

Cu(II) and Ni(II) β -dycarbonyl complexes as precursors of functional materials

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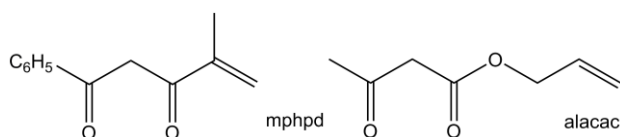
Abstract. The copper(II) and nickel(II) complexes with unsaturated β -dycarbonyl ligands methacrylaceto phenon and allyl acetoacetate were synthesized and studied. The Cu(II) complexes were found to have a square-planar structure. The Ni(II) complexes have a tetragonal distorted octahedral structure with two water molecules in the axial positions. By means of radical polymerization the corresponding metallopolymers were obtained and the kinetic of polymerization process was studied by volume dilatometry. The reactivity of the monomeric metal complexes was shown to be determined by both electronic and structure factors.

Keywords: β -dycarbonyl, complexes, polymers, nanomaterials, thermal analysis.

Introduction. The chemistry of coordination compounds is one of the major areas of modern science nowadays. Arousing interest in the metal-containing polymers is observed every year, which is due to their potential application in the design of functional materials with desired properties. The polymerization of metal complexes containing unsaturated substituents is one of the methods for synthesizing metallopolymers. This route is attractive since it makes feasible to obtain polymers with uniform chemical composition in which all functional groups are bounded to metal ions. However, the polymerization of coordination compounds has not been studied thoroughly [1-4], so the research in this area is of great interest.

Metal complexes to be use as monomers should have relatively high thermodynamic stability and solubility in organic solvents. From this viewpoint, unsaturated metal β -diketonates are suitable objects for studying the polymerization of coordination compounds. Metallopolymers based on them can combine the valuable properties of β -diketonates with the manufacturability of polymers. Therefore, the design of new synthetic routes for obtaining such complexes and the study of their structure and properties is one of the topical tasks of modern chemistry.

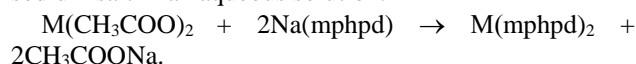
The present work deals with monomeric and polymeric copper(II) and nickel(II) coordination compounds with two unsaturated β -dycarbonyl ligands, namely, methacrylaceto phenone (2-methyl-5-phenyl-1-penten-dione-3,5, mphpd) and allyl acetoacetate (allyl-3-oxobutanoate, alacac). The complexes were studied using a number of physicochemical methods including thermal analysis, absorption, infrared (IR), electronic spin resonance (ESR) spectroscopy and dynamic light scattering. The polymerization kinetics of the monomeric complexes was also investigated by volume dilatometry.



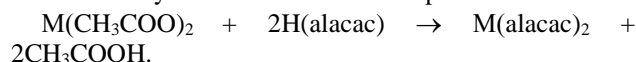
Materials and methods. Copper(II) acetate monohydrate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, nickel(II) acetate tetrahydrate $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, allyl acetoacetate, reagents used for the preparation of methacrylaceto phenone and organic solvents were of analytical grade. Sodium salt of mphpd was synthesized from methyl methacrylate and acetophe-

none according to [5] in a 72 % yield as a yellow crystalline substance (melting point 216 °C). ^1H NMR for $\text{Na}(\text{mphpd})$ (CDCl_3), δ (ppm): 1.98 (s., 3H, CH_3); 3.25 (s., 1H, $=\text{C}(\text{H})\text{H}$); 3.62 (s., 1H, $=\text{C}(\text{H})\text{H}$); 4.82 (s., 1H, CH_2); 7.05 – 7.96 (mult. br., 5H, C_6H_5).

Synthesis of the Cu(II) and Ni(II) complexes with mphpd was carried out by the exchange reaction between the equimolar amounts of metal (M) acetates and mphpd sodium salt in an aqueous solution:



Synthesis of metal complexes with alacac was performed in a hydroalcoholic solution at pH = 8.5 – 9.0:



The precipitates were filtered off and recrystallized from benzene at room temperature. One of the special features of unsaturated metal β -diketonates is that their synthesis and purification should be carried out at room temperature because even little heating results in partial oligomerization, which significantly decreases their solubility. For the same reason the complexes were not purified by sublimation.

Polymerization was performed at 80°C in dimethylformamide (DMF) during 20 hours in an incubator. 2,2'-azobis(isobutyronitrile) was used as an initiator. The concentrations of the complexes and initiator were 0,03 and 0,0003 $\text{mol} \cdot \text{L}^{-1}$ respectively. The metallopolymers obtained were precipitated from solutions by isopropanol. The polymerization kinetics was studied under the same conditions during the first 3 hours by volume dilatometry. The polymerization rate on the initial linear section of the polymerization curve (V_p), the reduced polymerization rate (V_{red}) and the total rate constant (K_Σ) were calculated using the following equations:

$$V_p = \frac{10Um}{MV\tau}$$

$$V_{red} = V_p / C_0$$

$$K_\Sigma = V_{red} / \sqrt{C_i}$$

where U and τ are the degree of conversion and the time for the last point on the linear section of the polymerization curve, m and M are the mass of the sample and the molar mass of the monomeric complex, C_0 is the initial concentration of the monomeric complex and C_i is

the concentration of the initiator.

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Q-1500D type derivatograph (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 20 to 500°C (heating rate 5°C/min) in a platinum crucible in the presence of anhydrous carrier Al₂O₃ in a static air atmosphere. IR spectra were recorded on a Spectrum BX II FT-IR spectrophotometer (Rerkin-Elmer) in the range from 400 to 4000 cm⁻¹ in a KBr tablet. The electronic absorption spectra were recorded on UV-VIS-IR Shimadzu UV-3600 spectrophotometer in the range from 300 to 700 nm. Particle size determination of monomeric and polymeric complexes was performed by dynamic light scattering at 25°C on a ZetaSizer system (Malvern Instruments). Powder microphotographs were taken on a Hitachi H-800 scanning electron microscope. For the Cu(II) β-diketonates the ESR spectra were recorded in a chloroform solution at 77 and 293 K on a CMS 8400 spectrometer (ADANI).

Results and Discussion. The coordination mode of the ligands functional groups to the metal ions was determined by IR spectroscopy. Table 1 lists the characteristic IR frequencies of the metal complexes and uncoordinated ligands. The CO and CC stretching vibrations observed in the spectra of the metal β-diketonates in the 1560 – 1600 cm⁻¹ (mphpd) and 1620 – 1640 cm⁻¹ (alacac) regions indicate the bidentate-cyclic coordination mode via carbonyl groups. The higher frequency band is attributed mainly to a C=O stretching and the lower one – to a C=C stretching [6-9]. The frequencies of these bands are intermediate between the characteristic frequencies of single and double CC and CO bonds [8], which indicates the

presence of conjugation in the chelate ring of both ligands. For the metal complexes with alacac the bands of C=O and C=C stretching vibrations are shifted towards higher wavenumbers compared to the corresponding mphpd complexes due to the electron density redistribution caused by the oxoallyl substituent. It may indicate the higher stability of the alacac chelates [7]. The carbonyl groups are involved in metal complex formation is evident from the appearance of medium intensity bands in the region 400-510cm⁻¹ due to ν(M-O) vibrations [9], also in this area there are bending vibrations of the chelate rings [6]. The broad band of coordinated water molecules presents in the spectra of the Ni(II) complexes in the 3200 – 3400 cm⁻¹ region.

The medium intensity stretching of the double C=C bond presented in the IR spectra in the 1600 – 1650 cm⁻¹ region is a characteristic feature of β-diketonates, containing unsaturated substituents. The disappearance or a significant reduction in intensity of this band can be used for a qualitative characterization of the metal complexes polymerization. The band in the mentioned region is absent in the spectra of the Ni(II) metallopolymers, whereas a slight shoulder at 1620 – 1630 cm⁻¹, indirectly indicating the presence of only terminal unsaturated groups, is observed for the Cu(II) metallopolymers. The C=O and C=C stretching vibrations for the polymeric complexes are slightly shifted towards higher wavenumbers in comparison with the monomeric β-diketonates. It indicates the redistribution of the electron density in the chelate ring due to the influence of adjacent molecules in the polymeric matrix.

	$\nu(\text{MO})$ + $\delta_{\text{chel. ring}}$	$\nu_s(\text{CC})$	$\nu_{\text{as}}(\text{CO})$	$\nu_{\text{as}}(\text{CC})$	$\nu_s(\text{CO})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu(\text{H}_2\text{O})$
Na(mphpd)	-	1459	1411	1568	-	1677	1726	
Halacac	-	1360	1410	-	-	1650	1713, 1725	
Cu(mphpd) ₂	406, 417, 478, 506, 518	1460	1416	1554	1592	1680	-	-
Cu(alacac) ₂	420, 435, 488, 530	1459	1414	1529	1589	1635	1715	-
Ni(mphpd) ₂ ·2H ₂ O	419, 460, 495, 530	1480	1450	1554	1592	1670	-	3435
Ni(alacac) ₂ ·2H ₂ O	425, 455, 490	1452	1410	1545	1580	1625	1715	3382
[Cu(mphpd) ₂] _n	415, 480	1458	1430	1558	1590	-	-	
[Cu(alacac) ₂] _n	410, 470	1450	1420	1536	1601	-	-	3441
[Ni(mphpd) ₂] _n	410, 485	1460	1415	1550	1595	-	-	
[Ni(alacac) ₂] _n	415, 470	1460	1420	1540	1600	-	-	

Table 1. Assignments of the characteristic bands in the IR spectra

Thermal analysis was performed in order to determine the hydrate composition of the β-diketonates under study and their behavior under heating. There are different opinions regarding the behavior of β-diketonate complexes under heating in the literature [9-15]. The TG and DTA curves contain a number of effects associated with the loss of water, polymerization and decomposition. The dehydration of the metal complexes with mphpd is known to occur at rather high temperatures (150 – 250°C) [16]. Since the polymerization takes place in the same temperature range, on the DTA curves the endothermic effect of dehydration is often masked by more intense exothermic polymerization effects. For Cu(mphpd)₂ the endothermic effect observed in the range of 80 – 140°C is due to the loss of adsorbed water (weight loss Δm = 1,8 %). The

exothermic effect at 158°C can be attributed to the formation of oligomeric structures. The decomposition of the complexes begins with the loss of one ligand molecule resulting in the pronounced exothermic effect at 212°C. Further heating above 350°C leads to the complete decomposition resulting in the formation of copper oxide.

The decomposition of Ni(mphpd)₂·2H₂O starts with the endothermic effect in the 80 – 155°C range, which is due to the loss of two coordinated water molecules (Δm = 6,9 %, Δm_{theor} = 7,6 %). The endothermic effect in the range of 155 – 188°C can be attributed to the melting of the complex. Further heating up to 500°C is accompanied with a number of endothermic and exothermic effects which are due to the decomposition of the organic part of the complex, which starts with the loss of one ligand mol-

ecule ($\Delta m = 31,2\%$, $\Delta m_{\text{theor}} = 32,8\%$). The complete weight loss in the temperature range studied is 62,6 %.

The dehydration of $\text{Cu}(\text{alacac})_2$ begins at 86°C and results in the loss of adsorbed water ($\Delta m = 2,1\%$). Further heating in the range of 182 – 352°C is accompanied with the endothermic effects at 257 and 296°C and the weight loss of 9,9 %, which is due to the detachment of oxoallyl substituent of one ligand molecule. The pronounced endothermic effects at 434 and 496°C indicate the thermal decomposition of the β -diketonate, however, the weight loss is rather small. Further heating results in the complete decomposition of the organic part of the complex. The metal–oxygen stretching vibrations observed at about 500, 600 and 640 cm^{-1} in the IR spectrum of the sample after thermolysis indicate that $\text{Cu}(\text{alacac})_2$ decomposes to copper oxide. The bands of these vibrations are shifted to the short-wave region compared to the spectra of the $\text{Cu}(\text{II})$ β -diketonate, which indicates the covalent nature of the Cu–O bonds in the complex.

Thermal analysis of metallopolymers reveals, that they are thermally stable up to 180 – 200°C, which indicates their potential use as precursors of film materials.

Electronic absorption spectra of the complexes under study were recorder in order to determine the shape of the coordination polyhedrons of the metal ions. In the UV region (240-280 nm) all complexes exhibit split bands of the $\pi \rightarrow \pi^*$ transition [9]. The spectra of copper complexes in the visible region (600-730nm) contain a wide line with two maxima corresponding to the $B_{1g} \rightarrow A_{1g}$, and $B_{1g} \rightarrow E_g$ transitions. The absorption spectra of both monomeric and polymeric $\text{Cu}(\text{II})$ complexes are similar to the spectra of square-planar β -diketonates. In the spectra of the $\text{Ni}(\text{II})$ complexes the charge-transfer band is shifted to ultraviolet region and both allowed transitions can be observe.

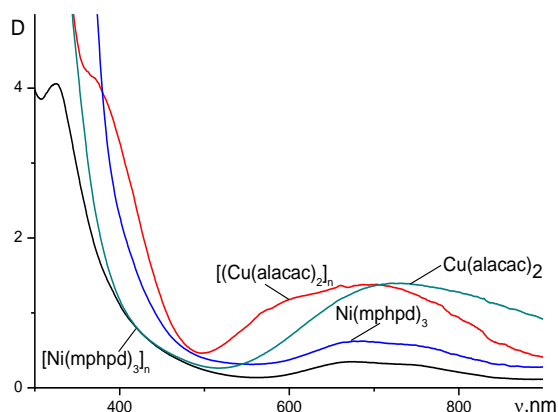


Figure 1. Absorption spectra of some complexes

The band of the ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ transition is shifted towards low-frequency region compared to $\text{Ni}(\text{II})$ acetylacetonate. It leads to the considerable spin-orbit coupling of the ${}^3T_{1g}(\text{F})$ and 1E_g states, resulting in the increasing intensity of the spin-forbidden ${}^3A_{2g} \rightarrow {}^1E_g$ transition and doublet splitting of the absorption band. Thus, the shape of the electronic spectra indicates that the coordination polyhedron of the $\text{Ni}(\text{II})$ ion is a tetragonal distorted octahedron. The inner coordination sphere consists of four carbonyl oxygen atoms of the β -diketonate ligands in the equatorial positions and complements with two water

molecules in the axial positions [12, 17-20]. The absorption spectra of the monomers and polymers are similar (fig.1). A slight shift of the main metallopolymers bands in the shortwave region indicates a weakening bond of the metal with oxygen.

It is well-known, that from the ESR spectra of paramagnetic polycrystalline complexes the rhombic, cubic and axial symmetries can be distinguished. For the axial symmetry the shape of the ESR spectra depends on the ground state of the central ion. For instance, if a $\text{Cu}(\text{II})$ complex has the $d_{x^2-y^2}$ ground state (square plane or prolate octahedron), the anisotropic values of the g -factors obey the following relation: $g_{\parallel} > g_{\perp} > 2$.

On the other hand, in the case of the d_{z^2} ground state (trigonal bipyramid or oblate octahedron) the relation between the g -factors will be as follows: $g_{\parallel} > g_{\perp} \approx 2$. As can be seen from Table 2 and Fig.2 for the $\text{Cu}(\text{II})$ β -diketonates under study the shape of the ESR spectra and the parameters calculated indicate the axial symmetry with the $d_{x^2-y^2}$ ground state. The coordination polyhedron of the $\text{Cu}(\text{II})$ ion is a square plane, which is in agreement with the results of the absorption spectroscopy. ESR spectrum of $\text{Cu}(\text{alacac})_2$ contains isotropic signal similar to complexes described in [12].

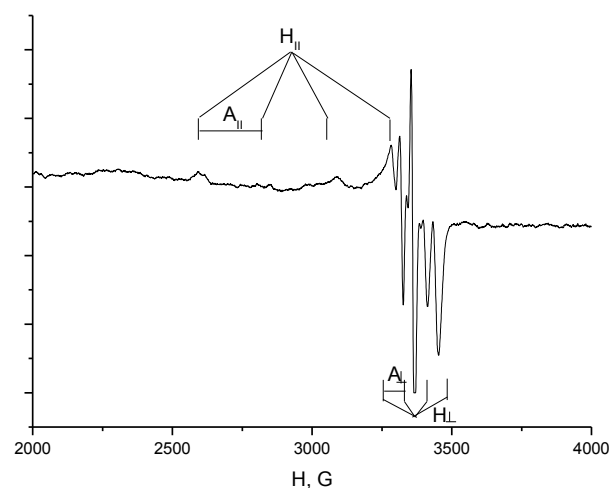


Figure 2a. ESR spectra $\text{Cu}(\text{mphpd})_2$ in CHCl_3 at 77 K

Complex	g_0	a_0	g_{\parallel}	A_{\parallel}	g_{\perp}	A_{\perp}
$\text{Cu}(\text{mphpd})_2$	2.132	77	2.256	170	2.070	30

Table 2. Parameters of the ESR spectra of the $\text{Cu}(\text{mphpd})_2$ complexes

Thus, the spectral study revealed the coordination mode of the ligands and the structures of the coordination polyhedrons of the monomeric complexes in question. However, the results obtained do not make feasible to predict the properties of the metal β -diketonates as monomers in the polymerization reaction.

When the unsaturated double bond is conjugated with the chelate moiety in ligand molecule, the redistribution of the electron density due to complexation with the metal ion increases the bond order of the C=C bond. It leads to the diminution of the metal complex reactivity compared to the “free” ligand in the polymerization reaction. In order to increase the reactivity, the charge redistribution in the ligand should be equilibrated. It can be done by using donor solvents, so the polymerization was carried out in DMF solutions. The kinetic parameters and kinetic lines of polymerization listed in Tab.3 and Fig.3 reveal that the

reactivity of the monomeric β -diketonates depends on the electronic structure of the central ion and is determined by both electronic and structure factors.

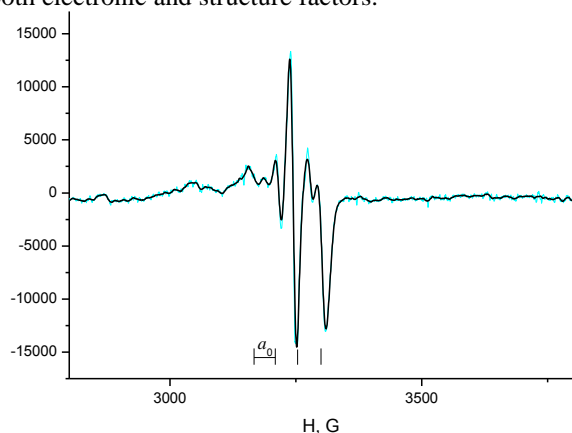


Figure 2b. ESR spectra $\text{Cu}(\text{mphpd})_2$ in CHCl_3 at 298 K

Parameter	$\text{Cu}(\text{alacac})_2$	$\text{Ni}(\text{mphpd})_2 \cdot 2\text{H}_2\text{O}$
$V_p (\times 10^4 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1})$	0.47	1.34
$V_{red} (\times 10^4 \text{ s}^{-1})$	1.56	6.38
$K_\Sigma (\times 10^3 \text{ L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{s}^{-1})$	2.84	8.16

Table 3. Kinetic parameters of polymerization

In order, to investigate the dispersion of the complexes under study and to choose the solvent for obtaining uniform thin films, the monomeric and polymeric metal β -diketonates were studied by dynamic light scattering in DMF and chloroform solutions.

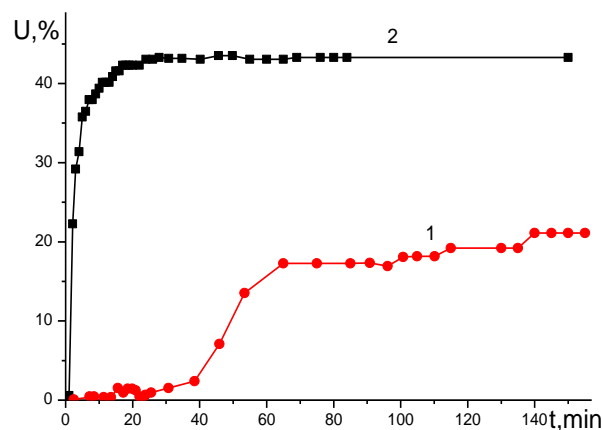


Figure 3. Kinetic of polymerization $\text{Cu}(\text{alacac})_2$ (1) and $\text{Ni}(\text{mphpd})_2 \cdot 2\text{H}_2\text{O}$

The results have shown that in a chloroform solution the sizes of the monomeric and polymeric particles are close to each other (about 10 – 20 nm) and the systems are monodisperse. In a DMF solution the particles are within 20 – 50 nm and the systems are polydisperse. At first glance, the dimension of a polymeric system should be higher than for the corresponding monomer. However, the monomer units in polymeric molecules are known to connect in the long chains, which results in a rather rigid structure with low entropy. For this reason polymer systems are prone to self-organization. Therefore, the dimension of a polymer depends on its structure: about 100 nm for a polymer twisted into a ball and about 10 nm for a polymer twisted into a globule. In view of the aforementioned, the metallopolymers are assumed to have a ball structure (fig.4).

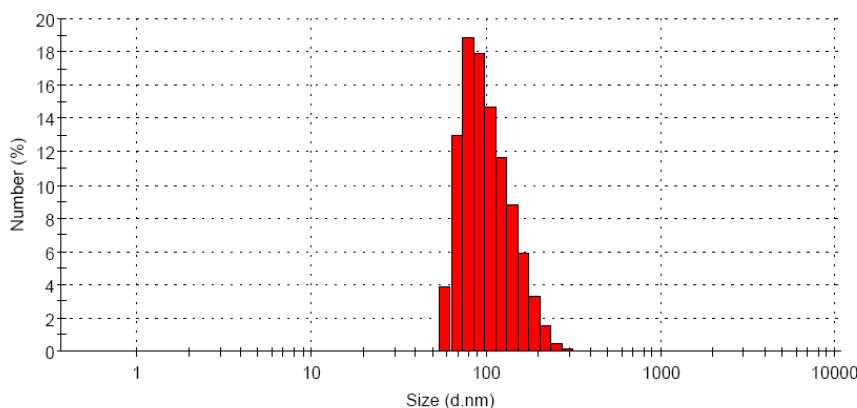
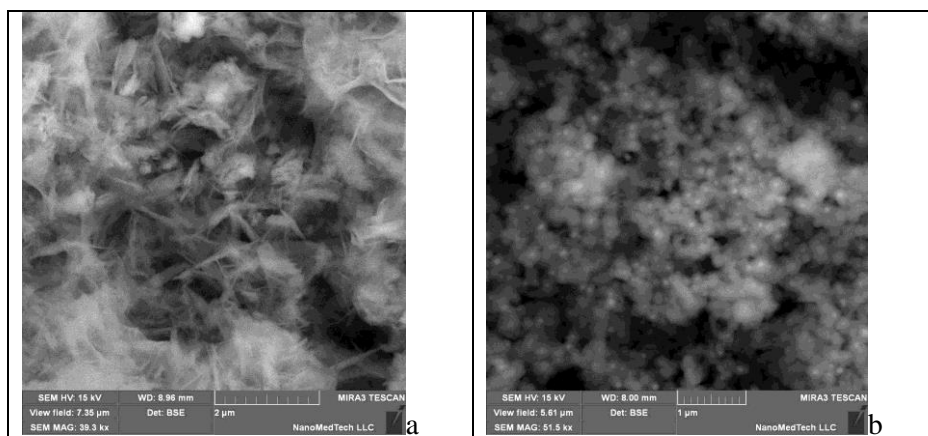


Figure 4. The diagram of distribution by radius of $[\text{Cu}(\text{mphpd})_2]_n$

Powder microphotographs support this assumption. As can be seen from the SEM images (fig.5), the structural units in the monomeric complexes and the polymeric globules have the size of 10 – 20 nm. The sizes of the particles in a chloroform solution and in powder coincide, which makes feasible to use both solutions and powders of the metallopolymers under study depending on a given task.

Conclusions. To sum up, the monomeric and polymer-

ic metal complexes of copper(II) and nickel(II) were synthesized and studied by a number of physicochemical methods in solid state and in solutions. Both monomeric and polymeric complexes were found to be nanosized. It was shown that the structure of the coordination polyhedrons doesn't change after polymerization. The polymeric metal complexes are chemically homogeneous compounds, which are thermally stable up to 220 °C



Figures 5. Microphotography of Cu(mphpd)_2 (a) and $[\text{Cu(mphpd)}_2]_n$ (b).

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β -Дикарбонильные комплексы Cu(II) и Ni(II) как прекурсоры функциональных материалов

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Аннотация. Были синтезированы и изучены комплексы меди (II) и никеля (II) с ненасыщенными β -дикарбонильными лигандами метакроилацетофеноном и аллилацетоацетатом. Показано, что комплексы Cu (II) имеют плоскочетырёхугольное строение, а комплексы Ni (II) - тетрагональную искажённую октаэдрическую структуру с двумя молекулами воды в экваториальных позициях. Путём радикальной полимеризации были получены соответствующие металлополимеры и методом дилатометрии изучена кинетика процесса полимеризации. Показано, что реакционная способность мономерных комплексов металлов определяется как электронными, так и структурными факторами.

Ключевые слова: β -дикарбонильные комплексы, полимеры, наноматериалы, термический анализ