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Chemistry

ROLE OF SUPRAMOLECULAR STRUCTURES IN MECHANISMS OF CATALYTIC OXIDATION AND ACTION OF Ni(Fe)ARD DIOXYGENASES ON MODEL SYSTEMS

***Ludmila Matienko*[1, ✉], *Vladimir Binykov*[1], *Elena Mil*[1], *Gennady Zaikov*[1]**

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Abstract. The AFM technique was used to research the possibility of the supramolecular structures formation due to H-bonds based on Ni(Fe)(acac)$_n$-systems, that are catalysts of alkylarens oxidations and also models Ni(Fe)ARD dioxygenases: {M(acac)$_n$+L^2+L^3} triple systems (M=Ni^{II}, Fe^{III} , L^2 = NMP (NMP = *N*-methyl-2-pirrolidone), L-histidine, L^3 = PhOH, L-tyrosine), n = 2, 3). Role of H-bonding and supramolecular structures in alkylarens oxidations, catalyzed with Ni(or Fe) complexes catalysts, and also role of supramolecular structures and Tyr-fragment in mechanisms of Ni(Fe)ARD-actions is discussed.

Keywords: AFM, supramolecular structures, catalytic oxidation, O_2, Ni(or Fe)(acac)$_n$, Ni(Fe)ARD dioxygenases.

1. Introduction

The mechanism of catalysis often involves the formation of supramolecular structures due to hydrogen bonds during the catalytic reaction. Hydrogen bonds play an important role in biology, in the structure of proteins and DNA, in receptor binding of drugs, and in catalysis [1, 2]. The importance of H-bonds for the coordination of molecular oxygen O_2 and the activation of O_2 by enzymes P450 is well studied [1]. H-bonding in the case of porphyrins is a type of bond that is usually observed in nature. One of the simplest artificial types of self-organizing supramolecular porphyrin systems is the formation of a dimer based on the carboxylic acid functional group [3].

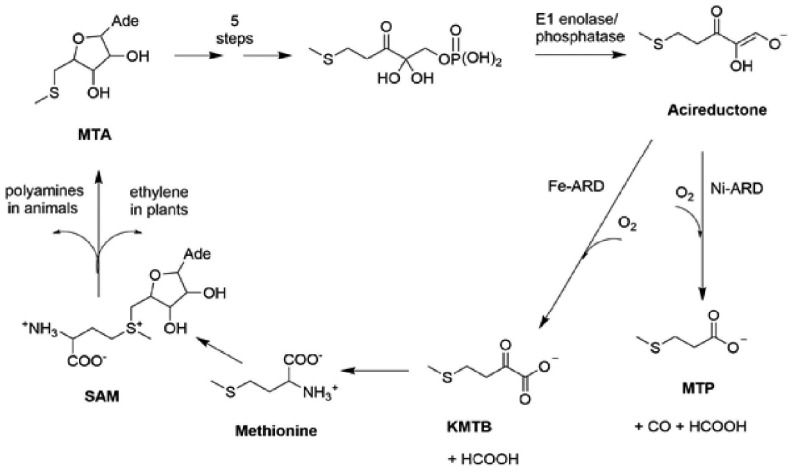
On the other hand surface-based supramolecular chemistry is an area of research that has grown extensively over the recent years. Researchers have developed the concept of exploiting supramolecular interactions, including coordination bonds, halogen bonds, and, notably, hydrogen bonding, to control molecular organization on surfaces [4].

[1] The Federal State Budget Institution of Science,
Emanuel Institute of Biochemical Physics,
Russian Academy of Sciences, Russian Federation
✉ *matienko@sky.chph.ras.ru*

We were the first to offer a new approach to research a role of supramolecular structures and H-bonding in the mechanism of catalysis. AFM method was first used successfully by us to investigate the possibility of supramolecular structures forming due to intermolecular H-bonds based heteroligand nickel and iron complexes, $Ni_2(acac)(OAc)_3$·NMP·$2H_2O$ (“A”), $Fe^{III}_x(acac)_y18C6_m(H_2O)_n$ (“B”), {Ni(acac)$_2$·L^2·PhOH} (“C”) (L^2 = NMP, HMPA, MSt (M = Na, Li)) (NMP = *N*-methyl-2-pyrrolidone). Complexes are effective catalysts for the oxidation of alkylarens by molecular oxygen to hydroperoxides [5], and structural and functional models of acireductone dioxygenase Ni(Fe)ARD ("A"-"C") [6-9] and Fe^{II}-Dke1 ("B") [6-10]. The stability of catalysts ("A"-"C") seemed to be caused by the formation during the catalytic reaction of stable supramolecular structures due to intermolecular H-bonds.

Ni(Fe)ARD enzyme that was discovered in the laboratory of Prof. R. Abeles [11] performs important functions in this process. FeARD catalyzes the penultimate step in the pathway, the oxidative (O_2) decomposition of acireductone to formate and 2-keto-4-(thiomethyl)butyrate (KMTB), the keto-acid precursor of methionine. The acireductone oxidation (O_2), catalyzed with NiARD, does not lead to methionine formation (NiARD produces methylthiopropionate, CO, and formate). However, neurotransmitter CO, formed due to this reaction, has been identified as an antiapoptotic molecule in mammals [11] (Scheme 1).

Earlier Ni(Fe)ARD activity was discovered for bacteria and plants [9, 11]. Later Deshpande *et al*. [11] showed that this dual chemistry of Ni(Fe)ARD, connected with the nature of metal ion (Ni or Fe), can also occur in mammals (MmARD). Interestingly, in the case of KoARD (*Klebsiella oxytoca* ARD, bacterial enzyme ARD) unlike MmARD, Ni-bound form has higher activity than Fe-KoARD. All forms remain monomeric regardless of bound metal ion. While both Fe- and Ni-ARD from *Klebsiella oxytoca* are monomers, Fe-ARD from *Oryza sativa L* (OsARD) is a trimer, and Ni-bound OsARD is a polymer consisting of several types of oligomers [9].



Scheme 1

It was possible to assume a guiding role of H-bonds, as one of the important factors in the regulation of methionine synthesis at participation of Ni(Fe)ARD.

We assumed that one of the reasons for the different activity of Ni(Fe)ARD in the functioning of enzymes in relation to the common substrates (acireductone and O_2) can be the association of catalyst in various macrostructure due to intermolecular H-bonds. These assumptions were confirmed by our AFM-studies [6-8].

Here we demonstrate AFM- and UV-data regarding H-bonding role in the self-organization of complexes $Fe(acac)_3$ with L-histidine and L-tyrosine in supramolecular systems that simulate the FeARD active center and discuss the possible role of Tyr-fragment in the functioning of FeARD.

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 [6-8].

The polished chemically modified silicone surface was used as substrate.

Waterproof modified silicone surface was exploit for the self-assembly-driven growth due to H-bonding of systems $\{Fe(acac)_3$+His$\}$ and $\{Fe(acac)_3$+His+Tyr$\}$, (as in the case of $\{Ni(acac)_2 \cdot NMP \cdot PhOH\}$, $\{Ni(acac)_2$+ +His+Tyr$\}$, $\{Ni(acac)_2\}$+His$\}$ [14] with silicone surface. The water solution of researched system was put on a surface, maintained for some time, and then solvent was deleted from the surface by means of special method – spin-coating process.

In the course of investigated samples scanning, it has been found that the structures are fixed on a surface strongly enough due to H-bonding. The self-assembly-driven growth of the supramolecular structures on modified silicone surface based on researched complexes, due to H-bonds and perhaps the other non-covalent interactions was observed.

Method of UV-spectroscopy was used first to prove the role of His-fragment in the formation of complexes $\{Fe(acac)_3 \cdot$His$\}$ (His =L-Histidine). Quartz cuvettes 1 mm thick were used to record the spectra in the UV regions. The spectra were recorded on a sensitive spectrophotometer "UV-VIS-SPECS" with UV-VIS-Analyst software.

3. Results and Discussion

3.1. Role of Tyr-Fragment in the Mechanism of (Ni)ARD Action on Model Systems

We assumed previously that in the case of operation of Ni(Fe)ARD it is necessary to consider the role of the second coordination sphere comprising the Tyr-fragment (Fig. 1), namely, regulatory role of Tyr-fragment in the mechanism of NiARD action, resulting in reduction of NiARD activity and CO formation.

In our previous works, we have shown that formation of multidimensional forms based on nickel complexes, in particular, forming of the stable nano structures based on $Ni_2(acac)(OAc)_3 \cdot NMP \cdot 2H_2O$, that are structural and functional model of NiARD, can be one of the regulating ways of two enzymes activity [6-8].

It is known that Tyr-fragment can take part in different enzymatic reactions. So, Tyr-fragment may be involved in substrate H-binding in the step of O_2-activation by iron catalyst, and this can decrease the oxygenation rate of the substrate, as it is assumed in the case of homo-protocatechuate 2,3-dioxygenase [12]. Tyr-fragment is

discussed as important in methyl group transfer from *S*-adenosylmethionine (AdoMet) to dopamine [13].

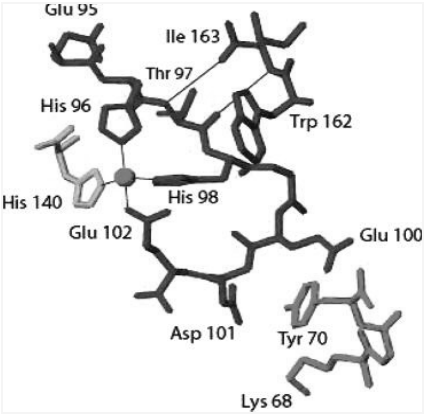


Fig. 1. Structure of NiARD with Tyr-fragment i n the outer coordination sphere of Ni-center [11]

We have found earlier [1, 5, 6] that the inclusion of PhOH in complex $Ni(acac)_2 \cdot L^2$ (L^2 = *N*-methyl-2-pirrolidone), which is the primary model of NiARD, leads to the stabilization of formed triple complex $Ni(acac)_2 \cdot L^2 \cdot PhOH$. We have found that in the ethylbenzene oxidation by molecular O_2, catalyzed by a triple system $\{Ni(acac)_2 + L^2 + PhOH\}$, complexes $Ni(acac)_2 \cdot L^2 \cdot PhOH$, formed during the initial stages of the oxidation reaction, do not undergo oxidative transformation for a long time. Unlike binary systems, the $acac^-$ ligand in nickel complex in this case is not oxidized with O_2 in the course of ethyl benzene oxidation. (The formation of triple complexes $Ni(acac)_2 \cdot L^2 \cdot PhOH$ at very early stages of oxidation was established with kinetic methods [1, 5, 6] and later, in the case of complexes $Ni(acac)_2 \cdot L^2 \cdot Tyr$ – with UV-spectroscopy [14]). Therefore, the reaction rate remains practically the same during the oxidation process.

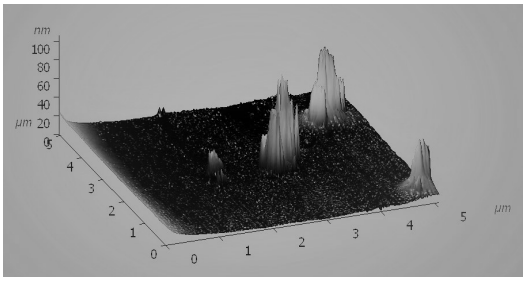


Fig. 2. The AFM three-dimensional image (4.0×4.0 μm) of the structures (h ~ 80–100 nm) based on triple complexes $Ni(acac)_2 \cdot NMP \cdot PhOH$ [7-9]

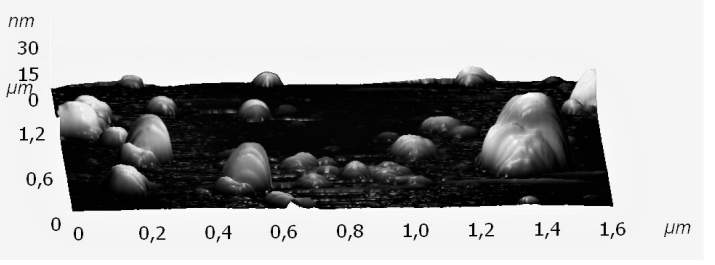


Fig. 3. The AFM three-dimensional image (1.2×1.6 μm) of the nanostructures (h ~ 30 nm) based on triple systems $\{Ni(acac)_2 + His + Tyr\}$ formed on a surface of modified silicone

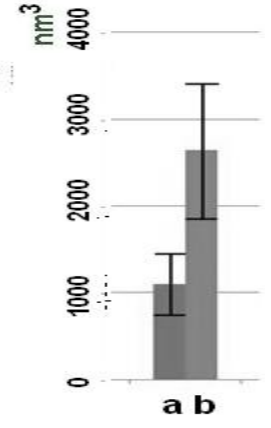


Fig. 4. Diagram of the mean values of volumes of the particles based on (binary $\{Ni(acac)_2 + His\}$(a) and triple systems $\{Ni(acac)_2 + His + Tyr\}$ (b). The diagram marked 95% confidence interval

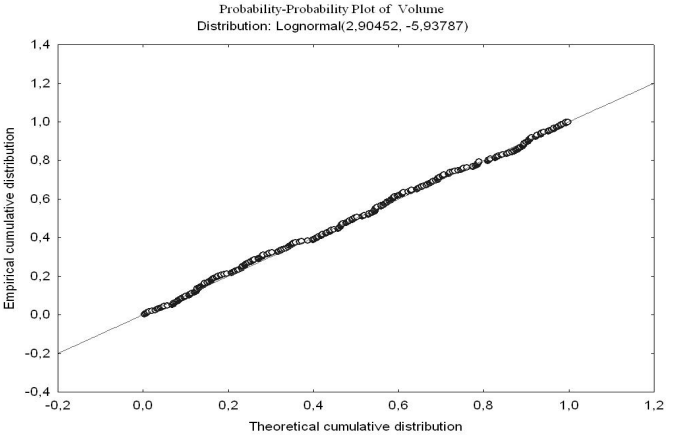


Fig. 5. The empirical and theoretical cumulative Log-normal distribution of volumes of the particles based on system $\{Ni(acac)_2 + His + Tyr\}$[14]

Previously, we established the transformation of binary complexes $Ni(acac)_2 \cdot L^2$ into more selective catalysts during the ethylbenzene oxidation in α-phenyl ethyl hydroperoxide [2]. We established transformation mechanism of binary complex $Ni(acac)_2 \cdot L^2$, that took place only due to molecular O_2. This mechanism of the Ni-catalyst conversion during the oxidation of ethylbenzene, resulting in the formation of more efficient catalytic particles, is similar to the action of NiARD dioxygenase discovered later [11]. Namely, the mechanism of $Ni(acac)_2 \cdot L^2$ transformation includes the incorporation of O_2 into C=C bond of the chelate acac-ring, accompanied by the proton transfer and the redistribution of bonds in the transition complex leading to the formation of the chelate ligand OAc^-, acetaldehyde and CO (*via* the Criegee rearrangement). At that formed intermediate binuclear complex $Ni_2(acac)(OAc)_3 \cdot NMP \cdot 2H_2O$ ("A") is the real effective catalyst of the ethyl benzene oxidation in α-phenyl ethyl hydroperoxide [1, 2]. As mentioned before, the high stability of the effective catalytic complexes ("A") may be connected with the forming of supramolecular structures due to intermolecular H-bonds based on complexes ("A"). This possibility was confirmed with AFM method [5-7].

We were the first to make the assumption that the stability of the triple complexes Ni(acac)2·L2·PhOH can also be connected with the formation of stable supramolecular macrostructures due to intra- and intermolecular hydrogen bonds [2, 5]. Formation of supramolecular macrostructures based on ternary compexes $Ni(acac)_2 \cdot L^2 \cdot PhOH$ due to intermolecular (phenol-carboxylate) H-bonds and, possibly, other non-covalent interactions, established by us with the AFM-method [6-8] is in favor of this hypothesis (Fig. 2). Using the AFM method, we obtained the convincing evidence in favor of the regulatory role of the Tyr-fragment in the functioning of Ni(Fe)ARD. We observed for the first time not only the self-organization that resulted in supramolecular structures based on $\{Ni(acac)_2 \cdot NMP \cdot PhOH\}$ model systems (Fig. 2, [14]), but also the formation of macrostructures under conditions that were closer to real biological systems. The active center of NiARD as a member of the super family of cupins includes histidine ligands. Really, we observed for the first time the self-organization due to H-bonding of model triple systems $\{Ni(acac)_2$+His+Tyr$\}$ [15] (Tyr = L-tyrosine, His = L-histidine) into stable supramolecular structure (AFM) (Figs. 3-5).

Spontaneous organization process, *i.e.*, self-organization, is driven by the balance between interaction of molecules with surface, and intermolecular interaction, which may be the consequence of hydrogen bonds and other non-covalent interactions. These data testified in favor of regulatory role of Tyr-fragment leading to reduce the NiARD activity.

3.2. Role of Tyr- and His-Fragments in the Mechanism of (Fe)ARD Action on Model Systems

Here we assume for the first time the possible role of Tyr-fragment in the second coordination sphere of FeARD, Fig. 6 [11], in the mechanism of FeARD action.

Based on kinetic data [1] we established earlier that the favorable combination of the electronic and steric factors that appeared as the result of the inner and outer sphere (hydrogen bonding) coordination of electron-donating ligand to iron complex, may promote oxygenation of the acetylacetonate ligand by another route, unlike Ni complex. We suggested a hypothetical mechanism for the transformation of the iron complexes [1], by analogy with the action of Dke1 or FeARD [10, 11]. In this case oxygen is included in the C−C bond (rather than in the C=C bond, as in the case of nickel complexes) to form another intermediate complex, *i.e.*, the Fe complex with the chelate ligand containing 1,2-dioxetane moiety**.** The process is completed by the formation of (OAc) ~ chelate ligand and methylglyoxal as the second degradation product of a modified acac-ring [2, 10] without CO formation. By analogy with Dke1 action [10] the FeARD operation seems to comprise the step of dioxygen activation ($Fe^{II}+O_2 \rightarrow Fe^{III}-O_2^-$) [6, 10]. Specific structural organization of iron complexes may facilitate the dioxygen activation and the following regioselective addition of activated oxygen to acireductone ligand and the reactions leading to formation of methionine.

Earlier we really observed the specific self-organization of heteroligand iron(III) complexes with 18C6 in the presence of small amounts of H_2O, $Fe^{III}_x(acac)_y 18C6_m(H_2O)_n$ (Fig. 7a, b) [6, 8]. As one can see the generated structures formed at putting a uterine solution of $Fe^{III}_x(acac)_y 18C6_m(H_2O)_n$ on a hydrophobic surface of modified silicone, are organized in certain way forming structures resembling the shape of tubule micro fiber cavity (Fig. 7c). The heights of particles are about 3–4 nm. In control experiments it was established that these iron constructions are not formed in the absence of the aqueous environment. It was shown that for similar complexes of nickel $Ni(acac)_2 \cdot 18C6 \cdot (H_2O)_n$ (as well as complexes $Ni_2(OAc)_3(acac) \cdot NMP \cdot 2H_2O$) this structures organization is not observed.

Earlier we showed the participation of small amounts of water in mechanism of $Fe^{III,II}_x(acac)_y 18C6_m(H_2O)_n$ transformation by analogy with Dke1 action, in the ethyl benzene oxidation [1]. Study of the effect of addition of small amounts of water to catalytic systems $\{Fe(acac)_3$ + 18C6$\}$ confirmed the important role of H-bonds in the formation of active catalytic complexes. It was found that the introduction of small portions of water

to catalytic systems based on iron complexes leads to the higher catalytic activity of these systems. We observed the increase in oxidation rate due to the increasing chain propagation rate. The outer-sphere coordination of water with the complex $[Fe^{II}(acac)_2]_p \cdot (18C6)_q$ formed during oxidation, may explain the increase in the conversion rate of the complex $[Fe^{II}(acac)_2]_p \cdot (18C6)_q$ into active species such as $Fe_x^{II}(acac)_y(OAc)_z(18C6)_n(H_2O)_m$.

After our research [16] it was found that the possibility of decomposition of the β-diketone in iron complex by analogy with FeARD and Dke1 action increases in aquatic environment. That apparently is consistent with the data obtained in our previous work [1]. It is possible that the self-organization of iron complexes into structures resembling the shape of a tubuline micro tubule (as, for example, in the case of $Fe^{III}{}_x(acac)_y18C6_m(H_2O)_n$ [6, 8]), may favor the dioxygen activation and reactions leading to the formation of methionine [10].

The active center of the FeARD enzyme, like the active NiARD center, includes histidine ligands. Here we show for the first time the self-organization into supramolecular structures due to the H-bonds of binary-{$Fe(acac)_3$+His} (His = L-histidine) and triple systems {$Fe(acac)_3$+His+Tyr} (Tyr = L-tyrosine). Based on the data obtained by us in this and earlier articles [5, 14, 15] and the literature data [18, 19], we could assume the formation of model complexes $Fe^{III}{}_x(acac)_y(His)_m(H_2O)_n$, and $Fe^{III}{}_x(acac)_y(His)_m(Tyr)_n(H_2O)_p$. due to the inner- and outer-sphere coordination of the amino acids L-histidine and L-tyrosine to the iron complex. The possibility of the coordination of L-histidine with $Fe(acac)_3$ is evidenced from spectral data shown in Fig. 8. We observed a decrease in the maximum of the absorption band at λ = 274 nm, connected with the π–π* transition of the conjugated cycle of the acetylacetonate ion $(acac)^-$ and a slight batochromic shift of the band in the presence of additives of L-histidine. The decrease in the absorption at $\lambda \sim 354$ nm, connected with charge transfer $(acac)^-$ ligand–metal was also observed. Such a change in the spectrum of iron-acetylacetonate indicates the influence of L-histidine coordinated in the outer sphere of iron complex. Earlier [1] in the case of $Fe(acac)_3 \cdot R_4NBr$, we also observed the similar changes in UV-spectrum of (acac) ion ($CHCl_3$).

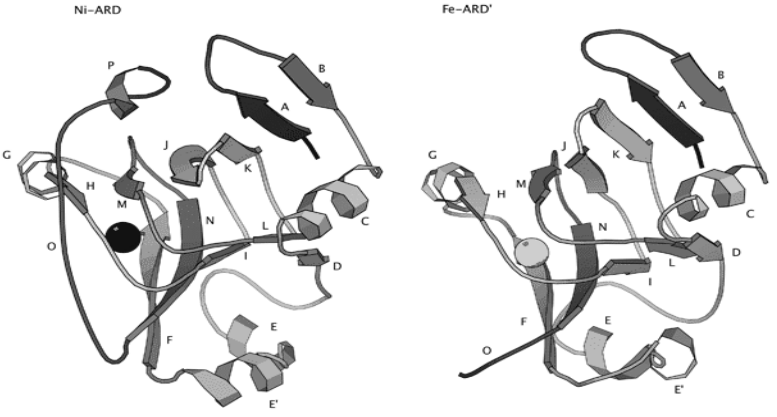


Fig. 6. Comparison of the structures of NiARD and FeARD. Letters reference to the ARD sequence as follows: A (Ala 2-Phe 6), B (Leu 15-Ser 18), C (Glu 23-Lys 31), E (Thr 50-Tyr 57), E' (Ile 61-Lys 68), F (Ser 72-Leu 78), G (Lys 85-Glu 90), H (Phe 92-Glu 95), I (Arg 104-Val 107), J (Gly 111-Ile 117), K (Glu 120-Leu 125), L (Asn 129-Ile 132), M (His 140-Met 144), N (Phe 150-Phe 156), O (Gly 161-Gly 168), P (Ile 171-Ala 174) [11]

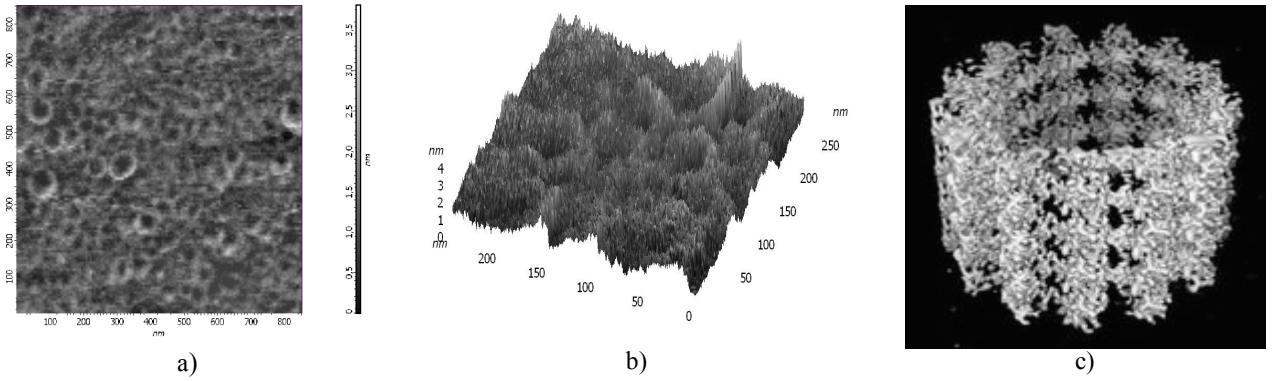


Fig. 7. The AFM two- (a) and three-dimensional (b) images of nanoparticles based on $Fe^{III}{}_x(acac)_y18C6_m(H_2O)_n$ formed on the surface of modified silicone; the structure of the cell microtubules (c)

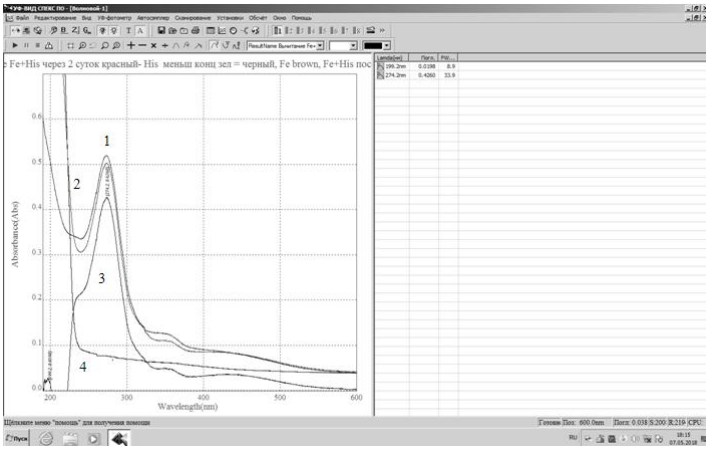


Fig. 8. Electron absorption spectra of aqueous solutions: $Fe(acac)_3$ (1); $\{Fe(acac)_3+His\}$ (2); $\{Fe(acac)_3+His\}$- His (3) and His (4). $[Fe(acac)_3] = 2.5\cdot10^{-4}$ mol/l, $[His] = 4.3\cdot10^{-4}$ mol/l, $T = 293$ K

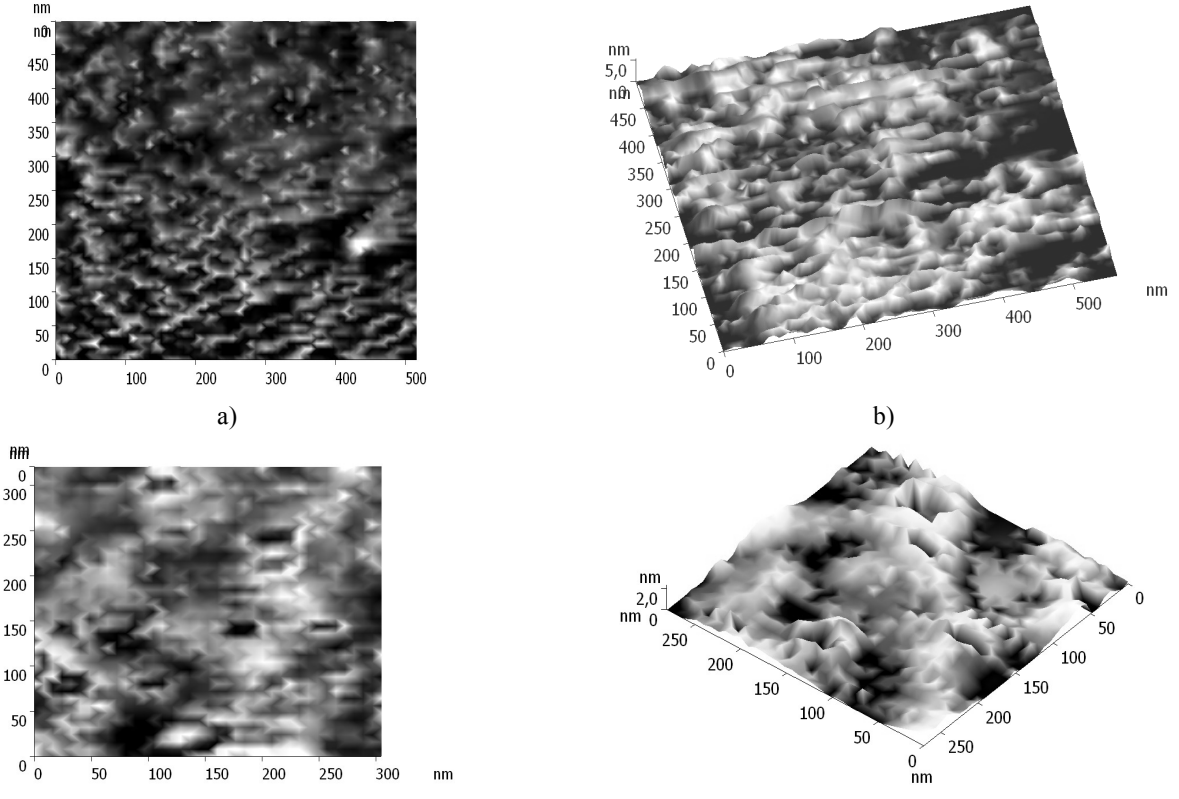


Fig. 9. The AFM two- (a) and three-dimensional images (b) of nanoparticles based on triple system $\{Fe(acac)_3+His+Tyr\}$ formed on the surface of modified silicone; the AFM two- (c) and three-dimensional images (d) of nanoparticles based on binary system $\{Fe(acac)_3+His\}$ formed on the surface of modified silicone

We fail to get a clear picture of the changes in UV-absorption of $(acac)^-$ ligand of $Fe(acac)_3$ in the presence of L-histidine and L-tyrosine additives due to complete coincidence of absorption bands of L-tyrosine and $(acac)^-$ ligand of Fe complex.

In Fig. 9 we observed the self-organization of binary $\{Fe(acac)_3+His\}$ and triple $\{Fe(acac)_3+His+Tyr\}$ systems in nanostructures due to H-bonds. It is visible that the generated structures are organized in certain way forming structures resembling the shape of tubule micro cavity like structures in Fig. 7 or structures like tau protein (Fig. 10, [20]).

$\{Fe(acac)_3+His+Tyr\}$ structures are better organized in tubuline (or tau)-like structures and characterized by a greater height (h = 5 nm, Figs. 9a, b) in comparison with the particles based on binary systems $\{Fe(acac)_3+His\}$ (h = 2–3 nm, Figs. 9c, d). We established also that unlike structures based on Ni- triple systems the nanostructures

based on Fe-bi- and Fe-triple systems were less stable. It is possible to assume that in the case of formation of triple complexes $Fe^{III}_x(acac)_y(His)_m(Tyr)_n(H_2O)_p$, Tyr-fragment does not lead to reduction of the enzyme activity. On the contrary, the outer-sphere coordination of Tyr-fragment can promote the formation of tubulin-like structures and the activation of O_2 (due to H-bonds) and the formation of structures analogous to the tube tubuline (or tau)-like structures based on $Fe^{III}_x(acac)_y(His)_m(Tyr)_n(H_2O)_p$, – may facilitate the following regioselective addition of activated oxygen to acireductone ligand and the reactions leading to formation of methionine.

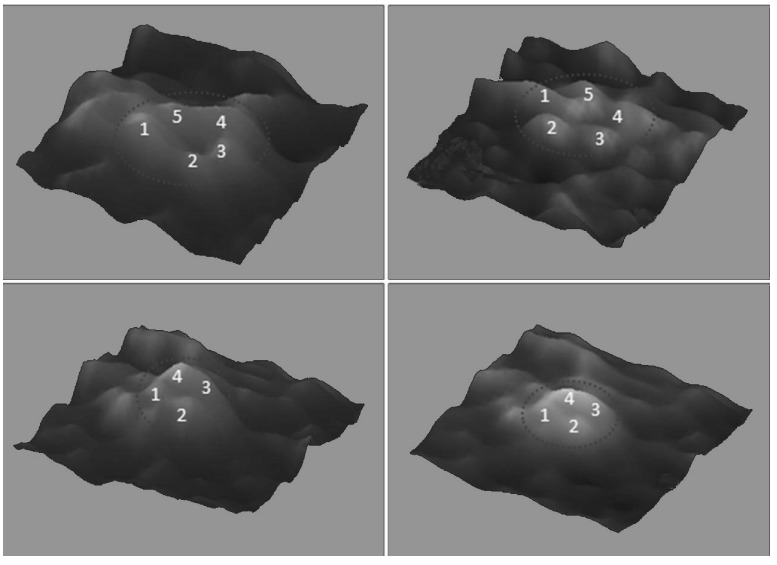


Fig. 10. AFM three-dimensional representation of pore like structures of tau protein in a lipid bilayer [20]

4. Conclusions

Earlier, for the first time we assumed the participation of Tyr-fragment, which is in the second coordination sphere of Ni(Fe)ARD enzymes, in the mechanism of Ni(Fe)ARD operation, the role of tyrosine residue as regulatory factor, and received experimental facts in favor of this assumption. With AFM method we observed the formation of very stable supramolecular macrostructures based on triple systems {Ni(acac)2+His+Tyr}, that included His = L-histidine and Tyr = L-tyrosine as extra ligands, formed on a surface of modified silicone due to intermolecular (phenol–carboxylate) H-bonds and, possibly, the other non-covalent interactions. These data testified in favor of regulatory role of Tyr-fragment leading to reduction of the NiARD activity.

Here we first demonstrate self-organization of complexes $Fe^{III}_x(acac)_y(His)_m(Tyr)_n(H_2O)_p$ (Tyr = L-tyrosine, His = L-histidine), which modulate Fe-ARD active center, into the supramolecular structures resembling tubuline structures due to H-bonds. The data of UV spectroscopy indicate the outer-sphere coordination of L-Histidine ligand (H-bonds) with $Fe(acac)_3$. Formation of structures similar to the tubuline protein or tau-like structures may favor the activation of O_2 (with the participation of Tyr-fragment) and the subsequent reactions leading to the formation of methionine. The data obtained can bring us closer to understanding of the processes occurring as a result of operation of Ni(Fe)ARD, Tyr-fragment role in the synthesis of methionine and CO in the mechanism of normal homeostasis.

Acknowledments

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Abbreviations

AFM method – Atomic-Force Microscopy method
$(acac)^-$ – Acetylacetonate ion
ARD – Acireductone ligand
18C6 – 18-Crown-6
CO – Carbon monoxide
$CHCl_3$ – Chloroform
Hacac – Acetylacetone
His – L-Histidine
NMP – *N*-methyl-2-pirrolidone
Ni(Fe)ARD – Ni(Fe) Acireductone dioxygenase
$(OAc)^-$ – Acetate ion
QX – quaternary ammonium salt
Tyr – L-tyrosine
UV-spectrum – Ultra violet spectrum

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РОЛЬ СУПРАМОЛЕКУЛЯРНИХ СТРУКТУР В МЕХАНІЗМАХ КАТАЛІТИЧНОГО ОКИСНЕННЯ ТА ДІЯ ДІОКСИГЕНАЗ Ni(Fe)ARD НА МОДЕЛЬНИХ СИСТЕМАХ

Анотація. *За допомогою методу АСМ досліджено можливість утворення супрамолекярних структур внаслідок водневих зв'язків на основі Ni(або Fe)(асас)$_n$-систем, які є каталізаторами окиснення етилбензену, а також моделями Ni(Fe)ARD діоксигеназ: потрійні системи {M(асас)$_n$ + L^2 + L^3} (M = Ni^{II}, Fe^{III}, L^2 = NMP (NMP = N-метил-2-піролідон), L-гістидин, L^3 = PhOH, L-тирозин), n = 2, 3). Визначено роль H-зв'язків і супрамолекулярних структур при окисненні алкіларенів (етилбензен), який каталізується Ni(або Fe)-комплексними каталізаторами, а також роль супрамолекулярних структур і Tyr-фрагменту в механізмах дії Ni(Fe)ARD діоксигеназ.*

Ключові слова: *АСМ, супрамолекулярні структури, каталітичне окиснення, O_2, Ni(або Fe)(асас)$_n$, Ni(Fe)ARD діоксигенази.*