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PYRIDINE-CONTAINING METAL-ORGANIC COORDINATION POLYMERS: SYNTHESIS AND PROPERTIES

The article presents the results of our research on the synthesis of pyridine-containing coordination polymers based on zinc and copper. At the moment, metal-organic coordination polymers are considered one of the most interesting and rapidly developing areas of organic chemistry. This determines their use in petrochemistry, pharmaceuticals, construction and much more. The introduction presents a literature review on the methods of synthesis of metal-organic coordination polymers, their structure and the main pyridine ligands used. The structure of a known polymer based on pyridine-3,5-dicarboxylic acid and europium is presented.

The materials and methods describe the reagents used and the synthesis techniques. The discussion results present data on the obtained metal-organic polymers based on pyridine-2,6-dicarboxylic acid, and provide photographs of the polymer crystals obtained using a light microscope. The absorption spectra of the synthesized polymers were recorded in comparison with pyridine-2,6-dicarboxylic acid. It was shown that the absorption spectra of the initial acid and the obtained polymers exhibit a hypochromic effect of the carboxyl group signal, indicating the formation of a polymer. The polymer obtained on the basis of copper has a more ordered structure, gives a higher yield of the product and better strength properties in contrast to the zinc polymer.

Key words: metal-organic polymers, pyridine, solvent evaporation, dicarboxylic acid, ligand.

Introduction

Organometallic coordination polymers are compounds consisting of metal ions or clusters linked together by rigid organic molecules to form one-, two- or three-dimensional structures that must also be porous [1]. In general, the structural design of organometallic coordination polymers is a simple approach known as building block methodology [1]. Organometallic polymers have great potential for further industrial applications.

Synthesis of organometallic coordination polymers is carried out by solvothermal, ionothermal, diffusion, microwave methods, synthesis using ultrasound, directed at the matrix, and others [2]. One of the most common and simple methods for obtaining polymers is the solvent evaporation method. In this method, the organic ligand and inorganic component are dissolved in a mixture of an organic solvent and water [3].

MOFs contain organic and inorganic components. The organic units (linkers/bridging ligands) are composed of carboxylates or anions such as phosphonate, sulfonate, and heterocyclic compounds [4]. The inorganic units are metal ions or clusters. Their geometry is determined by the coordination number, coordination geometry of metal ions, and the nature of the functional groups [5]. The pore size can be tuned and the spatial arrangement of the cavities can be controlled by a judicious choice of metal centers and organic ligands, as well as by adjusting the conditions of their synthesis. Their high porosity allows them to be used in adsorption and separation of gaseous molecules, catalysis, microelectronics, optics, sensor applications, bioreactors, drug delivery, and others [6]. Figure 1 alone shows several possible pyridine-based organic ligands such as pyridine-2,3-dicarboxylate and pyridine-2,6-dicarboxylic acid [7].

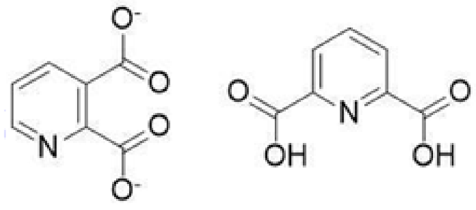

Figure 1 – Pyridine-based organic ligands

It is worth considering in more detail the structure of MOFs with pyridine ligands, since pyridine can have substituents in 3 positions and depending on their location, the structure and shape of the MOFs will change [8]. Figure 2 shows a Eu(III) complex in which the linker was pyridine-3,5-dicarboxylic acid [9].

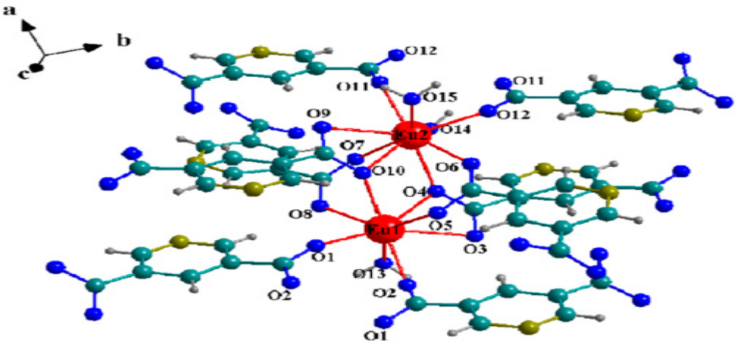

Figure 2 – Spatial model of the Eu(III) polymer

This structure shows that the bond between the metal and the ligand is formed by the oxygen atoms that are part of the carboxylic acid.

Material and methods

Reagents used in the synthesis: pyridine-2,6-dicarboxylic acid – a product of Sigma-Aldrich. Zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$, copper nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ (chemically pure).

In this experiment, to obtain polymers, an organic ligand in the form of pyridine-2,6-dicarboxylic acid and an inorganic component, zinc nitrate hexahydrate, as well as copper nitrate trihydrate, were dissolved in a mixture of ethanol and water.

Preparation of zinc-MOF: 0.2 mmol (0.024 g) of pyridine-2,6-dicarboxylic acid was dissolved in 12.5 ml of aqueous solution (H2O and C_2H_5OH in a ratio of 1.5:1), after which 0.05 mmol (0.0148 g) of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ was added. The contents were dispersed in an ultrasonic bath GA008G (GRANBO, China) for 1 minute. The solution was left at room temperature for 6 days to evaporate the solvent. The yield was 52 %.

Preparation of copper-MOF: the preparation of copper polymer was carried out by the same method as the preparation of zinc. 0.2 mmol (0.024 g) of pyridine-2,6-dicarboxylic acid was dissolved in 12.5 ml of aqueous solution (H_2O and C_2H_5OH in a ratio of 1.5:1), after which 0.05 mmol (0.0121 g) of copper nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ was added, dispersed in an ultrasonic bath for 1 minute and left for complete evaporation of the solvent for 4 days. The yield was 53 %.

Results and discussion

Despite the variety of methods for synthesizing MOFs, as a rule, only the solvent evaporation synthesis method allows obtaining a polymer in a crystalline state, which allows further study of its structure by X-ray structural analysis. This technique shows a good yield of polymers and practicality [10].

The polymer yield averaged about 50 %. Scaling the process allows obtaining a product with a higher yield, which is associated with the acceleration of the crystallization process. The obtained polymers were examined under a microscope, Figure 4. A study of the polymer structures under a microscope showed that the Cu-MOF crystal shape corresponds to the orthorhombic syngony, in which the unit cell is determined by three perpendicular, but not equal to each other, base vectors. A similar structure was found in the polymer obtained by solvent evaporation [10]. Zn-MOF has a monoclinic structure, which corresponds to three vectors of different lengths, forming two right angles and one angle greater than 90. The polymer obtained in work [10], also by solvent evaporation, had the same structure.

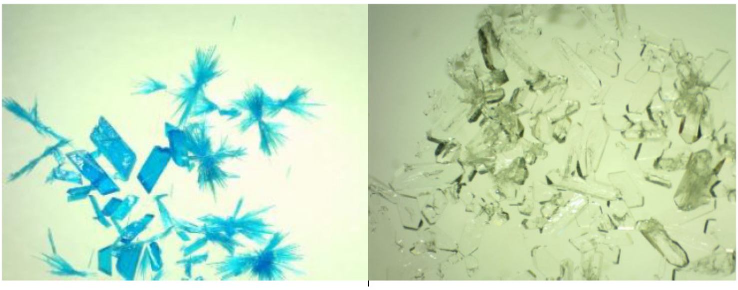

Figure 4 – Copper-zinc MOFs under a microscope with illumination from below

MOFs obtained from copper have a characteristic bluish color, while zinc polymers are colorless.

The absorption spectra of the obtained polymers and pyridine-2,6-dicarboxylic acid were studied using a CM 2203 spectrofluorimeter (SOLAR, Russia).

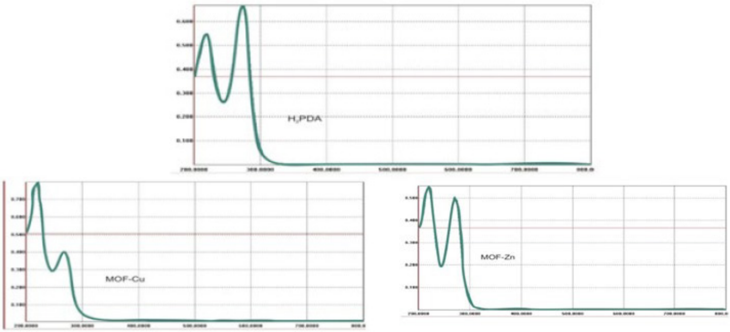

Figure 5 – Spectra of polymers and organic ligand

In the absorption spectrum of pyridine-2,6-dicarboxylic acid, two absorption maxima are observed in the region of 220 and 275 nm, which indicates the aromaticity of the acid structure and the formation of carboxylate anions, respectively (Figure 5). In the absorption spectra of Cu-MOF and Zn-MOF, the presence of an aromatic structure is confirmed by the retention of the absorption maximum at 220 nm. In this case, the second absorption maximum in the case of polymers is subject to a hypochromic effect and a hypsochromic shift by 270 nm.

Conclusion

Organometallic coordination polymers have become an integral part of modern science and technology due to their unlimited variations in structural construction, which is an amazing opportunity to create a new layer of functional materials with desired properties. Over time, improving synthesis techniques, as well as more extensive research in this direction, will open new boundaries for the use of metal-organic coordination polymers. In this article on MOCPs, a new method for obtaining polymers based on pyridine-2,6-dicarboxylic acid was proposed, and the main characteristics of the obtained polymers with metal centers from zinc and copper were studied based on micrographs and absorption spectra. It was shown that the obtained structures completely coincide with the known literature data. This study was carried out with the financial support of Ministry of Science and Higher Education of the Republic of Kazakhstan, project AP 08856049

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МЕТАЛДЫҚ – ОРГАНИКАЛЫҚ КОРДИНАЦИЯЛЫҚ ПОЛИМЕРЛЕР: СИНТЕЗІ ЖӘНЕ ҚАСИЕТТЕРІ

Жұмыста мырыш пен мыс негізінде пиридин бар координациялық полимерлердің синтезі бойынша өзіміздің зерттеулеріміздің нәтижелері берілген. Қазіргі уақытта металл-органикалық координациялық полимерлер органикалық химияның ең қызықты және тез дамып келе жатқан салаларының бірі болып саналады. Бұл оларды мұнай химиясында, фармацевтикада, құрылыста және т.б. пайдалануға әкеледі. Кіріспеде металл-органикалық координациялық полимерлерді синтездеу әдістері, олардың құрылымы және қолданылатын негізгі пиридин лигандтары туралы әдебиеттерге шолу берілген. Пиридин-3,5-дикарбин қышқылы мен еуропий негізіндегі белгілі полимердің құрылымы берілген.

Материалдар мен әдістер қолданылатын реагенттер мен синтез процедураларын сипаттайды. Талқылау нәтижелері пиридин-2,6-дикарбон қышқылы негізінде алынған металл-органикалық полимерлер туралы мәліметтерді және жарық микроскопынан алынған полимер кристалдарының фотосуреттерін ұсынады. Синтезделген полимерлер үшін абсорбциялық спектрлер жазылып, пиридин-2,6-дикарбон қышқылымен салыстырылды. Бастапқы қышқылдың және алынған полимерлердің абсорбциялық спектрлерінде полимердің түзілуін көрсететін карбоксил тобының сигналының гипохромды әсері байқалатыны көрсетілген. Мыс негізіндегі полимер негұрлым реттелген құрылымға ие, мырыш полимерінен айырмашылыгы жогары өнім шыгымдылыгын және жақсы беріктік қасиеттерін береді.

Кілтті сөздер: металл-органикалық полимерлер, пиридин, еріткіштің булануы, дикарбон қышқылы, лиганд.

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ПИРИДИНСОДЕРЖАЩИЕ МЕТАЛЛ-ОРГАНИЧЕСКИЕ КООРДИНАЦИОННЫЕ ПОЛИМЕРЫ: СИНТЕЗ И СВОЙСТВА

В работе представлены результаты собственных исследований по синтезу пиридинсодержащих координационных полимеров на основе цинка и меди. На данный момент металл-органические координационные полимеры, считаются одним из самых занимательных и быстро развивающихся направлений органической химии. Это обуславливает их использование в нефтехимии, фармацевтике, строительстве и многое другое. Во введении представлен литературный обзор по методам синтеза металл-органических координационных полимеров, их структуре и основным используемым пиридиновым лигандам. Представлена структура известного полимера на основе пиридин-3,5-дикарбновой кислоты и европия.

В материалах и методах описаны используемые реактивы и методики синтеза. В результатах обсуждения представлены данные о полученных металл-органических полимерах на основе пиридин-2,6-дикарбоновой кислоты, приведены фотографии кристаллов полимера, полученных со светового микроскопа. Для синтезированных полимеров сняты спектры поглощения с сравнении с пиридин-2,6-дикарбоновой кислотой. Показано, что в спектрах поглощения исходной кислоты и полученных полимеров наблюдается гипохромный эффект сигнала карбоксильной группы, что свидетельствует об образовании полимера. Полимер, полученный на основе меди, обладает более упорядоченной структурой, дает больший выход продукта и лучшими прочностными свойствами в отличии от цинкового полимера.

Ключевые слова: металлоорганические полимеры, пиридин, испарение растворителя, дикарбоновая кислота, лиганд.

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