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INVESTIGATION OF THE PHYSICO-CHEMICAL PROPERTIES OF CUCURBIT[5]URIL USING IR SPECTROSCOPY AND THERMAL ANALYSIS

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ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ КУКУРБИТ[5]УРИЛА С ПОМОЩЬЮ ИК-СПЕКТРОСКОПИИ И ТЕРМИЧЕСКОГО АНАЛИЗА

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Аннотация. *В настоящей работе мы синтезировали смесь кукурбитурилов и выделили кукурбит[5]урил. Впервые написали о более глубоком физико-химическом анализе и распознавании кукурбит[5]урила. Синтезированный кукурбит[5]урил был охарактеризован методами ИК-Фурье и термогравиметрического анализа (ТГА). Впервые была исследована удельная теплоемкость CB[5].*

Abstract. We synthesized a mixture of cucurbiturils and isolated cucurbit[5]uril. Deeper physical and chemical analysis and recognition of cucurbit[5]uril reported for the first time. The synthesized cucurbit[5]uril was characterized by FTIR and thermogravimetric analysis (TGA). The specific heat capacity of CB[5] was investigated for the first time.

Introduction. CB[5] is the smallest macrocycle in the cucurbit[n]uril family. With its synthesis and isolation first reported by Kim and coworkers in 2000, it has a portal diameter of 2.4 A^0 and a cavity volume of 82 $Å^3$(which is under half the volume of CB[6]) [1]. The method of IR spectroscopy was used to study the results of a quantum-chemical study of the structure formation of water in the cavities of cucurbit[n]urils (CB[n]), n=5–8, obtained in the framework of the density functional theory [2]. IR spectroscopy helps to know the functional groups present in the sample from its stretching and bending frequencies. The Powder X-ray diffraction studies show sharp peaks in the molecule and the mixed ligand complexes with specific 2θ values, this indicates that crystallinity is maintained in the complexes [3].

Research methods. *Synthesis of CB[5].* The synthesis of a mixture of cucurbiturils was carried out in a three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser. For the synthesis, a weighed portion of 100 g of glycoluril and 142 ml of 37% hydrochloric acid was placed in a flask. The mixture was stirred until the glycoluril was completely dissolved, then 42.2 g of paraformaldehyde was placed in the flask. The mixture quickly gelled, the gel was held for 30 minutes and then heated to 100°C. The gel was dissolved, the solution was kept at 100°C for 24 hours. The resulting solution was evaporated under vacuum to

100 ml. To the resulting solution was added 800 ml of acetone. The solution was stirred for 24 hours. The dropped is CB[5]. The precipitate was filtered off and recrystallized from concentrated hydrochloric acid.

Fourier-transform infrared spectroscopy (FTIR). A Nicolet iS10 FT-IR Spectrometer was used to confirm the presence of certain functional groups and bonds in the structures of CB[5]. Analysis measurement conditions: KBr, number of scans – 32, resolution – 2.

Thermal analysis. TG and DSC measurements were carried out on a Perkin Elmer STA-6000 simultaneous thermal analyzer. The experiments were performed in the nitrogen and air flows (20 cm^3/min), at heating rates of 10°C min-1; the sample mass was kept ca. 12.0–16.0 mg.

Results. We obtained the following element data during elemental analysis of cucurbit[5]uril: w(C) = 43.37%, w(H) = 4.27%, w(N) = 36.45% and w(O) = 18.45%.

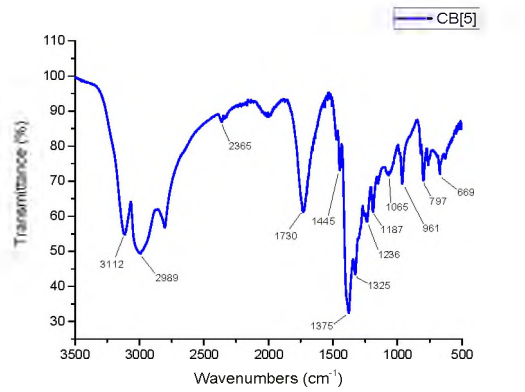

Fig. 1. IR spectrum of cucurbit[5]uril

The IR spectrum of CB[5] shows significant variation especially in 3000 cm^{-1} and between 1700 to 1200 cm^{-1} indicating prevalence of enhanced hydrogen bonding which are shown in Fig.1. In this spectrum a peak is seen at 3112 cm^{-1} which indicates the presence of CO-N bond, the C-N stretching gives a small absorption peak at 2989 cm^{-1}. The sharp peak at 1730 cm^{-1} indicates C=O stretching. In the spectrum, a peak at 2365 cm^{-1} is due to C-H stretching, and absorption peaks at 1375, 1325, 1236, 1187, 1065 cm^{-1} are due to C-N bonds. The peak at 961 cm^{-1} corresponds to the N-H bond, and at 1445 cm^{-1} to the CH_3 group. We found C-H bonds at 797 cm^{-1} and 669 cm^{-1}.

Table 1

Description of the peaks of cucurbit[5]uril in the IR spectrum

Peaks	Cucurbit[5]uril
3112	N-C=O bond
2989	C-N stretch
2365	C-H stretch
1730	C=O stretch
1445	–CH_3 methyl group
1375	C-N bond (amine)
1325	C-N bond (amine)
1236	C-N bond
1187	C-N bond
1065	C-H stretch
961	N-H bond
797	C-H bond
669	C-H bond

Thermal gravimetric analyses were applied to investigate the thermal stability of the free CB[5] (Fig. 2). A simultaneous TG analysis is performed with the same heating rate of 5°Cmin^{-1}. The profile of the thermogram from CB[5] shows the total decomposition of the structure at around 310°C. The thermal stability of the CB[5] in N_2 atmosphere is similar to the CB[5] in air; nevertheless, there occurred a small increase in the temperature of total decomposition of the structure. The onset of the main mass loss of CB[5] in nitrogen and air atmospheres begins at 180°C, and ends in nitrogen at 330°C, and in air at 337°C. Further, in both curves, it reaches the baseline and we see insignificant weight loss when heated to 950°C. Based on these data, we can conclude that cucurbit[5]uril behaves equally in an inert atmosphere and in the air. Based on the DSC data, we plotted curves to determine the specific heat capacity. According to the graph, we found the specific heat capacity of CB[5], in an inert nitrogen atmosphere Cp is 33.7 J/g°C and in air is 21.76 J/g°C.

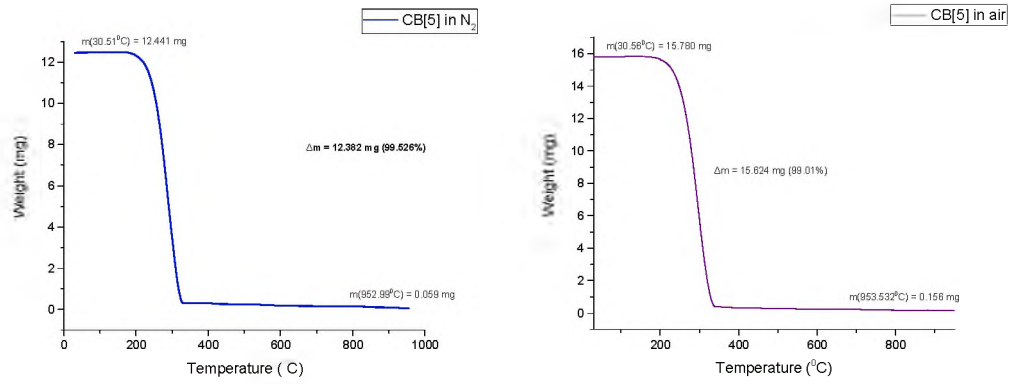

Fig. 2. TGA curves of cucurbit[5]uril: a) in N_2 atmosphere; b) in air

Conclusion. The IR spectrum of Cucurbit[5]uril shows the following peaks 3112 cm^{-1}, 2989 cm^{-1} to 2365 cm^{-1} and a sharp peak at 1730 cm^{-1} these frequencies indicate the presence of CO-N, C-H and C=O stretching respectively. In summary, the CB[5] have been successfully isolated and fully characterized. We are currently trying to isolate other CB homologues and optimize the separation and purification processes. The discovery and isolation of the cucurbituril homologues provides new opportunities in molecular recognition, separation, catalysis, and many other applications. We are actively working along this line.

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