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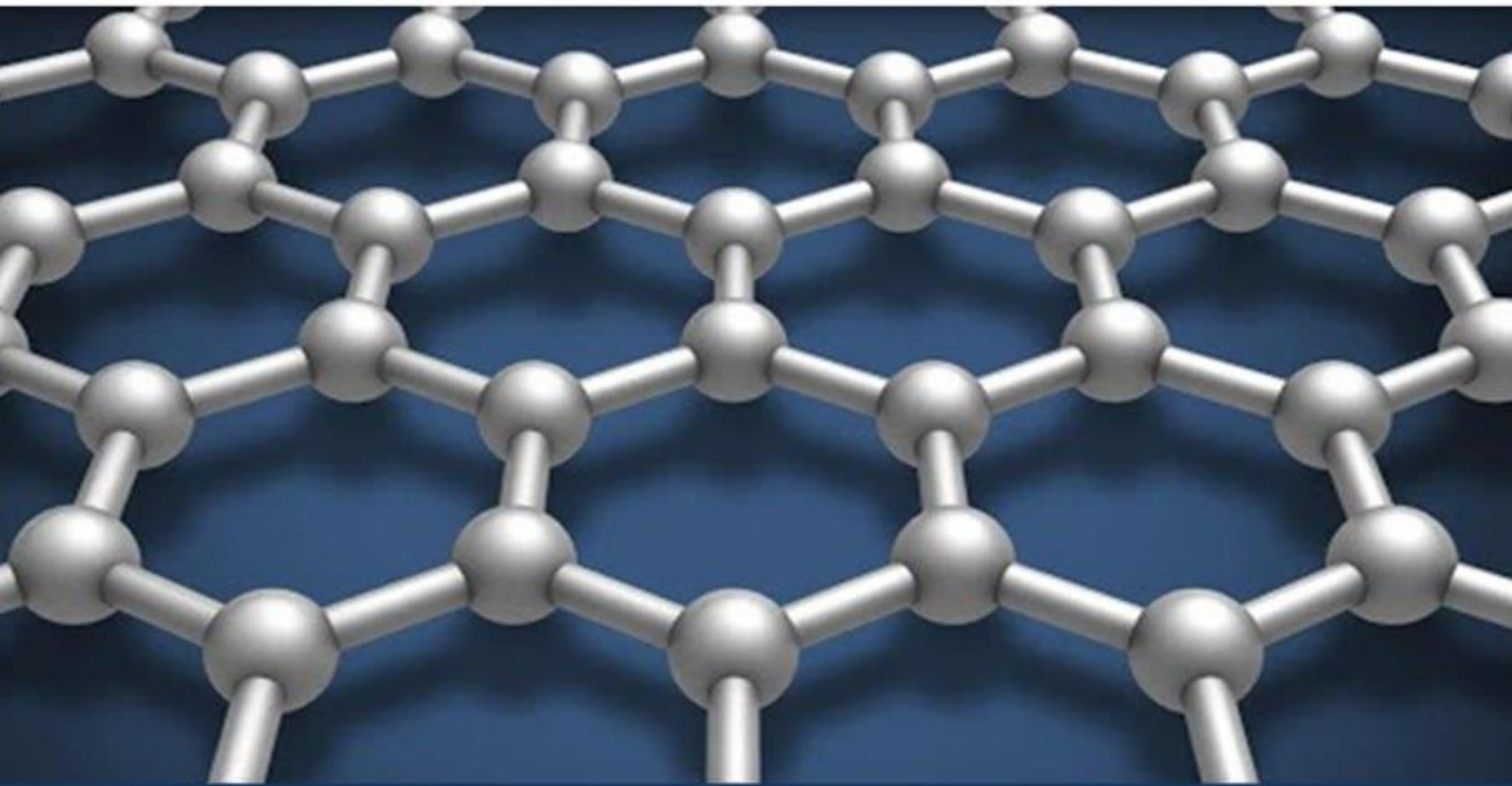

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Композиционные материалы

SYNTHESIS AND PROPERTIES OF A MONOMERIC COMPLEX COMPOUND BASED ON ACRYLAMIDE

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Introduction. Metal-containing polymers and copolymers have a number of unique properties: biological and catalytic activity, biocidal, electrical and magnetic properties, etc. [1, 2].

At present, three main methods for obtaining metal-containing polymers are described in the literature: 1) the interaction of linear polymers with metals; 2) the reaction of polycondensation of the corresponding precursors with the incorporation of a metal ion into the main chain; 3) reactions of (co)polymerization of metal-containing monomers [2]. Each of these methods has its own advantages and disadvantages. However, one of the promising methods in this area is the third one, i.e. synthesis of metal-containing monomers, which are convenient systems for studying the regularities of the radical polymerization process, since they contain a chemically bound metal atom capable of coordinating interaction with a macroradical and other components of the reaction system.

The results of the synthesis and study of metal-containing monomers and their polymerization are reflected in numerous works of Pomogailo A.D., Jardimalieva G.I., Savostyanova V.S. and others [3,12]. The paper considers methods for the synthesis of metal-containing monomers that differ in the type of bond between the metal and the organic part of the molecule; a classification of these monomers is given. The influence of the nature of the metal on the polymerization process and the properties of the resulting products, the fields of application of metal-containing polymers, and the technological aspects of the synthesis of metal-containing monomers have been studied. The classification of metal-containing monomers takes into account the type of bond between the metal and the organic part of the monomer. Based on this, metal-containing monomers can be divided into the following main types: monomers with covalent, ionic, donor-acceptor, and π-bonds [3,5].

The authors chose unsaturated dicarboxylic acids as the base compound for the preparation of metal-containing monomers. [6]. They synthesized Co (II), Ni (II), Cu (II), Zn (II) Fe (II), Fe (III), Cr (III) maleates, fumarates, and itoconates in up to 95% yield. Other authors have synthesized iron(III) carboxylates with acrylic, crotonic, linoleic, methacrylic, oleic, and sorbic acids [7]. The paper presents generalized data on the synthesis and reactivity of metal-containing monomers based on mono- and dicarboxylic unsaturated acids, the identification of the kinetic patterns of their polymerization and thermal transformations, as well as the study of the main properties of the resulting products [8].

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 [9,15]. Vinyl porphyrin complexes of palladium and cobalt have also been synthesized [16].

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 [17,19].

Chlorine-containing compounds of anthranilamide with cobalt, nickel, and copper were obtained in an ethanol solution [20]. 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 [21]. 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 [22]. 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 $[Co(AAm)_4(H_2O)_2](NO_3)_2$, $[Cu(AAm)_4(NO_3)_2]$, $[Co(AAm)_4Cl_2]$, and $[Co(AAm)_6][CoCl_4]$.

The authors synthesized acrylamide complexes of cobalt: blue dichlorotetrakis (acrylamide) cobalt(II) (1) and pink (acrylamide) cobalt(II) tetrachlorocobaltate (2) [23]. 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 [24]. The work presents comparative data of the crystal structure of acrylamide and complexes of acrylamide with metals formed with divalent transition metal chlorides [25]. Also, the authors determined the structure of the synthesized acrylamide complexes of metal nitrates using single-crystal X-ray diffraction analysis [26]. 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.

Experimental part. Acrylamide (2-propenamide) $CH_2=CHC(O)NH_2$ - acrylic acid amide, is a colorless crystals with $T_{melt.}$=84.5 °C, $T_{boil.}$=215 °C, density 1.122 g/cm^3. Soluble in water, ethanol, acetone. Ethanol (ethyl alcohol, methylcarbinol) - CH_3CH_2OH - monohydric aliphatic alcohol, colorless, easily mobile liquid with a characteristic odor. Tm.=-114.15 °C, Tboil.=78.39 °C, density 0.7893 g/cm³. It was absolutized by dehydration with calcium oxide, then it was distilled and a fraction with Tbp was taken. = 78 °C. Copper chloride - $CuCl_2$ is a bluish-green odorless crystals with T_{melt} = 498 ºC; $T_{boil.}$=993 ºC; density 3.386 g/cm^3.

The IR spectra of the starting reagents and the synthesized monomers were recorded on an IRTracer-100 IR-Fourier spectrophotometer developed by SHIMADZU (Japan) in the wavenumber range 400-4000 cm^{-1} in KBr tablets. The PMR spectra of the initial reagents and synthesized substances were recorded on a Varian-T-6- spectrometer with an operating frequency of 60.0 mHz on H nuclei at a temperature of 30 °C. Sample preparation requires 5-10 mg of the substance. The solvent used should ideally not contain its own protons (CD_3COCD_3). A small amount (~1%) of TMS is also introduced into the ampoule as internal ethanol.

NMR spectra were recorded on an Avance 500 spectrometer (Bruker, Germany) with an operating frequency of 500 MHz for 1H nuclei and 126 MHz for 13C nuclei at a temperature of 293 K. The following parameters for recording 13C NMR spectra were used: sampling time for the decay of free induction (AQT = 0,5 s); relaxation delay time (RD = 2 s); number of savings (NS = 22,000); the number of points describing the real spectrum (SI=32 K). The number of accumulations in recording 1H NMR spectra was 128.

The structure of the synthesized acrylamide complex compounds was determined by X-ray diffraction analysis (XRD). Reflection sets were obtained at 293 K on Xcalibur R autodiffractometers (Oxford Diffraction, England). (CuK_α-radiation, λ=1.54184 E, ω-scanning, graphite monochromator). All non-hydrogen atoms were localized in difference syntheses of electron density and refined by F2hkl in the anisotropic approximation. The positions of all H atoms were calculated geometrically and included in the refinement in the isotropic approximation. The single crystal has the form of a thin transparent plate 0,42x0,12x0,1 mm in size.

Elemental analysis for carbon, hydrogen, and nitrogen was performed on a CHNS-3 FA 1108 Elemental Analyzer (Carlo Erba) automatic gas analyzer; for boron and manganese, by ICP MS on an iCAP 6300 Duo inductively coupled plasma atomic emission spectrometer.

Procedure for Synthesizing a Monomeric Complex Based on Acylamide and $CuCl_2$ Weighed 0,4 mol of acrylamide and 0,1 mol of $CuCl_2$ salt were dissolved in 50 ml of ethanol and heated at 60 °C for 5 hours. The mixture was then evaporated to 1/3 volume. After cooling to room temperature, a green crystalline precipitate formed. Chlorine ions were removed from the $AgNO_3$ solution by precipitation. The resulting precipitate was filtered off, washed twice with acetone, and dried in air. The precipitate formed has the composition [$C_{12}H_{24}N_4O_4Cu$].

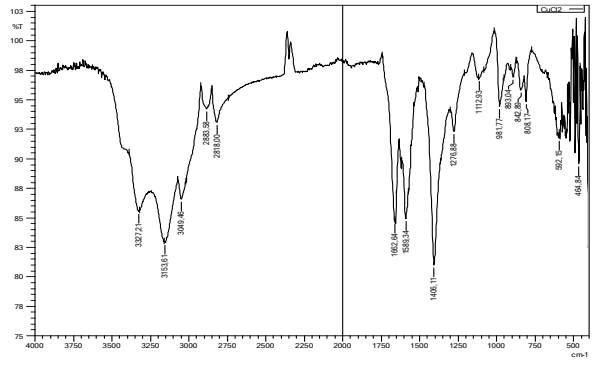

Fig.2. IR spectrum of a monomeric complex compound based on acrylamide and copper(II)

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

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