70%. The chemical analysis was carried out with an HCNS-0 EA 1112 Flash Elemental Analyser (Perkin-Elmer, England). The analysis results of (**1**) (w.%): found: H 6.45, C 32.2, N 9.26, S 10.5. Calc. H 6.37, C 31.9, N 9.31, S 10.7. The analysis results of (**2**) (w.%): found: H 6.35, C 32.1, N 9.17, S 10.6. Calc. H 6.37, C 32.0, N 9.32, S 10.7.

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 α radiation source. The absorption corrections were applied using the SADABS program. The structures were solved by direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [31]. All the hydrogen atoms of the Detba[−] ligands in (**1**) and (**2**) were positioned geometrically as riding on their parent atoms with d(C–H) = 0.93 Å for the C5–H5 bond and 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 H₂O 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. The DIAMOND program was used for the crystal structure plotting.

The powder X-ray diffraction data were obtained using diffractometer D8 ADVANCE (Bruker) equipped by a VANTEC detector with a 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 performed using program TOPAS 4.2. The low R-factors and good refinement results shown in (Figs. 1S and 2S) indicate the crystal structures of the powder samples to be representative ones of the (**1**, **2**) bulk structures, respectively.

2.3. Physical measurements

TGA had been carried out on the simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under dynamic air atmosphere (50 ml/min flow rate) within 25–800 °C at the scan rate of 10 °C/min. The compound weight was 7.729 mg for (**1**) and 11.267 mg for (**2**). Platinum crucibles with perforated lids were used. The qualitative composition of the evolved gases was determined by 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 and TG data, and composition of the released gas phase. The time dependence of the optical density for each

released gas component was obtained from their IR spectra. The IR absorption spectra of the compounds in KBr were recorded over the range of 400–4000 cm^{−1} at room temperature on a VECTOR 22 Fourier spectrometer (Bruker, Germany). The spectral resolution during the measurements was 5 cm^{−1}.

3. Results and discussion

3.1. Crystal structures

The main structural characteristics of (**1**) and (**2**) are shown in Table 1. The main defined bond lengths are shown in Table 1S. The Co–O and Ni–O bond distances range from 2.037(2) to 2.066(2) Å and from 2.062(2) to 2.104(2) Å, respectively, which is comparable to the values earlier reported for Co–O (aqua) and Ni–O (aqua) bonds in other six-coordinated complexes of these d-metals [32].

The asymmetric unit of the M(H₂O)₆(Detba)₂·2H₂O (M = Co, Ni) unit cells contains half of the M²⁺ ion, one Detba[−] ion and four H₂O (Figs. 1 and 2a, b). Crystal structures (**1**) and (**2**) are isostructural and can be presented by one scheme (Fig. 1). Ion M²⁺ is coordinated by six H₂O and forms an octahedron. The octahedra are not contacted directly, but they are linked through hydrogen bonds. There are seven O–H...O and one O–H...S intermolecular hydrogen bonds in the structure which form the 2D layer (Fig. 3, Table 2). All H atoms of all water molecules are involved in bonding with the formation of structural motifs R₄⁴(12), R₁¹²(40), C₃²(8), C₄⁴(16), R₃²(8), R₂¹(6) (Fig. 3). The structural analysis reveals the π – π interactions between the Detba[−] rings of the head-to-tail type in (**1**) and (**2**) (Fig. 4, Table 2S) using program PLATON. The bond lengths C2–S in (**1**, **2**) are in the range of 1.684–1.685 Å (Table 1S), that exceeds

Table 1
(**1**) and (**2**) crystal structure parameters.

Single crystal	[Co(H ₂ O) ₆](Detba) ₂ ·2H ₂ O (1)	[Ni(H ₂ O) ₆] (Detba) ₂ ·2H ₂ O (2)
Formula sum	C ₁₆ H ₃₈ CoN ₄ O ₁₂ S ₂	C ₁₆ H ₃₈ N ₄ NiO ₁₂ S ₂
Dimension (mm)	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
Color	Pink	Pale green
Molecular weight	601.55	601.33
Temperature (K)	298	298
Space group, Z	C2/c, 4	C2/c, 4
a (Å)	18.573 (1)	18.526 (1)
b (Å)	18.001 (1)	17.906 (1)
c (Å)	8.8812 (5)	8.9010 (5)
β (°)	114.882 (1)	114.856 (1)
V (Å ³)	2693.7 (3)	2679.2 (3)
ρ_{calc} (g/cm ³)	1.483	1.491
μ (mm ^{−1})	0.854	0.942
Reflections measured	12945	10956
Reflections independent	3621	2773
Reflections with $F > 4\sigma(F)$	2745	2202
2 θ_{max} (°)	52.62	52.96
h, k, l limits	−24 ≤ h ≤ 25; −24 ≤ k ≤ 24; −12 ≤ l ≤ 12	−23 ≤ h ≤ 23; −22 ≤ k ≤ 22; −11 ≤ l ≤ 11
R _{int}	0.0273	0.0910
The weighed refinement of F ²	w = 1/[$\sigma^2(F_o^2)$ + (0.0422P) ² + 1.0567P]	w = 1/[$\sigma^2(F_o^2)$ + (0.0395P) ²]
No. of refinement parameters	185	185
No. of restraints	8	8
R1 [$F_o > 4\sigma(F_o)$]	0.0344	0.0328
wR2	0.0801	0.0840
Goof	1.027	1.034
$\Delta\rho_{\text{max}}$ (e/Å ³)	0.300	0.285
$\Delta\rho_{\text{min}}$ (e/Å ³)	−0.329	−0.406
$\Delta/\sigma_{\text{max}}$	0.001	0.001

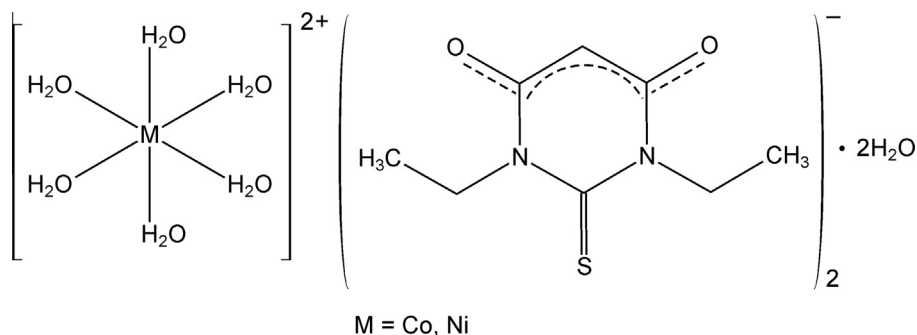


Fig. 1. $[M(H_2O)_6](Detba)_2 \cdot 2H_2O$ scheme, M = Co, Ni.

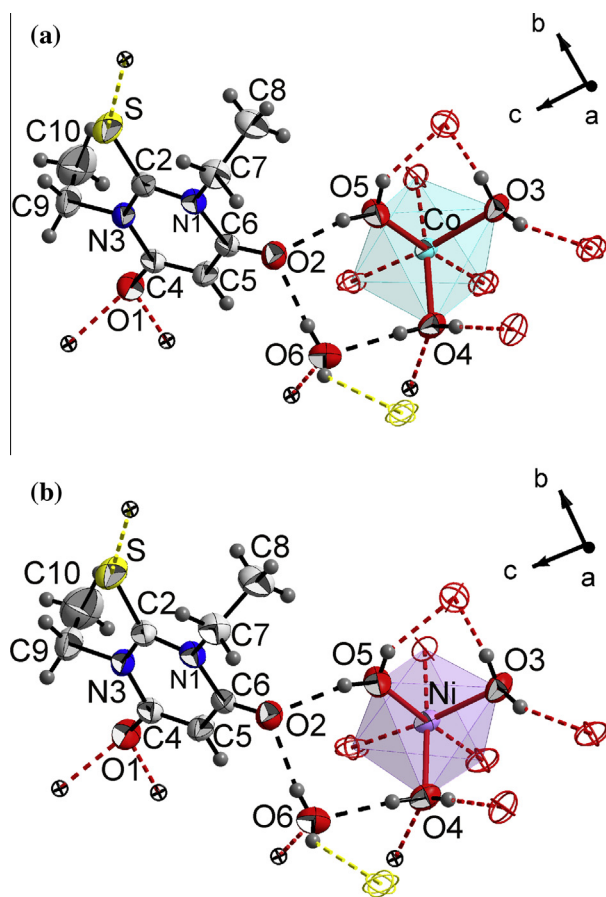


Fig. 2. The asymmetric unit of the $[M(H_2O)_6](Detba)_2 \cdot 2H_2O$ unit cell: (a) M = Co (1); (b) M = Ni (2). All atoms in the asymmetric unit are labeled. The directly neighboring symmetry-generated atoms are represented by principal ellipsoids with an individual color. The bonds linking asymmetric unit atoms with the symmetry-generated atoms 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the range previously defined for HDetba (1.658–1.681 Å) [33,34], and this indirectly confirms the S atom participation in the hydrogen bond. Compounds (1) and (2) have very similar bond lengths O1–C4, O2–C6 and C4–C5, C5–C6 (Table 1S), and that indicates the charge delocalization in the O=C–CH–C=O group. Such delocalization was observed in alkali and other metal compounds of 2-thiobarbiturates. [25–27,35–48]. Previously, two different conformational states: conformer (A) with large value of torsion angle C8–C7–C9–C10 ($\sim 150^\circ$) and conformer (B) with a small value of

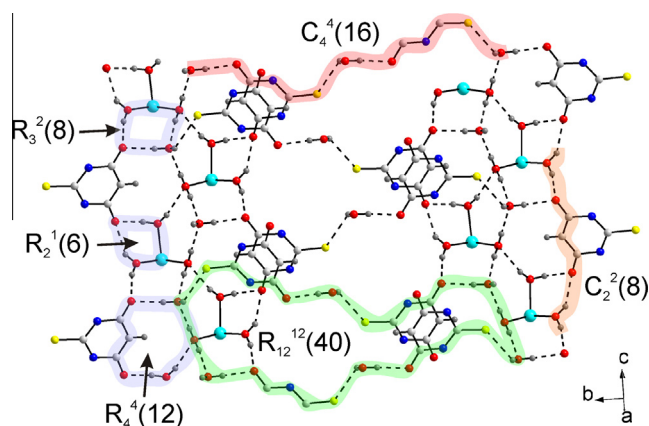


Fig. 3. Hydrogen bonding in 1. The CH_2-CH_3 groups are deleted for clarity, the H-bonds are marked by dashed lines, the H-bond motifs are marked by circles and broad lines.

this angle ($\sim 0 \dots 12^\circ$) were observed for Detba[−] ion in HDetba and its coordination compounds [21,25–27]. The present investigation shows that (1) and (2) have conformational state (A).

3.2. Supramolecular structures of $[Ni(H_2O)_6] X_2$ (X = Detba, Htba)

The peculiarity of (1) and (2) structures, contrary to HDetba and almost all its known coordination compounds with metals [25–27], besides AgDetba [21], are the $\pi-\pi$ interactions between the Detba[−] rings. Like AgDetba, the packing of Detba[−] ions should be classified as head-to-tail type. Previously, similar compound $[Ni(H_2O)_6](Htba)_2 \cdot 4H_2O$ with 2-thiobarbituric ions in the outer-sphere was obtained and structurally characterized. In solid and liquid states, $[Ni(H_2O)_6](Htba)_2 \cdot 4H_2O$ transformed to inner-sphere coordination compound $[Ni(H_2O)_2(Htba)_2]$ [19]. At room temperature, such transformation was not observed in (1) and (2). This stabilization of the outer-sphere compound, probably, is associated with steric obstacles in the coordination of volumetric Detba[−] ligand. The attempts to synthesize single crystals of Co(II) and Ni(II) compounds containing coordinated Detba[−] ion from ethyl alcohol and acetone or by dehydration of (1) and (2) under heating were unsuccessful. The geometrical parameters of octahedral cations $[Ni(H_2O)_6]^{2+}$ in $[Ni(H_2O)_6](Htba)_2 \cdot 4H_2O$ and in (2) are little different, but insertion of alkyl substituents in the H₂tba affects the supramolecular organization of the matter. Thus, the intermolecular hydrogen bonds between Htba[−] ions in $[Ni(H_2O)_6](Htba)_2 \cdot 4H_2O$ link the ions in infinite chains. There are no such chains of Detba[−] ions in (2) and, moreover, they do not directly link each other, but participate in hydrogen bonding with water molecules only. The difference is also evident in the formation of different supramolecular

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

D—H	d(D—H)	d(H···A)	∠ D—H···A	D···A	A	Transformation for A atom
<i>[Co(H₂O)₆](Detba)₂·2H₂O (1)</i>						
O3—H3WA	0.90(2)	1.74(2)	174(2)	2.527(2)	O1	x, y, -1 + z
O3—H3WB	0.83(2)	2.16(2)	167(2)	2.970(2)	O4	x, -y, -0.5 + z
O4—H4WA	0.85(2)	1.88(2)	167(2)	2.709(2)	O6	x, y, z
O4—H4WB	0.85(3)	1.94(3)	177(3)	2.790(2)	O6	x, -y, -0.5 + z
O5—H5WA	0.82(2)	2.03(2)	146(2)	2.749(2)	O1	x, y, -1 + z
O5—H5WB	0.83(2)	1.90(2)	165(2)	2.713(2)	O2	x, y, z
O6—H6WA	0.77(3)	2.85(2)	136(2)	3.440(2)	S	0.5 - x, -0.5 + y, 1.5 - z
O6—H6WB	0.84(2)	1.87(2)	174(3)	2.705(2)	O2	x, y, z
<i>[Ni(H₂O)₆](Detba)₂·2H₂O (2)</i>						
O3—H3WA	0.89(2)	1.74(2)	173(2)	2.625(2)	O1	x, y, -1 + z
O3—H3WB	0.84(2)	2.18(3)	163(2)	2.998(2)	O4	x, -y, -0.5 + z
O4—H4WA	0.83(3)	1.91(2)	166(3)	2.714(2)	O6	x, y, z
O4—H4WB	0.85(3)	1.94(3)	178(3)	2.785(3)	O6	x, -y, -0.5 + z
O5—H5WA	0.80(3)	2.04(2)	148(2)	2.750(2)	O1	x, y, -1 + z
O5—H5WB	0.79(3)	1.95(2)	165(3)	2.719(2)	O2	x, y, z
O6—H6WA	0.80(3)	2.74(2)	142(2)	3.411(2)	S	0.5 - x, -0.5 + y, 1.5 - z
O6—H6WB	0.82(2)	1.88(2)	172(3)	2.699(2)	O2	x, y, z

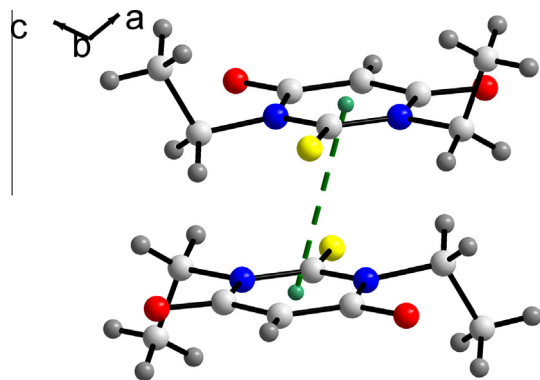


Fig. 4. π - π interaction between the rings of the Detba⁻ ions.

motifs in the compared compounds (Fig. 3, [19]). As far as [Co(H₂O)₆](Htba)₂·4H₂O compound was not obtained, the similar relations can be only supposed for [Co(H₂O)₆](Htba)₂·4H₂O and (1).

3.3. IR spectroscopy

Currently complete assignments of infrared and Raman spectra of HDetba and its coordination compounds are absent in the literature. The similarity of the IR spectra of compounds (1) and (2) confirms that these compounds are isostructural. The following bands were found in the IR absorption spectrum of (1), as shown in Fig. 3S, curve 2 (cm⁻¹): 3430 m., 2980 w., 2934 w., 2872 w., 1583 vs., 1415 vs., 1344 m., 1319 m., 1281 s., 1256 s., 1204 m., 1195 w., 1161 vw., 1107 s., 1057 vw., 953 vw., 923 vw., 839 vw., 797 w., 735 vw., 709 w., 661 w., 632 vw., 596 vw., 513 w., 493 w. and 407 w. (vs. – very strong, s. – strong, m. – medium, w. – weak, and v.w. – very weak). The IR absorption spectrum of (2) (Fig. 3S, curve 3 (cm⁻¹)): 3422 m., 2980 m., 2932 w., 2872 w., 1603 vs., 1402 vs., 1344 w., 1319 m., 1298 s., 1255 s., 1200 w., 1195 w., 1164 vw., 1107 s., 970 vw., 926 vw., 876 vw., 837 vw., 792 w., 698 vw., 631 vw., 592 vw., 508 w., 480 w., 443 w. and 405 w.

The IR spectra of (1) and (2) drastically differ from the IR spectra of HDetba (Fig. 3S, curve 1). The broad band in the range of ~3700–3300 cm⁻¹ with its maximum at 3430 cm⁻¹ for (1) and 3422 cm⁻¹ for (2) in IR spectra of coordination compounds, which is absent in the spectrum of Hdetba, corresponds to ν (OH) vibrations of water molecules. The IR spectra of each complex contains two very strong bands at 1583 cm⁻¹ and 1415 cm⁻¹ for (1) and 1603 cm⁻¹

and 1402 cm⁻¹ for (2) in the region typical of C—O stretching vibrations, as shown in Fig. 3S. For pure Hdetba, the ν (CO) bands are located at 1646 and 1521 cm⁻¹. Similarly to other compounds containing Detba⁻ ions, compounds (1) and (2) show the charge delocalization in the O=C—CH—C=O group (Table 1S, Fig. 1), and both C—O groups of Detba⁻ ion participate in the O—H···O(carbonyl) intermolecular hydrogen bonds (Fig. 3, Table 2S). This induces the shift of C—O stretching vibrations to shorter wavelengths. The medium intensity band at 1158 cm⁻¹ observed in the IR spectrum of Hdetba, which can be attributed to the ν (CS) vibration by analogy with H₂tba [35,36], is very weak in the IR spectra of the compounds (1) and (2) and it is located at 1161 cm⁻¹ in (1) and 1164 cm⁻¹ in (2). The C = S group of Detba⁻ ion practically does not participate in conjugation with the π -electron system of heterocyclic ligand [21,25–27]. However, the S atoms participate in O—H···S intermolecular hydrogen bonds (Fig. 3, Table 2S), which leads to a slight shift of the ν (CS) band vibration (on 3–6 cm⁻¹) and lower band intensity.

3.4. Thermal decomposition

Thermal decomposition of coordination compounds (1) and (2) in the air consists of several overlapped stages, and this complicated determination of the intermediate compound composition. Compound (1) begins to lose weight even at ~70 °C (Fig. 5a), IR spectroscopic analysis of released gaseous fractions showed that water molecules were removed during this stage (Fig. 5b). The dehydration process is associated with endoeffect at 104.8 °C. The value of experimental mass lost (Δm) at this stage well agrees to the loss of 4 water molecules (observed 12.8%; calculated 12.0%). The mass change over the temperature range of ~100–200 °C is insignificant. On further heating of compound (1) the continuous mass decrease occurs up to ~520 °C. The SO₂, CO₂, NH₃, isocyanate and H₂O gases released in the range of ~270–450 °C during oxidation of the Detba⁻ ion (Fig. 5c). The transformations over this temperature range are accompanied by a strong exothermal effect with the maximum at 312.7 °C. The penultimate thermal decomposition stage in the range of ~480–520 °C showed a drastic mass loss and an intense release of SO₂, CO₂, isocyanate and H₂O gases. This stage is accompanied by a strong exoeffect at 519.8 °C. Then, in the range of 520–700 °C, the mass is almost unchanged. However, under further heating, the mass is decreased by 3.6% additionally, and that can be explained by decomposition of partly formed CoSO₄, and this is consistent with a release of a small amount of SO₂. According to the XRD analysis of Co(H₂O)₂(HTBA)₂ [19], one can suppose

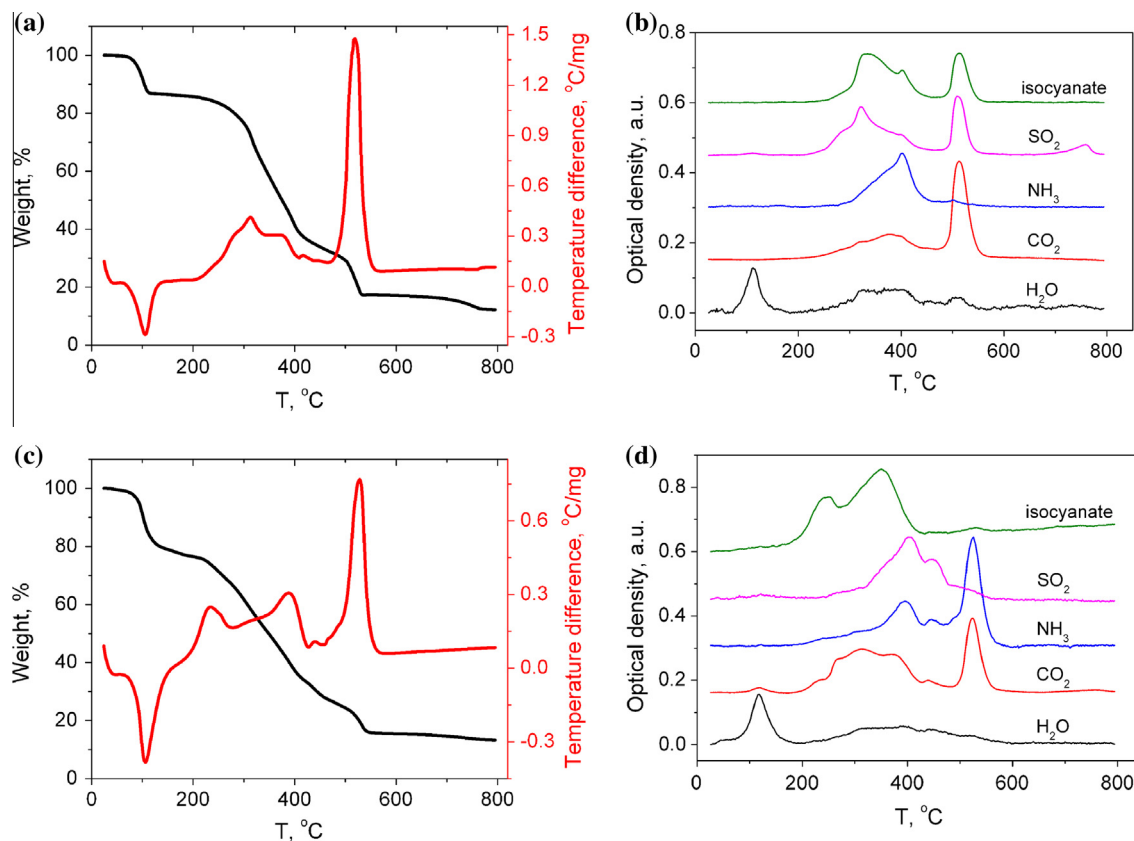


Fig. 5. TG и DSC curves of the thermal decomposition of (1) (a) and (2) (c). Gas evolution curves recorded during thermal decomposition (1) (b) and (2) (d).

that the final product for the oxidative decomposition of (1) is Co_3O_4 . At 795 °C, the theoretical values of Δm for Co_3O_4 formation is 86.7%. The observed mass loss in experiment is equal to 87.8%.

A noticeable weight loss by the thermal decomposition of (2) starts at ≈ 90 °C, as shown in Fig. 5c. Herewith, initially, the substance loses water (Fig. 5d). The dehydration process corresponds to a strong endothermic effect at 106.6 °C. Under heating up to ≈ 150 °C, the mass of the compound rapidly decreases ($\Delta m = 20.9\%$) and, then, the mass decrease is much slower up to ≈ 200 °C (Fig. 5c). The dehydration partly overlapped with a further stage of the Detba^- ion degradation by oxidation. The main gaseous product of the thermolysis below ≈ 190 °C is water, but a small amount of SO_2 was observed in parallel. The total mass loss at 190 °C is equal to 23.5%, that is consistent with the calculated value ($\Delta m = 24.0\%$) in case of losing all 8 molecules of coordinated and crystallized water in compound (2). In the range of 200–450 °C, the oxidative decomposition of organic component proceeds with a release of SO_2 , CO_2 , H_2O , NH_3 and isocyanate gases (Fig. 5d). The oxidation is accompanied by the exothermic effects on the DSC with the maxima at 233.3 °C and 389.1 °C. The sharp decrease of the mass is observed at ≈ 500 °C, which is mainly accompanied by a release of CO_2 and NH_3 . This stage corresponds to a strong exothermal effect with a maximum at 527.9 °C. In the range of ≈ 550 –800 °C, the mass is almost persistent. The total mass loss corresponds to the formation of NiO as the final decomposition product. The theoretical value of Δm for NiO formation is 87.6% and it is in excellent relation to the measured mass loss of 87.5%.

4. Conclusions

The reaction of HDetba with basic cobalt carbonate or basic nickel carbonate in water results in the formation of compounds

$[\text{M}(\text{H}_2\text{O})_6](\text{Detba})_2 \cdot 2\text{H}_2\text{O}$, M = Co (1), Ni (2). In the structures, the octahedral $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ions are linked through the $\text{O}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{S}$ intermolecular hydrogen bonds which are formed between the water and the outer-sphere Detba^- ions (Fig. 3, Table 2). Crystallization of (1) and (2), and the previously obtained $[\text{Ni}(\text{H}_2\text{O})_6](\text{Htba})_2 \cdot 4\text{H}_2\text{O}$ [19], which contains Htba^- anions in the second coordination sphere, let us assume that the formation of such compounds can be common for thiobarbituric acid derivatives. The structures of (1) and (2), contrary to HDetba and most their metal coordination compounds, are stabilized by the π - π interactions between the Detba^- rings (Fig. 4S, Table 2S). The introduction of the ethyl groups in the N,N'-position of H_2tba reduces the number of the intermolecular hydrogen bonds. Like in 1,3-diethyl-2-thiobarbiturate coordination compounds of alkali metals [25,26], Ag(I) [21], and Pb(II) [27], the Detba^- anion in (1) and (2) has short contacts $\text{C}-\text{H} \cdots \text{O}$ ($d(\text{C} \cdots \text{O}) = 2.644(3)-2.667(3)$ Å) and $\text{C}-\text{H} \cdots \text{S}$ ($d(\text{C} \cdots \text{S}) = 3.002(3)-3.018(3)$ Å), which can be attributed to weak intermolecular hydrogen bonds in accordance with conventional classification [49]. The thermal decomposition of (1) and (2) under oxidative conditions starts at a higher temperature than that in HDetba ($T > 112$ °C) [25,50], and it comprises the steps of dehydration and oxidation of the organic ligand with gases release and formation of oxides (Fig. 5).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2016.04.059>.

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