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Bis(μ_3 -barbiturato–O,O,O′)-(μ_2 -aqua)-aqua-barium(II): crystal structure, spectroscopic and thermal properties

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ABSTRACT

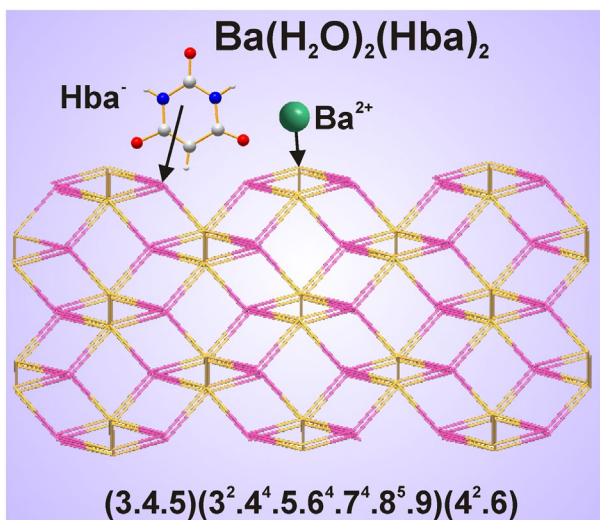
A polymeric coordination compound, $[\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2]$ (**1**) (H_2ba – barbituric acid, $\text{C}_4\text{H}_4\text{N}_2\text{O}_3$), was obtained. The structure of **1** was solved using powder X-ray diffraction methods. The Ba^{2+} ion in **1** formed a three-capped trigonal prism. The BaO_9 polyhedra, connected with each other by the edges and faces, formed a chain. Several 4- and 12-membered cycles due to the bridging μ_2 - H_2O and bridging μ_3 - Hba^- also formed implementing a 3-D polymer structure. The structures of **1** and other thiobarbiturate complexes were compared. The replacement of a S atom by an O atom in the heterocyclic ligand Htba^- (thiobarbiturate ion) of the compound $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ resulted in changes of the coordination number $\text{Ba}(\text{II})$ and supramolecular structure. The intermolecular hydrogen bonds $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ formed a 3-D net where pronounced 2-D layers of Hba^- ions could be found. A new topological net in **1** was observed. The IR and thermal stability were investigated.

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1. Introduction

Barbituric acid ($C_4H_4N_2O_3$, H_2ba) is a key compound of a wide class of drugs called barbiturates which are used in medicine as central nervous system depressants [1]. It contains three O atoms of carbonyl groups and two N amino groups, with their location being favorable for the formation of coordination polymers. Such polymers attract the attention of scientists due to their various topologies and their possible applications in catalysis, adsorption, and separation [2, 3]. Some barbituric acid coordination compounds with metals are considered to be prospective materials for nonlinear optics, and to have potentially useful biological activity, luminescence, and catalytic properties [4]. Despite the commercial value of metal-organic coordination polymers with alkaline earth metals [5], they are still not well investigated [6]. For example, the coordination compounds with barbituric acid [7], which would find practical application, are still not structurally characterized. The complexes of a barbital anion (5,5-diethylbarbiturate, Bar^-) with alkaline earth metals, for example, $[Ba_2H(Bar)_5]$, exhibit higher antibacterial activity against bacterial strains while barbital is not active [8]. A concept of trapping of radioactive barium ions from aqueous media based on a metal-organic framework was proposed [9]. Highly efficient detection of metal ions and nitroaromatic compounds is achieved using fluorescent barium metal-organic coordination polymers [10]. These factors make the synthesis of Ba(II) coordination polymers a strategic challenge.

The current study describes the synthesis, crystal structure, thermal decomposition, and IR spectra of a polymeric Ba(II) coordination compound with barbituric acid, $Ba(H_2O)_2(Hba)_2$.

2. Experimental

2.1. Reagents and synthesis

Barbituric acid with the purity >99%, $BaCO_3$, $BaCl_2$, and NaOH were commercially available from Aldrich and used without purification. H_2ba acid of 0.20 g (1.56 mmole) was mixed with 5-mL water and further with 0.154 g (0.78 mmole) $BaCO_3$, then the mixture was stored at 90 °C in an oven for 8 h to complete the reaction; the volume of the mixture was kept approximately constant (≈ 5 mL) by adding necessary amounts of water. The resulting colorless crystalline precipitate obtained after cooling to room temperature was isolated by filtration, washed with 2 mL of acetone, and dried in air to a constant weight. The obtained compound contained unidentified impurities; therefore, it was recrystallized from aqueous solution. For this purpose, the entire product (~ 0.3 g) was dissolved in excess water (100 mL) while heating to 90 °C until complete dissolution. The resulting solution was heated at 90 °C to evaporate the solvent. A white flocculent precipitate was formed with the volume of solution about 50 mL. After evaporation of water at 90 °C for 5 h to 20 mL, the solution was cooled to room temperature, the white precipitate was recovered by filtration, washed with 2 mL of acetone, and dried in air at room temperature to constant weight. Compound mass 0.241 g. The yield on H_2ba was 73%.

Compound **1** can also be prepared using well-soluble salts of Ba(II), for example, $BaCl_2$, instead of $BaCO_3$. To the mixture, 0.2 g (1.56 mmol) of H_2ba in 5 mL H_2O an equivalent amount of solid NaOH (0.062 g) was added. To this solution, 0.162 g (7.80 mmol) of $BaCl_2$ was added. The resulting white voluminous precipitate was recovered by filtration, washed with 2 mL of acetone, and dried in air to constant weight. The pH of the filtrate was 5. Further

recrystallization was carried out similarly to the above-mentioned method. Compound mass 0.234 g. The yield, based on H_2ba , was 70%.

Anal. Calcd for $C_8H_{10}BaN_4O_8$ (1): C, 22.5; H, 2.36; N, 13.1. Found: C, 22.8; H, 2.20; N, 13.4 (%). Yield = 70–80%.

2.2. X-ray diffraction analysis

The powder X-ray diffraction data were obtained using an X'pert PRO (PANalytical) diffractometer with a PIXcel detector equipped with a Ni filter. The measurements were made using $Cu K\alpha$ radiation. All peaks were indexed as triclinic cells and the space group $P-1$ was used as a starting group for the model. The structures were obtained using the FOX program [11] with the simulated annealing algorithm. Two Hba^- ions were treated as a rigid body whose position and orientation were optimized by the program. Good R-factors and reasonable coordination of a Ba^{2+} ion by the Hba^- ions were obtained. The refinement was performed using the program DDM [12]. The thermal parameters of C and N atoms of the Hba^- ions were the same during the refinement, the Ba^{2+} ion was refined using the anisotropic approach. All the hydrogen atoms of the Hba^- ligands were positioned geometrically, with the thermal parameters fixed at $U_{iso}(H) = 0.0507 \text{ \AA}^2$. The hydrogen atoms of the water molecules were found via Fourier difference maps and fixed during the refinement; their thermal parameters were also fixed at $U_{iso}(H) = 0.0760 \text{ \AA}^2$. The refinement was stable and gave low R-factors (table 1, figure 1). The atomic coordinates and the main bond lengths are listed in tables 1S and 2S, respectively. The structural tests for the presence of missing symmetry elements and possible voids were made using the PLATON program [13]. The DIAMOND program was used for plotting the crystal structure.

2.3. Physical measurements

The chemical analysis was carried out with a HCNS-0 EA 1112 Flash Elemental Analyser (Perkin-Elmer, England). The TGA characteristics were recorded with the simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under a dynamic air atmosphere at a 50 mL min^{-1} flow rate from 25 to $800 \text{ }^\circ\text{C}$, the scan rate being $10 \text{ }^\circ\text{C min}^{-1}$. The sample weight

Table 1. Main parameters of processing and refinement of $Ba(H_2O)_2(Hba)_2$.

Chemical formula	$C_8H_{10}BaN_4O_8$
Sp.Gr.	$P-1$
a (Å)	7.5017(3)
b (Å)	9.5304(12)
c (Å)	9.8090(6)
α (°)	65.533(5)
β (°)	74.971(4)
γ (°)	83.420(5)
V (Å ³)	616.46(9)
Z	2
2θ -interval (°)	9–100
Number of reflections	1277
Number of parameters of refinement	80
R_{wp} (%)	2.96
R_{exp} (%)	2.59
χ^2	1.14
R_B (%)	2.22

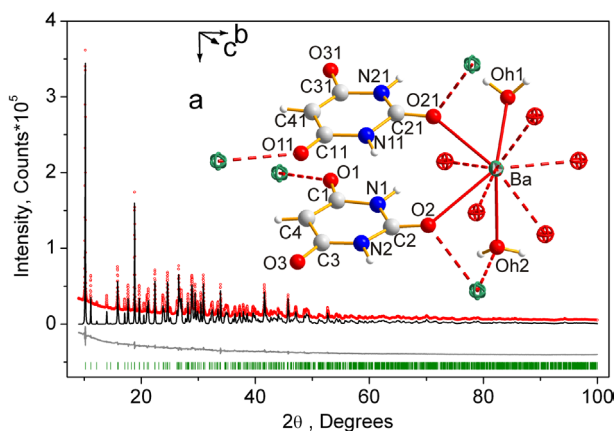


Figure 1. Difference DDM plot of $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$. Inset shows the asymmetric unit of the $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ unit cell. All atoms in the asymmetric unit are labeled. The directly neighboring symmetry-generated atoms are represented by principal ellipsoids with an individual color. The bonds linking asymmetric unit atoms with the symmetry-generated atoms are represented by dashed lines. The ellipsoids of Ba^{2+} ions are drawn at the 50% probability level.

was 5.81 mg. Platinum crucibles with perforated lids were used as the sample containers. The IR absorption spectra of the compounds were recorded from 400 to 4000 cm^{-1} at room temperature using 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 asymmetric unit of the $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ unit cell contains a Ba^{2+} ion, two Hba^- ions, and two H_2O molecules (figure 1). Barium(II) is surrounded by an O_9 donor set (figure 2(a)) in an approximate three-capped trigonal prism with the Ba–O distances ranging from 2.732(6) to 2.906(10) Å. The C–O bond lengths in $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ are 1.22(1)–1.29(1) Å (Table 2S) and it is seen that they slightly differ. The higher $d(\text{C}3\text{--O}3)$ and $d(\text{C}31\text{--O}31)$ values (1.28–1.29 Å) as compared with the smaller values of other $d(\text{C--O})$ lengths (1.22–1.27 Å) can be explained by the involvement of the O3, O31 atoms in three H-bonds (Table 3S).

One can see that $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ [14] has a similar content and structure (figure 2(b)), but Hba^- is replaced by Htba^- and both H_2O molecules are terminal instead of there being one terminal molecule and one μ_2 bridging molecule in the case of $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ (figure 2(a)). In particular, these differences lead to different coordination numbers (CN): CN = 9 and CN = 8 for the Ba^{2+} ions in $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ and $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$, respectively. It is interesting that $\text{Pb}(\text{H}_2\text{O})(\text{Htba})_2$ [15] (figure 2c) and $\text{K}(\text{H}_2\text{O})(\text{Htba})(\text{H}_2\text{tba})$ [16] (figure 2c) have very similar structures, and Pb^{2+} with the K^+ ions also have the coordination number CN = 8, but only one terminal H_2O molecule was observed in our case. Taking into account the single terminal H_2O molecule, the large coordination number in $\text{Pb}(\text{H}_2\text{O})(\text{Htba})_2$ and $\text{K}(\text{H}_2\text{O})(\text{Htba})(\text{H}_2\text{tba})$ can be explained by the fact that one Htba^- ion becomes a μ_4 -ligand instead of a μ_3 -ligand in the case of $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ with $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ (figure 2). Therefore, the Htba^- ions compensate for the absence of H_2O by additional coordination to the metal. It should

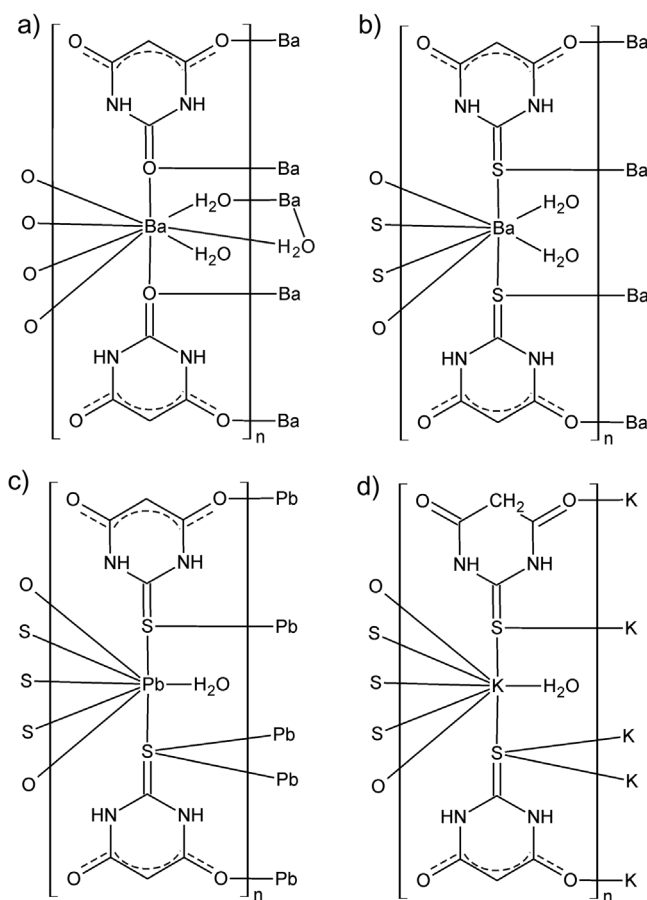


Figure 2. Schemes of (a) $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$; (b) $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$; (c) $\text{Pb}(\text{H}_2\text{O})(\text{Htba})_2$; (d) $\text{K}(\text{H}_2\text{O})(\text{Htba})(\text{H}_2\text{tba})$. Schemes (c) and (d) are similar in spite of different charges of Pb^{2+} and K^+ ions; scheme (b) violates similarity due to additional H_2O molecule and due to reducing connectivity of one Htba from μ_4 to μ_3 . Scheme (a) further violates similarity because one H_2O becomes μ_2 bridge instead of terminal.

be noted that changing $M = \text{Pb}^{2+}$ into $M = \text{K}^+$ with its markedly different ion radius IR (Pb^{2+} , CN = 8) = 1.29 Å, IR (K^+ , CN = 8) = 1.51 Å) and the charges does not lead to any noticeable changes of the structures and coordination numbers, but changing the formula $L = \text{Htba}^-$ to $L = \text{Hba}^-$ in $\text{Ba}(\text{H}_2\text{O})_2L_2$ leads to a pronounced change in the structures and CN. The observed distinctions may be related to the fact that the substitution of O to S increases the Htba ion size anisotropically, leading to qualitatively different effects on the structure organization compared to the isotropic change in the metal ion radii.

One can see that the Ba^{2+} ion forms a square antiprism in $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ [14], but the Ba^{2+} ion in $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ forms a three-capped trigonal prism (figure 3(a)). $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ shows several $r(4)$, $r(12)$ motifs due to the bridge $\mu_2\text{-H}_2\text{O}$ and bridge Hba^- (figure 3(b)) implementing a 3-D polymer structure, but $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ shows only $r(4)$ motifs formed by the bridge Htba^- and 1-D chains are formed only. Meanwhile, all the Htba^- ions are located in the parallel planes the same as the Hba^- ions (figure 3(a)). In addition, in $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ and $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$, the ligands are linked by hydrogen bonds and form chains. The chains

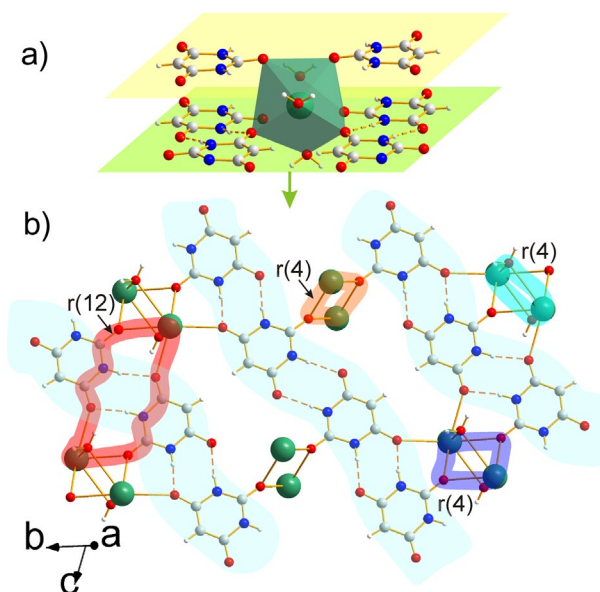


Figure 3. Six Hba^- ions and three H_2O molecules coordinate Ba^{2+} ion forming three-capped trigonal prism (a). All Hba^- ions lay in parallel planes (a); in these planes they are linked by hydrogen bonds forming chains (b). Chains, in turn, are linked with each other by Ba^{2+} ions and $r(4)$, $r(12)$ motifs can be seen (b). Hydrogen bonds are marked by dashed lines; main structural motifs are marked by solid broad lines.

are linked with each other through the Ba^{2+} ions (figure 3(b)) in both compounds. The BaO_9 polyhedra in $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ are linked with each other by edges and faces and they also form chains along the a -axis (figure 1S). Since the BaO_9 polyhedra are linked by the faces, it is interesting to compare the shortest distances $d(\text{M}\cdots\text{M})$ of $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ with other related compounds (table 2S) [14, 15, 17, 18]. One can see that $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ has the value of $d(\text{M}\cdots\text{M}) = 4.269(1)$ Å, which is intermediate as related to the range of 4.1092(6)–6.1141(4) Å of other compounds.

There are eight intermolecular hydrogen bonds in the structure $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$, four $\text{O}\cdots\text{H}$, and four $\text{N}\cdots\text{H}\cdots\text{O}$ which form a 3-D net where the pronounced 2-D layers of the Hba^- ions can be found (figure 2S, Table 3S). All the H atoms of all water molecules and all the H atoms of N–H groups of the Hba^- ions are involved in bonding with the formation of the structural motifs $S(6)$, $R_2^2(8)$, $R_4^2(8)$, $R_4^2(14)$ (figure 2S). The analysis of the π – π interactions between the Hba^- rings carried out using the program PLATON [13] did not reveal them because the shortest contact between the centers of the rings was 5.251(6) Å.

3.2. Topological analysis of $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$

Topological analysis of the 3D-networks in the compounds was implemented using the representation of the Hba^- ions and H_2O molecules in the form of spheres located in their centroids. The ToposPro program was used to make the structure simplification by the standard method [19] and, after the procedure, the 0,1,2-coordinated nodes were omitted. The

obtained networks were used to calculate the topological indices in ToposPro [19], which were further used to identify the nets and assignment to the topological type.

In $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$, the Ba^{2+} ions are linked by six Hba^- ligands, two H_2O bridge molecules, and one terminal H_2O ; both Hba^- ligands bridge three Ba^{2+} ions. The simplification and omission of the 0,1,2-coordinated nodes results in only three nodes: the (Ba^{2+}) node coordinated by a (Ba^{2+}) node and six (Hba^-) nodes, and the two different (Hba^-) nodes coordinated by three (Ba^{2+}) nodes. Consequently, $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ has a trinodal (3,3,7)-connected 3D-net with the point symbol $(3.4.5)(3^2.4^4.5.6^4.7^4.8^5.9)(4^2.6)$ which is a new topological net and, currently, it was added to the ToposPro database [19] and named **mol3** net. (figure 4(a)).

In $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$, the Ba^{2+} ion is linked by six Htba^- ligands and two terminal H_2O molecules. The Htba^- ligand bridges three Ba^{2+} ions. The simplification and omission of the 0,1,2-coordinated nodes results in only two nodes. Finally, $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$ has the binodal (3,6)-connected 3D-net with the point symbol $(4^2.6)_2(4^4.6^2.8^9)$ (figure 4(b)) and is called **flu-3,6-Pnma**. There are only six compounds having the same net topology. An apparently small difference between $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ and $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$, namely the existence/absence of the bridge H_2O , leads to a noticeable difference of the 3D-network topology. In addition, this small difference leads to a pronounced increase of the $\text{Ba} \cdots \text{Ba}$ contact (Table 4S), and it seems that these two compounds, in spite of the similar formula, are actually different.

Similar topological analysis for $\text{Ba}(\text{H}_2\text{O})_5(\text{Htba})_2$ reveals that it forms a 2D-net instead of a 3-D one. It is found that this net is a binodal (4,5) network with the point symbol $(3.4^3.5^2)(3^2.4^4.5^2.6^2)$ (figure 4c). This net is referred to as **4,5L28** and, currently, there are 61 compounds having the same net. The detected diversity of the net topology for the $\text{Ba}(\text{H}_2\text{O})_x\text{L}_2$ ($x = 2,5$; $\text{L} = \text{Hba}, \text{Htba}$) compounds is interesting. It shows bi- and trinodal nets, as well as 3-D and 2-D ones. The main reason for this diversity is the existence or absence of the bridging H_2O molecules.

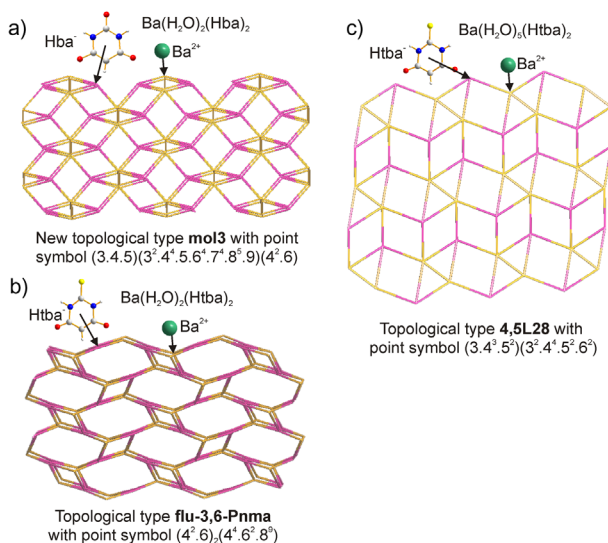


Figure 4. A schematic representation of the network topology: (a) $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$; (b) $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$; (c) $\text{Ba}(\text{H}_2\text{O})_5(\text{Htba})_2$.

3.3. IR spectroscopy

IR spectra of barbituric acid and **1** dispersed in KBr pellets were recorded from 4000 to 400 cm^{-1} as shown in figure 3S. The bands obtained for H_2ba (figure 3S, curve 1) are virtually identical to those reported earlier [20]. The following bands were observed in the IR absorption spectrum of **1**, as shown in figure 3S, curve 2 (cm^{-1}): 3392 m., 3254 w., 3115 w., 2906 m., 2802 m., 1692 vs., 1651 vs., 1505 w., 1405 m., 1362 s., 1295 s., 1212 w., 1109 vw., 1093 vw., 1010 vw., 873 w., 822 vw., 790 w., 769 w., 653 vw., 628 w., 545 s., 534 s., 431 w. (vs. – very strong, s. – strong, m. – medium, w. – weak, and vw. – very weak). The IR spectra of **1** drastically differ from those of H_2ba (figure 3S, curve 1). The broadband at 3392 cm^{-1} with a shoulder at ~ 3500 cm^{-1} in the IR spectra of **1**, which is absent in the H_2ba spectrum, corresponds to the $\nu(\text{OH})$ vibrations of the water molecules. The IR spectra of **1** have two very strong bands at 1692 cm^{-1} and 1651 cm^{-1} in the region typical of the C=O stretching vibrations, as shown in figure 3S, curve 2. For pure H_2ba , the $\nu(\text{C}=\text{O})$ strong bands are located at 1752 cm^{-1} ($\nu_s(\text{C}=\text{O}_{1,3})$), 1710 cm^{-1} ($\nu_{as}(\text{C}=\text{O}_{1,3})$), and 1695 cm^{-1} ($\nu_{as}(\text{C}=\text{O}_{1,3})$) [20]. The carbonyl absorption bands $\nu(\text{C}=\text{O})$ of H_2ba are shifted to lower frequencies from the spectra of **1**. The comparison of the frequencies $\nu(\text{C}=\text{O})$ in the complex compound and in the free ligand is usually used to analyze the coordination of ligand to ion metal through oxygen ions of carbonyl groups [21]. The noticeable shift of $\nu(\text{C}=\text{O})$ bands in the IR spectra of **1** to the low-frequency region, in comparison with H_2ba , is consistent with the coordination of Hba^- through O atoms.

3.4. Thermal decomposition

According to the TG curve (figure 4S), the initial weight reduction of **1** occurs in two apparently separate steps: at ~ 180 $^\circ\text{C}$ the weight loss amounts to $\sim 2.5\%$ (Δm) and at ~ 280 $^\circ\text{C}$ it is 3.8%. The weight loss is associated with two endothermic effects at 128.6 and 251.6 $^\circ\text{C}$. The sum value Δm at ~ 280 $^\circ\text{C}$ (6.3%) is consistent with the loss of $1.5\text{H}_2\text{O}$ ($\Delta m = 6.31\%$) per a formula unit **1**. It can be assumed that the terminal water is removed at the first stage of decomposition. The remaining water is removed only at ~ 350 $^\circ\text{C}$. The sum value Δm at ~ 350 (8.3%) is close to the calculated one given the assumption of the total dehydration of $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ (8.43%). Further temperature increasing leads to oxidation of the Hba^- ion, which is accompanied by exothermic effects with the maximum at 458.4 $^\circ\text{C}$ and shoulder at 491.8 $^\circ\text{C}$. The end-product of thermal decomposition at ~ 550 $^\circ\text{C}$ according to the chemical analysis and X-ray data is BaCO_3 . The total Δm at 550 $^\circ\text{C}$ is 53.8%, and the calculation value in the assumption of the BaCO_3 formation should be 53.9%.

4. Conclusion

As a result of the BaCO_3 neutralization of the aqueous solution of barbituric acid, the polymeric compound $\text{Ba}(\text{H}_2\text{O})_2(\text{Hba})_2$ (**1**) was obtained. The X-ray powder diffraction showed that one Ba^{2+} ion was linked by six Hba^- ligands, two bridging H_2O molecules, and one terminal H_2O ; both Hba^- ligands bridged three Ba^{2+} ions. Comparison of **1** with $\text{Ba}(\text{H}_2\text{O})_2(\text{Htba})_2$, which are close to each other in composition, reveals differences in the polyhedra form (three-capped trigonal prism and square antiprism, respectively) and a different supramolecular structure. As mentioned above, the crystal structures of the coordination compounds of barbituric acid with metals are not well studied [7]. It can be assumed that they would

have original topologies as in the case of **1**. Its new topology was added to the ToposPro database [19] and referred to as a **mol3** net. All the H atoms of all the water molecules and of the N–H groups of the Hba[−] ions are involved in intermolecular hydrogen bonds O–H···O and N–H···O with the formation of the 3-D net. The changes in the position of the carbonyl band of H₂ba in the IR spectra of **1** indicate that the carbonyl groups in Hba[−] are coordinated to the Ba²⁺ cation. The thermal decomposition of Ba(H₂O)₂(Hba)₂ in air starts with dehydration occurring in two stages at ~90–180 °C and ~200–280 °C. The end-product of the thermal decomposition is BaCO₃.

Supplementary data

The crystallographic data for the structural analysis has been deposited with Cambridge Crystallographic Data Center (**1**) - CCDC#1511478. 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, or www: www.ccdc.cam.ac.uk). Electronic supplementary information (ESI) is available on-line.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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