SPECTROSCOPIC ANALYSES

OF Cu (II) COORDINATION POLYMER BASED ON 4-NITROPHENYLACETIC ACID

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Аннотация:

В присутствии 4-нитрофенилуксусной кислоты, паранитроанилина (ПНА), метанола, диметилформамида (ДМФ) и ацетата меди был синтезирован новый координационный полимер на основе Cu(II). Кристаллическая структура синтезированных 4-нитрофенилуксусной кислоты и ПНА была определена с помощью рентгеноструктурного анализа монокристаллов. В данной работе представлены результаты ИК-, ТГА и ДТА, а также рамановской спектроскопии. Полученные результаты подтверждают, что 4-нитрофенилуксусная кислота и ПНА являются перспективными многофункциональными материалами.

Ключевые слова:

4-нитрофенилуксусная кислота, паранитроанилин (ПНА), ацетат меди, диметилформамид (ДМФ).

Annotatsiya:

Cu(II) asosidagi yangi koordinatsion polimer 4-nitrofenilsirka kislotasi, paranitroanilin (PNA), metanol, dimetilformamid (DMF) va Mis atsetat ishtirokida sintez qilindi. Sintezlangan 4-nitrofenilsirka kislotasi va PNAning kristall tuzilmasi monokristalli rentgen difraksiyasi yordamida aniqlandi. Ushbu ishda TGA va DTA hamda Raman tahlillar keltirilgan. Olingan natijalar 4-nitrofenilsirka kislotasi hamda PNAning istiqbolli ko‘p funksiyali material ekanligini tasdiqlaydi.

Kalit so‘zlar:

4- nitrofenilsirka kislotasi, paranitroanilin (PNA), Mis atsetat, dimetilformamid (DMF).

Annotation:

A new coordination polymer based on Cu (II) was synthesized in the presence of 4-nitrophenyl acetic acid, paranitroaniline (PNA), methanol, dimethylformamide (DMF), and copper acetate. The crystalline structure of the synthesized 4-nitrophenyl acetic acid and PNA was determined using single-crystal X-ray diffraction. TGA and DTA, as well as Raman analyses, are presented in this work. The obtained results confirm that 4-nitrophenyl acetic acid and PNA are promising multifunctional materials.

Key words:

4-nitrophenyl acetic acid, paranitroaniline (PNA), copper acetate, dimethylformamide (DMF).

Introduction:

The results of the study of 4-nitrophenylacetic acid showed that the solubility of 4-nitrophenylacetic acid by mole fraction increases with increasing temperature and is arranged by solvents in the following sequence: DMF > methanol > ethanol[1]. 4-Nitrophenylacetic acid (4-NPAH) and its complex compounds with alkaline earth metal ions are currently of great scientific interest in terms of structure, spectroscopic and thermal properties.

It serves as an important theoretical basis for in-depth study of the crystal chemistry of metal complexes based on 4-nitrophenylacetic acid and the mechanisms of their molecular interactions[2]. Four new single-dimensional (1D) coordination polymers with the formula [M (4-npa) 2 (μ2-H2O) (H2O) 2]·2H2O were synthesized, and their spectral, thermal, magnetic, and structural properties were studied (where M = Mn (II), Co (II), Ni (II), and Cu (II); 4-npa-4-nitrophenyl acetate). The results of IR, thermogravimetric, and elemental analysis confirm the close proximity of the structure of the polycrystalline complex (4) to other 4-npa analogues. These results have important scientific significance in the study of the coordination geometry and supramolecular stability of metal complexes based on 4-nitrophenylacetic acid [3]. A new monoclinic polymorphic form of 4-nitrophenylacetic acid (C8H7NO4) has been identified, which differs from the previously known orthorhombic form by molecular conformation and types of intermolecular interactions. These structural differences provide an important scientific basis for a more in-depth study of the polymorphic properties of the 4-nitrophenylacetic acid crystal, their stability, and the nature of intermolecular bonds [4]. Creates an important scientific basis for in-depth study of the structural features of organometallic complexes based on 4-nitrophenylacetic acid and determination of the directions of their potential functional applications [5]. As a result of the interaction of 2,6-diaminopyridine as a donor and 4-nitrophenylacetic acid as an acceptor in a methanol medium at room temperature, a new hydrogen-bonded charge-conducting complex (CCD) was synthesized. The complex was described using elementary analysis, IR spectroscopy methods, and thermal analysis [6].

P-nitrophenylacetic acid, obtained by electrosynthesis, is an important intermediate product widely used in pharmaceuticals and organic synthesis and serves as the main raw material in the synthesis of biologically active compounds such as biphenyl acetic acid, aminosentrin, and nilapanib. In addition, p-nitrophenylacetic acid can be converted into p-aminophenylacetic and p-hydroxyphenylacetic acids through side reactions, which are of great importance in the production of pharmaceuticals and pesticides[7]. The new monoclinic form of 4-nitrophenylacetic acid (C8H7NO4) differs from the known orthorhombic polymorph in molecular conformation and intermolecular interactions. In the new form, the carboxylic acid group is located almost perpendicular to the plane of the aromatic ring[8]. Monocrystals of 4-nitrophenylhydrazone were grown by slow evaporation using an acetone solvent. The obtained crystals were comprehensively studied using X-ray diffraction, UV-visible spectral analysis, thermo-

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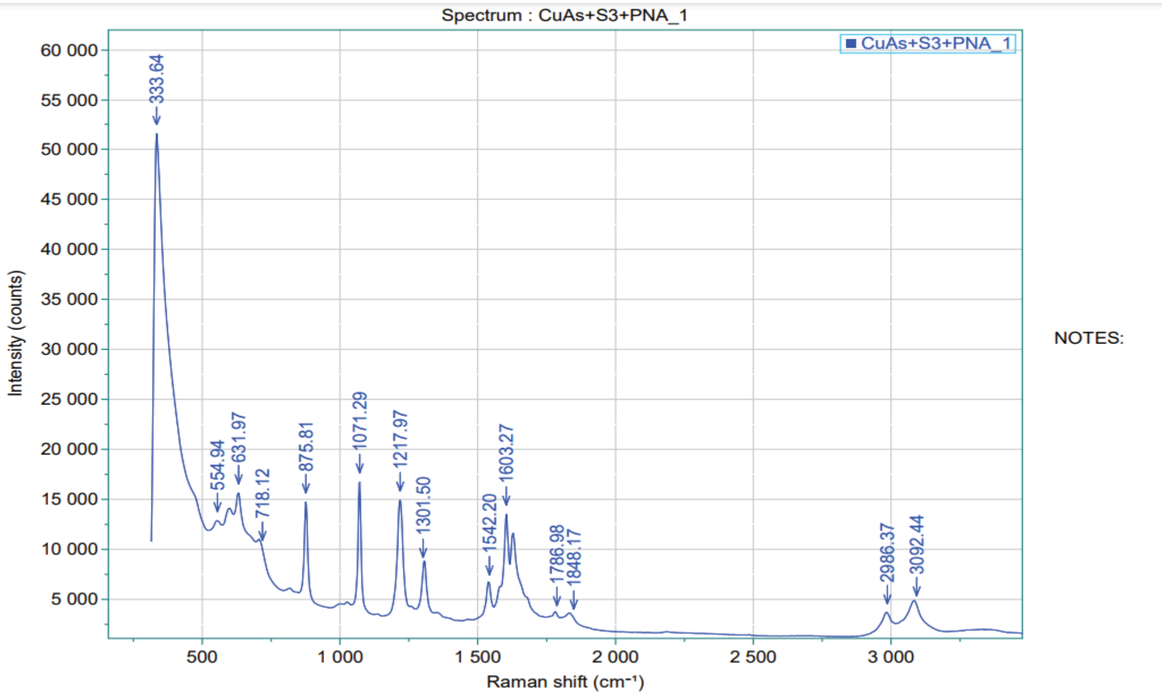

Figure 1. Raman spectrum of the Cu (II) coordination polymer based on 4-nitrophenyl acetic acid

gravimetric (TGA), differential thermal (DTA) analyses[9]. Cocrystals formed on the basis of 4-nitrophenylacetic acid in a 2:1 ratio are distinguished by their common supramolecular structural features. In these cocrystals, the formation of three-molecular aggregates is observed as a result of hydrogen bonds of the O-H···N (pyridyl) type, which indicates the stability of supramolecular synthesis[10].

Synthesis of a Coordination Polymer:

Copper (II) acetate dihydrate (Cu (CH3COO) 2·H2O), 4-nitrophenyl acetic acid, and paranitroaniline (PNA) were used as starting materials in the synthesis of the complex compound. Initially, 0.199 g (1 mmol) of Cu (CH3COO) 2·H2O was dissolved in 10 ml of water. In another vessel, 0.362 g (2 mmol) of 4-nitrophenyl acetic acid was dissolved in 20 ml of water. In another vessel, 0.276 g (2 mmol) of paranitroaniline (PNA) was dissolved in 20 ml of water.

When all three solutions were ready, a solution of 4-nitrophenyl acetic acid was added sequentially to a solution of Cu (II) acetate, and then to a solution of paranitroaniline (PNA). Then the solution was kept in a thermostat at 60°C for 15 days. During this process, crystals separated from the solution. After crystallization, the resulting substance was filtered and washed several times with cold distilled water and ethanol. The purified crystals were dried in a drying oven at 50°C for 8 hours. As a result, the yield of the coordination compound formed on the basis of Cu (II) was approximately 75%.

Results and Discussion:

The composition and properties of the synthesized coordination polymer were studied using modern physicochemical analysis methods. Raman spectroscopy is based on the study of scattered light, while IR spectroscopy is based on the absorption of light. Raman spectroscopy, like IR spectroscopy, analyzed the IR spectra of samples located in the region from 4000 cm-1 to 400 cm-1 to determine what type of bond exists and what class the samples belong to. The absorption spectral lines of the obtained new coordination polymer were determined.

The Raman spectrum obtained as a result of the coordination polymer of 4-nitrophenyl acetic acid with copper (II) acetate crystal hydrate and paranitroaniline is shown in Figure 1, according to which the valence vibration frequency of the -C=C bond is in the region of 1603.27 cm-1, the valence vibration frequency of the -OH bond is in the region of 3092.44 cm-1, and the deformation vibration frequency of the -OH bond is in the region of 1301.50 cm-1.

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Table-1

Absorption frequencies (cm-1) in the Raman spectra of the coordination polymer formed by 4-nitrophenyl acetic acid with copper (II) acetate crystalline hydrate and paranitroaniline

Vibration classifications	4-nitrophenyl acetic acid, copper (II) acetate crystal hydrate and paranitroaniline	
ν(C=C)	1616.35	sm^{-1}
ν(OH)	3381.21	
δ(OH)	1313.52	

The thermal stability of the coordination compound synthesized with 4-nitrophenyl acetic acid and p-nitroaniline ligands based on Cu (II) ions was studied using the TGA and DTA methods. The thermogram results show that the decomposition of the complex compound occurs in several stages.According to the TGA curve, the first phase of mass loss is observed in the temperature range of 18.48-235.68 °C, with a mass loss of 0.657 mg (34.76%). This process is explained by the separation of adsorbed or coordinated water molecules present in the crystal lattice and the release of some low molecular weight fragments. On the DTA curve, a distinct thermal effect corresponding to this process is observed, the maximum point of which is recorded at 235.62°C. The initial temperature of the thermal effect is 224.41 °C, the final temperature is 240.39 °C, and a thermal effect of 148.08 J/g was determined for the process. These values indicate that the complex compound undergoes structural changes in this temperature range.The second stage occurs in the temperature range of 237.82-742.95 °C, where a mass loss of 0.399 mg (21.11%) is observed. At this stage, the decomposition of organic ligands in the complex - molecules of 4-nitrophenyl acetic acid and p-nitroaniline occurs. At high temperatures, oxidation of the metal center can result in the formation of CuO or other thermally stable residue.

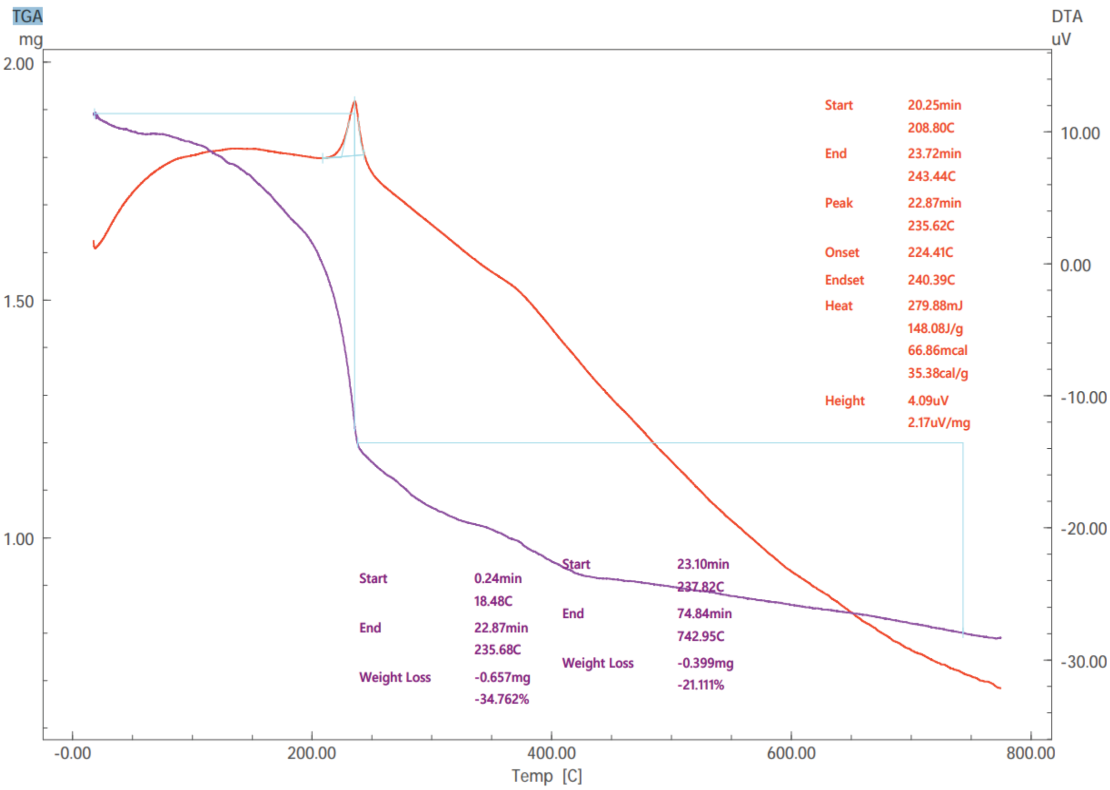

Figure 2. Derivatogram of the Cu (II) coordination polymer based on 4-nitrophenyl acetic acid

Table-2

Thermal decomposition stages of the Cu (II) -4-nitrophenylacetic acid-p-nitroaniline complex

Phase	Temperature range (°C)	Mass loss (mg)	Mass loss (%)
I Phase	18.48 – 235.68	0.657	34.76
II Phase	237.82 – 742.95	0.399	21.11
Balance	>742	–	–

Table-3

Mass change of the complex according to TGA results

Phase	Starting weight (mg)	Lost mass (mg)	Remaining mass (mg)	Weight loss (%)
Beginner	1.89	–	1.89	–
I Phase	1.89	0.657	1.233	34.76
II Phase	1.233	0.399	0.834	21.11
Final balance	–	–	0.834	44.13

Conclusion.

The properties of the complex compound synthesized on the basis of 4-nitrophenyl acetic acid as a result of the coordination polymer reaction were studied. The properties of the synthesized coordination polymer and its complexes with copper (II) acetate were studied by TGA and DTA, Raman spectroscopic methods using modern physicochemical analysis methods. The results of TGA and DTA, Raman spectroscopy were analyzed and presented in accordance with the table. The tables show the absorption frequencies corresponding to the groups in 4-nitrophenyl acetic acid and its complexes with copper (II) acetate.