Metal chelate monomers based on nickel(II) cinnamate and chelating N-heterocycles as precursors of nanostructured materials

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\textbf{ABSTRACT}

Metal chelate monomers (MCMs) have been widely used as precursors for the production of advanced functional polymers and nanomaterials. In this article, new metal chelate monomers based on nickel(II) cinnamate (cinn) and various chelating N-heterocycles, \(\text{[Ni(cinn)_2(bpy)(C}_2\text{H}_5\text{OH})]}\) and \(\text{[Ni(cinn)_2(phen)(C}_2\text{H}_5\text{OH})_2]}\) (bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline), were first synthesized and characterized. A detailed analysis of the main stages and features of the kinetics of thermolysis of MCMs was carried out. Metal-polymer nanocomposites with a core-shell structure containing metal nanoparticles evenly distributed in a stabilizing nitrogen-containing polymer matrix were obtained by thermolysis at 300°C. Thermolysis at 450°C resulted in pure nickel oxide nanoparticles. The nature of the ligand has been shown to affect the structure and size of the product obtained. The tribological characteristics of nanoparticles as additives to lubricating oils were studied using the pin-on-disc tribometer. At the optimum concentration of nanoparticles, the coefficient of friction is the smallest, and an increase in the concentration above the optimum level leads to an increase in the coefficient of friction.

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1. Introduction

Metal chelate monomers (MCMs) containing chelated metal and unsaturated bonds for various polymerization transformations has become the object of researchers [1, 2], due to the fact that MCMs have increased stability in comparison with other metal-containing monomers due to the chelate or macrocyclic effect. In addition, they are effective precursors of polymeric metal chelates, in which the chelated metal ion is contained in each monomer unit in a predetermined spatial configuration [3]. Conjugated thermolysis of MCMs, including the simultaneous thermal polymerization of the monomer and thermolysis of the resulting metal-containing polymer, allows one to obtain advanced nanomaterials [4]. It should be emphasized that during the thermolysis of such MCMs, nanoparticles of metals, metal oxides, or carbides are formed, which are stabilized by the products of thermolysis of the polymer matrix. The conditions of thermolysis (temperature, gas medium), ligand environment, and the nature of the metal in the MCM are the determining factors of the conjugated thermolysis and allow targeted production of various nanoparticles inserted into the polymer matrix. The most extensive studies of MCMs were carried out using various unsaturated carboxylates of metals, in particular cinnamates of transition [5–18], alkaline earth [19, 20], and rare earth metals [21–23]. Trans-cinnamic acid is a natural compound, a metabolite in the biosynthetic shikimate and phenylpropanoic pathways, as well as other biochemical transformations [24]. In addition, cinnamic acid and its metal complexes have a wide range of interesting applications [25–33].

One of the promising classes of MCMs are mixed-ligand complexes, which include unsaturated carboxylic acids and N-heterocycles: 1,10-phenanthroline (phen) [34–39], 2,2′-
bipyridine (bpy) [40, 41], 4,4'-bipyridine [42], benzimidazole derivatives [11, 43, 44], 4,4'-dipyridylamine [45], bis(4-pyridyl)ethane [46], and others. As typical examples, we note MCMs based on cobalt acrylate complexes with bpy and phen [47]. The conjugated thermolysis of these MCMs leads to metal-polymer nanocomposites containing metal nanoparticles uniformly distributed in a stabilizing nitrogen-containing polymer matrix, or Co$_3$O$_4$ nanoparticles, depending on thermolysis conditions. However, a detailed study of the kinetics of conjugated thermolysis of mixed-ligand complexes has not yet been carried out.

Extensive studies of nanomaterials as lubricant additives for motor oils (nanolubricants) have shown their high tribological effectiveness [48–57]. It should be noted that the design of nanolubricants based on metal or metal oxide nanoparticles is a very complex process, depending on a large number of parameters, the importance of which is largely unknown. The mechanisms of action of nanolubricants are not well understood. Recent research has focused on environmentally friendly nanoparticles that minimize the use of hazardous materials and additives, and also meet the requirements of green tribology.

In previous studies, we described the conjugated thermolysis of unsaturated metal carboxylates and the properties of the nanomaterials obtained [47, 58–63]. In continuation of these studies, the present work is devoted to the synthesis of new metal chelate monomers based on nickel(III) cinnamate (cinn) and various chelating N-heterocycles, viz.: [Ni(cinn)$_2$(bpy)(C$_2$H$_5$OH)] (1) and [Ni(cinn)$_2$(phen)(C$_2$H$_5$OH)$_2$] (2), as well as the study of their conjugated thermolysis, the composition and structure of nanoparticles synthesized in various thermolysis conditions, and tribological performance of the resulting nanomaterials as lubricant additives.

2. Experimental

2.1. Chemicals

All reagents were purchased from Aldrich and Merck of reagent grade and were used without purification. Ethanol “chemically pure” and benzene label “pure” (Closed Joint Stock Company “Mosreaktiv”) were used without purification. Diethyl ether of the brand “analytical grade” (Khimmed) was distilled at atmospheric pressure over potassium hydroxide and the main fraction was collected at $t = 34 \, ^\circ\text{C}$ and stored over sodium metal.

**Synthesis of Ni(cinn)$_2$H$_2$O.** Cinnamic acid (17.76 g, 0.12 mol) is dissolved by heating in an aqueous solution of sodium hydrogen carbonate (8.4 g, 0.1 mol) in water (200 mL) until a uniform clear solution is obtained and the carbon dioxide evolution has stopped. If necessary, the resulting solution is quickly filtered hot through a dense porous glass plate. Nickel sulfate heptahydrate (14.05 g) is dissolved in warm water (100 mL) and gradually both solutions are mixed, aged for 24 h to ripen the precipitate and facilitate filtering. After settling, the clear supernatant is decanted, the residue is filtered under vacuum, washed with warm water to remove excess inorganic salts and alcohol to remove excess of cinnamic acid. The resulting precipitate is dried in air at a temperature of no higher than 50 $^\circ\text{C}$ to an air-dry state and dried in vacuo at room temperature. A light green powder is obtained, which is stable in air to 220 $^\circ\text{C}$, above which it loses water and undergoes thermal changes without melting. Yield: 8.347 g, 50.6% (based on anhydrous nickel sulfate). Found (%): C, 58.23; H, 4.39; Ni, 16.02.
C_{18}H_{16}O_{5}Ni·H_{2}O. Calcd (%): C, 58.38; H, 4.32; Ni, 15.94. IR (KBr pellet), $\nu/cm^{-1}$: 3450 (O–H); 3060 (=C–H); 1640 (as(C=O)); 1580 (C¼C); 980 (=CH–C).

**Synthesis of MCM 1.** To a suspension of nickel cinnamate (3.3 g, 0.9 mmol) in ethanol, an alcohol solution of bpy (1.56 g, 0.01 mol) at 40 °C is added dropwise with continuous stirring. By the end of the introduction of the reagent a clear blue solution is formed, the solution is filtered through a dense porous glass plate. The solvent is removed in vacuo at a temperature of 26–28 °C. The resulting gray blue residue is dried under vacuum at room temperature and the resulting powder is washed in a beaker in freshly distilled ether at a ratio of 1:30, separated by vacuum filtration on a porous glass plate and extracted with ether in a Soxhlet apparatus to remove excess bpy. The compound obtained after extraction of the pollutants is dried in vacuo at room temperature. The final product is hygroscopic light gray powder. Yield: 3.11 g, 69.04%. Found (%): C, 64.32; H, 5.1; N, 5.16; Ni, 10.725. C_{28}H_{22}O_{4}N_{2}Ni·C_{2}H_{5}OH. Calcd (%): C, 64.98; H, 5.054; N, 5.00; Ni, 10.65. IR (KBr pellet), $\nu/cm^{-1}$: 3420 (O–H); 3060 (=C–H); 1636 as(OCO); 1552 (C¼C); 984 (=CH–C).

**Synthesis of MCM 2.** To a suspension of nickel cinnamate (3.7 g, 0.01 mol) in ethanol (30 mL), an alcoholic solution of phen (1.98 g, 0.011 mol) at 40 °C was added dropwise with continuous stirring. By the end of the introduction of the reagent a clear purple solution is formed. The solution is filtered through a dense glass plate under vacuum. From the resulting solution, the solvent is removed under vacuum, and the product obtained is dried under vacuum. Then the product is washed in freshly distilled ether at a ratio of 1:30, separated by vacuum filtration on a glass plate and washed with ether in a Soxhlet apparatus to remove excess phen. The material obtained after washing is dried under vacuum at room temperature. Yield: 3.28 g, 30.5%. Found (%): C, 66.04; H, 5.039; N, 5.04; Ni, 10.065. C_{30}H_{22}N_{2}O_{4}Ni·C_{2}H_{5}OH. Calcd (%): C, 66.3; H, 4.83; N, 4.83; Ni, 10.1. IR (KBr pellet), $\nu/cm^{-1}$: 3408 (O–H), 3056 (=C–H); 1636 as(OCO); 1552 (C¼C); 980 (=CH–C).

**Preparation of the nanomaterials in air.** Weighed portions (0.6–0.8 g) of MCM were placed in a porcelain crucible and placed in a muffle furnace for 30–80 min. The furnace was heated at a rate of 5 °C/min until the temperature reached 450 °C and was kept for 1 h at this temperature. Then the furnace was cooled to room temperature, the porcelain crucible was taken out and the target product was crushed.

**Preparation of the nanomaterials in an inert atmosphere.** A portion of the substance (0.6–0.8 g) is placed in a quartz tube with a minimum height of 10 cm and a diameter of 1 cm. The assembled unit is evacuated, filled with argon, heated at a rate of 5 °C/min until reaching a temperature of 300 °C and kept at this temperature for 1 h. After the specified time, the unit is again evacuated, continuing to maintain the specified temperature. Vacuuming is carried out until the walls of the external vessel are freed from volatile decomposition products. The resulting substance is cooled in vacuum to room temperature, the target product is removed in the form of a porous column with a height of 20–25 mm and crushed.

### 2.2. Characterization

Elemental analyses were carried out on a CHNOS vario EL cube analyzer (Elementar Analysensysteme GmbH, Germany). Nickel was determined on an energy dispersive
X-ray fluorescence spectrometer “X-Art M” (Comita, Russian) or atomic absorption spectrometer “MGA-915” (Lumex, Russia). IR spectra were performed on the Perkin-Elmer Spectrum 100 FTIR spectrometer using KBr tablets and Softspectra data analysis software. Thermal analysis (TA) and differential scanning calorimetry (DSC) were carried out on a synchronous thermal analyzer STA 409CLuxx coupled to quadrupole mass spectrometer QMS 403CAeolos (NETZSCH, Germany) and on a Perkin-Elmer Diamond TG/DTA derivatograph under air (powders, m = 0.3–0.4 g) with the standard α-Al₂O₃ at a rate of 10 K/min in the range of 20–800°C.

X-ray diffraction (XRD) analysis was carried out on the diffractometers DRON-UM-2, “Philips PW 1050” and ARL™ XTRA Powder (Thermo Fisher Scientific, USA) with CuKα radiation (λCu = 1.54184 Å) from 2θ = 5–80° with a scan rate of 50/min and a temperature of 25°C to determine the phase composition and the size of the crystallites. The sizes of crystallites of nanomaterials (D, nm) were determined by the Debye-Scherrer Equation (1) [64]:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos(\theta)},$$

where K is a constant (ca. 0.9); λ is the X-ray wavelength used in XRD (1.5418 Å); θ is the Bragg angle; β is the pure diffraction broadening of the peak at half-height that is, broadening due to the crystallite size.

Nanomaterials synthesized by thermolysis of MCMs were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) on a ZEISS Crossbeam 340 with an accelerating voltage of 3 kV. Detection of secondary electrons was carried out using the Everhart-Thornley detector (SE2), increasing the samples from 1.92 to 50 thousand times.

Atomic force microscopy (AFM) was performed on a PHYWE Compact AFM (probe type Tap 190Al-G) in the semicontact mode using a wide range piezoelectric scanner enabling up to 100 mm lateral scanning (x-y) and 5 mm scanning in the vertical (z)
direction with a scan rate of $1 \text{ mm} \times 1 \text{ mm/min}$. The Gwyddion 2.10 software was used to analyze AFM images.

### 2.3. Study of thermolysis kinetics

The kinetics of the isothermal transformations of MCMs was studied based on gas evolution in a static nonisothermal reactor (Figure 1) using a membrane zero manometer. Thermolysis was carried out under static isothermal conditions at temperatures $T_{\text{exp}}$ in an argon atmosphere. The weight loss of the sample ($\Delta m$, wt.%) and the amounts of gaseous products (GPs) at $\sim 20 \, ^\circ\text{C}$ were determined at the end of the experiments. The volume of the heated tube did not exceed $0.05 \, V$, where $V$ is the total reactor volume. The ratio $m_0/V = (0.60 - 3.85) \times 10^{-3} \, \text{g cm}^{-3}$, where $m_0$ is the initial weight of the sample.

### 2.4. Tribological tests

Nanomaterials synthesized by MCM thermolysis were mixed in a glass beaker with liquid paraffin and simultaneously dispersed in a PSB-Hals ultrasonic shaker for 15 min to ensure uniform dispersion and good suspension stability. The lubricating composition was prepared with a different percentage of the additive content in the oil: 0.05, 0.1, 0.5, and 0.8 wt.%.

Tribological tests of the friction system were carried out on a universal testing machine (Figure 2, left) of the UMT-200 type (Research and Production Center “Konvers-resurs”, Russia). The speed of rotation of the disc without load does not exceed 2900 rpm, the pressing force of the tested samples is in the range from 0 to 200 kg. The friction unit is a steel disc and three steel pins (Figure 2, middle). The pin-on-disk tribo-testing geometric configuration is shown in Figure 2, right. The total diameter of the flat specimen is 50 mm, the diameter of each of the movable pins (3 pcs) is 8 mm (for a thick lubricant, a pin with a diameter of 20 mm was used). The initial surfaces of the steel disc and steel pins were prepared by grinding and polishing.
using emery paper of 600 grit size, washed with distilled water, then cleaned by hex-
ane and dried at room temperature in air. The lubricant composition was placed in a
metal container which was attached to a thread with a hole under the steel disc. The
tests were carried out with pure liquid paraffin, as well as with the addition of nano-
material at different loads: 49, 98, 147, and 196 N and the time of rolling steel pins on
the disc for each load of 30 min. Each test was repeated three times.

The coefficient of friction is calculated by Equation (2):

$$f = \frac{F}{P}$$

where F is the friction force, N; P – pressing force, N.

3. Results and discussion

3.1. Synthesis and structure of metal chelate monomers

In the present study, nickel (II) cinnamate complexes with bpy (1) and phen (2) were
synthesized by reacting an excess of a chelating N-heterocycle (bpy or phen) with the
original complex in ethanol. MCMs 1 and 2 are light gray and purple crystalline sub-
stances, easily soluble in water, ethanol and DMF. According to the elemental analysis
data, the complexes can be formulated as [Ni(cinn)₂(bpy)(C₂H₅OH)] (1) and
[Ni(cinn)₂(phen)(C₂H₅OH)₂] (2), respectively. A comparison of the IR spectra of the syn-
thesized MCMs (Supplementary material Figures S1 and S2) with the spectra of previ-
ously obtained related compounds [5–18] allows us to conclude that the coordination
node of the nickel ion contains a chelating N-heterocycle, a monodentate cinn⁻ anion
and solvent molecules.

3.2. Thermal properties of metal chelate monomers

The study of thermal transformations of MCMs showed an overall pattern of the
nature of their conjugated thermolysis, consisting of three successive key stages [4]:

![Figure 3. TG and DTA curves for MCM 1 (a) and 2 (b).](image-url)
dehydration (desolvation) of the initial MCM; solid-phase polymerization of dehydrated MCM; decarboxylation of the obtained metallopolymer with the formation of a metal-containing phase and an oxygen-free polymer matrix, accompanied by intense gas evolution. Similar patterns were observed for MCMs 1 and 2 (Figure 3). In particular, when MCM 1 is heated at temperatures ranging from 60 to 90°C, there is a loss of 8.5 wt.% of the original sample, which corresponds to the removal of one ethanol molecule (8.3%), accompanied by an endothermic effect with a maximum at 82°C. When MCM 2 is heated in the temperature range of 87–114°C and from 121 to 150°C, there are minor endothermic effects associated with desolvation. Weight loss, according to the thermogram, is about 8%, which corresponds to the loss of ethanol, which is 7.7 wt.% of the original substance.

Our previous studies [65] showed that the dehydration (desolvation) of MCMs causes a nonequivalence of M–O bonds. The polymerization reaction is initiated in accordance with the Borodin-Hunsdiecker mechanism; the initial insignificant decarboxylation leads to formation of radicals, which, in turn, causes the polymerization process and the formation of polymers with a linear or three-dimensional network structure (Scheme 1). It should be noted that at this stage the chain growth proceeds with strong steric hindrance and is characterized by a high level of internal stress.

In particular, for MCM 1, polymerization begins to occur at 100 to 155°C without significant loss of sample weight. From 157 to 273°C, there is an intense weight loss of 36.5% of the weight of the original sample against the background of the almost unchanged DSC curve. It can be assumed that the processes of decarboxylation (which make the main contribution to the endothermic effect) and polymerization (which make a significant contribution to the exothermic effect) occur simultaneously in this temperature interval. The dependence of the evolution of GPs of thermolysis on the temperature in the range of temperatures of intense gassing (Figure 4) allows you to calculate the degree of conversion ($\eta$):

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I. Initiation

\[
\begin{align*}
\text{n M(PhCH = CHCOO)_2L} & \xrightarrow{\text{M(PhCH = CHCOO)_2L}} \text{PhCH = CHCOO}^* + L \\
\text{PhCH = CHCOO}^* + \text{M(PhCH = CHCOO)_2L} & \rightarrow \text{PhCH = CHCOOH} + (\text{Ph}^*\text{CH = CHCOO})\text{M(PhCH = CHCOO)_2L} \\
\end{align*}
\]

II. Polymerization

\[
\begin{align*}
R'[n + \text{M(PhCH = CHCOO)_2L}]
\end{align*}
\]

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**Linear structure**

**Cross-linked structure**

**Scheme 1.** Scheme of second stage of conjugated thermolysis of MCMs.
where $D_{\text{aR},t} = a_{\text{R},t} - a_{\text{R},0}; D_{\text{aR},f} = a_{\text{R},f} - a_{\text{R},0}; a_{\Sigma,t}$, and $a_{\Sigma,0}$ are the final, current, and initial number of moles of GPs released per mole of the initial sample at room temperature, respectively.

The gas evolution rate $W = \frac{dg}{dt}$ decreases monotonically with increasing conversion.

The kinetics of gas evolution $g(t)$ in the general case (up to $g/C_20 < 0.95$) is described by the equation for two parallel reactions:

$$
\eta = \frac{\Delta x_{\Sigma,f}}{\Delta x_{\Sigma,t}},
$$

where $\Delta x_{\Sigma,t} = x_{\Sigma,t} - x_{\Sigma,0}; \Delta x_{\Sigma,f} = x_{\Sigma,f} - x_{\Sigma,0}; x_{\Sigma,t}$ and $x_{\Sigma,0}$ are the final, current, and initial number of moles of GPs released per mole of the initial sample at room temperature, respectively.

The gas evolution rate $W = \frac{dg}{dt}$ decreases monotonically with increasing conversion. The kinetics of gas evolution $\eta(t)$ in the general case (up to $\eta \leq 0.95$) is described by the equation for two parallel reactions:

$$
\eta(t) = \eta_{1f}[1 - \exp(-k_1 t)] + (1 - \eta_{1f})[1 - \exp(k_2 t)],
$$

where $t = t - t_0$ ($t_0$ is the heating time), $\eta_{1f} = \eta(t)|_{k_2 \to \infty}$. $k_1$, $k_2$ are the effective rate constants.

Parameters $(k_1, k_2, \eta_{1f}, \Delta x_{\Sigma,t})$ depend on the thermolysis temperature ($T_{\text{therm}}$):

$$
\eta_{1f}, \Delta x_{\Sigma,f} = A \exp\left[-E_{\text{a},\text{eff}}/(RT_{\text{therm}})\right]
$$
\[ k_{\text{eff}} = k_{0,\text{eff}} \exp \left[ -\frac{E_{a,\text{eff}}}{RT_{\text{therm}}} \right], \]  

where \( A \) and \( k_{0,\text{eff}} \) are the pre-exponential factors and \( E_{a,\text{eff}} \) is the effective activation energy.

The dependence of the logarithm of the decarboxylation reaction rate constant on \( 1/T \cdot 10^3 \) is shown in Figure 5.

When \( k_2 \ll 0, \eta_{1f} \rightarrow 1 \)

\[ \eta(\tau) \approx 1 - \exp \left( -k_1 \tau \right) \]  

\[ W_0 \approx k_1. \]

Equations (7) and (8) describe the kinetics of gas evolution during thermolysis of MCMs with activation energy values given in Table 1.

### 3.3. Characterization of thermolysis products

The products of thermolysis of MCMs 1 and 2 in a self-generated atmosphere at 300 °C for 1 h are shiny powders of black color, which is explained by the presence of amorphous carbon [66]. The elemental composition of the products obtained is shown in Table 2.

Products obtained by thermolysis of MCMs were examined by XRD analysis, which made it possible to obtain data on their phase composition. As shown in Supplementary material Figures S3 and S4, strong and sharp diffraction peaks indicate that the product obtained is crystalline. XRD patterns of MCM thermolysis product powders at 300 °C in an inert atmosphere allow diffraction peaks to be indexed as a metallic nickel enclosed in a polymer matrix (region of amorphous substance in a diffractogram). The size of nickel crystallites calculated by the Scherrer formula is 10.98 and 11.29 nm for the products of thermolysis of MCM 1 and 2, respectively.

The IR spectra for the two products almost coincide both in the characteristic absorption bands and in intensity (the difference in intensity is 5–7%). Taking into account the data of IR spectroscopy (Supplementary material Figure S5) and elemental analysis (see Table 2), as well as the results of previous studies [47, 67], it can be proposed that the resulting polymers are subjected to thermal polymerization with the formation of a network containing conjugated double bonds and polypyridine fragments.

Thermolysis of MCMs leads to formation of metal-polymer nanocomposites with a core-shell structure, which contain metal and metal oxide nanoparticles uniformly

| Table 1. Activation energy of decarboxylation reaction for MCMs. |
|------------------|------------------|
| Compound         | \( E_{a,\text{eff}}, \text{kJ mol}^{-1} \) |
| Nickel cinnamate | 137.0            |
| MCM 1            | 103.4            |
| MCM 2            | 248.2            |

| Table 2. Elemental composition of the thermolysis products. |
|-----------------|-----------------|
| Thermolysis product | C, % | H, % | N, % | Ni, % |
| MCM 1            | 69.55 | 4.21 | 11.16 | 13.01 |
| MCM 2            | 71.75 | 3.81 | 12.23 | 12.23 |
distributed in a stabilizing nitrogen-containing polymer matrix (Scheme 2). This matrix provides encapsulation of nanoparticles, which is an important fact, since the high dispersion of metals in the composites leads to their strong interaction with the components of the medium, both during preparation and during further storage. The resulting nanocomposites are stable over time; during their long-term storage, no changes in the chemical composition, size and shape of the nanoparticles occur. Thus, the conjugated thermolysis of MCMs may be the best embodiment of the idea of stabilizing nanoparticles in situ.

When the thermolysis temperature of MCMs rises above 300 °C, there is a significant weight loss, which indicates destructive changes occurring in the organic matrix. Products obtained by thermolysis of MCM 1 in air at 450°C with exposure times of 60, 50, and 30 min were examined by XRD analysis (Figure 6). Powder XRD patterns allow

Scheme 2. Scheme of formation of core-shell NPs.

Figure 6. XRD pattern of a metal oxide nanopowder obtained by thermolysis of MCM 1 at 450°C for 30 min (a), 50 min (b), and 60 (c) min.
indexing the diffraction peaks on the diffractogram as a cubic phase of NiO. Three characteristic peaks for the face-centered cubic lattice of nickel oxide are marked by the indices (111), (200), and (220) at 37.25°, 43.34°, 62.75° (ICDD data 00-004-0835). The study of diffraction patterns of the products of thermolysis of MCM 1 at different times of thermolysis showed that the qualitative and quantitative composition of the products does not depend on the time of thermolysis. When comparing diffraction patterns, one can trace an increase in the intensity and a decrease in the width of the peaks, which indicates the process of crystallization of the thermolysis product. The average sizes of crystallites vary within small limits, which may be related to the process of formation of the porous structure during boiling up of the coordination compound during thermolysis.

A comparative analysis of the results was carried out for the thermolysis products of MCM 1 and 2, obtained in air at 450°C for 60 min. The intensity of the diffraction peaks of the thermolysis products of MCM 1 is significantly higher than that of the thermolysis products of MCM 2 (Figure 7), but the width of the peaks shows a reverse trend. The average crystallite size of the thermolysis products of MCM 1 is 10 nm less on average than that of the thermolysis products of MCM 2. Given that MCMs used to produce NiO differ only in the composition of chelating N-heterocycles, it can be concluded that the nature of the ligand affects the structure and size of the resulting product. Consequently, the introduction of bpy into coordination compound, in contrast to phen, as a ligand leads to a decrease in the thermolysis time and crystallite size. In addition, in both cases, the dependence of crystallite sizes on the thermolysis time of the studied compounds is traced.

The surface topography of nickel oxide nanoparticles obtained by the thermolysis of MCM 1 and 2 was studied using AFM. Samples were prepared using the PSB-Hals ultrasonic bath, mixing the powder with alcohol when it was dispersed. Figure 8 shows 2-D and 3-D images of the surface topography of the thermolysis products of MCM 1 and 2, respectively. The thermolysis product of MCM 1 consists of irregularly shaped nanoparticles ranging in length from 200 to 400 nm. The particle height ranges from 11 to 20 nm (Figure 8(a)). In the AFM image of the thermolysis product of MCM 2 (Figure 8(b)), the individual powder particles are distinguishable. The distribution of particle size is non-uniform; its constituent particles have a length from 300 to 550 nm. It can be assumed that the synthesized powder consists of aggregated nanoparticles. The distribution in height for all particles is approximately the same at 20 nm.
The morphology of NiO nanopowders was investigated using SEM (Figure 9). The thermolysis of MCMs at 450°C produces a layered product observed in SEM photographs. The chemical composition and purity of the synthesized nanostructures were investigated using EDS analysis. Ni and O are observed in the EDS spectra, and the product is pure and does not contain any surfactants or impurities. Thus, from the results of the EDS analysis, it follows that the main component of thermolysis of the Ni-containing MCMs at 450°C is NiO.

Figure 8. 2D and 3D visualization of the obtained nickel oxide nanopowders as a result of thermolysis of MCM 1 (a) and MCM 2 (b) at 450°C.

Figure 9. SEM and EDS analysis of nickel oxide nanopowder obtained by thermolysis of MCM 1 (a) and MCM 2 (b) at 450°C.
3.4. Tribological tests

Considering that nickel oxide nanoparticles have high surface activity and can easily settle on sliding steel surfaces, lubricant compositions with different content of nickel oxide nanopowder based on liquid paraffin were designed and their tribological characteristics were studied. NiO nanoparticles were suspended in liquid paraffin at various concentrations to produce nanolubricant, which is used in small amounts at the sliding interface between three steel pins and the steel disc in a pin-on-disc tribometer in accordance with ASTM G-99 standard. Figure 10 shows a plot of the coefficient of friction versus the load at a constant concentration of the additive of 0.05%. The optimum value of the load was found, at which a decrease in the friction coefficient is observed, and with increasing concentration, nickel oxide works as an abrasive, increasing the coefficient of friction. The increase in load has little effect on the friction

Figure 10. The dependence of the tribological characteristics on the applied normal load of nickel oxide nanoparticles obtained by thermolysis of MCM 1 (a) and MCM 2 (b). The concentration of NiO in the lubricant is 0.05%.

Figure 11. The dependence of tribological characteristics on the concentration in the lubricant of nickel oxide nanoparticles obtained by thermolysis of MCM 1 (a) and MCM 2 (b). Normal load 98 H.
coefficient, however, when the load increases above 198 N, an increase in the friction coefficient is observed. As follows from the obtained results (Figure 11), the greatest efficiency is achieved when the concentration of additive obtained as a result of the thermolysis of MCM 1 and 2 in the lubricant is 0.05 wt.%. The results of tribological studies show that the addition of 0.05% nickel oxide reduces the coefficient of friction by almost two times. At a concentration of 0.05 wt.%, a maximum mixing of the components of nickel oxide-liquid paraffin is observed. A further increase in the NiO concentration leads to an increase in the friction coefficient, which may be due to the abrasive action of the nanoparticles. In addition, an increase in nickel oxide concentration during the frictional interaction of the steel-steell pair leads to the separation of components, and friction occurs in liquid paraffin. It should be noted that a higher concentration of nanoparticles increased the tendency to agglomerate particles. In general, there is an optimum concentration at which the coefficient of friction is minima, but it is highly dependent on the system, since the composition of the lubricant must be adjusted for each operating condition.

The presence of nickel oxide nanoparticles improves anti-wear properties, and the improvement in tribotechnical characteristics is explained by the formation of a nickel oxide film in the contact zone of rubbing surfaces (tribo-film). With the relative motion of the two surfaces, the forming structure of the metal layer has a number of asperities and pores that are capable of capturing not only the lubricant, but also the nickel oxide particles present in it, contributing to the formation of thin modified surface layers on the friction path of the steel. Nanoparticles have a micropolishing effect on steel surfaces, the powder begins to cut the surface, wiping out microcracks, and forming a compact protective layer. The film formed by nanoparticles inserted into the oil, acts as a protective film, reduces direct contact and facilitates smoothing of the friction surface. Deposition of nanoparticles on the friction surface is the main explanation for the reduction of friction, since the presence of a thin layer interferes with the metal-to-metal contact and determines the tribological behavior of the interacting surfaces [50]. Tribo-film formation is initiated by the reaction between rubbing material and additives under ambient conditions [68–72]. The mechanism of lubrication is a crucial parameter for a complete understanding of the tribological action of nanoparticles. Determination of active mechanisms in nanolubricants based on NiO nanoparticles is the subject of our further research.

4. Conclusion

New metal chelate monomers based on nickel(II) cinnamate and various chelating N-heterocycles (2,2'-bipyridine and 1,10-phenanthroline) were synthesized and characterized. Analysis of the presented data shows that conjugated thermolysis at 300 °C of metal chelate monomers leads to the formation of metal-polymer nanocomposites with a core-shell structure containing metal nanoparticles evenly distributed in a nitrogen-containing polymer matrix. Thermolysis at 450 °C consists in formation of nickel oxide nanoparticles. The resulting nanomaterials are characterized by stability, and their storage for a long time does not lead to any changes in the chemical composition, size and shape of the nanoparticles. The proposed method for producing
nanoparticles is simple and cheap, which makes it very suitable for large-scale production. It was found that the size of the crystallites of nickel oxide varies depending on the conditions and the nature of the initial MCM. The study of tribological parameters in the steel-steel friction pair made it possible to choose the optimum concentrations of NiO additives in lubricants. By changing the nature of the ligand, it is possible to purposefully change the characteristics of the powders, which makes it possible to use them in the future when creating a wide range of new functional materials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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