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SYNTHESIS OF MONOMER COMPOUNDS BASED ON ACRYLAMIDE

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Introduction. The authors synthesized nickel(II) salts with unsaturated monocarboxylic acids: acrylic, methacrylic, sorbic, 4-pentic, propiolic, crotonic, linoleic, and oleic acids, studied their thermal properties, and synthesized nickel-containing nanocomposites by controlled thermolysis of the resulting carboxylates [1,6]. Vinyl porphyrin complexes of palladium and cobalt have also been synthesized [7].

In recent years, the attention of many researchers has been attracted by metal chelate monomers (MCM), whose characteristic features are the presence of unsaturated bonds and a metal chelate cycle for obtaining polymers and copolymers with desired properties [8,9].

Chlorine-containing compounds of anthranilamide with cobalt, nickel, and copper were obtained in an ethanol solution [10]. Using elemental analysis, vibrational and electronic spectra, it was shown that the synthesized solid compounds have an octahedral structure.

The authors synthesized metal complexes of manganese(II), iron(II), and nickel(II) chlorides with acrylamide [11]. It is shown that in all three complexes the coordination geometries of the metal centers include tetragonally distorted octahedral structures with four O-donor acrylamide atoms bound in equatorial and two chloride ligands. This paper presents a review of the literature on the coordination chemistry of acrylamide with various transition metals [12]. A general review of the structure and possible ways of coordinating acrylamide is discussed and data are given on the synthesis and structure of nitrate and chloride complexes of acrylamide coordinating exclusively through carbonyl oxygen [Co(AAm)₄(H₂O)₂](NO₃)₂, [Cu(AAm)₄(NO₃)₂], [Co(AAm)₄Cl₂], and [Co(AAm)₆][CoCl₄].

The authors synthesized acrylamide complexes of cobalt: blue dichlorotetrakis(acrylamide)cobalt(II) (1) and pink

(acrylamide)cobalt(II) tetrachlorocobaltate (2) [13]. They found that the coordination of CoII in 1 includes a tetragonally distorted octahedral structure with four O-donor acrylamide atoms in equatorial positions and two chloride ions in apical positions. The second complex 2 in ionic form contains Co⁺² cations surrounded by an octahedral array of O-coordinated acrylamide ligands. In other works, the authors present the results of the synthesis, spectroscopy, and single-crystal X-ray structure of the acrylamide ligand N-pyrazolylpropanamide and its complexes with copper(II) and cobalt(II) chlorides [14]. The work presents comparative data of the crystal structure of acrylamide and complexes of acrylamide with metals formed with divalent transition metal chlorides [15]. Also, the authors determined the structure of the synthesized acrylamide complexes of metal nitrates using single-crystal X-ray diffraction analysis [16]. It has been established that all synthesized complexes crystallize in the triclinic space group.

As can be seen, acrylamide has a high complexing ability and is an interesting type of ligand containing three donor atoms: the nitrogen atom of the amide group, the double bond between the carbon atoms and the oxygen of the carboxyl group.

The aim of this work is the targeted synthesis and study of the composition and structure of a metal-containing monomer without chloride ions with a MO-bond of the donor-acceptor type based on acrylamide with copper.

Discussion. A molecular complex compound based on acrylamide with copper chloride was synthesized at a reagent ratio of 4:1.

The structure and composition of the resulting complex compound were confirmed by IR spectroscopy and elemental analysis (fig. 1,2).

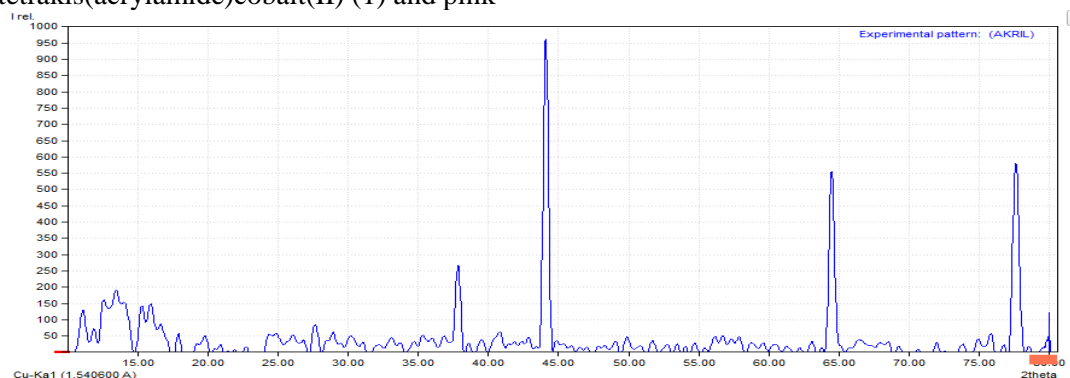


Fig.1. Elemental composition of a monomeric complex compound based on acrylamide and copper(II)

The synthesized complex compound of copper chloride with acrylamide is an air-stable green crystal having the following composition:

Found (%): C - 41.10; H - 6.71; O - 18.12; Cu - 18.11; N-15.80;

Calculated (%): C- 41.00; H - 6.81; O -18.20; Cu-18.17; N-15.90

The structure of the synthesized complex compound was established by the IR spectroscopic method from the shift of the characteristic absorption bands of acrylamide [17].

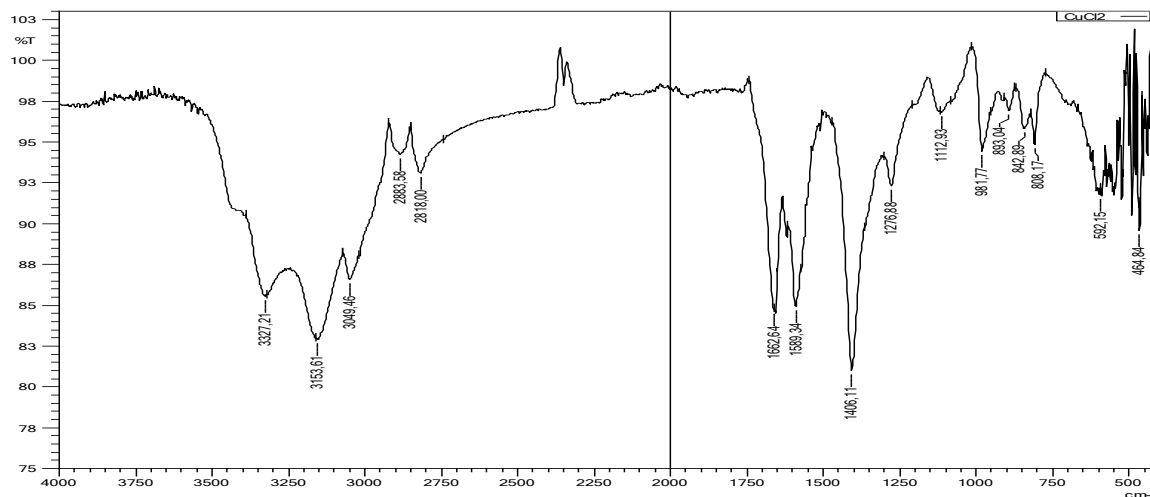


Fig.2. IR spectrum of a monomeric complex compound based on acrylamide and copper(II)

By comparing the IR spectra of free acrylamide and the complex compound, it was found that the strong broad band observed at 1673 cm^{-1} in free acrylamide shifted during complexation to lower frequencies at 1662 cm^{-1} (fig. 2). The absorption band of free acrylamide at 1614 cm^{-1} shifted in the IR spectrum of the complex compound to lower wave numbers at 1599 cm^{-1} . The absorption band of the NH_2 group at 1138 cm^{-1} in free acrylamide shifted to 1112 cm^{-1} ; $\text{C}=\text{C}$ absorption bands in the region of 981 cm^{-1} and 1276 cm^{-1} , characteristic of the region of out-of-plane bending vibrations $=\text{CH}$, and $\text{C}=\text{C}$ stretching vibration bands in the region of 1589 cm^{-1} show the preservation of double bonds. The results of IR spectroscopy show that the acrylamide ligands are bound to the complexing agent through the oxygen atoms of the carbonyl groups.

The results obtained show that the acrylamide ligands are bound to the complexing agent through the oxygen atoms of the carbonyl groups.

Also, the structure of the monomeric complex compound based on acrylamide and copper(II) was studied by ^{13}C NMR and ^1H PMR spectroscopy (fig. 3,4). It is known that, due to the presence of an unpaired electron, the copper(II) cation has paramagnetic properties [28]. It can be seen that in the ^{13}C NMR spectra of solutions of copper(II) ions with acrylamide and a number of carbon signals with shifts from 35 to 180 ppm are observed. Broadened signals corresponding to carbon atoms of carboxyl groups are in the region of 180 ppm. Such a shift and broadening of the signal of the carbon atom suggests participation in the donor-acceptor coordination of the carboxyl groups of acrylamide with copper (II) ions.

In the ^1H NMR spectrum of a solution of acrylamide and copper(II) in a molar ratio of 4:1, a chemical shift of the signals of the hydrogen atoms of the methylene groups is observed in the range of 3.5–3.6 ppm. and broadening of these signals (Fig. 4). This phenomenon confirms the assumption that acrylamide carboxyl groups are involved in the coordination.

Also, the structure of the synthesized compound was studied by X-ray diffraction analysis (XRD) (table-1, Fig. 5).

According to X-ray diffraction data, in the crystal lattice of the complex compound based on acrylamide and copper(II), coordination of oxygen atoms $-\text{C}=\text{O}$ of acrylamide fragments to the metal center is observed; one copper atom in the complex is bonded to four acrylamide molecules, and the coordination geometries of metal centers have a tetragonal structure with four O-donor acrylamide atoms [29–31]. It can be seen that the carbonyl groups of acrylamide c are bound to the copper atom and the double bond is not involved in the coordination (Fig. 5).

Conclusion. Monomeric complex compounds based on acrylamide and Cu (II) were synthesized at a ratio of 4:1. The composition and structure of the synthesized monomers were established using elemental analysis, IR spectroscopy, and X-ray diffraction analysis.

It is shown that the complex compound based on acrylamide and copper has a high degree of crystallinity, consists of 12,63% amorphous and 87,37% crystalline structure.

X-ray diffraction analysis has shown that in the crystal lattice of the complex compound based on acrylamide and copper(II) the coordination of oxygen atoms $-C=O$ of acrylamide fragments to the metal

center is observed; tetra dentate coordination of copper with acrylamide and O-chelation due to donor-acceptor bonds of the carbonyl group with the formation of $[C_{12}H_{24}N_4O_4Cu]$ were identified.

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Key words: monomer, acrylamide, copper chloride, complex salts, coordination, carbonyl group.

Monomeric complex compounds based on acrylamide and copper chlorides have been synthesized. The reaction of interaction of acrylamide with copper chloride was carried out by heating in solutions, followed by washing and drying of the precipitated crystalline precipitates of monomeric salts. It has been established that

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