*Ludmila Matienko, Vladimir Binyukov, Larisa Mosolova, Elena Mil
and Gennady Zaikov*

# SOME SUPRAMOLECULAR NANOSTRUCTURES BASED ON CATALYTIC ACTIVE NICKEL AND IRON HETEROLIGAND COMPLEXES. FUNCTIONAL MODELS OF Ni(Fe) DIOXYGENASES

*N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,
4, Kosygina str., 119334 Moscow, Russian Federation
matienko@sky.chph.ras.ru; chembio@sky.chph.ras.ru*

**Abstract.** The possibility of the supramolecular nano structures formation on the basis of iron and nickel heteroligand complexes: $Fe_x(acac)_y18C6_m(H_2O)_n$, and $Fe_x(acac)_y(CTAB)_p(H_2O)_q$, or $Ni_2(OAc)_3(acac)L^2 \cdot 2H_2O$ ($L^2$ = MP) – with the assistance of H-bonding, is researched using the AFM method. Formation of different supramolecular nanostructures on the basis of nickel and iron heteroligand complexes as models for Ni(Fe)ARD Dioxygenases may be used for understanding of different actions of these enzymes.

**Keywords**: nanostructure, heteroligand iron and nickel complexes, H-bond, catalysis, ethylbenzene, dioxygen, Ni(Fe)ARD Dioxygenases.

## 1. Introduction

Research of structure and catalytic activity of complexes of nickel in different reactions of oxidation with molecular $O_2$ has been causing heightened interest of researchers in the recent years due to the fact that nickel as an essential catalytic cofactor of enzymes is found in eubacteria, archaebacteria, fungi, and plants. These enzymes catalyze a diverse array of reactions that include both redox and nonredox chemistries [1, 6].

Methionine salvage pathway (MSP) plays a critical role in regulating a number of important metabolites in prokaryotes and eukaryotes. Acireductone Dioxygenases (ARDs) Ni(Fe)ARD are enzymes involved in the methionine recycle pathway, which regulates aspects of the cell cycle. The relatively subtle differences between the two metal protein complexes are amplified by the surrounding protein structure, giving two enzymes of different structures and activities from a single polypeptide [2-5].

The products of the two enzymatic Acireductone oxidations differ in the following: one enzyme $Fe^{II}ARD$ or (ARD′) converts Acireductone to the R-ketoacid precursor of methionine, and formate, while the other enzyme $Ni^{II}ARD$ (or ARD) produces methyl-thiopropionate, CO, and formate. The precise function of the $Ni^{II}ARD$ reaction in the K. pneumoniae is unclear. Its products are not precursors for methionine. The $Ni^{II}ARD$-catalyzed reaction may thus be considered a shunt in the methionine salvage pathway, aiding in the regulation of methionine [2-5].

We have offered the new approach to research of mechanism of catalysis with heteroligand complexes of nickel (iron), which can be considered as model for $Ni^{II}(Fe^{II})ARD$.

We developed a method for enhancing the catalytic activity of transition metal complexes in the processes of alkylarens (ethyl benzene, cumene) oxidation with dioxygen to afford the corresponding hydro peroxides [6, 7], intermediates in the large-scale production of important monomers [8]. This method consists in introducing additional mono- or multidentate modifying ligands into catalytic metal complexes. The activity of systems $\{ML^1_n + L^2\}$ (M=Ni, Fe, $L^1$ = acac$^-$, $L^2$ = N-methylpirrolidon-2 (MP), HMPA, MSt (M = Na, Li, K), crown ethers or quaternary ammonium salts) is associated with the fact that during the ethyl benzene oxidation, the primary $(M^{II}L^1_2)_x(L^2)_y$ complexes and the real catalytic active heteroligand $M^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ complexes are formed to be involved in the oxidation process [6, 7, 9]. We established that the mechanism of formation of active heteroligand $M^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ complexes is analogous to mechanism of action of NiII(FeII)ARD (and Fe-Acetylacetone Dke1[20]) Dioxygenases. Therefore

$M^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ complexes seem to be useful as models for $Ni^{II}(Fe^{II})$ARD (and Dke1). The conclusions obtained in the present work can be used at discussion of mechanisms of $Ni^{II}(Fe^{II})$ARD Dioxygenases operation.

Nanostructure science and supramolecular chemistry are fast evolving fields that are concerned with manipulation of materials that have important structural features of nanometer size (1 nm to 1 μm) [10, 11]. Nature has been exploiting no covalent interactions for the construction of various cell components. For instance, microtubules, ribosomes, mitochondria, and chromosomes use mostly hydrogen bonding in conjunction with covalently formed peptide bonds to form specific structures. The self-assembled systems and self-organized structures mediated by transition metals are considered in connection with increasing research interest in chemical transformations with the use of these systems [12].

H-bonding can be a remarkably diverse driving force for self-assembly and self-organization of materials. H-bonds are commonly used for the fabrication of supramolecular assemblies because they are directional and have a wide range of interactions energies that are tunable by adjusting the number of H-bonds, their relative orientation, and their position in the overall structure. H-bonds in the center of protein helices can be 83.8 kJ/mol due to cooperative dipolar interactions [13, 14].

As one of the reasons of stability of heteroligand complexes $M^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ ($L^1_{ox}$ = $CH_3COO^-$) in the conditions of hydrocarbon oxidation there can be formation of intermolecular H-bonds. [6, 9]. On the other hand the different activity of nickel and iron complexes in the oxidation processes as well as in biological systems can be connected with different structures characteristics of formed complexes. In this article AFM method was used with analytical aim, for research of possibility of different supramolecular structures formation on the basis of nickel and iron heteroligand complexes: $Fe_x(acac)_y18C6_m(H_2O)_n$, and $Fe_x(acac)_y(CTAB)_p(H_2O)_q$, or $Ni_2(OAc)_3(acac)L^2·2H_2O$ ($L^2$ = MP) − with the assistance of H-bonding.

## 2. Experimental

AFM SOLVER P47/SMENA/ with Silicon Cantilevers NSG11S (NT MDT) with curvature radius 10 nm, tip height: 10–15 μm and cone angle ≤ 22° in taping mode on resonant frequency 150 kHz was used. As substrate the special chemically modified polished silicone surface was used. Hydrophobic modified silicone surface was exploit for the self-assembly-driven growth due to H-bonding of heteroligand nickel and iron complexes $Ni_2(OAc)_3(acac)MP·2H_2O$ and $Fe_x(acac)_y18C6_m(H_2O)_n$ with Silicone surface. The solutions of complexes in water (or $CHCl_3$) was put on a surface, maintained for some time, and then water was deleted from the surface by means of a special method – spin-coating process.

## 3. Results and Discussion

It is well known that transition metal $\beta$-diketonates are involved in various substitution reactions. Methine protons of chelate rings in $\beta$-diketonates complexes can be substituted by different electrophiles. Formally, these reactions are analogous to the Michael addition reactions [15, 16]. This is a metal-controlled process of the C−C bond formation [17]. The complex $Ni^{II}(acac)_2$ is the most efficient catalyst of such reactions.

In our works we have established that the electron-donating ligand $L^2$, axially coordinated to $M^{II}L^1_2$ (M = Ni, Fe, $L^1$ = $acac^-$), controls the formation of primary active complexes $M^{II}L^1_2·L^2$ and the subsequent reactions in the outer coordination sphere of these complexes. The coordination of an electron-donating extra-ligand $L^2$ with an $M^{II}L^1_2$ complex favorable for stabilization of the transient zwitter-ion $L^2[L^1M(L^1)^+O_2^-]$ enhances the probability of regioselective $O_2$ addition to the methine C−H bond of an acetylacetonate ligand, activated by its coordination with metal ions. The outer-sphere reaction of $O_2$ incorporation into the chelate ring depends on the nature of the metal. Transformation routes of a ligand $(acac)^-$ for Ni and Fe are various, but lead to formation of similar heteroligand complexes $M^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m(L^1_{ox}=CH_3COO^-)$ [6, 7]. Thus for nickel complexes, the reaction of acac-ligand oxygenation follows a mechanism analogous to those of $Ni^{II}$-containing Dioxygenase ARD [2-5] or Cu- and Fe-containing Quercetin 2,3-Dioxygenases [18, 19]. Namely, incorporation of $O_2$ into the chelate acac-ring was accompanied by the proton transfer and the redistribution of bonds in the transition complex leading to the scission of the cyclic system (**A**) to form a chelate ligand $OAc^-$, acetaldehyde and CO (in the Criegee rearrangement) (Scheme 1).

In the effect of $Fe^{II}$-acetylacetonate complexes, we have found [6,7] the analogy with the action of $Fe^{II}$ARD (ARD′) [2] and with the action of Fe(II) containing Acetylacetone Dioxygenase (Dke1) [20]. For iron complexes oxygen adds to C−C bond (rather than inserts into the C=C bond as in the case of catalysis with nickel(II) complexes) to afford intermediate, *i.e.* a Fe complex with a chelate ligand containing 1,2-dioxetane fragment **B** (Scheme 2). The process is completed with the formation of the $(OAc)^-$ chelate ligand and methylglyoxal as the second decomposition product of a modified acac-ring (as it has been shown in [20]) (see Scheme 2).
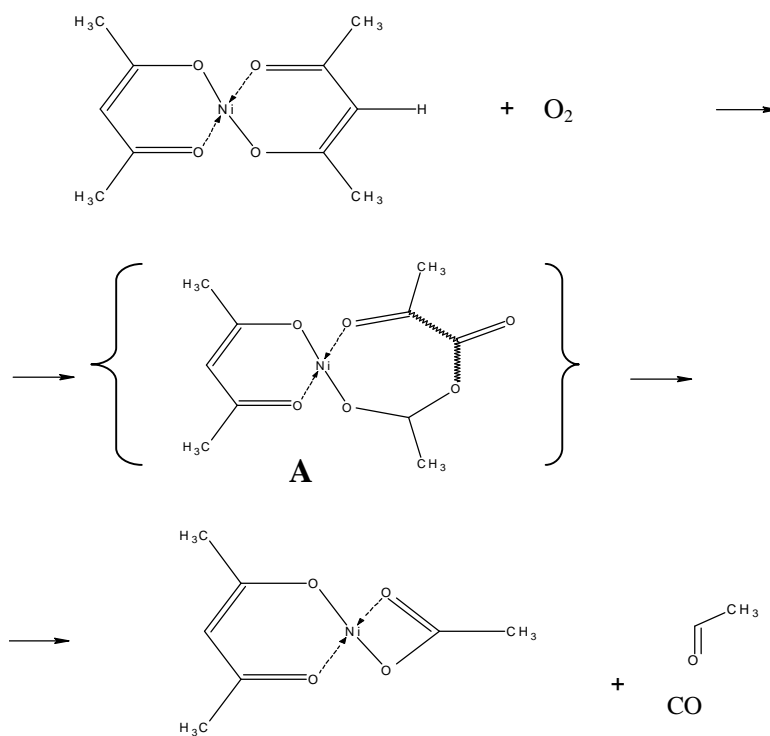
**Scheme 1**
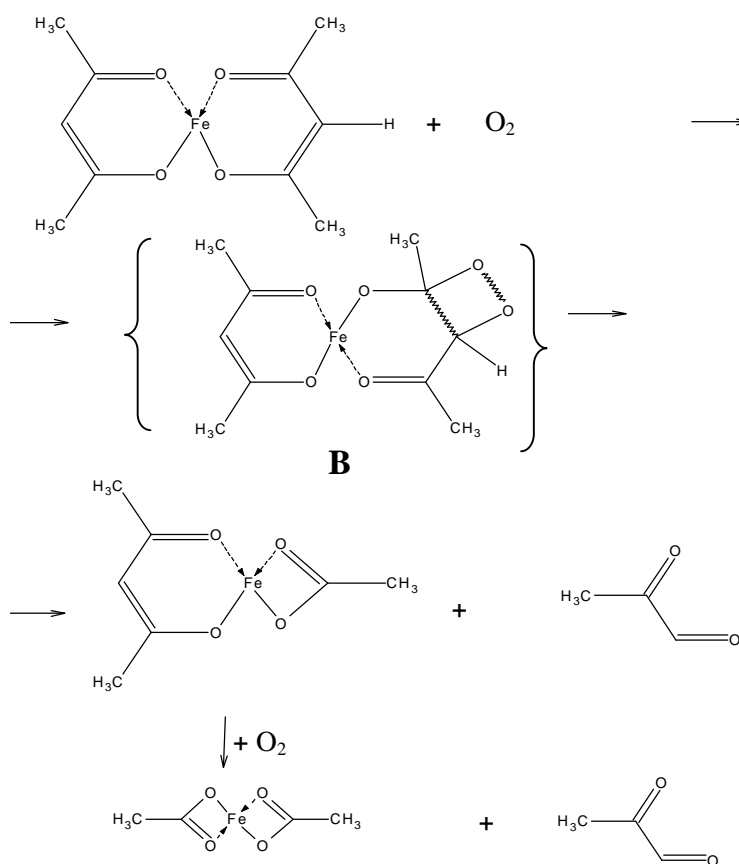


**Scheme 2**

## 3.1. Role of H-Bonding in Stabilization of Catalytic Complexes $Ni_x(acac)_y(OAc)_z(L^2)_n(H_2O)_m$

It is known that heteroligand complexes are more active in relation to reactions with electrophiles in comparison with homoligand complexes [6]. Thus the stability of heteroligand complexes $Ni_x(acac)_y(OAc)_z(L^2)_n(H_2O)_m$ with respect to conversion into inactive form $Ni(OAc)_2$ seems to be due to the formation of intermolecular H-bonds.

The complex formed in the course of ethyl benzene oxidation, catalyzed with the system $\{Ni^{II}(acac)_2 + MP\}$, has been synthesized by us and its structure has been defined with mass spectrometry, electron and IR spectroscopy and element analysis [6, 7]. The certain structure of a complex $Ni_2(OAc)_3(acac) \cdot MP \cdot 2H_2O$ corresponds to structure that is predicted on the basis of the kinetic data [6,7]. Prospective structure of the complex $Ni_2(OAc)_3(acac) \cdot MP \cdot 2H_2O$ is represented with Scheme 3.

On the basis of the known from the literature facts it was possible to assume that heteroligand complexes $Ni_2(OAc)_3(acac)MP \cdot 2H_2O$ are capable to form macro structures with the assistance of inter- and intramolecular H-bonds ($H_2O – MP$, $H_2O – (OAc^-)$(or $(acac^-)$) [21, 22].

The association of $Ni_2(AcO)_3(acac) \cdot MP \cdot 2H_2O$ to supramolecular structures as a result of H-bonding is demonstrated in Figs 1-3. Tree-dimensional and two-dimensional AFM image of the structures formed at drawing of a uterine solution on a hydrophobic surface of modified silicone is presented. It is visible that the majority of the generated structures have rather similar form of three almost merged spheres.
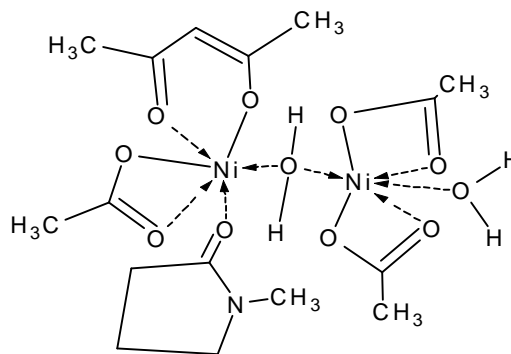


**Scheme 3**

As it is possible to see in Figs.1a and 3, except particles with the form resembling three almost merged spheres (Fig. 1b), there are also structures of more simple form (with the height approximately equal to 3–4 nm). A profile of one of the particles of the 3–4 nm in height is presented in Fig. 3c.

The distribution histogram (Fig. 2) shows that the greatest number of particles - is particles of the size 3–4 nm in height.
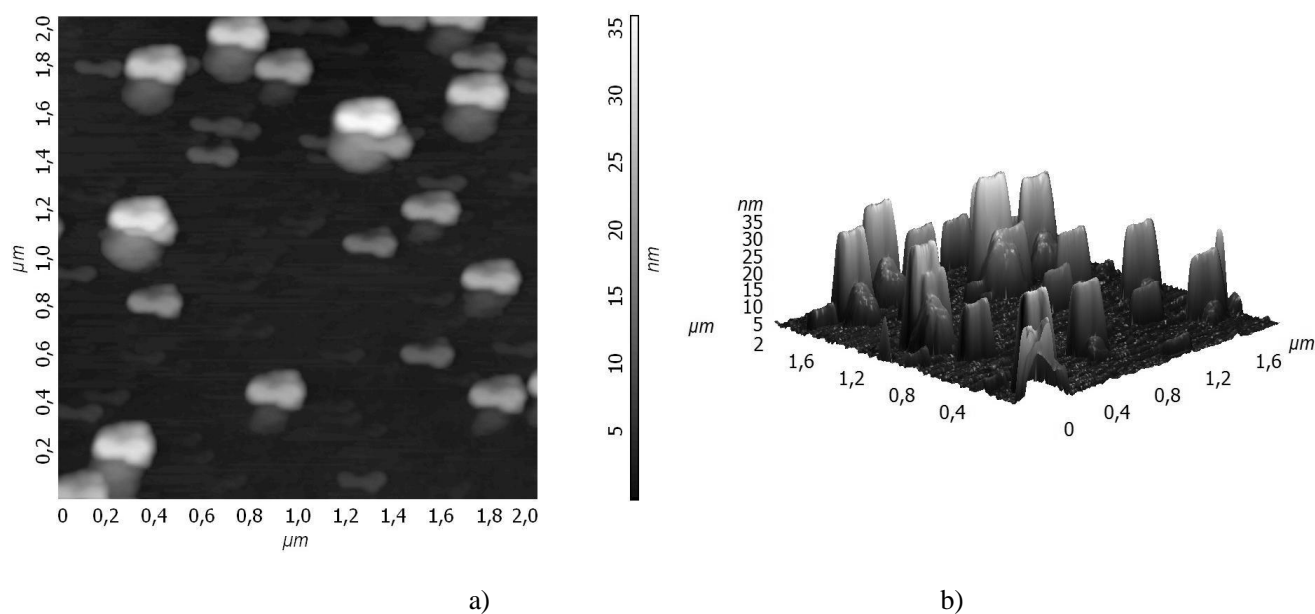


a)                                                          b)

**Fig. 1.** The AFM two- (a) and three-dimensional (b) image of nanoparticles on the basis $Ni_2(AcO)_3(acac) \cdot L^2 \cdot 2H_2O$ formed on the hydrophobic surface of modified silicone

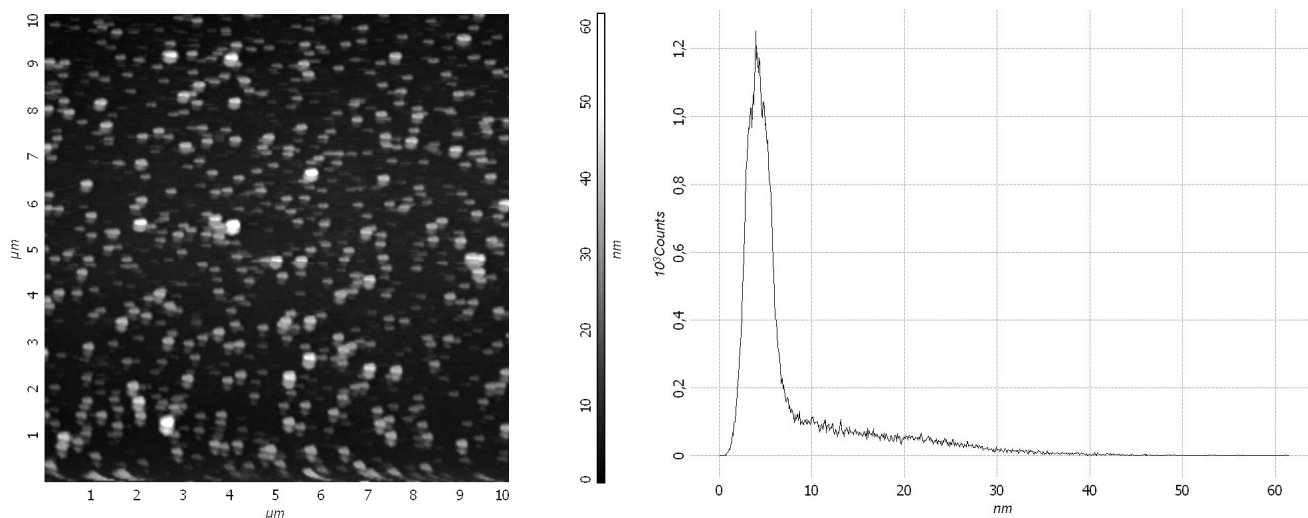**Fig. 2**. AFM image of structures on the hydrophobic modified silicone surface 10×10 µm (at the left). The distribution histogram in height of nanoparticles (at the right)
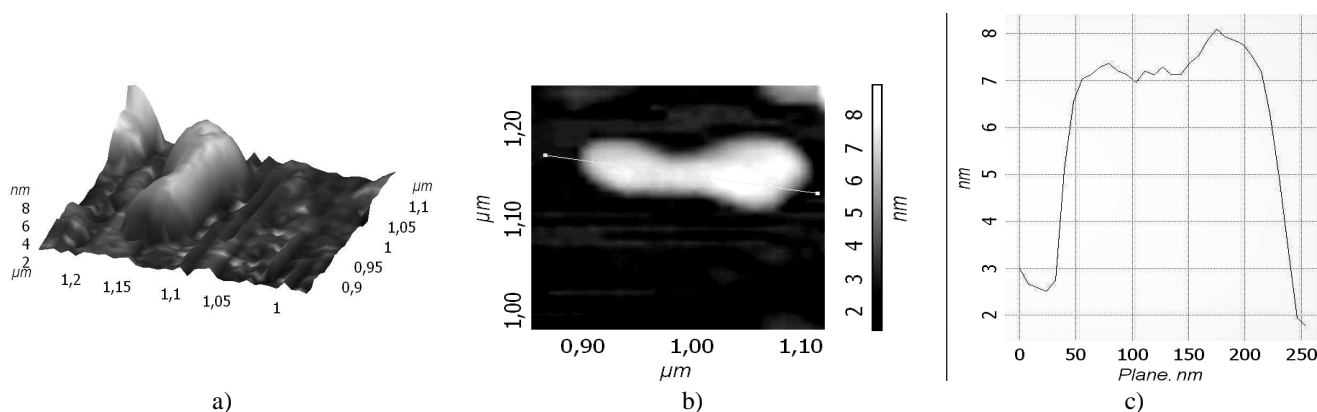


a)   b)   c)

**Fig. 3.** The AFM three- (a) and two-dimensional (b) image and profile of the structure with minimum height (c) along the greatest size in plane XY

From the data in Figs.1-3 the following is visible. It is important to notice that for all structures the sizes in plane XY do not depend on height in Z. They make about 200 nm along a shaft which are passing through two big spheres, and about 150 nm along a shaft crossing the big and smaller spheres (particles with the form resembling three almost merged spheres). But all structures are various in heights from the minimal 3–4 nm to ~ 20–25 nm for maximal values. In distribution in height there is a small quantity of particles with maximum height 20–25 nm and considerably smaller quantity with height to 35 nm (Fig. 1b).
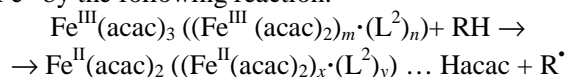
Thus, in this article we have shown that the self-assembly-driven growth seems to be due to H-bonding of binuclear heteroligand complex $Ni_2(OAc)_3$ (acac)·MP·2H$_2$O with a surface of modified silicone, and

further due to directional intermolecular H-bonds, apparently at precipitation of H$_2$O molecules, acac, acetate groups, MP [21, 22] (see Scheme 3).

## 3.2. Role of H-Bonding in Formation of Catalytic Complexes $Fe_x(acac)_y L^2_m(H_2O)_n$ (L$^2$ = 18C6, CTAB)

Participation of hydrogen bonds in the step of $O_2$ activation was found by us in the oxidation of ethylbenzene in the presence of catalytic systems {Fe(acac)$_2$ + L$^2$} (L$^2$ = 18C6, CTAB, DMF). In the oxidation of ethylbenzene ion FeIII rapidly transformed to Fe$^{II}$ by the following reaction:

$$Fe^{III}(acac)_3 \ ((Fe^{III}(acac)_2)_m \cdot (L^2)_n) + RH \rightarrow$$
$$\rightarrow Fe^{II}(acac)_2 \ ((Fe^{II}(acac)_2)_x \cdot (L^2)_y) \ \ldots \ Hacac + R^{\bullet}$$

Then the complex of $Fe^{II}$ was involved in the chain initiation reaction (activation of $O_2$) and the reactions leading to the conversion of primary complexes $Fe^{II}(acac)_2)_x \cdot (L^2)_y$ in the active species (through step of $O_2$ activation). It was also found that complexes with HMPA, which do not form hydrogen bonds are not transforming into the active species in Scheme 2 [6, 7]. The role of H-bonds in the mechanism of catalysis with chemical and biological systems follows from the AFM data presented below.

The surrounding protein structure give two enzymes $Ni^{II}(Fe^{II})ARD$ of different structures and activities. Conversion from monomeric to multimeric forms could be one of the ways of regulating $Ni^{II}(Fe^{II})ARD$ activity [4]. Association of the catalyst in macrostructures with the assistance of the intermolecular H-bonds may be one of the reasons of reducing $Ni^{II}ARD$ activity in mechanisms of $Ni^{II}(Fe^{II})ARD$ operation. On the other hand the $Fe^{II}ARD$ operation seems to comprise the step of oxygen activation ($Fe^{II}+O_2 \rightarrow Fe^{III}-O_2^-\cdot$) (by analogy with Dke1 action [20]). Specific structural organization of iron complexes may facilitate the following regioselective addition of activated oxygen to Acireductone ligand and the next reactions leading to formation of methionine. Here for the first time we demonstrate the different structures organization of complexes of nickel and iron in aqueous and hydrocarbon medium.

First we received UV-spectrum data, testified in the favor of the complex formation between $Fe(acac)_3$ and 18C6. In Fig. 4 the spectrums of solutions of $Fe(acac)_3$ (1) and mixture {$Fe(acac)_3$+18C6} (2) are presented.

One can see that at the addition of a solution of 18C6 to the $Fe(acac)_3$ solution (1:1) an increase in absorption intensity of acetylacetonate ion $(acac)^-$, broadening of the spectrum and a bathochromic shift of the absorption maximum from $\lambda \sim 285$ nm to $\lambda = 289$ nm take place. The similar changes in the intensity of the absorption band and shift of the absorption band are characteristic of narrow, crown unseparated ion-pairs [6]. Earlier similar changes in the UV-absorption band of $Co(II)(acac)_2$ solution we observed in the case of the coordination of macrocyclic polyether 18C6 with $Co(II)(acac)_2$ [6, 7]. The formation of a complex between $Fe(acac)_3$ and 18C6 occurs at preservation of acac ligand in internal coordination sphere of $Fe^{III}$ ion because in another case the short-wave shift of the absorption band should be accompanied by a significant increase in the absorption of the solution at $\lambda = 275$ nm, which correspond to the absorption maximum of acetylacetone [6]. It is known that $Fe^{II}$ and $Fe^{III}$ halogens form complexes with crown-ethers of variable composition (1:1, 1:2, 2:1) and structure dependent on the type of crown-ether and solvent [23]. It is known that $Fe(acac)_3$ forms labile OSCs (Outer Sphere Complexes) with $CHCl_3$ due to H-bonds [24].
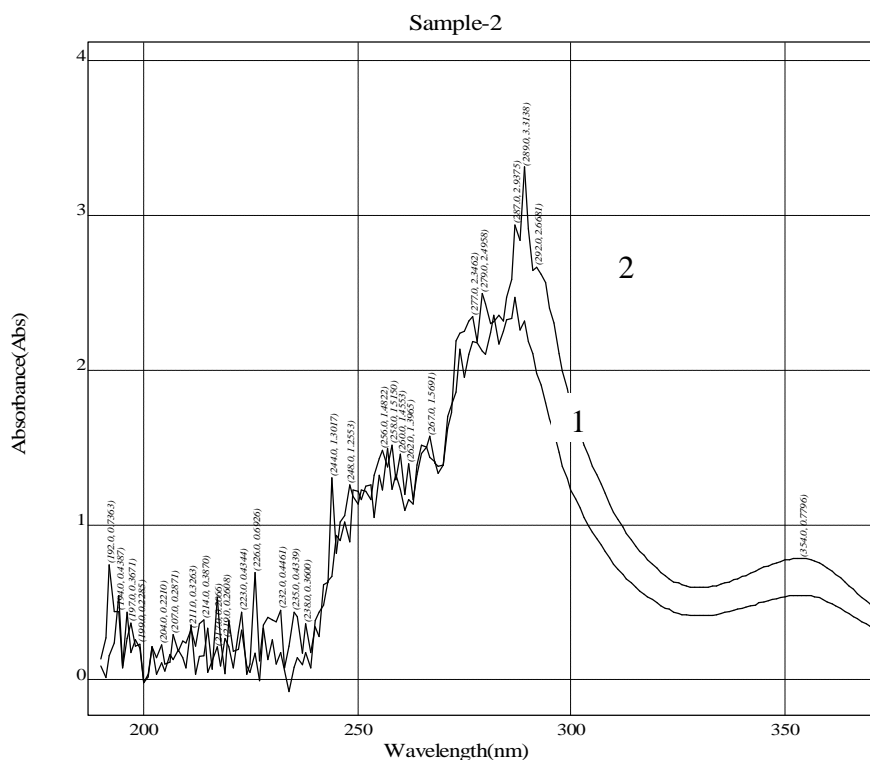


**Fig. 4**. Absorption spectra of $CHCl_3$ solutions: of $Fe(acac)_3$ (1) and {$Fe(acac)_3$+ 18C6}(1:1) mixture (2). $T$ = 293 K

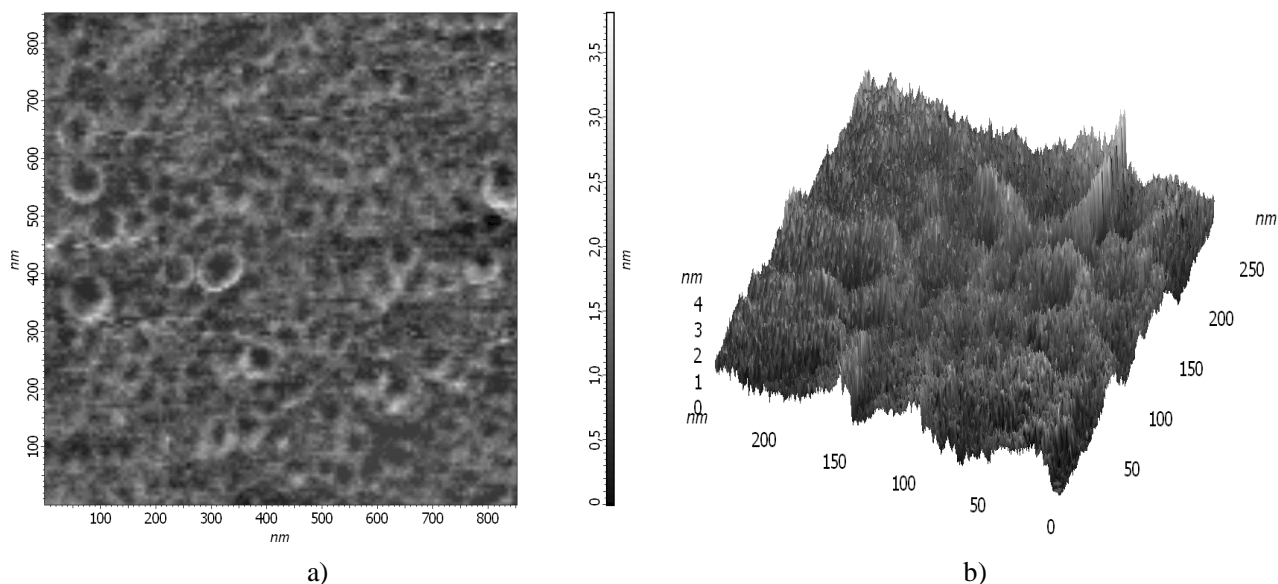**Fig. 5.** The AFM two- (a) and three-dimensional (b) image of nanoparticles
on the basis of $Fe_x(acac)_y18C6_m(H_2O)_n$ formed on the surface of modified silicone



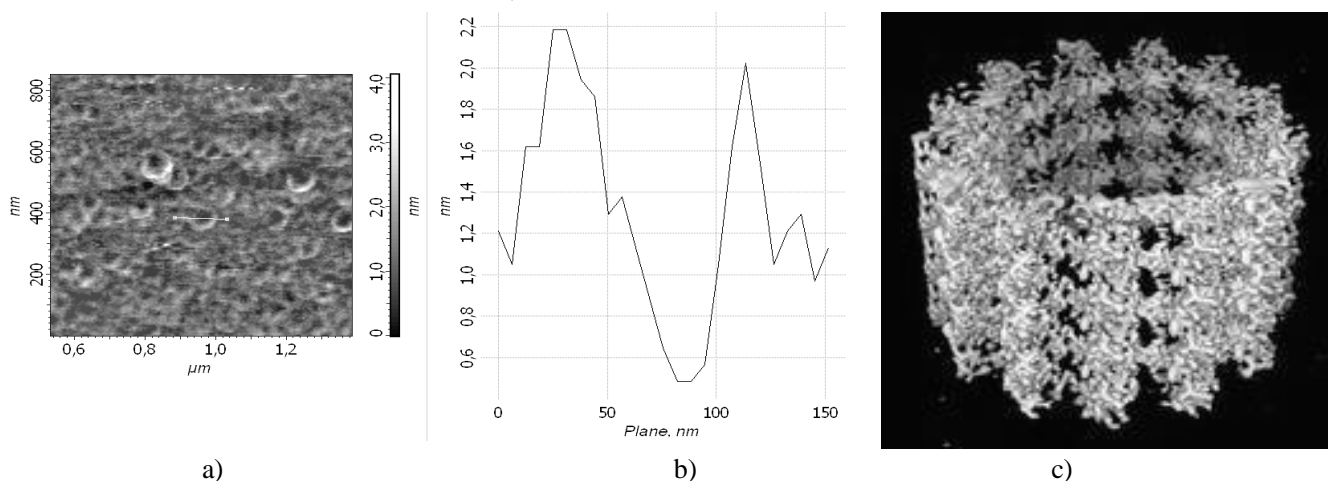**Fig. 6.** The AFM two-dimensional image (a) of nanoparticles on the basis of $Fe_x(acac)_y18C6_m(H_2O)_n$ formed
on the hydrophobic surface of modified silicone. The section of a circular shape with fixed length and orientation is about 50–80 nm
(b). The structure of the cell microtubules (c)

In an aqueous medium the formation of supramolecular structures of generalized formula $Fe^{III}_x(acac)_y18C6_m(H_2O)_n$ is quite probable.

In Fig. 5 three-dimensional (a) and two-dimensional (b) AFM image of the structures on the basis of iron complex with 18C6 $Fe^{III}_x(acac)_y18C6_m(H_2O)_n$, formed at drawing of a uterine solution on a hydrophobic surface of modified silicone are presented. It is visible that the generated structures are organized in certain way forming structures resembling the shape of tubule micro fiber cavity (Fig. 6c). The heights of the particles are about 3-4 nm. In control experiments it was shown that for similar complexes of nickel $Ni^{II}(acac)_2·18C6·(H_2O)_n$ (as well as complexes $Ni_2(OAc)_3(acac)·MP·2H_2O$) this structures organization is not observed. In addition, in the absence of the aqueous environment these iron constructions are not formed. As another example we researched the possibility of the supramolecular nano structures formation on the basis of $Fe_x(acac)_yCTAB_m$ at putting of solutions of $Fe_x(acac)_yCTAB_m$ in $CHCl_3$ (Fig. 7) or $H_2O$ (Fig. 8) on the hydrophobic surface of modified silicon ($CTAB=Me_3(n-C_{16}H_{33})NBr$). We used CTAB concentration 5–10 times less in comparison with $Fe(acac)_3$ with the aim to decrease the possibility of micelles formation in water. However, formation of sphere micelles at these conditions can not be excluded. It is known that salts QX can form complexes with metal compounds of variable composition, which depends on the nature of solvent [6, 7]. So, the formation of heteroligand complexes $Fe_x(acac)_yCTAB_m(CHCl_3)_p$ (and $Fe^{II}_x(acac)_y(OAc)_z(CTAB)_n(CHCl_3)_q$ also) seems to be probable [24].

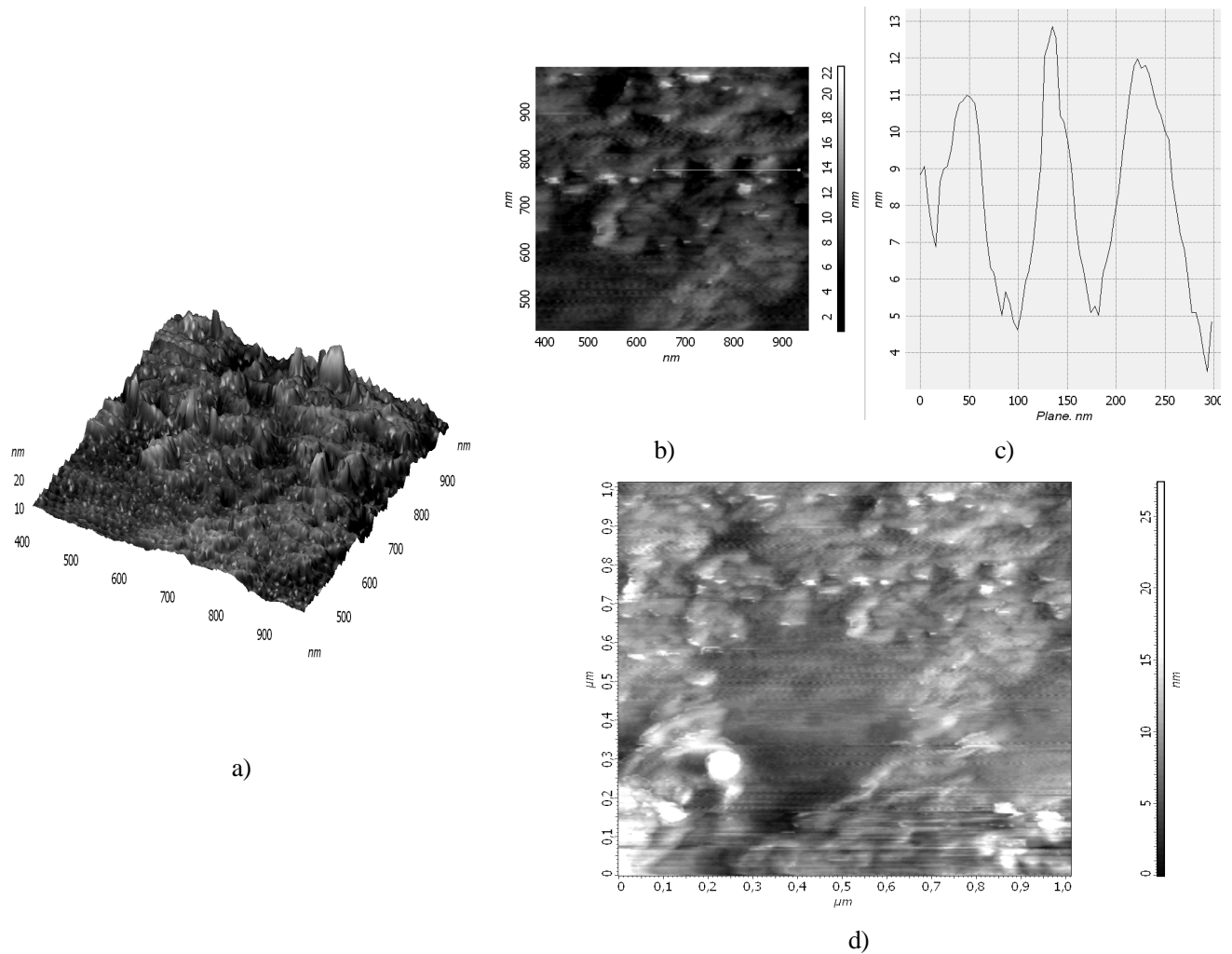**Fig. 7.** The AFM three- (a) two-dimensional image (b, d) of nanoparticles on the basis of $Fe_x(acac)_yCTAB_m(CHCl_3)_p$ formed on the hydrophobic surface of modified silicone. The section of a circular shape with fixed length and orientation is about 50–70 nm (c)



**Fig. 8.** The AFM two-dimensional image (a, b) of nanoparticles (the remains of the micelles) on the basis of $Fex(acac)yCTABp(H_2O)q$ formed on the hydrophobic surface of modified silicone. The section of a circular shape with fixed length and orientation is about 100–120 nm (c)
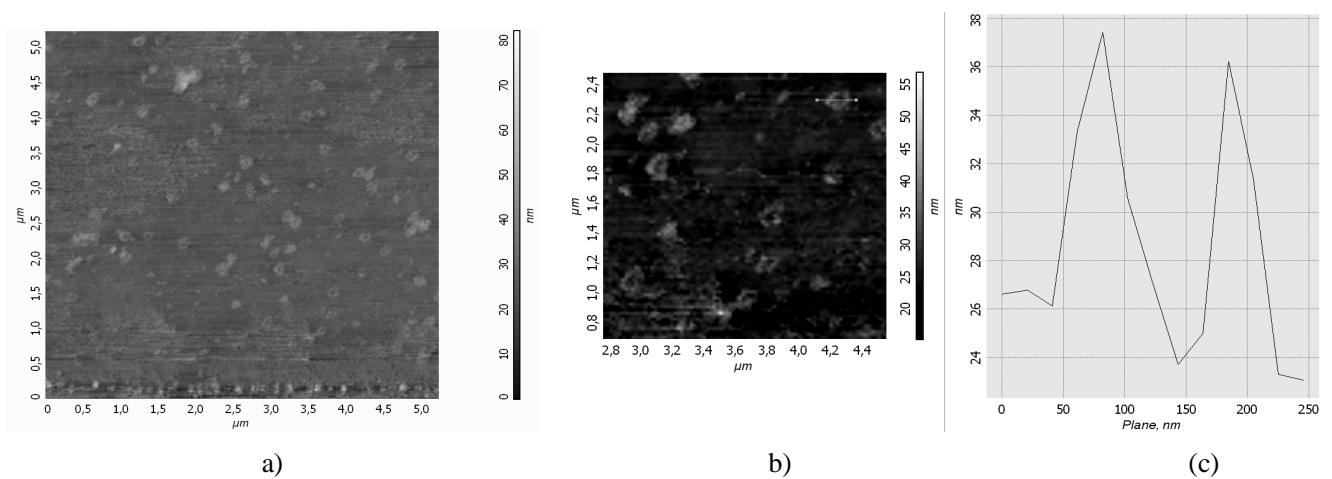
Earlier we established outer-sphere complex formation between $Fe(acac)_3$ and $R_4NBr$ with different structure of R-cation. Unlike the action of 18C6 in the presence of salts $Me_4NBr$, $Me_3(n-C_{16}H_{33})NBr$ (CTAB), $Et_4NBr$, $Et_3PhNCl$, $Bu_4NI$ and $Bu_4NBr$, a decrease in the maximum absorption in this band and its bathochromic shift ($\Delta\lambda \approx 10$ nm) were observed (in $CHCl_3$). Such changes in the UV-spectrum reflect the effect of $R_4NX$ on the conjugation in the $(acac)^-$ ligand in the case of the outer-sphere coordination of $R_4NX$. A change in the conjugation in the chelate ring of the acetylacetonate complex could be due to the involvement of oxygen atoms of the acac ligand in the formation of covalent bonds with the nitrogen atom or hydrogen bonds with CH groups of alkyl substituents [6].

In Fig. 7 three-dimensional (a) and two-dimensional (b, d) AFM image of the structures on the basis of iron complex – $Fe_x(acac)_yCTAB_m(CHCl_3)_p$, formed at drawing of a uterine solution on a surface of modified silicone are presented.

As one can see in this case also the generated supramolecular nano structures are organized like the generated structures on the basis of $Fe_x(acac)_y18C6_m(H_2O)_n$, but with less clear form as compared with the structures, presented in Figs.5 and 6, which resemble the sabout 7-8 nm (Fig. 7c), which is higher when comhape of tubule micro fiber cavity (Fig. 6c). The heights of the particles on the basis of $Fe_x(acac)_yCTAB_m(CHCl_3)_p$ are pared to the same parameters for $Fe_x(acac)_y18C6_m(H_2O)_n$. We showed that complexes $Ni^{II}(acac)_2 \cdot CTAB$ (1:1) (in $CHCl_3$) do not form similar structures.

In Fig. 8 two-dimensional (a-c) AFM image of the structures on the basis of iron complex with CTAB: $Fe_x(acac)_yCTAB_p(H_2O)_q$, – formed at drawing of a uterine water solution on a hydrophobic surface of modified silicone are presented. In this case, we observed apparently phenomenon of the particles, which are the remnants of the micelles formed. Obviously, the spherical micelles, based on $Fe(acac)_3$ and CTAB, in a hydrophobic surface are extremely unstable and decompose rapidly. The remains of the micelles have circular shaped structures different from those observed in Figs. 6 and 7. The heights of particles on the basis of $Fe_x(acac)_yCTAB_p(H_2O)_q$ are about 12–13 nm, which is greater than in the case of the particles presented in Figs. 6 and 7. The particles in Fig. 8 resemble micelles in sizes (particle sizes in the XY plane are 100–120 nm (Fig. 8c)) and also like micelles, probably due to the rapid evaporation of water needed for their existence, they are very unstable and destroyed rapidly (even during measurements).

## 4. Conclusions

AFM method was used by us in the analytical purposes to research the possibility of the formation of supramolecular structures on the basis of heteroligand complexes $Ni_2(OAc)_3(acac) \cdot MP \cdot 2H_2O$ ($L^2 = MP$), $Fe_x(acac)_y18C6_m(H_2O)_n$ and $Fe_x(acac)_yCTAB_m(CHCl_3)_p$ with the assistance of intermolecular H-bonding.

Here for the first time we showed the different structures organization of nickel and iron complexes with the assistance of intermolecular H-bonds in aqueous and hydrocarbon medium.

The experimental data confirm the possibility of formation of supramolecular structures on the basis of complex $Ni_2(OAc)_3(acac) \cdot MP \cdot 2H_2O$ with the assistance of intermolecular H-bonds in the course of alkylarens oxidation. H-bonding seems to be one of the factors responsible for the stability of real catalysts – heteroligand complexes $Ni_2(OAc)_3(acac) \cdot MP \cdot 2H_2O$, in the course of alkylarens (ethyl benzene, cumene) oxidation by dioxygen into hydro peroxide (intermediates in the large-scale production of important monomers) in the presence of catalytic systems $\{Ni^{II}(acac)_2 + L^2\}$.

The data obtained in this work can be useful in treatment of biological effects in $Ni^{II}(Fe^{II})ARD$ enzymes operation. Conversion of monomeric to multimeric forms could be one of ways of regulating $Ni^{II}(Fe^{II})ARD$ activity. Association of catalyst in different macrostructures with the assistance of the intermolecular H-bonds may be one of reasons of different actions of $Ni^{II}$- and $Fe^{II}ARD$. The different supramolecular nanostructures organization based on nickel and iron heteroligand complexes may facilitate the understanding of $Ni^{II}(Fe^{II})ARD$ operation mechanisms. Specific structural organization of iron complexes may facilitate the first step in $Fe^{II}ARD$ operation: $O_2$ activation and following regioselective addition of activated oxygen to Acireductone ligand (unlike mechanism of regioselective addition of nonactivated $O_2$ to Acireductone ligand in the case of $Ni^{II}ARD$), and reactions leading to formation of methionine.

At the same time it is necessary to note that an important function of $Ni^{II}ARD$ in cells has been established. Namely, carbon monoxide, CO, is formed as a result of action of nickel-containing dioxygenase $Ni^{II}ARD$. It was established, that CO is a representative of the new class of neural messengers, and seems to be a signal transducer like nitrogen oxide.

## Abbreviations:

AFM method – atomic-force microscopy method
$(Acac)^-$ – acetylacetonate ion
Bu – butyl radical
CTAB – cetyltrimethylammonium bromide ($Me_3(n-C_{16}H_{33})NBr$)

18C6 – 18-Crown-6
CO – carbon monoxide
DMF – dimethylformamide
Et – ethyl radical
HMPA – hexamethylphosphorotriamide
Hacac – acetylacetone
Me – methyl radical
MP – N-methylpirrolidon-2
Ni(Fe)ARD – Ni(Fe) Acireductone Dioxygenase
NO – nitrogen monoxide
$(OAc)^-$ – acetate ion
QX – quaternary ammonium salt
MSt – stearates of alkaline metals (M = Li, Na, K)
UV-spectrum – ultra violet-spectrum

# References

[1] Li Y. and Zamble D.: Chem. Rev., 2009, **109**, 4617.

[2] Dai Y., Pochapsky Th. and Abeles R.: Biochemistry, 2001, **40**, 6379.

[3] Al-Mjeni F., Ju T., Pochapsky Th. and Maroney M.: Biochemistry, 2002, **41**, 6761.

[4] Sauter M., Lorbiecke R., OuYang B. *et al*.: The Plant J., 2005, **44**, 718.

[5] Chai S., Ju T., Dang M. *et* al.: Biochemistry, 2008, **47**, 2428.

[6] Matienko L., Mosolova L. and Zaikov G.: Selective Catalytic Hydrocarbons Oxidation. New Perspectives. Nova Science Publ., Inc., New York 2010.

[7] Matienko L.: Ch. 2 [in:] D'Amore A. and Zaikov G. (Eds.), Reactions and Properties of Monomers and Polymers. Nova Sience Publ., Inc., New York 2007, 21.

[8] Weissermel K. and Arpe H.-J.: Industrial Organic Chemistry, 3$^{nd}$ edn., VCH: New York 1997.

[9] Matienko L. and Mosolova L.: Oxid. Commun., 2010, **33**, 830.

[10] Leninger St., Olenyuk B. and Stang P.: Chem. Rev., 2000, **100**, 853.

[11] Stang P. and Olenyuk B.: Acc. Chem. Res., 1997, **30**, 502.

[12] Beletskaya I., Tyurin V., Tsivadze A. *et al*.: Chem. Rev., 2009, **109**, 1659.

[13] Drain C., Varotto A. and Radivojevic I.: *ibid*, 1630.

[14] Chu C-C., Raffy G., Ray D. *et al*.: J. Am. Chem. Soc., 2010, **132**, 12717.

[15] Uehara K., Ohashi Y. and Tanaka M.: Bull. Chem. Soc. Jpn., 1976, **49,** 1447.

[16] Nelson J., Howels P., Landen G. *et al*.: [in:] Fundamental Research in Homogeneous Catalysis. Plenum, New York- London 1979, 921.

[17] Daolio S., Traldi P., Pelli B. *et al*.: Inorg. Chem., 1984, **23**, 4750.

[18] Gopal B., Madan L., Betz S. and Kossiakoff A.: Biochemistry, 2005, **44**, 193.

[19] Balogh-Hergovich E., Kaizer J. and Speier G.: J. Mol. Catal. A, 2000, **159**, 215.

[20] Straganz G. and Nidetzky B.: J. Am. Chem. Soc., 2005, **127**, 12306.

[21] Basiuk E., Basiuk V., Gomez-Lara J. and Toscano R.: J. Incl. Phenom. Macrocycl. Chem., 2000, **38**, 45.

[22] Mukherjee P., Drew M., Gomez-Garcia C. and Ghosh A.: Inorg. Chem., 2009, **48**, 4817.

[23] Belsky V. and Bulychev B.: Usp. Khim., 1999, **68,** 136.

[24] Nekipelov V. and Zamaraev K.: Coord. Chem. Rev., 1985, **61**, 185.

## СУПРАМОЛЕКУЛЯРНІ НАНОСТРУКТУРИ НА ОСНОВІ КАТАЛІТИЧНО АКТИВНИХ ГЕТЕРОЛІГАНДНИХ КОМПЛЕКСІВ НІКЕЛЮ І ЗАЛІЗА. ФУНКЦІОНАЛЬНІ МОДЕЛІ Ni(Fe) ДІОКСИГЕНАЗ

**Анотація.** *За допомогою методу АСМ дослідженo можливість утворення супрамолекулярних наноструктур на основі гетеролігандних комплексів: $Fe_x(acac)_y18C6_m(H_2O)_n$, та $Fe_x(acac)_y(CTAB)_p(H_2O)_q$, або $Ni_2(OAc)_3(acac)L^2 \cdot 2H_2O$ ($L^2$ = MP) внаслідок міжмолекулярних Н-зв'язків. Отримано дані про формування різних супрамолекулярних наноструктур на основі комплексів нікелю і заліза, які є моделями Ni(Fe)ARD діоксигеназ. Такі дані можуть бути використані для пояснення механізму різного функціонування цих ферментів.*

**Ключові слова:** *наноструктура, гетеролігандні комплекси нікелю і заліза, Н-зв'язок, каталіз, етилбензол, молекулярний кисень, Ni(Fe)ARD діоксигеназа.*