REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Science

STRUCTURE, PROPERTIES AND REACTIONS OF OXIDATIVE DEHYDROGENATION OF METAL COMPLEXES WITH RESTORED SCIFF BASES

Specialty 2303.01- Inorganic chemistry

Field of science: Chemistry

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GENERAL CHARACTERISTICS OF THE WORK

Modern state and urgency of the problem:

Coordination compounds are catalysts, sensors, drugs, etc. in various fields of chemistry occupies a leading position in the world scientific literature for its use. In the last decade, researches have been conducted on the possibility of using coordination compounds in nanotechnology - molecular magnets, molecular conductors and etc.

The structure and properties of coordination compounds are determined by the structure of the organic ligand. Many different types of organic ligands are now known that are able to bind metal ions strongly. In this case, the structure of complex compounds depends on the electronic properties of the hetero atoms that make up the ligand, the number of coordinating atoms (dentate), their relative position, and the elasticity of the ligands. In this regard, metal complexes with reduced Schiff bases are of great interest. The reduction of the azometin bond leads to new, more elastic ligands than the original Schiff bases, and accordingly the coordination nature of the metal ion must be different.

The collection of information on the synthesis and structure of new complex compounds, the study of their X-ray structure, can help to establish the relationship between the structure of the ligand and the resulting metal complex. The synthesis of molecular magnets and conductors, catalysts for various reactions, and new, bi- and polydenate ligands that can be used in the field is very promising.

A more complex problem is the prediction and implementation of the synthesis of dual and multinucleated metal complexes. One solution to this problem is to increase the dentate of the ligand by introducing functional groups that can form anions by separating protons.

In this regard, hydrazones of hydrazides, mono- and dicarboxylic acids open up a wide range of possibilities for the production of polydentate ligands. Due to their high biological activity, this class of compounds has been intensively studied in recent years. They have antimicrobial and fungicidal properties, have anti-cold and anti-cancer properties. Like reduced Schiff bases, reduced hydrazones and their complexes with metals are of great interest both in terms of the theory of coordination compounds and their practical application. However, to date, such compounds have not been studied.

Thus, the study of new, multi-dent ligands of reduced Schiff bases and reduced hydrazones and their complexes is one of the urgent directions. Very little is known in the literature on the study of oxidative dehydrogenation reactions in coordinated ligands.

Object and subject of research:

Reduced Schiff Basics. Hydrazones of hydrazides of mono- and dicarboxylic acids and their complexes with transition metals. Metal complexes with reduced Schiff bases and reduced hydrazones.

Aims and objectives of the dissertation: The aim is to study the synthesis, structure, properties and reactivity of metal complexes of reduced Schiff bases and reduced hydrazone ligands. The dissertation includes the following tasks:

- obtaining new reduced Schiff bases based on aromatic oxyaldehydes and aromatic amines, study of their synthesis, structure and properties of metals and complexes;
- study of oxidative dehydrogenation reactions in ligands coordinated on the basis of reduced Schiff;
- study of the kinetics and mechanism of oxidative dehydrogenation reactions;
- synthesis of reduced hydrazones of carbonic acids;
- obtaining metal complexes of the first transition period with reduced hydrazones of carbonic acid hydrazides;
- study of the structure and properties of metal complexes with reduced hydrazones of carbonic acids.

Research methods: Synthesized compounds - ligands and metal complexes studied by IR-, electron spectroscopy, EPR, magnetic permeability, RSA and etc. methods.

The main provisions submitted for defense:

- new coordination compounds with reduced Siff bases;
- rate and mechanism of oxidative dehydrogenation reaction in coordinated ligands;
- complexes of transition metals with reduced hydrazones of mono- and dicarboxylic acid hydrazides;
- structural features of complexes of transition metals with

hydrazones of hydrazides of mono and dicarboxylic acids;

- reduced Schiff bases, reduced hydrazones of carbonic acids and biological activity of their complexes;
- catalytic activity of complexes with reduced hydrazones of carbonic acids.

Scientific innovation:

- Cu(II) and Pd(II) complexes were obtained with N-(2-hydroxybenzyl) -aminopyridines. Molecular and crystal structures of complexes were studied. Cu(II) complex of N- (2-hydroxybenzyl) -2-aminopyridine (Hs2amph) $[Cu(s2amph)_2(CH_3COO)_2]$ coordinates with 2 oxygen atoms of two acetate groups and two nitrogen atoms of two pyridine rings, which are coordinated in the fog state. The distorted plane has a square structure. The remaining two oxygen atoms of the two carboxyl groups form an 8-membered 2-body structure linked by a hydrogen bond joined by four coordinated copper (II) ions.

IR-, electron spectra, magnetic moment, as well as thermogravimetric analysis show that the complexes $[Cu(s3amph)_2(CH3COO)_2{\cdot}2H_2O]$ and $[Cu(s4amph)_2\ (CH_3COO)_2{\cdot}2H_2O]{\cdot}2H_2O$ have a single-nucleated octahedral structure.

X-ray structural analysis of the $[Pd\ (s2amph){\cdot}2Cl_2{\cdot}2C_2H_5OH]$ complex showed that the Pd(II) complex has a plane-square structure due to two chlorine atoms coordinated in the trans state and two nitrogen atoms of the pyridine rings. Spectral data show that the complexes obtained by ligand exchange between $[PdCl_2(PhCN)_2]$ and the hydroxybenzyl derivatives of 3-amino and 4-aminopyridine have similar structures.

- 2-hydroxybenzyl derivatives of 4-aminoantipyrine and their complexes with transition metals were synthesized. The molecular and crystalline structure of 3 new complexes of this class of compounds was studied by X-ray structural analysis. The results show that the coordination polyads in the complexes have an equatorial plane octahedral structure due to two nitrogen atoms of amine groups and oxygen atoms of 2 carbonyl groups of two 4-aminoantipyrine fragments, and phenolic oxygen is located apical to this plane. The solvent molecules entering the crystal lattice, O-H (water molecule and methyl alcohol), form a hydrogen bond with the nitrogen atom of the amine group, the oxygen atom of the phenol group and the carbonyl group.

– (2-hydroxy-R^1, R^2-benzyl) -4-aminopyridines in alcoholic solutions are obtained by complexes with appropriate Schiff bases instead of complexes with reduced Schiff bases expected in the interaction with copper 2-acetate, oxidative dehydrogenation reaction takes place in ligands. It was possible to obtain suitable complexes by reducing the sodium salts of reduced ligands by reacting them with copper 2-sulfate in aqueous medium.

– It has been shown that the oxidative dehydrogenation reaction takes place in mixed ligand complexes. But doesn't take place in these complexes of Cu(tbsaah-dtbsaah)(CH_3COO)X. X=H_2O, CH_3OH, CH_3CH_2OH). Cu(tbsaah-dtbsaah)$_2$·H_2O. This is due to the octahedral structure of the Cu^{+2} ion in the Cu(tbsaah-dtbsaah)$_2$ complexes and the lack of a coordinating space for the combination of molecular oxygen. As a result of the oxidative dehydrogenation reaction, two single crystals of the Cu(II) complex based on Schiff were obtained as the final product, and their molecular and crystalline structures were studied by X-ray analysis.

–Schiff bases based on 8-aminoquinoline and 5-bromine and 3,5-ditretbutyl salicyl aldehyde derivatives and Cu(II), Ni(II), Co(II) complexes were synthesized with their reduced analogues. The structure of the complexes obtained was studied by elemental analysis, IR-, electron spectroscopy methods. It has been shown that the Cu(II), Co(II) complexes of reduced 8-aminoquinoline and 5-bromosalicyl aldehyde are easily oxidatively dehydrogenated in the process of complex formation.

– New Cu(II), Co(II), Ni(II) and VO(II) complexes were synthesized with ligand obtained by reduction of hydrazone obtained from the interaction of salicylic acid hydrazide and 3,5-ditretbutyl salicyl aldehyde. The structure of complexes was studied by IR, electronic spectrometry, thermogravimetry and element analysis methods. It has been shown that the coordination of the metal ion is formed by the oxygen atom of the amide group in the enol form, the nitrogen atom of the hydrazine group and the oxygen atom of the salicylaldiminate fragment. The metal-ligand ratio in the complexes is 1:1.

– Co(II), Ni(II), Cu(II), Mn(II), Fe(II) complexes of salicylhydrazone were synthesized with nicotinic acid hydrazide. It has been shown that the metal ion coordinates with the oxygen atom of the phenol fragment, the nitrogen atom of the azometine group, and the oxygen atom of the amide group. In this case, the ligand dianion is a tridentate.

– Mn(II) and Fe(II) complexes were synthesized by the reduced derivative of salicyl aldehyde dihydrazone, 3,5-ditretbutyl was synthesized with malonic acid dihydrazide. The structure of complexes was studied by IR, electronic spectrometry, thermogravimetry, EPR and element analysis methods. The reduced analogue of 3,5-ditretbutyl salicyl aldehyde dihydrazone with malonic acid dihydrazide forms binuclear complexes with manganese and iron ions. Measurement of magnetic permeability shows that there is a ferromagnetic interaction between metal ions.

– Ni(II), Co(II), Cu(II), Mn(II), Fe(III) complexes were obtained and studied with reduced analogues of dihydrazones of maleic and amber acids. It has been shown that the metal ion coordinates with the ligand through the enol form of the oxygen atom of the amide group and the nitrogen atom of the amine group. Element analysis and thermographic analysis showed that the metal-ligand ratio was 1:1. These complexes are thought to have two nuclear.

– X-ray structural analysis shows that when 4-salicylidenimine-3-hydrazine-5-mercapto-1,2,4-triazole interacts with Ni(II) acetate, a complex with salicylic thiosemicarbazone is obtained instead of the corresponding Schiff-based complex.

A mechanism for the hydrolysis of the triazole ring has been proposed. It has been shown that the interaction of nickel (II) acetate with 4-salicylidenimine-3-hydrazine-5-mercapto-1,2,4-triazole breaks down the triazole ring and forms a thiosemicarbazonate complex of nickel (salicylide). This, in turn, proves that salicylic aldehyde, based on the original Schiff, forms a bond between the nitrogen atom in the triazole ring and the nitrogen atom next to the amine group. The mechanism of hydrolysis of the triazole ring is shown.

Theoretical and practical significance of the work:

The study of the mechanism of the oxidative dehydrogenation reaction in ligands allows to clarify the oxidative ammonolysis reaction. The methods developed for reactions with 4-aminoantipyrine are simple, allow the production of compounds in various combinations of substitutes, and these compounds can be used in drug synthesis. It has been found that a number of compounds may be included in anti-cold and analgesic drugs used in medicine.

Reduced hydrazones of carbonic acid hydrazides and their metal complexes have a strong antibacterial and fungicidal effect. They can be used as antimicrobials, fungicide additives and medicines for petroleum products.

Approbation of the results of the work

Conference dedicated to the 100th anniversary of academician H.B.Shakhtakhtinsky, Baku (2000), Days of Kazakhstan-2001. II International Scientific-Practical Conference of Young Scientists (2001), Conference dedicated to the 75th anniversary of corresponding member of the Azerbaijan National Academy of Sciences Kh.M. Mammadov (2002), Conference dedicated to the 95th anniversary of academician M.F.Naghiyev (2003), IX Republican scientific conference, BSU, (2004), Conference dedicated to the 90th anniversary of corresponding member of ANAS Z.Sh. Zulfugarov, (2005), Proceedings of the IV International Conference on Solving Waste Problems, Kharkov (2007), III Republican Scientific Conference "Synthesis and Transformation of Chemical Compounds", Baku, (2007), Scientific Conference dedicated to the 90th anniversary of Baku State University and the 75th anniversary of the Faculty of Chemistry (2009), Republican Conference “Organic Reagents in Analytical Chemistry” dedicated to the 95th anniversary of professor A.Verdizade, November 24-25, ADPU (2009), 44thWorld Chemistry Congress 11-16 August, Istanbul/Turkey (2013), II Republican Scientific Conference "Organic Reagents in Analytical Chemistry", dedicated to the 100th anniversary of Professor A.A. Verdizade, Baku, (2014), European Journal of Natural History №5 (2015), Conference Proceedings, Kyoto, Japan, may (2015), I All-Russian Youth Conference on "Success of Synthesis and Complex Formation", abstracts of reports, Moscow, April 25-28 (2016), XXVI Russian Youth Scientific Conference "Problems of Theoretical and Experimental Chemistry" dedicated to the 120th anniversary of Academician N.N. Semyonov, abstracts of reports, Yekaterinburg, April 27-29 (2016), 27th International Chugaev conference on Coordination chemistry, October 2-6, Nizhny Novgorod (2017), H85. III International Interdisciplinary Youth Forum "New Materials", Moscow, November 21-24 (2017).

The place where the dissertation work is done.

The dissertation work was carried out in accordance with the scientific research plan of the Azerbaijan National Academy of Sciences. Registration number 0115 Az 2102.

STRUCTURE AND VOLUME OF WORK

The dissertation consists of an introduction, a literature review (chapter I), an experimental part (chapter II), discussion of the results of the study of metal complexes with reduced Schiff bases (chapter III), metal complexes with mono- and dihydrazides of carboxylic acids (chapter IV), the study of biological and the catalytic activity of the synthesized complex compounds (chapter V), conclusions and list of references, referred to in 286 titles.. The total volume of the dissertation contains 361 pages of printed text, 205 figures, 21 schemes and 10 tables. The total volume of the dissertation is 320270 characters (excluding tables, figures and bibliography).

The first chapter provides a literature review on studies in the field of the structure and properties of complex compounds with o-hydroxybenzylamines, 4-aminoantipyriminium and also on the synthesis and study of reduced hydrazides and hydrazone of carboxylic acids, which are of interest in terms of structure and biological activity.

The second chapter summarizes the experimental data, which provide methods for the synthesis of derivatives of o-hydroxybenzylamine, 4-aminoantipyrine, reduced hydrazides and hydrazone of carboxylic acids, complexes of 4-salicylidenamino-3-hydrazino-5-mercapto-1,2,4-triazole and their complexes with transition metals Cu(II), Ni(II), Co(II), Pd(II), VO(II), Mn(II), Fe (II), studying the possibility of obtaining aminocarboxylic acid by carboxymethylation 2,2,6,6-tetramethyl-4-hydroxypiperidine (TMHP) as well as the oxamide of this compound using oxalyl chloride.

The third and fourth chapters discuss the results of experimental studies and the structure and properties of the obtained compounds.

The fifth chapter provides data on the bactericidal, antifungal and catalytic activity of metal complexes of 2-aminopyridine, derivatives of 4-aminoantipyrine and metal complexes with hydrazides and hydrazones of carboxylic acids.

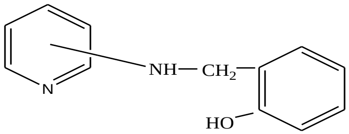
1. Cu(II) and Pd(II) complexes with N- (2-hydroxybenzyl) aminopyridines

The Schiff bases of aminopyridines are very interesting due to the fact that they contain two biologically active fragments at the same time - the pyridine ring and the CH = N bond. Many works have been published on the biological activity of Schiff's bases. They will be discussed in the "Schiff Basics" section. Depending on the structure of aminopyridine (2, 3 or 4 aminopyridine), different structures of the formed complex compounds are possible. For example, in the complex formed by the Schiff base of 2-aminopyridine and salicyl aldehyde, the metal ion coordinates with the endicyclic nitrogen atom of the two pyridine rings, the nitrogen atom of the azometine group, and phenolic oxygen. In the complex formed by the Schiff base of salicyl aldehyde and 3-aminopyridine, the metal ion coordinates with the phenolic oxygen and the nitrogen atom of the azometine group. (The endocyclic nitrogen atom of the pyridine ring is not involved in coordination. The same is true for the Schiff base complexes of 4-aminopyridine).

A number of works are known on complexes of transition metals with Schiff bases of aminopyridines. Basically, in these compounds, the metal ion is coordinated through phenolic oxygen and azomethine nitrogen, and the endocyclic nitrogen atom is usually not involved in coordination. There is practically no data on complexes of “hydrogenated” analogues of the above compounds.

This section presents the results of the work on the synthesis and study of the structure of complexes of Cu(II) and Pd(II) with reduced hydroxybenzyl aminopyridines.

According to elemental analysis and thermogravimetric measurements, the ligands Hs2amph, Hs3amph, and Hs4amph form Cu(II) complexes of the composition-$Cu(s2amph)_2(CH_3COO)]_2$, $Cu(s3amph)_2(CH_3COO)_2 \cdot 2H_2O]$ and $Cu[(s4amph)_2 \cdot (CH_3COO) \cdot 2H_2O]$.



s2amph- derivatives of 2-aminopyridine
s3amph- derivatives of 3-aminopyridine
s4amph- derivatives of 4-aminopyridine

In IR spectra, the absorption band of N-H stretching vibrations of secondary amine groups appears at different frequencies depending on their position in the pyridine ring, for example, 3328 cm^{-1} for Hs2amph; 3360 cm^{-1} for Hs3amph; and 3355 cm^{-1} for Hs4amph. The stretching vibrations of the phenolic hydroxyl groups of O-H clearly appeared at 3400 cm^{-1} only for Hs4amph.

A characteristic feature of the IR spectra of N-(2-hydroxybenzyl) aminopyridines is the presence of two broad absorption bands in the region of 2500-1650 cm^{-1}, which indicate the presence of an intramolecular hydrogen bond between the phenolic hydroxyl and the secondary amino group. Although the position of the band at about 2500 cm^{-1} does not change for all ligands, the position of the low-frequency bands depends on the basicity of the secondary amino group.

In the IR spectra of the Cu(II) complexes shifts of the absorption bands towards lower frequencies were observed, and wide peaks appeared due to stretching vibrations of OH and NH, with absorption maxima at 3328, 3260, and 3280 cm^{-1} for $[Cu(s2amph)_2(CH_3COO)_2]$, $[Cu(s3amph)_2(CH_3COO)_2 \cdot 2H_2O]$ and $[Cu(s4amph)_2(CH_3COO)_2 \cdot \cdot 2H_2O] \cdot 2H_2O$, respectively. The bands at 3420 and 3400 cm^{-1} in the spectra of the s3amp-Cu(II) and s4amph-Cu(II) complexes, related to the O – H vibrations in a water molecule, appear as weak and strong peaks, respectively.

In the NMR spectrum of 2-hydroxybenzylamine-2-pyridine (Fig. 1), the methylene group is located at a chemical shift of 4.3 m.h. Multiplets in the field of 6.5-7.4 m.h. belong to the protons of the pyridine and phenolic moieties. Doublet with chemical shift at ~ 8 m.h. refers to a proton located in the pyridine ring next to the endocyclic nitrogen atom. The proton of the amino group NH has a large chemical shift and is located at 15.5 m.h.

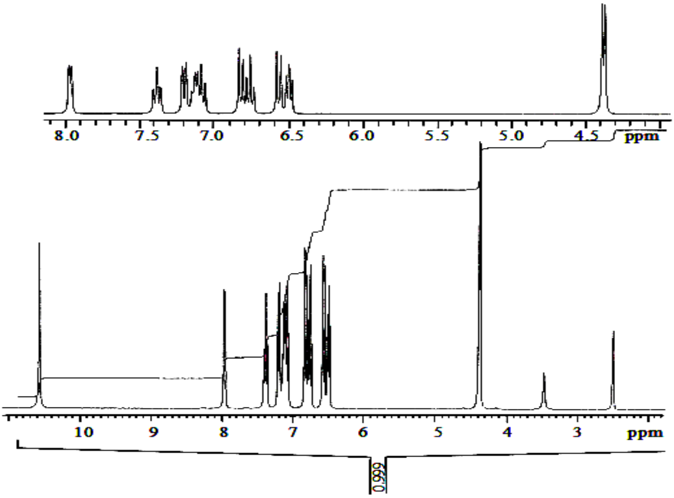


Fig. 1. NMR spectrum of the ligand Hs2amph

In the case of 2-hydroxybenzylamine-3-pyridine, the protons of the methylene group are at a chemical shift of 4.4 m.h., while the phenolic and pyridine rings are observed in the range of 6.3-8 m.h. The protons located in the ortho position in the pyridine ring have $\delta = 8.05$ ppm. and a proton adjacent to the hydroxyl group in the phenolic ring with $\delta = 7.77$ ppm.

Single crystals of two complexes of Cu(II) and Pd(II) with N-(2-hydroxybenzyl)-aminopyridines were obtained and their molecular and crystalline structure was studied by RSA method.

X-ray structural analysis shows that the ligands in the complexes are monodentate and are coordinated with the metal atom by pyridine nitrogen. Comparison of spectral data shows the accuracy of similar results for complex formation for other similar ligands.

The Cu(II) complex of the N-(2-hydroxybenzyl)-2-aminopyridine $[Cu(s2amph)_2(CH_3COO)_2]$ has a flat square structure distorted by oxygen atoms of 2 carboxyl groups and nitrogen atoms of 2 pyridine rings, which are coordinated in the fog state. The remaining 2 oxygen atoms of the 2 carboxyl groups form two Cu - H bridged structures consisting of 8 members joined by a hydrogen bond to the Cu(II) ion (Fig. 2).

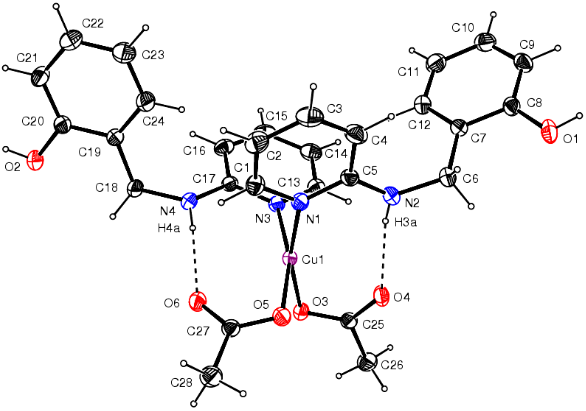


Fig.2. Molecular structure of the $[Cu(s2amph)_2(OOCCH_3)_2]$ complex

$[Cu(s3amph\text{-})_2(CH_3COO)_2 \cdot 2H_2O]$ and $[Cu(s4amph)_2\text{-}(CH_3COO)_2 \cdot 2H_2O]$, (s3amph and s4amph are the derivatives of N-(2-hydroxybenzene) -3 or 4-aminopyridine, respectively) have octahedral structure.

X-ray analysis of the $[Pd(s2amph)_2Cl_2 \cdot 2C_2H_5OH]$ complex has a plane-square structure due to the chlorine atoms in the trans state around the Pd(II) ion and the nitrogen atoms of the 2 pyridine ring (Fig.3). Spectral indicators show that the complexes of the salt $[PdCl_2(PhCN)_2]$ obtained with 3-amino and 4-aminopyridine derivatives have a similar structure.

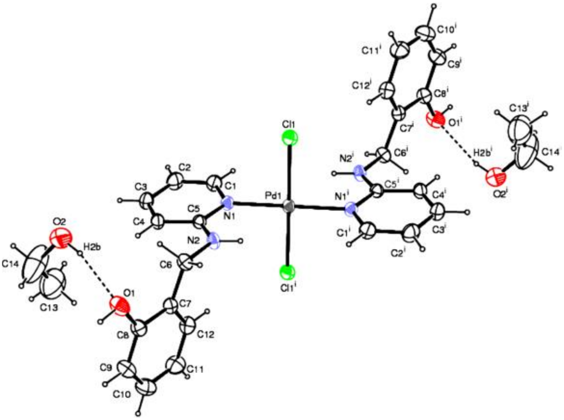


Fig.3. Molecular structure of the complex $[Pd(s2amph)_2Cl_2] \cdot 2C_2H_5OH$.

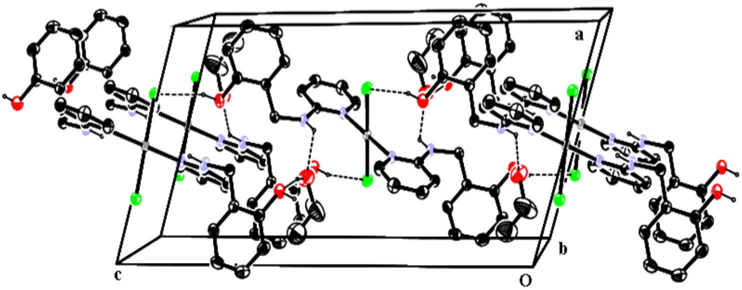


Fig.4. Elemental cage of the complex [Pd(s2amph)$_2$Cl$_2$]·2C$_2$H$_5$OH.

For all Pd(II) complexes, the valence oscillations of phenol hydroxyl appear in the range of 3350-3500 cm^{-1}, the deformation oscillations in the range of 1210-1270 cm^{-1}. Coordination of the metal ion with the ligand is possible only with the help of the endocyclic nitrogen atom, phenol hydroxyl and the dual amine group do not participate in the coordination, which has been proved by X-ray analysis.

In the 3-amino- and 4-aminopyridine complexes with Pd (II), aminopyridinate ligands also behave as monodentate ligands that coordinate with pyridine nitrogen. In this case, the phenol oxygen and the nitrogen atom of the amine group do not participate in coordination. Neither the aromatic hydroxyl nor the dual amine group was deprotonated. They are stabilized by intramolecular and intermolecular hydrogen bonds.

These coordination properties are fundamentally different from the Schiff base complexes in which the synthesized complexes coordinate with phenolic oxygen and nitrogen nitrogen and pyridine nitrogen plays no role.

Similarly, Pd(II) complexes were obtained in aqueous ethanol (90%) using [Pd(C$_6$H$_5$CN)$_2$Cl$_2$] by displacement of the benzonitrile ligand with hydroxybenzyl pyridine. N-(2-hydroxybenzyl) aminopyridines give light yellow complexes of the composition [Pd(s3amph)$_2$Cl$_2$]·2C$_2$H$_5$OH and [Pd(s4amph)$_2$Cl$_2$].

X-ray structural analysis of the [Pd(s2amph)$_2$Cl$_2$]·2C$_2$H$_5$OH complex shows that coordination is carried out by means of 2 pyridine nitrogen and chlorine atoms in the trans state. Similar spectroscopic values are obtained for other complexes.

2. Cobalt(II) and nickel(II) complexes of 2-hydroxybenzyl-4-aminoantipyrine.

Heterocycles play a major role in biochemical processes. These compounds attract attention for many reasons and mainly for their biological activity. Many drugs contain heterocycles. Sulfur, nitrogen and oxygen, which contain various chemical groups - amines, azomethine, phenol, thiol and others, are of great interest as donor atoms.

In the last decade, five-, six- and seven-membered piperazine, piperidine, imidazole, benzodiazene, etc. containing oxygen, nitrogen, sulfur atoms and other pharmaceuticals with heterocycles are widely used.

Heterocyclic compounds have important anticonvulsant, antihistamine, analgesic and anti-pneumonic properties. In addition, they are used as metalprotein models in bio-inorganic systems. They are also known to be used as photosensors and catalysts. Among the pyrazolone derivatives, 4-aminoantipyrine forms various Schiff bases with aldehydes and ketones. They show high biological and pharmacological properties and find their clinical, analytical application. It has the N-phenyl group of 4-aminoantipyrine, the NH group in the same direction and the polar carbonyl group. In this respect, it is reminiscent of the replaced amide. There are articles in the literature on the study of medicinal and analytical properties of this compound, as well as coordination chemistry. In the 4-aminoantipyrine, the carbonyl group has a large dipole moment (5.48 D) and exhibits strong basic properties. Therefore, the oxygen of the carbonyl group can coordinate with the metal ion.

Thus, due to the oxygen and nitrogen atoms of 4-aminoantipyrine, it can behave as a monodentate ligand or form a chelate due to the oxygen atom and the nitrogen atom of the amine group. Many Schiff bases of 4-aminoantipyrine are obtained mainly by condensation with ketones and aldehydes in water or alcohol solution. Metal complexes with Schiff bases are obtained with high yield in polar solvents, mainly in alcohol solution and with low heating. Depending on the substitute for the nitrogen atom, complexes of different structures can be formed in the antipyrine fragment. The Schiff base copper (II) complex obtained by the interaction of 2-oxinaftoy aldehyde and 4-aminoantipyrine has a flat square structure, the Schiff base copper (II) complex obtained with chloric salicylic aldehyde has an octahedral structure. The main focus is on the condensation reaction of 4-aminoantipyrine with the amine group and the carbonyl group with various aliphatic and aromatic aldehydes and ketones to form amine >C = N-' or -CH = N- groups. These compounds are used in catalysts, dyes, pigments, in the manufacture of sensors, in the food industry, analytical reagents, therapeutic substances, etc. found application areas such as. 4-aminoantipyr has the potential to form chelates, which can form different types of complexes with almost all transition metals and lanthanides. These complexes include sensors, light emitting diodes, electrochemical thin films, anti-pneumonia, antioxidants, analgesic drugs, carriers, etc. has found its application in the fields.

A new Schiff base was synthesized by condensation of 4-aminoantipyrine and 2-hydroxy-1,2-diphenylethanol. The obtained Schiff base is used as an analytical reagent in the determination of iron (II), cobalt (II), copper (II), zinc (II), aluminum (III), magnesium (II), calcium (II), barium (II), lead (II), cadmium. By adding iron (III) ions to the solution, the solution becomes pur-pur. This can be seen visually and quantified in the visible range of the spectrometer. The same ligand forms a fluorescent compound with aluminum (III) ions, so the concentration of aluminum ions can be determined using a fluorescent spectrometer. Thus, this ligand allows to determine the concentration of iron (III) and aluminum (III) ions, even in the presence of other ions.

The antimicrobial activity of 4-aminoantipyrine and its complexes has been observed by many researchers. Copper (II), nickel (II), cobalt (II), zinc (II) complexes were obtained on the basis of Schiff obtained by condensation of 4-aminoantipyrine and vanillin o-aniside, their antimicrobial properties against *Esherichia Coli*, fungicides against *Aspergillius niger*, *Aspergillius fumigantus* and *Candida albicans* have been studied.

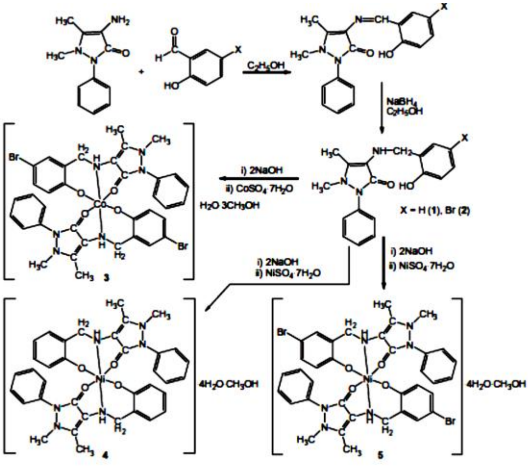
Similarly, Schiff bases with other aldehydes and ketone derivatives of 4-aminoantipyrine are also highly active against various microorganisms.

Schiff bases of 2-hydroxybenzyl derivatives of 4-aminoantipyrine (Hs4aap and Hbs4aap) were obtained by condensation of 4-aminoantipyride salicyl and Br-salicyl aldehyde, and the reduced derivatives were obtained by their reduction with $NaBH_4$ in ethanol.

The dissolution of Hs4aaph and Hbs4aaphc ligands with subsequent deprotonation and the introduction of nickel (II) sulfates or cobalt (II) allowed us to isolate the complexes [Co(bs4aaph)$_2$·H_2O·$3CH_3OH$ (3), [Ni(s4aaph)·$4H_2O$ (4) and [Ni(bs4aaph)$_2$] $4H_2O$ (5) as their crystalline solvates (Scheme 1).

The complexes [Co(bs4aaph)$_2$·H_2O·$3CH_3OH$ (3), [Ni(s4aaph)·$4H_2O$ (4) and [Ni(bs4aaph)$_2$]·$4H_2O$ (5) are light brown, dark brown and light blue colors, respectively. In s4aaph and bs4aaph compounds, wide IR signals, absorption bands at 3360, 3480 and 3341, 3184 cm^{-1}, can be assigned to the functional groups OH and NH, while narrow intense peaks at 1630 and 1638 cm^{-1} can be assigned to ν vibrations (C=O). After restoration, the characteristic IR signal for the azomethine group ν (C=N) at 1653 cm^{-1} disappears. The loss of the characteristic band δ 9.60-9.75 CH = N in the ^1H NMR spectra confirms the reduction reaction.

The ^1H NMR peaks at δ13.11 (for Hs4aaph) and 12.94 (for Hbs4aaph) relate to the intramolecular hydrogen bond of the phenolic OH group with benzylamine. In addition, peaks of -CH_2- and N-H protons are observed at δ 4.23 and 11.08 (for Hs4aap) and 4.32 and 11.42 (for Hbs4aap).



Scheme 1. Synthesis of 4-aminoantipyrine derivatives and complexes

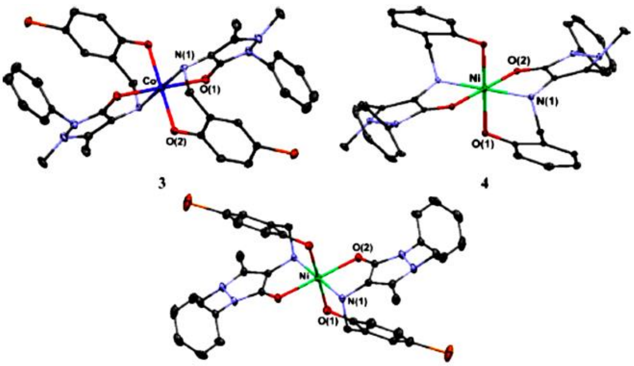


Fig.5. Ellipsoid graphs of 3-5 complexes. H atoms and solvent molecules entering the crystal are not shown for clarity.

In the IR spectra $[Co(bs4aaph)_2\cdot$H2O$\cdot 3CH_3OH$ (3), [Ni (s4aaph)$\cdot$ $4H_2O$ (4) and $[Ni(bs4aaph)_2]$ correspond to $4H_2O$ (5) ν(C=O) communication oscillations 1650, 1652 and 1648 cm^{-1} for ligands (1630 and 1638 cm^{-1} for s4aaph and bs4aaph, respectively) move to a higher frequency field (≈14-20 cm^{-1}), this, in turn, proves that coordination takes place through the oxygen atom (Fig. 5).

In all complexes, positive metal charges are neutralized by deprotonated phenol groups. The surrounding metal ion has an octahedral structure distorted by each ligand (Hs4aaph and Hbs4aaph), 2 oxygen atoms, and one nitrogen atom from each ligand. Oxygen atoms occupy the main positions (Fig. 6).

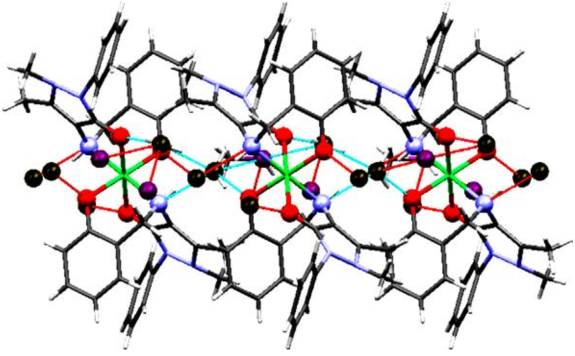
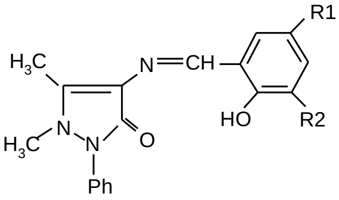


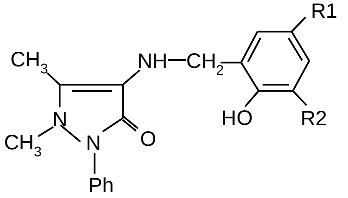
Fig. 6. Chain 1D-arrangement of solvent molecules (water, methanol) along the b-axis of the $[Ni(s4aaph)\cdot 4H_2O\cdot CH_3OH]$ complex. "Spheres and rods" model.

3. Oxidative dehydrogenation reaction in the process of complex formation with N(2-hydroxy-3,5-R^1, R^2-benzyl) 4 aminopyridines.

In the study of metal complexes of aminoantipyrine derivatives, it was found that in the production of Cu(II) complexes with N-(2-hydroxy-3,5-R^1, R^2-benzyl)-4-aminopyridines (Hsaah – Hdtbsaah) instead of complexes with ligands (Hsaa - Hdtbsaa) are obtained by complexes and the structure of these complexes was studied by X-ray structural analysis.



Hsaa-$R^1=R^2=H$
Hbsaa- $R^1=Br, R^2=H$
Hmsaa -$R^1=OCH_3, R^2=H$
Htbsaa - R^1=трет-C_4H_9, $R^2=H$
Hdtbsaa - $R^1= R^2=$ трет-C_4H_9



Hsaah - $R^1=R^2=H$
Hbsaah-$R^1=Br, R^2=H$
Hmsaah - $R^1=OCH_3, R^2=H$
Htbsaah R^1=трет-C_4H_9, $R^2=H$
Hdtbsaah $R^1= R^2=$ трет-C_4H_9

$Cu(saa)_2$ – $Cu(dtbsaa)_2$ complexes can be obtained by direct exposure to copper-2-acetate in methanol-ethanol solution.

The interaction of Hsaah – Hdtbsaah ligands with copper-2-acetate undergoes an oxidative dehydrogenation reaction in methanol-ethanol solution (1:1) and replaces the expected $Cu(saah)_2$ – $Cu(dtbsaah)_2$ complexes with $Cu(saa)_2$ - $Cu(dtbsaa)_2$ complexes are obtained. The oxidation process of Hsaah ligand can be summarized as follows:

$$\mathbf{2(Hsaah) + Cu(CH_3COO)_2 + O_2 \rightarrow Cu(saa)_2 + 2CH_3COOH + H_2O_2}$$

In the electronic spectra of these complexes, the absorption bands 373-366, 427-409 nm belong to the ligand-metal transition band, and the low-intensity absorption bands at 526-500 nm belong to the d-d transition. The IR spectra of the complexes include 1640–1650 cm^{-1} absorption band ν(C=O), ~ 1580–1600 cm^{-1}- absorption band ν(C=N).

In the region visible in the electronic spectrum of the $Cu(saah)_2{\cdot}2H_2O$ complex, ligand-metal at 420 nm and d-d transition bands at 575 and 680 nm are observed. Similarly, for the $Cu(bsaah)_2{\cdot}2H_2O$ complex, these bands are observed at 425, 560 and 675 nm.

Reduced Schiff bases react with copper 2-acetate to oxidize-dehydrogenate in alcohol solutions to form Cu(saa)-Cu(dtbsaa) complexes. During the interaction of sodium salts of these ligands with metal sulfates and chlorides in the aqueous medium, it is possible to synthesize complexes containing $M(tbsaah)_2$, $M(dtbsaah)_2$. They are resistant to oxidation-dehydrogenation reactions.

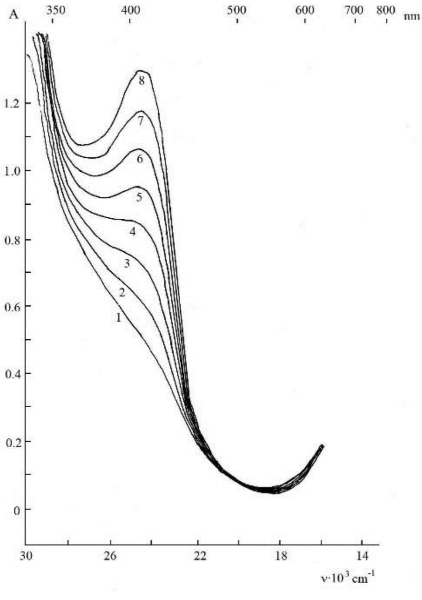


Fig.7. Interaction of Hsaah ligand with $Cu(CH_3COO)_2{\cdot}\ H_2O$ (1–8). Time dependence of optical density. The time between notes is 3 minutes. $c_{saah} = 7.5 \times 10^{-5}$, $c_{Cu\ (CH3COO)2{\cdot}H2O} = 5 \times 10^{-3}$ mol/l.

In the interaction of ligands and an alcoholic solution of copper 2-acetate, a rapid OD reaction takes place, and in the electron spectrum we observe the formation of an absorption band corresponding to the bond of azometine (Fig. 7). It should be noted that the OD reaction is not observed in the absence of oxygen.

During the decomposition of the $Cu(saah)_2$ complex, an oxidative dehydrogenation reaction is also observed. Thus, when small amounts of acetic acid are added to the $Cu(saah)_2$ alcohol solution, its absorption spectrum disappears at a wide absorption peak at 420 nm (the initial complex decomposes) and then a relatively narrow peak appears at 415 nm, related to the mixed ligand complex with the dehydrogenated ligand $Cu(saa)(CH_3COO)$. This peak grows in time (Fig. 8).

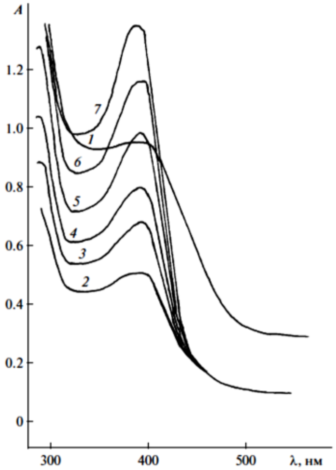


Fig. 8. Changes in the ESP of $Cu(saah)_2{\cdot}H_2O$ upon addition of acetic acid: the initial solution of $Cu(saah)_2$ H_2O (*1*), after addition of acetic acid (2), changes in the ESP with time (2–6). The interval between recording spectra is ~ 6 min. $c_{(saah)2{\cdot}H2O} = 10^{-4}$, $c_{CH3COOH} = 10^{-1}$ mol/l, solvent C_2H_5OH.

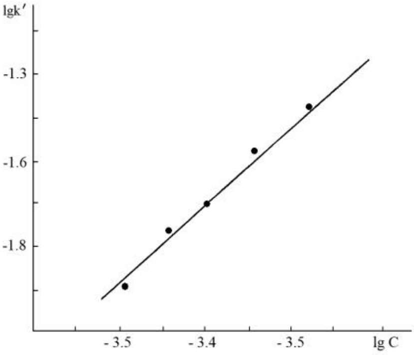
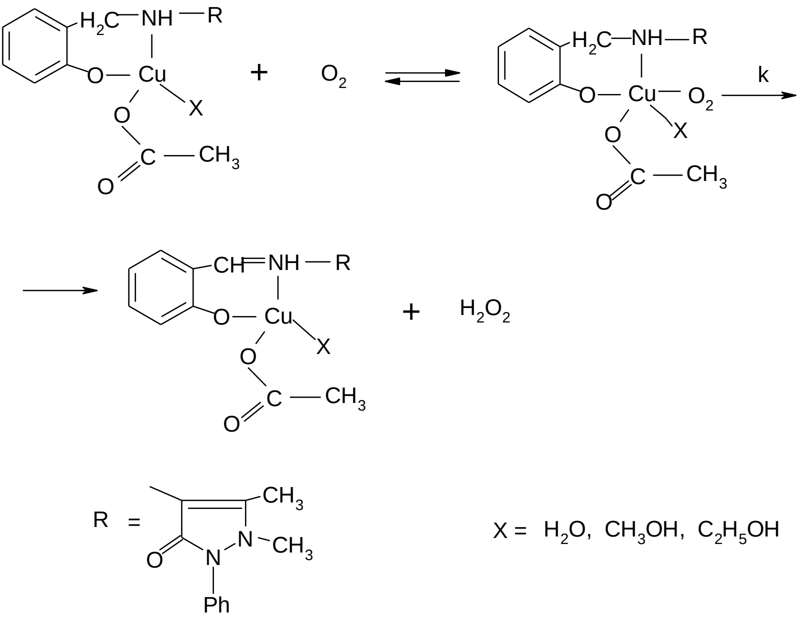


Fig. 9. Dependence of the lgw of the oxidative dehydrogenation reaction on the lgc of the Hsaah ligand.

All these data indicate that the coordinated ligand OD occurs in the mixed ligand complex Cu(saah)(CH_3COO), in which the ratio of metal ion:ligand is 1:1.This process can be represented by the following scheme:



Scheme 2. Oxidative dehydrogenation of Cu(saah)(CH_3COO), a mixed ligand complex in which the ratio of metal ion: ligand is 1:1.

Kinetic studies of the interaction of Hsaah with copper acetate in a methanol-ethanol solution (1:1) showed that the reaction rate for [$Cu(CH_3COO)_2 \cdot H_2O$] >> [saah] obeys the first-order kinetic equation for Hsaah concentration (Fig. 8) At the same concentrations of the reaction components or under the condition [$Cu(CH_3COO)_2 \cdot H_2O$] < [saah] the OD reaction slows down significantly and stops due to the formation of an inactive Cu(saah)$_2$ complex.

The equilibrium of the complex formation process (1), (2), (4) and the general scheme of OD reactions (3) can be shown as follows:

$$Cu(CH_3COO)_2H_2O \;+ saah \xrightleftharpoons[k_{-1}]{k_1} Cu(saah)CH_3COO \;+\; CH_3COOH \qquad (1)$$

$$Cu(saah)CH_3COO \;+ saah \xrightleftharpoons[k_{-1}]{k_1} Cu(saah)_2 \;+\; CH_3COOH \qquad (2)$$

$$Cu(saah)CH_3COO \;+O_2 \xrightarrow{k} Cu(saa)CH_3COO \;+H_2O_2 \qquad (3)$$

$$2Cu(saa)CH_3COO \rightleftharpoons Cu(saa)_2 \;+ Cu(CH_3COO)_2 \qquad (4)$$

Scheme 3. The kinetic scheme of the reaction, including the equilibrium of complexation (1), (2), (4) and the OD reaction (3).

At low ligand concentrations and high concentrations of copper acetate, equilibrium (2) can be neglected. Experimental data indicate that the Hsaah ligand is exclusively in the form of a mixed ligand complex, i.e. $k_1 >> k_{-1}$.

If we take the reaction of interaction of $Cu(saah)CH_3COO$ with oxygen as a limiting stage, then for $[Cu(CH_3COO)_2{\cdot}H_2O] >> [saah]$ and k1>>k – 1, the expression for the reaction rate can be written as $w = k[Cu(saah)CH_3COO][O_2] = k[saah][O_2]$ or $w = k'\,[saah]$, where $k' = k[O_2]$, i.e. we obtain the pseudo-first order for the reaction rate according to the concentration of the initial ligand, which is confirmed experimentally.

The pseudo first order reaction rate constant found from the dependence of logw on logc (Fig. 9) has the value $k\,' = 0.1 \approx 10^{-1}\ s^{-1}$. Note that the pseudo-first order in ligand concentration under the above conditions ($[Cu(CH_3COO)_2{\cdot}H_2O]$ [saah] and $k_1 >> k_{-1}$) is obtained if equation (3) is taken as the limiting stage.

X-ray structural analysis of $Cu(tbsaa)_2$ and $Cu(dtbsaa)_2$ complexes shows that the ligands in the complexes are in a foggy state.

The products of the OD reaction were also identified by comparison of the initial and conversion complexes, IR-, electron absorption spectra (Fig.11).

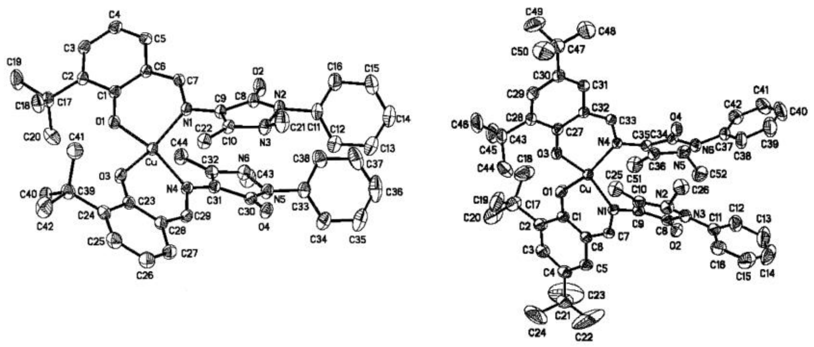


Fig. 10. Molecular structures of the complexes Cu(tbsaa)$_2$ and Cu(dtbsaa)$_2$.

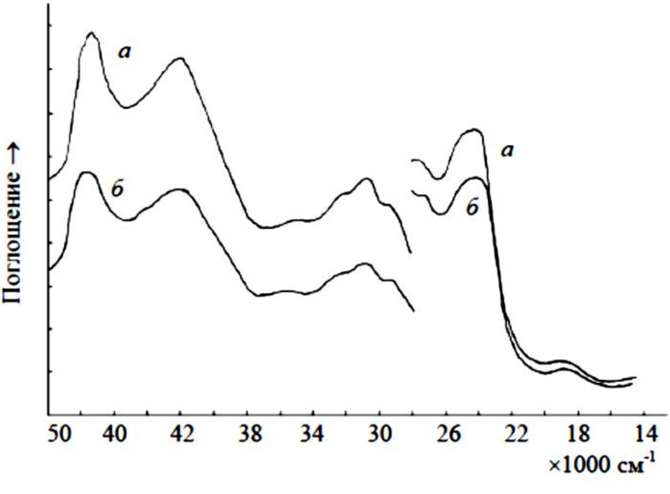


Fig. 11. Electronic absorption spectra in a solution of ethyl alcohol: a) complex Cu(tbsaa)$_2$, b) complex obtained by the interaction of Cu(CH_3COO)$_2$·H_2O with Htbsaah.

Thus, the reason that Cu(saah)$_2$ is not subjected to OD is the lack of coordination of molecular oxygen in the air, since the Cu^{2+} ion in Cu(saah)$_2$·H_2O is hexacoordinated. At the same time, this reaction easily proceeds in multi-ligand complexes, in which the coordination number of the metal ion is lower.

Table 2. Communication length [Å] and angles [°]

$[Cu(tbsaa)_2\cdot]2H_2O$		$[Cu(dtbsaa)_2]\ 2H_2O$	
Cu-O(3)	1.8819(15)	Cu-O(1)	1.888(4)
Cu-O(1)	1.8834(15)	Cu-O(3)	1.889(3)
Cu-N(4)	1.9525(17)	Cu-N(4)	1.952(4)
Cu-N(1)	1.9560(18)	Cu-N(1)	1.955(4)
O(3)-Cu-O(1)	90.28(7)	O(1)-Cu-O(3)	90.00(17)
O(3)-Cu-N(4)	93.54(7)	O(1)-Cu-N(4)	147.2(2)
O(1)-Cu-N(4)	150.72(8)	O(3)-Cu-N(4)	93.81(16)
O(3)-Cu-N(1)	148.43(8)	O(1)-Cu-N(1)	94.09(17)
O(1)-Cu-N(1)	93.85(7)	O(3)-Cu-N(1)	146.6(2)
N(4)-Cu-N(1)	97.85(7)	N(4)-Cu-N(1)	100.26(17)
C(1)-O(1)-Cu	128.91(14)	C(1)-O(1)-Cu	128.9(4)
C(23)-O(3)-Cu	126.45(14)	C(27)-O(3)-Cu	129.1(3)

3. Metal complexes of 8-aminoquinoline derivatives with Schiff bases and their reduced analogues.

Aminoxinoline is a heterocyclic compound with an amine group and is part of various bioactive compounds. Aminoxinoline derivatives have various pharmaceutical properties, including anticonvulsants, antibacterials, fungicides, antimalarials, etc.

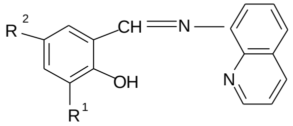
8-aminoquinolines are the first organic compounds to have antimalarial properties. 8-aminoquinoline and its derivatives form complexes with transition metal ions. Chelate complexes form five-membered metalcycles due to the endocyclic nitrogen atom and the nitrogen atom of the amine group.

A lot of work is known about Schiff's bases, which contain a fragment of quinoline, and many of their transition metal complexes. These substances are used in pharmacetic research, adsorption, metabolism, etc. used as a medicine.

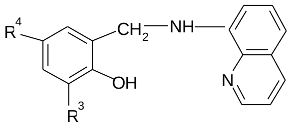
Although the oxidative dehydrogenation reaction is of great interest, metal complexes with reduced Schiff bases of 8-aminoquinoline have not been studied in practice.

This section describes the synthesis and properties of Cu(II), Ni(II), Co(II) and Pd(II) complexes of 8-aminoquinoline derivatives and salicylaldiminate with Schiff bases and their reduced analogues.

According to the results of elemental analysis, Cu(II) forms complexes with Schiff bases with bamch and dtbsamch with a metal-ligand ratio of 1: 1, in which case the complex includes a deprotonated carboxyl group. In the ultraviolet region of the electron spectra of the Hbsamch ligand, the absorption bands are subjected to a batochromic shift due to the formation of the [Csam (bsamch) (CH3COO)] complex, with d-d transition bands appearing in the visible region at ~ 560 nm. At 477 nm, the absorption band of the Hbsamch ligand group attached to the azometine group undergoes a hypsachromic shift during complex formation and is observed at 455 nm.



bsamch - R^1=H, R^2=Br
dtbsamch -t-Bu, R^2=t-Bu



Hbsamch-R^3=H, R^4=Br
Hdtbsamch - R^3=t-Bu, R^4=t-Bu

IR spectra of this complex show 1610 cm-1 absorption bands belonging to the azometine group and 1579 and 1377 cm^{-1} absorption bands belonging to the carboxyl group. If we consider that the ligand is a tridentate, then we can write the following structure for the complex [Cu(bsamch) (CH_3COO)] (Fig. 12).

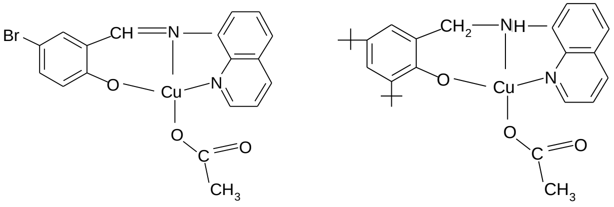
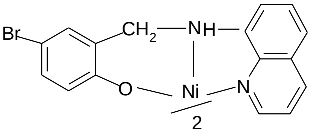


Fig. 12: Structures of the complexes [Cu(bsamch)CH_3COO] və [Cu(hdtbsamch)CH_3COO]

The ligands Hhbsamch and Hhdtbamch behave differently upon complexation with Cu(II) ions. During complexation, the Hhbsamch ligand undergoes oxidative dehydrogenation, so that the Cu(bsamch) complex is ultimately formed. In contrast, Hhdtbamch with Cu(II) gives complexes of the composition Cu(II):Hhdtbamch =

1:1, in which the Hhdtbamch ligand remains in its reduced form and oxidative dehydrogenation does not occur. This is confirmed by IR and electron spectrometry. In the IR spectrum of the [Cu(hdtbsamch)CH_3COO] complex, a coordinated amino group band is observed at 3474 cm^{-1} and there is no absorption band of the azomethine group at ≈1600 cm^{-1}. At 1587 cm^{-1} and 1384 cm^{-1}, absorption bands of ν_{sim} and ν_{asim} are observed coordinated carboxyl group. These data indicate that the following structure can be adopted for the [Cu(hdtbsamch)CH_3COO] complex.

The interaction of the Hhbsamch ligand with Ni(II) acetate gives complexes of the composition [Ni(hbsamch)$_2$]. The IR spectra of this complex contain valence absorption bands of a coordinated amino group at 3400 and 3120 cm^{-1}.



[Ni(hbsamch)$_2$].

When interacting with Cu(II) and Co(II) ions, the Hhbsamch ligand undergoes oxidative dehydrogenation, as a result of which complexes with a Schiff base are formed.

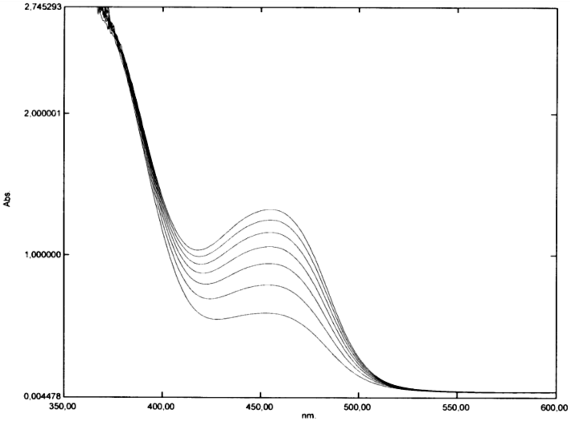
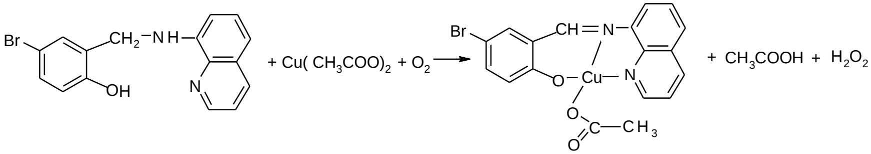


Fig. 13. Change in optical density at λ = 455 nm of a solution containing 10^{-3} moles of Hhbsamch and 10^{-3} moles of $Cu(CH_3COO)_2{\cdot}H_2O$. Spectra were recorded after 2 minutes.

Thus, the reduced Schiff base derivatives of 8-aminoquinoline and salicylaldehyde, depending on the nature of the metal ion and substituents in the salicylic moiety, can either undergo oxidative dehydrogenation or complex with these ligands without being oxidized. Thus, the Hhbsamch ligand forms a stable complex [Ni(hbsamch)$_2$], with the Ni(II) ion, while light oxidative dehydrogenation occurs with the Cu(II), Co(II) ions, with the formation of [Cu(bsamch)·(CH_3COO)] and [Co(bsamch)·-(CH_3COO)]. The oxidative dehydrogenation reaction of Hhbsamch ligand takes place in the process of complex formation. The oxidative dehydrogenation reaction of Hhbsamch ligand with copper 2-acetate can be shown by the following scheme:



Scheme 4. The scheme of the oxidative reduction reaction that takes place when Hhbsamch ligand interacts with copper 2-acetate.

It should be noted that the complex of Hhdtbsamch with copper acetate containing a di-tert-butyl fragment is less susceptible to oxidative dehydrogenation when interacting with Cu(II) acetate compared to Hhbsamch with copper 2-acetate and gives a stable complex with this ion.

It can also be noted that the reduced Schiff bases studied in this work are oxidized more readily than similar compounds with other aromatic amines. This can be explained by the influence of the quinoline ring.

4. Crystal and molecular structure of 2,2,6,6-tetramethyl-4-hydroxypiperidine (HTAA · HCl).

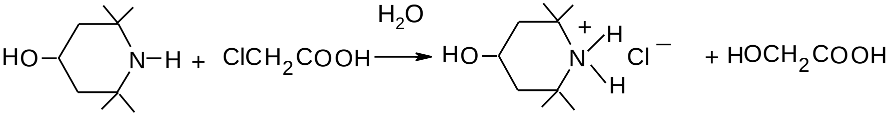
The reactions of acylation and carboxymethylation of secondary amines are widely used in organic synthesis and proceed under fairly mild conditions.

The carboxymethylation reaction of primary and secondary amines of chloroacetic acid is usually carried out in aqueous alkaline solutions at 80°C. Under milder conditions, amides are formed from amines and carboxylic acid chlorides.

In this work, an attempt was made to obtain aminocarboxylic acid by carboxymethylation of 2, 2,6,6-tetramethyl-4-hydroxypiperidine (TMHP), as well as the oxamide of this compound using oxalyl chloride.

However, instead of the expected products, in both cases, HTAA · HCl hydrochloride is formed, the structure of which was studied using X-ray diffraction analysis.

The interaction between TMHP and chloroacetic acid occurs according to the scheme:



Scheme 5. Interaction of TMHP with chloroacetic acid

Undoubtedly, the carboxymethylation reaction of 2,2,6,6-tetramethyl-4-hydroxypiperidine with chloroacetic acid does not occur due to steric shielding of the amino group by methyl groups.

A similar behavior of sterically hindered amines was observed with direct reductive amination of aldehydes and ketones to give amines with an additional alkyl group. It was shown that the yield of the reductive amination reaction products depends on the amount and nature of the substituents in the amino group.

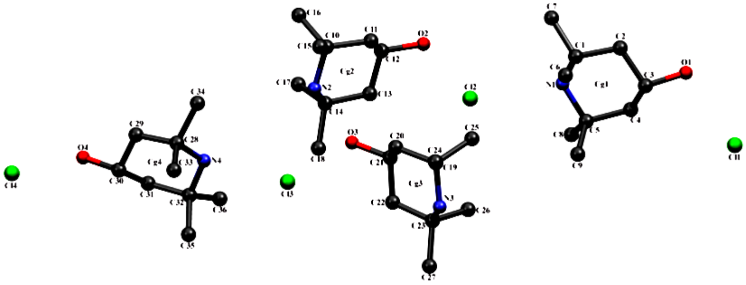


Fig. 14. HTAA · HCl molecular structure. For clarity, H atoms have been omitted.

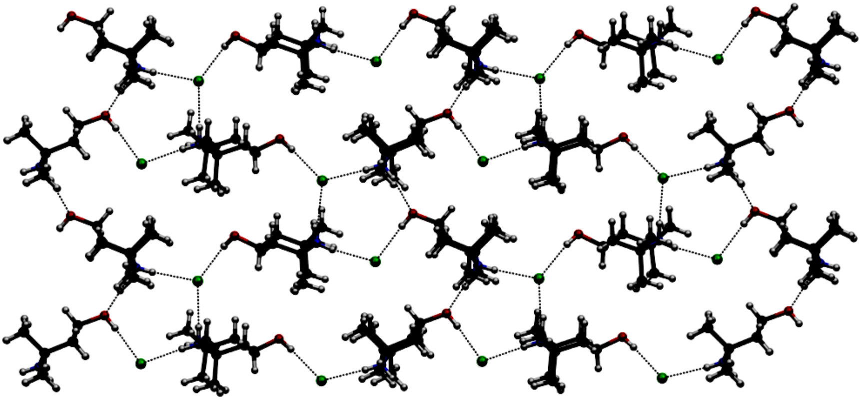


Fig.15. The part of the crystalline structure of HTAA · HCl, showing the formation of R53 (10) and R77 (30) rings with hydrogen bonds N-H ··· Cl, O-H ··· Cl and N-H ··· O.

6. Synthesis and structure of Cu (II) and VO (II) complexes with salicylic acid hydrazide and 3,5-ditretbutyl salicylic aldehyde hydrazone.

Complexes containing N, O-donor chromophores play a very important role in the determination of active sites of many metal enzymes and in catalytic reactions. Amino acids usually act as N, O-donor ligands. They are involved in the construction of the protein block and many important biochemical processes in the body. It is well known that the Cu complex of the amino acid L-valine is used as a model system in the study of pharmacology of drugs. Such N, O-donor can also be attributed to N-salicyloil-N'-2-hydroxy-3,5-ditret-butyl benzyl synthesized (H2sahz) in the dissertation. It is a potential 4-dentate ligand and behaves as a 3-charged anion due to the oxygen of the 2 hydroxyl groups attached to the aromatic ring and the hydrazide group, which can form an enol structure. However, in the divalent copper complex, it behaves like a tridentate monoanion ligand, as shown below.

In the dimeric structure of the ligand molecule (Figure 16), there are four strong molecular internal hydrogen bonds.

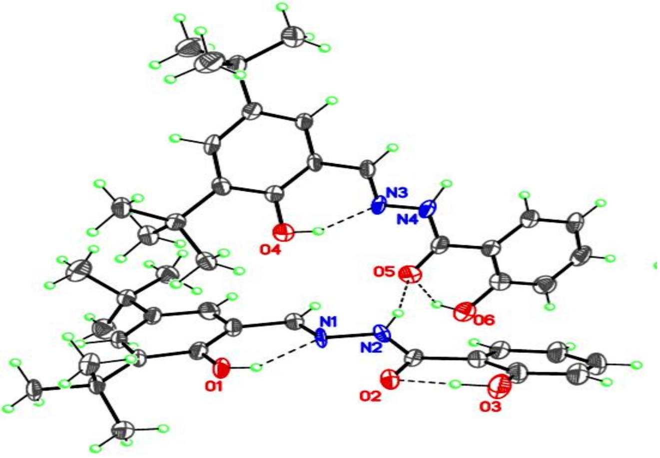


Fig. 16. Molecular structure of ligand $(H_2sahz)_2$

There are 2 hydrogen bonds between the nitrogen atoms of the hydrazine group and phenol hydrogen of di-tert-butyl salicyl aldehyde, and two more hydrogen bonds between the oxygen of the hydrazine group and the carboxyl group of salicylic acid.

The structure of the complex $Cu[H_2sahzNO_3H_2O]$

Crystals of the $Cu[H_2sahzNO_3H_2O]$ complex were obtained by the ligand reaction of Cu(II) nitrate in a methanol-ethanol medium. Crystals suitable for X-ray structural analysis obtained by recrystallization from methanol solution.

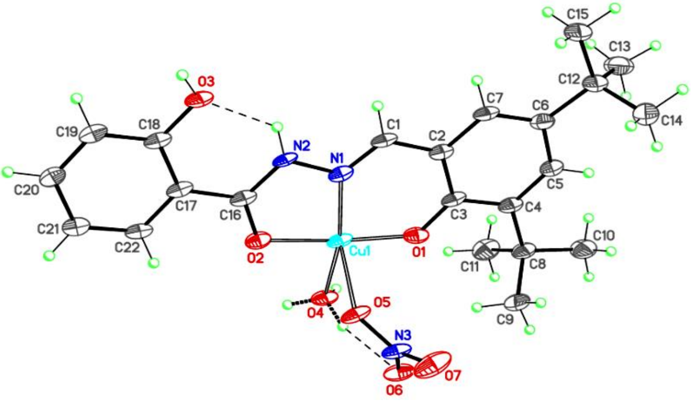


Fig. 17. Molecular structure of the Cu(II) complex

The coordination geometry around the center Cu(II) can be determined by calculating the geometric parameter $\tau = (\beta-\alpha)/60$, where α and β are the smallest and largest angles around the central atom. $\tau = 0$ for an ideal square pyramidal structure and $\tau = 1$. for an ideal trigonal bipyramidal structure. The value found $\tau = 1.16$ (95.130 / 81.410) indicates that the complex has a distorted square pyramidal structure. In the IR spectrum of benzylidene N-salicyloil-N '(3,5-di-tert-butyl-2-hydroxy) there is a vibration band of 1612 cm^{-1} of the C = N azomethine group and an absorption band of aromatic at 1600 cm^{-1}. At 3079 cm^{-1}, the absorption band has a very low intensity and refers to the absorption of aromatic rings. The presence of bands 1634 cm^{-1} and 3196 cm^{-1} indicates that the hydrazide carbonyl is in the ketone form.

In the free ligand coordinated with the Cu(II) ion, the absorption band of the carbonyl group observed at 1634 cm^{-1} shifts to lower frequencies and is observed at 1625 cm^{-1}. The absorption band of the hydrazide fragment (NH) narrows significantly as a result of complex formation and at the same time slides significantly towards higher frequencies and is observed at 3210 cm^{-1}. This change indicates that the carbonyl group is in coordination with the metal ion. In the IR spectrum of the $[Cu(sahzNO_3H_2O)]$ complex there is an absorption band of the hydroxyl group of the water molecule coordinated at ~ 3400 cm^{-1}.

In the thermogram of the Cu(II) complex in the temperature range of 50-102^{0}C, a mass loss of 7.30% is observed, which is accompanied by an endothermic effect and corresponds to a hygroscopic water loss. In the range of 102-167^{0}C, a mass loss of 5.43% is observed, corresponding to the loss of a coordinated water molecule. At temperatures above 240^{0}C, thermooxidative destruction of the complex occurs and turns into a process of burning organic residues in a wavy manner. The process is accompanied by a maximum slippery exothermic effect on the DTA curve in the 340^{0}C region. The decomposition process of the sample ends with a loss of 92.21% of its mass at 940°C.

The weight of the remaining metal is 7.8%, the metal in the complex corresponds to a ligand ratio of 1:1.

The coordination circle of the Cu^{2+} ion has a distorted square pyramidal structure. At the equatorial plane, the Cu(II) ion binds to three oxygen atoms: di-tert-butyl phenol fragment oxygen, water molecule oxygen, and hydrazide oxygen. The fourth position in the equatorial plane is occupied by the nitrogen atom of the hydrazine fragment. Completion of the pyramid is carried out with oxygen of the nitro group. Phenol does not participate in oxygen coordination (Figure 17).

The structure of the VO (II) complex.

In different ligand metal complexes, vanadium may have different oxidation states - II, III, IV and V. V(II) and V(III) are unstable and readily oxidize to higher oxidation states. At the same time, V(IV) vanadyl is very stable in the form of VO_2^+, although under certain conditions it can be converted to V(V) in the form of VO^{3-}vanadium anion. In particular, when vanadil salt is used as a starting material in the synthesis of a number of complex compounds, vanadium dioxovanadium compounds VO_2^+ are formed instead of the expected vanadil complexes.

In the dissertation it was shown that the reaction of vanadil sulfate with N-salicyloil-N'-2-hydroxy-3,5-di-tert-butyl benzylidene formed VO_2^+ complexes.

Vanadium is a very common element in nature and is part of a number of biological systems. Metal complexes of different compounds can have different oxidation states - II, III, IV and V. V (II) and V(III) conditions are unstable and easily oxidized to higher oxidation states. At the same time, V(IV) vanadil is extremely stable in the form of VO_2^+.

The dual-core structure of the vanadil complex consists of two non-equivalent monomer complexes. In both cases, the vanadium ion has an oxidation state of +4. In one of these monomer units, the vanadium ion is coordinated with three oxygen atoms in the equatorial plane: O1 (phenol oxygen of the di-tert-butylphenol fragment), O2-hydrazide oxygen, and O6 (deprotonated ethanol oxygen). The fourth position is occupied by the nitrogen atom of the azometine group - C = N.

In the axial position are two oxygen atoms - the oxygen of the alcohol molecule and the vanadyl oxygen.

The equatorial plane coordination of the V2 atom is the same as in V1, but in the axial position the coordination with the “vanadil” oxygen is not carried out with the oxygen of the ethanol molecule, but with the oxygen of the neighboring molecule (V = O). The length of this bond is longer than that of ordinary bonds (2.47 Å). However, this is sufficient for the formation of a dual-core complex.

As in the copper complex, so in the vanadil complex The phenolic oxygen in the salicylic fragment does not coordinate with the vanadium ion.

The complex $[(VO)_2(Hsahz)_2(C_2H_5O)_2\ (C_2H_5OH)]$ crystallizes in the space group P2(2). The structure of the complex consists of two nucleated units connected by intermolecular hydrogen bonds in a crystal lattice.

In a two-nucleated structure, monomer complexes differ from each other by the nature of coordination. Both vanadium atoms V1 and V2 have a distorted octahedral structure. At the equatorial plane, the coordination of the V1 ion is carried out with the deprotonated phenolic oxygen of the di-tert-butyl fragment, the nitrogen atom of the azomethene group C = N, the carbonyl oxygen of the hydrazide group and the oxygen atom of the deprotonated ethanol. The axial positions are occupied by vanadil oxygen and the oxygen atom VO (2) of the neighboring vanadil group. The coordination of the V2 ion in the equatorial plane is the same as that of the three oxygen atoms of the phenol, carbonyl, and deprotonated hydroxyl groups, and the nitrogen atom of the C = N group of nitrogen in V1. One of the axial locations is vanadil oxygen, the other is the oxygen molecule of ethanol hydroxyl. V1 = O (vanadyl oxygen) has a bond length of 1,585 Å and is close to what is published in the literature. In the equatorial plane, the shortest bond is observed with V-O vanadium with ethanol-1 anion with a value of 1.767Å. The length of the bond of the vanadium ion with the deprotonated phenolic oxygen in the di-tert-butyl salicyl fragment is 1.835 Å, and the length of the bond with the hydrazide oxygen is slightly longer - 1.96 Å. The length of the V(1) - N(1) bond (nitrogen nitrogen) is 2,114 Å. For the V (2) ion, the lengths of these bonds are either equal or slightly higher. Communication between monomer complexes is carried out by coordination

coordination between the ion V(1) and the vanadyl oxygen VO(2) of the neighboring molecule of the complex. The length of this connection is 2,471 Å. Short distances are observed between vanadil oxygen VO(2) and 3 oxygen atoms and one nitrogen atom located in the equatorial plane V1. In the dimer molecule, the ligand molecules are in a fog state with each other, ie in both cases the di-tert-butyl fragments are oriented in the same direction. The same is true for salicylic acid fragments.

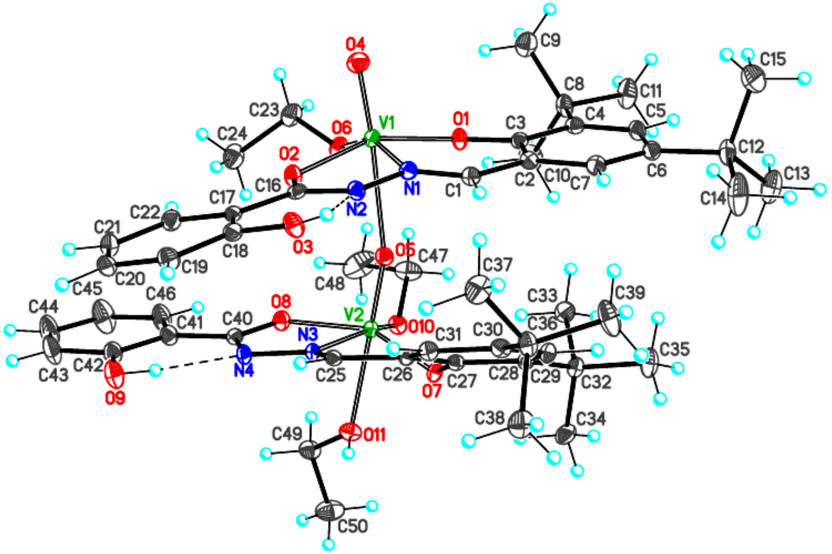


Fig.18. Molecular structure of the VO (II) complex

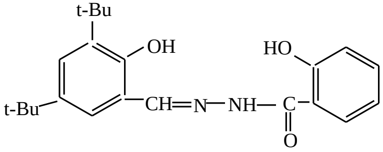
The dual-core structure of the vanadil complex consists of two unequal monomer complexes. In both cases, the vanadium ion is in the +4 oxidation state.

The V1 ion coordinates with three oxygen atoms in the equatorial plane: O1 (phenolic oxygen of the di-tert-butylphenol fraction), O2-hydrazide oxygen, and O6 (deprotonated ethanol oxygen). The fourth position is occupied by the nitrogen atom of the azometine group –C = N-

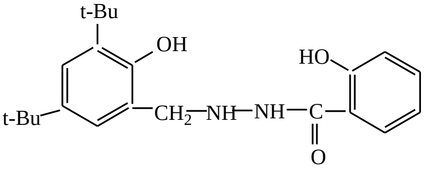
As with the copper complex, the phenolic oxygen of the salicylic fragment does not coordinate with the vanadium ion.

7. Synthesis, structure and properties of Cu(II) Co(II), Ni(II) and VO(II) complexes with 3,5-ditretbutyl-2-hydroxybenzoyl hydrazide.

New complexes Cu(II), Co(II), Ni(II) and VO(II) with hydrogenated ligand on the azometine group of Schiff's base consisting of salicylic acid and 3,5-ditretbutyl salicyl aldehyde were obtained. It should be noted that there is no information about similar items in the literature.



H_4sahz



H_4sahzh

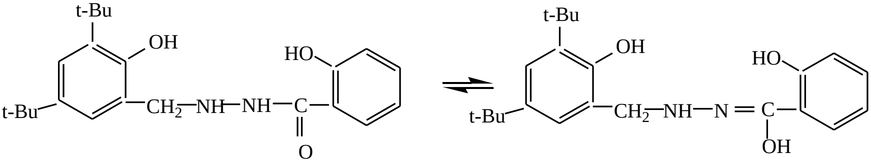
The reduced Schiff base was obtained by reducing N-(3,5-ditretbutyl 2-hydroxybenzyl) to salicyloilhydrazone under mild conditions (methyl alcohol, room temperature) with sodium borhydride.

Absorption bands 205, 265 in the electronic spectra of the Schiff base belong to the π-π * transition of the salicyloilhydrazone fragment. The absorption bands at 225, 310 nm belong to the π-π * transitions in the fraction of ditrebutyl-2-hydroxybenzylidene. The n-π * absorption band at 350 nm belongs to the C = N group attached to the benzene nucleus.

Based on the reduced Schiff, the H_4sahzh loses the absorption band at 265 nm and the absorption band is observed at 295, 285 and 310 nm.

In the IR spectra of the Schiff base (H_4sahz), the absorption bands C=N and C=O are observed at 1612 cm^{-1} and 1634 cm^{-1}, respectively. 3072 and 3196 cm^{-1} absorption bands belong to NH and HO-C=N groups. In the reduced H_4sahzh ligand, the absorption band of 1612 cm^{-1} azometine group is lost, and the absorption band of 1639 cm^{-1} band of carbonyl group is formed. The absorption band of the NH group occurs in the range of 3285 cm^{-1} and in the range of 3079 cm^{-1} with low intensity. The final absorption band is associated with the enolysis of the carbonyl group.

As mentioned earlier, this strip also has H4sahz based on Schiff, and its intensity is higher. This can be explained by the high degree of enolysis on the basis of Schiff compared to its reduced analogue.



Scheme 6. H_4sahzh-keto form H_4sahzh-enol form

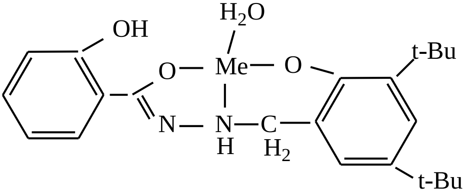
Upon the formation of Co(II), Ni(II), VO(II), and Cu(II) complexes with the H_4sahzh ligand, an additional band appears in the electronic absorption spectra at 400 nm, the position of which depends on the nature of the metal ion. This absorption band can be attributed to the ligand-metal charge transfer band. In the Cu(II) complex, it is located at 410 nm, in the Ni(II) complex at 423 nm, and in the Co(II) complex at 435 nm.

Along with this band in the visible region, d-d transitions are observed in the form of wide low-intensity absorption bands for the Cu(II) complex at 620 nm, for Co(II) at 560 nm and Ni(II) at 530 nm.

IR spectra indicate that the coordination of the ligand with the metal ion is carried out with the oxygen atom of the carbonyl group in the enol state. Indeed, the absorption band of the amide group at 1639 cm^{-1} disappears upon complexation. At the same time, at 3488 cm^{-1}, an absorption band of the hydroxyl group of the salicyl hydrazide fragment is observed, indicating that this group is not involved in coordination.

Derivatographic analysis confirms the data of elemental analysis, according to which the metal: ligand ratio in the complexes is 1:1. In addition, in accordance with thermogravimetric data, the molecules of the complexes contain one (Ni(II), Cu(II) complexes) or two (Co(II) complexes) water molecules, which are split off in the temperature range 120-250^{0}C. Next, several steps of weight loss are observed at 300-420^{0}C (37-58%), 420-500^{0}C (4.5-22%).

Taking into account the data of elemental analysis, IR and electron spectroscopy, as well as derivatography, the following structure can be attributed to the obtained complex compounds:



According to the given structure, the coordination of the metal ion is carried out due to the oxygen of the amide group in the enol form, the nitrogen atom of the hydrazine group and the oxygen atom of the salicyl aldiminate fragment.

Thus, the reduced Schiff base derivative of 3.5-di-tert-butyl phenol and salicylic aldehyde forms stable complexes with Co(II), Ni(II), VO(II) and Cu(II) ions, soluble in polar and non-polar organic solvents. The resulting complexes have compositions in which the metal: ligand ratio is 1:1.

8. Metal complexes of nicotinic acid hydrazide and salicylhydrazone.

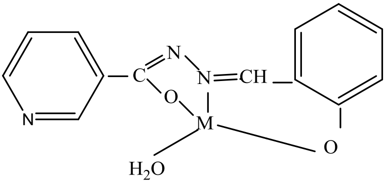
Salicylic hydrazides of nicotinic acid are potentially dianion tetradentate ligands; therefore, they can form various single-, dual- and multinucleated structures with metal ions.

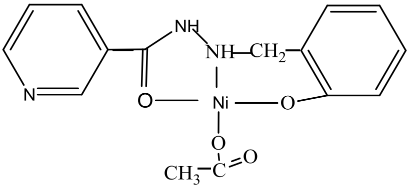
In almost all complexes, 1-nicotinoil 2-salicylidenhydrazone behaves as a tridentate and a mono- or dianion (depending on the nature of the metal ion) ligand. Interestingly, the nitrogen atom of pyridine is not involved in coordination in most cases, but in some cases it coordinates with neighboring metal atoms to form polymer structures. An analysis of the literature has shown that so far very little is known in the literature about metal complexes with reduced hydrazones on azomethane bonds. At the same time, such ligands are of interest due to their elastic structures. At the same time, such ligands are of interest due to their elastic structures. Comparison of the electron absorption spectra (Hshzna) of 1-nicotinoil-(2-salicylidene) hydrazone (Hshzna) and 1-nicotinoil-2-(2-hydroxybenzyl) hydrazine (Hshzna) confirms the predominance of the enol form. The long-wavelength absorption band at 360 nm (Hshzna) belongs to the double C = N-N = C fragment of the aromatic rings, and the absorption band at 300 nm belongs to the aromatic rings. In 1-nicotinoil-2-(2-hydroxybenzyl) hydrazine (Hshznah), the absorption band of the aromatic rings shifts to a shorter wavelength and is observed at 280 nm.

In this work, we obtained 1-nicotinoyl-2(2-hydroxybenzyl) hydrazine, complexes Co(II), Ni(II), Cu(II) with this ligand, and their structure and properties were studied.

We first synthesized 1-nicotinoyl-2-(2-hydroxybenzyl) hydrazine (Hshznah) by reducing 1-nicotinoyl-(2-salicylidene) hydrazone (H_2shzna) using sodium borohydride and their complexes with Co(II), Ni(II), Cu(II). For comparison, the Co(II), Ni(II), Cu(II) complexes without reduced ligand (H_2shzna) were obtained and studied.

The studies showed the possibility of reducing nicotinoylhydrazone salicylic aldehyde to the corresponding 2-hydroxybenzyl hydrazide, the different nature of the coordination of 1-nicotinoyl-2-salicylidenehydrazone and its reduced analog 1-nicotinoyl-2(2-hydroxybenzyl) hydrazine. In the first case, the ligand acts as a dianionic tridentate, while in the second case, it acts as a monoanionic tridentate.





H_2shzna **M=Co(II),Ni(II),Cu(II)** **H_3shznah**

Nicotinic acid hydrazones have been shown to have bactericidal and fungicidal properties.

9. Synthesis, structure and properties of complexes of manganese and iron with malonic acid dihydrazide derivatives.

Complexes with acylhydrazones and their transition metal ions are of great interest as anti-tuberculosis, anti-cancer drugs. They also have antimicrobial properties.

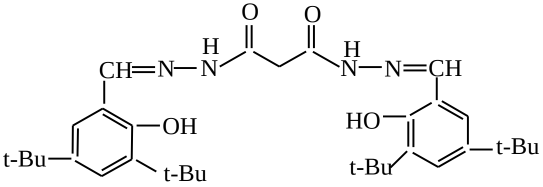
Dihydrazones of dihydrazides of dibasic acids are polydenate ligands and form different types of single-, dual-, and 3-nucleated complexes with transition metal ions: malic acid and salicylic aldehyde dihydrazone are monodentate ligands that can enter at least six coordinates with oxygen and nitrogen atoms and forms different types of complexes.

Malonic acid dihydrazide has a high elasticity due to its ability to rotate around the methylene group compared to other similar dibasic acids (oxalate, phthalic, etc.). Experiments show that higher elasticity can be achieved by reducing the azometine group in these ligands.

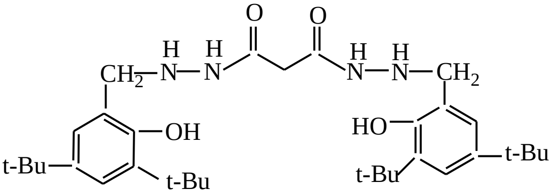
The carbonyl group combined with the hydrazine group can be converted to keto and enol forms, and the hydrogen atom can be deprotonated during coordination. Therefore, dihydrazone of malonic acid dihydrazide acts as a potential mono-, bi-, tetraanion ligand during coordination.

In this work, we synthesized complexes of Mn(II) and Fe(II) with reduced derivatives of malonic acid 3,5-ditretbutyl salicylhydrazones.

Complexes of transition metals with disalicylidene-malonoyl-dihydrazone usually form compounds insoluble in water and organic solvents, which limits the possibility of studying their properties. We have obtained malonoyl-dihydrazones 3,5-ditretbutyl salicylic aldehyde. The complexes of the latter with Mn(II) and Fe(II) ions are readily soluble in polar (methanol, ethanol) and low-polar (benzene, chloroform) solvents.



H_2shzma



H2shzmah

In the electronic spectra recorded in an ethanol solution, shzma observed absorption bands at 285 and 296 nm (doublet) and 340 nm. These bands can be assigned to π-π * and n-π transitions, respectively. The band at 370 nm is attributed to the absorption of the azomethine group conjugated to the benzene ring. In the reduced shzmah ligand, the band at 340 nm disappears, which confirms its belonging to the conjugated azomethine group, and a singlet band at 295 nm appears instead of the doublet band at 285 and 296 nm.

When a complex of manganese with the H_2shzma ligand is formed in the UV (ultraviolet) region, peaks appeared at 267, 290 nm and kinks at 320 and 340 nm.

In the visible region of the spectrum, three absorption bands are observed – at 445, 610 and 720 nm, corresponding, respectively, to the ligand-metal charge transfer band and two d-d transitions.

In the complex of manganese with the hydrogenated H_2shzmah ligand, the singlet band at 285 nm observed in the ligand noticeably broadens and shifts to the long-wavelength region (λ_{max} = 305 nm). In the visible region of the spectrum, absorption is observed at ~ 400 nm (kink) and a weak wide band with λ_{max} = 550 nm.

Iron complexes with H_2shzma ligand are identical to manganese complexes. A similar analogy exists in the complexes of Mn(II) and Fe(II) ions with H_4shzmah ligand.

In the IR spectrum of the Schiff base, absorption bands are observed related to the azomethine group CH = N- at 1630 cm^{-1} and the band at 1694 cm^{-1}, which can be attributed to vibrations of carbonyl C = O in the amide group. Two intense bands at 3200 and 3080 cm^{-1} can also be attributed to stretching vibrations of the interacting NH and OH. In the azomethine hydrogenated ligand shzmah, the bands of the azomethine and carbonyl groups at 1630 and 1694 cm^{-1} disappear and a broadened band appears with a maximum of 1620 cm^{-1}. In the IR spectrum of the complex of manganese with a Schiff base, the H_4shzma band at 1690 cm^{-1}, which is present in the ligand, disappears and the band at 1630 cm^{-1} shifts somewhat towards low energies (1609 cm^{-1}) and a new one appears at 1654 cm^{-1}, which can be attributed to the coordinated carbonyl group.

In the IR spectrum of the manganese complex with the reduced H_4shzmah ligand, they disappear in the region of 1600-1700 cm^{-1}, and weak absorption at 3200 and strong at 3400 cm^{-1}, which can be attributed to the N-H and OH vibrations in the amino and phenolic groups, disappear in the region of stretching vibrations. These data indicate that the carbonyl group in the complex is enolized and acts as an anion in coordination.

Attempts to obtain single crystals for X-ray measurements were unsuccessful. The obtained single crystals had a defective structure, however, with a high degree of probability, the molecular structure was established for the complex of manganese with the H_4shzmah ligand (Fig. 15).

It is binuclear with a ratio metal: ligand = 1:1. The coordination of each manganese ion is carried out by two phenolic oxygen atoms, two nitrogen atoms of the amino group and two oxygen atoms of the amide fragment (Fig. 15), so that an octahedral environment is carried out around the metal ion. Apparently, the iron complex has a similar structure, which has spectral and magnetic properties similar to the manganese complex.

Magnetic moments measured at room temperature indicate a high-spin state of iron and manganese ions in these complexes μ_{eff} = 7.2 m.B. for $[Mn_2(shzmah)_2]$ and μ_{eff} = 6.8 m.B. for $[Fe_2(shzmah)_2]$.

According to the magnetic measurement data, the manganese ion has an oxidation state of +2 (electronic configuration d^5) and therefore the ligand in this case behaves as a dianionic and the total formula of this compound can be represented as $[Mn_2(shzmah)_2]$.

In both complexes, the dependence of the magnetic permeability on the voltage of the magnetic field goes beyond the linear dependence. This indicates that there is an intramolecular ferromagnetic interaction between Mn (II) and Fe (II) ions.

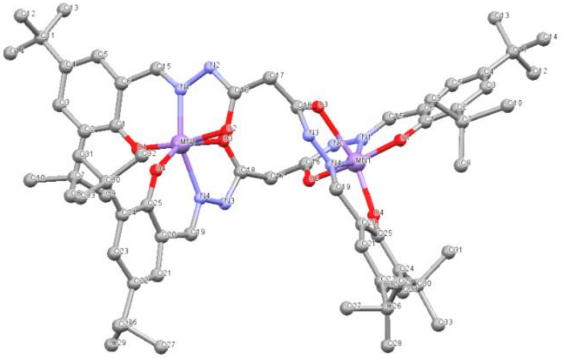
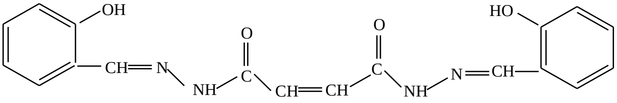


Fig. 19. Structural structure of $Mn_2(shzmah)_2$ complex.

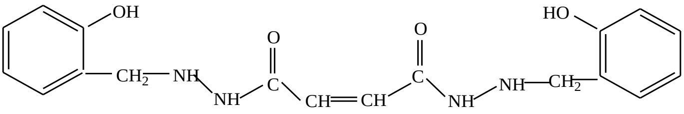
Thus, in the dihydrazone of 3,5-ditretbutyl salicyl aldehyde with malonic acid, the azometine group can be reduced to the amine group. Reduced hydrazone forms binuclear complexes with manganese (II) and iron (II) ions.

9. Metal complexes with maleic and amber acid dihydrazones.

Maleic acid dihydrazone and its reduced analogues in terms of azometine are of great interest in terms of the formation of di- and multinucleated complexes. We have studied and synthesized Ni(II), Co(II), Cu(II), Mn(II), Fe(II) complexes with this ligand.



$H_2dhzmaa$



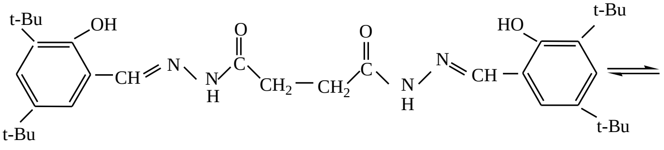
$H_2dhzmaah$

An absorption band of 1621 cm^{-1} is observed in the IR spectra of the Schiff base (H2dhzmaa), and this absorption band is lost at the reduced Schiff base (H2dhzmaah). At the same time, in the reduced ligand, an absorption band of 3343 cm^{-1} is observed due to the valence waves of the N-H group.

The hydroxyl group of the phenol fragment in both ligands manifests itself in the form of a very wide absorption band from 2000 cm^{-1} to 3500 cm^{-1} as a result of intramolecular hydrogen bonds. Electron absorption spectra also show that the azometine group is reduced. A very wide absorption band at 360 nm is observed in the electronic spectrum of (H2dhzmaa). This band belongs to the n-π * transition of the azometine group connected by a benzene ring.

This band (H2dhzmaah) does not exist in the spectrum, and instead an absorption band at 320 nm appears, which can be attributed to the combined group formed by the keto-enol equilibrium - N = COH - CH = CH-.

Salicylic dihydrazones of amber acid have catalytic activity, have a catalytic effect on the oxidation of alkenes, can bind to DNA and have antimicrobial activity. Dihydrazones of amber acid dihydrazides, like dihydrazones of other two basic acids, are 4-anionic due to the deprotonation of potential hexadentate and two phenolic hydroxyls, enolysis of two carbonyl groups (structure E).



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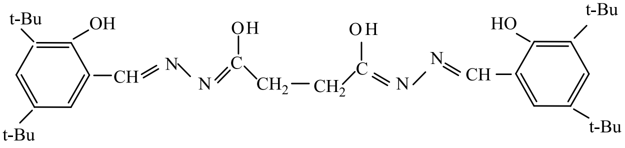


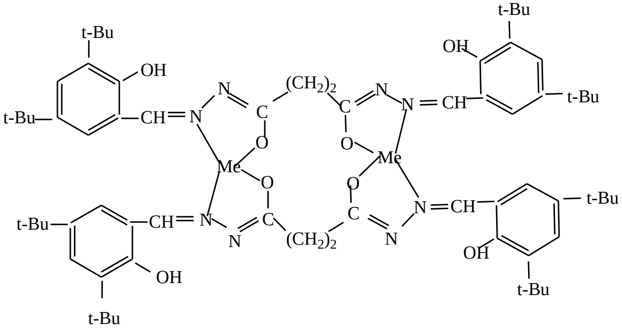
E

Therefore, this ligand has the ability to form complexes with different composition and structure. The acquisition of new dihydrazone complexes is of great interest due to their biological activity - antimicrobial and fungicidal properties. In this regard, the reduced hydrazones of the azometine group are of particular interest.

Dihydrazone with 3,5-ditretbutyl salicyl aldehyde of amber acid hydrazide is well soluble in organic and less polar solvents, unlike other dihydrazone derivatives.

Manganese and iron complexes were synthesized with amber acid dihydrazide, 3.5-ditretbutyl salicyl aldehyde hydrazone and its reduced analogue.

It was not possible to directly reduce the azometin bond in H_2dhzsa dihydrazone, as very small amounts of reduced ligand were observed in the reaction products. Therefore, the reduction reaction was carried out with the catalytic presence of palladium chloride. The Mn(II) ion coordinates with the ligand through the enolished oxygen atom of the amide group and the nitrogen atom of the azometine group.



Element analysis shows that the metal: ligand ratio is 1:1.

10. Disruption of the triazole ring by the interaction of salicylidenamine-3-tia-4-hydrazino-5-mercapto 1,2,4-triazole with Ni(II) ion.

1,2,4-triazoles and their derivatives are polydenate ligands. They coordinate with the metals of the first transition period, forming single-core and polymer complexes.

1,2,3-triazole and its derivatives are heterocyclic compounds of great interest with their interesting structures and large coordination differences. Heterocyclic π-connected systems, nitrogen atoms that are acceptors of hydrogen bonds, and luminescent and other properties due to their π-π- stacking interactions in aromatic systems.

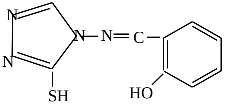
The 1,2,4-triazole nucleus is included in a wide list of therapeutically active molecules that can be converted into highly effective drugs. In addition to conventional medical applications, triazoles are also used as corrosion inhibitors, potential energy materials with optoelectronic properties due to their high electronic conductivity.

Derivatives of 3-hydrazino-4-amino-1,2,4-triazole have luminescent properties, and iron (III) complexes have a spin-crossover effect.

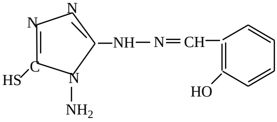
Substituted triazoles are particularly noteworthy due to the presence of three potential donor substituents associated with the 4-amino-3-hydrazino-5-mercapto-4H-1,2,4-triazole, 1,2,4-triazole nuclei. The presence of an expanded π-conjugation allows the creation of new molecular architectures. Studies show that 4-amino-3-hydrazino-5-mercapto-4H-1,2,4-triazole coordinates transition metal ions through the hydrazine and amine group nitrogen atoms.

Schiff bases of 3-tia-4-hydrazino-5-mercapto 1,2,4-triazole are biologically active substances with bactericidal and fungicidal activity. The use of 4-salicylidenamine-3-hydrazino-5-mercapto-1,2,4-triazole as an inhibitor of steel corrosion is also known.

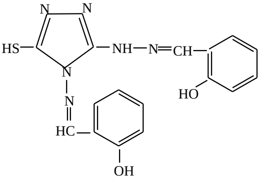
Because it contains two active NH_2 groups, 3-tia-4-amino-5-hydrazino-1,2,4-treazole aldehydes can form 3 types of Schiff bases.



I



II



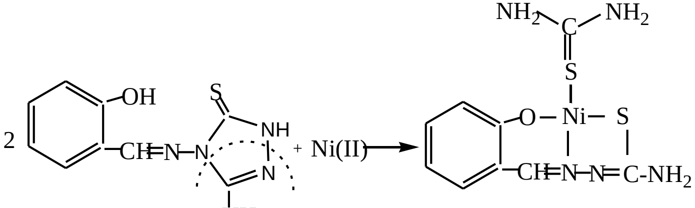
III

All three types of structures can be found in published articles. Some articles suggest that the Schiff base is formed from the direction of the 4-amine group. Some, on the contrary, show that the formation of the Schiff base is due to the nitrogen of the hydrazine group.

When the initial reagents are thiatreazole: salicyl aldehyde in a ratio of 1:2, a Schiff base can be formed from both amine groups. It should be noted that so far there is no X-ray structure with these ligands and their complexes.

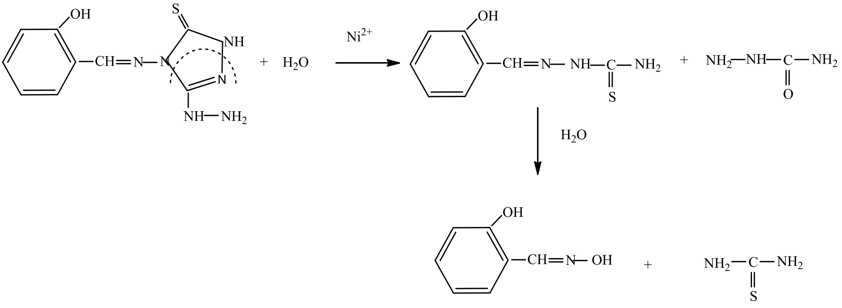
When synthesizing the Ni(II) complex on the basis of Schiff from salicylic aldehyde and 3-tia-4-amino-5-hydrazino-1,2,4-triazole, it was found that the treazole ring is broken down during the complex formation process. X-ray structural analysis shows that the ligand that coordinates the Ni(II) ion in the formed complex is N- (salicylidene) thiosemicarbazone and behaves as a tridentate dianion ligand.

Thiosemicarbazonate ligand can be formed if the treazole ring is broken down according to the following scheme:



NiTSC

The breakdown of the treazole ring can be explained by the catalytic effect of the nickel ion on the process. In this case, the hydrolysis reaction is most likely to take place in coordinated ligands. The formation of thiourea involved in the complex is possible due to the hydrolysis of thiosemicarbazide. The hydrolysis of the primary ligand can be shown as follows:



Scheme 7. Disruption of the triazole ring by interaction with Ni (II) acetate.

The molecular structure of the complex is shown in Figure 20. The environment around of the Ni(II) ion is a distorted square. The metal ion is coordinated by a phenolic oxygen atom, a hydrazine nitrogen atom, a thiosemicarbazonate ligand sulfur atom, and a sulfur atom of a thiosemicarbazide molecule. The ligand N-(salicylidene) thiosemicarbazone behaves as a dianionic ligand due to the phenolate oxygen of the sulfur atom, coordinating in thiolate form.

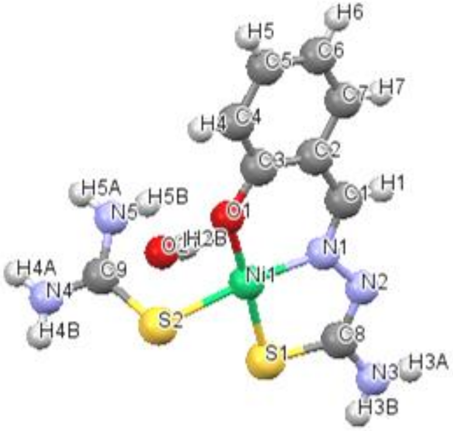


Fig. 20. Molecular structure of the complex
[Ni (TSC) $(NH_2)_2$CS)]·H_2O kompleksinin molekulyar quruluşu.

The Ni-S1 and Ni-S2 distances are significantly different and equal, respectively, to 2.158Å and 2.252Å, which indicates a stronger bond between the thiol sulfur atom and nickel ion than the thionic distances C1-N1 and C2-N2 have close values (1.311 and 1.327Å) and are conventional values for a double bond between nitrogen and carbon atoms. The distances of Ni-N1 and Ni-O1 are equal to 1.894 and 1.890Å, respectively.

In the IR spectra of the initial Schiff base of thiatriazole in the region of stretching vibrations of N-H bonds, absorption bands are observed at 3200, 3320 and 3400 cm^{-1}. Due to the strong hydrogen bond with the C=N group, the absorption band of the phenolic hydroxyl group is not visible in the spectrum. There is also no S-H absorption band, which indicates that the thiatriazole sulfur in the ligand is in thionic form. The intense band at 1620 cm^{-1} can also be attributed to vibrations of the azomethine group.

The IR spectra of the nickel complex in the region of NH stretching vibrations contain four absorption bands of 3160, 3280, 3400 and 3420 cm^{-1}, which relate to stretching vibrations of N-H in the thiosemicarbazonate fragment (the first two bands are ν_{symm} and ν_{asym}) and to stretching NH vibrations in coordinated thiourea molecule. A narrow band of medium intensity at 3520 cm^{-1} can be attributed to a crystalline water molecule.

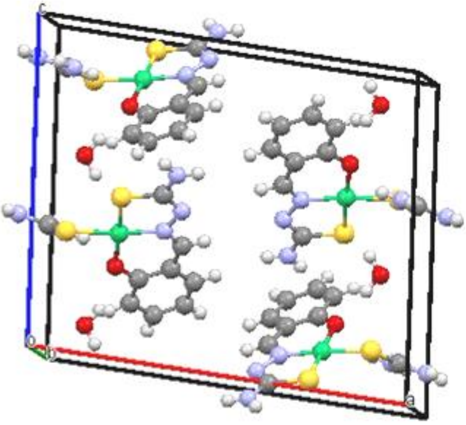


Fig. 21. Crystal cage of $[Ni(TSC) (NH_2)_2CS)]\cdot H_2O$ complex

The electronic spectrum of the initial ligand contains the following absorption bands: 210, 240, 300, and 330 nm. The band at 240 nm should be attributed to the absorption of the C = S chromophore group, since thiourea absorbs precisely at this wavelength (Fig. 23). We note the almost complete similarity of the electronic absorption spectra of thiourea and thiosemicarbazone. The remaining bands belong to π-π n-π transitions in the salicyl aldiminate and triazole fragments. The spectrum of the $[Ni(TSC) (NH_2)_2CS)] \cdot H_2O$ complex in the UV region also has absorption at 240 nm, which is due to the presence of coordinated thiocarbamide in the complex.

The decomposition of the initial ligand and the formation of the salicylicdene thiosemicarbazonate complex $[Ni(TSC)-(NH_2)_2CS)]\cdot H_2O$ occurs very quickly. The spectrum of the complex formed by mixing equimolar solutions of nickel acetate and the starting ligand-salicylidenamine-3-hydrazino-5-mercapto 1,2,4-triazole for 5 minutes completely coincides with the spectrum of the complex [Ni(TSC)$(NH_2)_2CS$)]·H_2O. When mixing solutions of thiosemicarbazide, salicylic aldehyde and nickel acetate, an electronic spectrum is obtained similar to the spectrum of [Ni(TSC)$(NH_2)_2CS$)]·H_2O, except of the fact that the absorption at 240 nm. low intensity (Fig. 22).

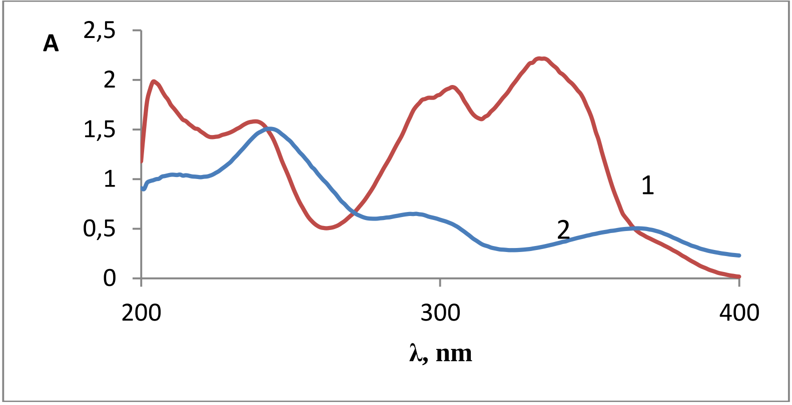


Fig.22. Electronic spers drawn in ethyl alcohol: 1-salicylidenamine-3-hydrazino-5-mercapto 1,2,4-triazole, 2-[Ni (TSC) $(NH_2)_2CS$)]·H_2O complex

This is due to the absence of urea in the resulting complex and its presence in [Ni (TSC) $(NH_2)_2CS$)]·H_2O (Fig.23).

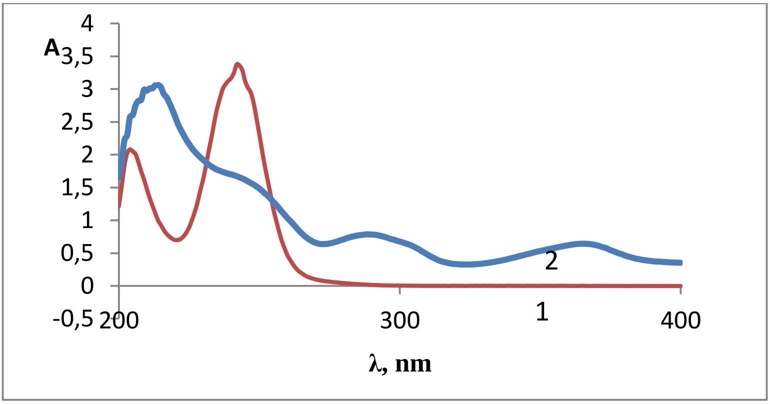


Fig.23. Electronic spectra in ethanol solutions: 1-thiosemicarbazide, 2- a mixture of nickel acetate, salicylic aldehyde and thiosemicarbazide.

Thus, the interaction of nickel 2-acetate with salicylidenamine-3-hydrazine-5-mercapto 1,2,4-triazole breaks down the triazole ring and the formation of a thiosemicarbazonate complex of nickel (salicylide) is observed. This, in turn, proves that Schiff-based salicylic aldehyde forms a bond between the amine group and the nitrogen atom in the triazole ring.

11. Study of the biological activity of synthesized metal complexes with hydrazides and hydrazones of carboxylic acids.

When lubricating oils are stored in unfavorable conditions (high temperature, humidity), they are exposed to microorganisms that change their composition, increase their acidity and therefore increase their corrosion resistance.

Pure bactericidal chemicals or mixtures are added to lubricants to prevent bacterial growth.

Many classes of bactericidal chemicals are currently known. However, to date, reduced ligands and their complexes have not been studied as antimicrobials and fungicides.

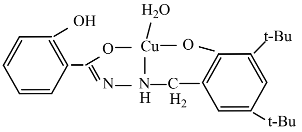
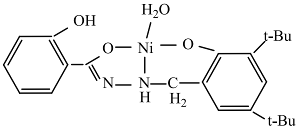
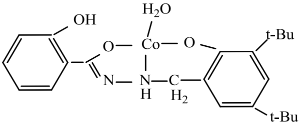
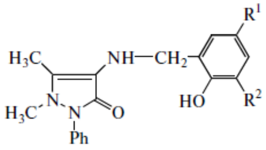
Table (Table 3) presents the reduced Schiff bases and test results of their complexes.

As can be seen from the table, all tested substances show antimicrobial and fungicidal properties. The most active of the studied compounds is the Co(II) complex of N-3,5-ditretbutyl 2-hydroxybenzyl-N-salicyloyl hydrazine.

Cu(II) and Ni(II) complexes are also quite active with this ligand. Derivatives of 4-aminoantipyrine also show high antimicrobial and fungicidal properties. It should be noted that high activity is also observed when reducing the concentration.

Table 3

Antimicrobial and fungicidal properties of synthesized complexes. The diameter of the inhibition zone is cm

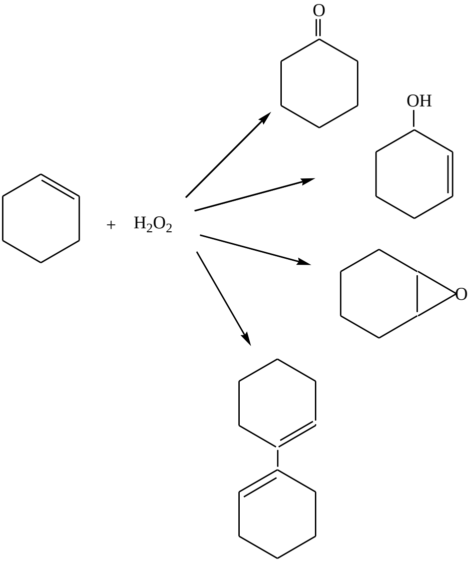
№	Cons. в %	Chemical formula	APA (atpeptideagar) bacteria in the environment	SA((suslo agar) fungi in the environment)
1	1 0.5 0.25	$[Cu(s2amph)_2(CH_3COO)_2]$	1.6-1.8 1.3-1.4 1.1-1.1	2.5-2.7 2.0-2.0 1.5-1.3
2	1.0 0.5 0.25	$[Pd(s2amph)_2Cl_2]\cdot 2C_2H_5OH$	1.8-1.8 1.5-1.5 1.1-1.2	+ + + + + + + + +
3	1 0.5 0.25		1.4-1.5 1.2-1.2 1.0-1.0	2.2-2.4 1.8-1.6 1.4-1.5
4	1 0.5 0.25		1.6-1.6 1.2-1.4 1.0-1.2	1.2-1.2 1.0-1.0 + + +
5	1 0.5 0.25		2.0-2.5 1.8-1.8 1.5-1.5	3.0-3.2 2.5-2.5 1.6-1.8
6	1 0.5 0.25		2.5-2.6 1.6-1.8 1.4-1.5	2.2-2.4 1.8-2.0 1.6-1.7
Конт СОЖ АзероЛ-5			+ + + +	+ + + +

+ +- full growth of microorganisms

12. Investigation of catalytic activity of hydrazide and hydrazone complexes. Catalysis of the interaction of cyclohexene with hydrogen peroxide.

The course of the epoxidation reaction of cyclohexene with hydrogen peroxide in the presence of Mn(II) and VO(II) complexes of H_2shzma and H_2shzmah ligands was studied.

The reaction was carried out for 3 h with intensive mixing with 30% hydrogen peroxide at 500°C. Chroma-to-mass spectroscopic analysis showed that the main products of the reaction were 2-cyclohexene-1-ol, 2-cyclohexene-1-on, epoxycyclohexane, and bis-cyclohexene-1-year (Scheme 8).



Scheme 8. Conversion products of cyclohexane.

The following table (Table 4) provides comparative data on the oxidation of cyclohexene in the absence and presence of catalysts. As can be seen, catalysts significantly increase the productivity of reaction products compared to non-catalyst reactions. The highest productivity of epoxycyclohexane is observed in the presence of $Mn_2(shzma)_2$ complex.

Table 4

Yield of oxidation products of cyclohexene with hydrogen peroxide.

Substances	2-cyclo-hexane -1-ol,%	2-cyclo-hexene -1-on,%	Epoxy hexane, %	bis-cyclo-hexane 1- y.,%
cyclohexene + hydrogen peroxide	5.295	4.016	0.444	0.288
$Mn_2(shzma)_2$	10.256	7.988	5.273	1.931
$(VO)_2(shzmah)_2$	14.627	9.800	3.806	1.331

CONCLUSIONS

1. There is a fundamental difference in coordination with N-(2-hydroxybenzyl) -2,3,4 aminopyridines and their reduced analogues. If in the complexes formed from Schiff bases the coordination with the metal ion is formed by oxygen of the phenol group and nitrogen of the azometine group, their reduced analogues behave as monodentate ligands and coordinate with the endocyclic nitrogen atom [272].
2. It was shown by the RSA method that the reduced analogues of Schiff bases formed by 2-hydroxybenzyl derivatives of 4-aminoantipyrine with Co(II) and Ni(II) ions form complexes with an equatorial plane distorted octahedral structure. The equatorial plane consists of two nitrogen atoms of the amine group and two oxygen atoms of the two carbonyl groups. The oxygen atom of the phenol group is in the apical position at this plane. The octahedral structure of the complexes formed by the reduced ligands is due to the fact that the ligands are more elastic in them. Schiff bases have a flat square structure [1,18,29,96].
3. It has been shown for the first time that the oxidation-dehydrogenation reaction of 4-aminoantipyrine derivatives in metal compounds with reduced Schiff bases takes place in mixed ligand complexes. This is due to the formation of a free coordination space as a result of the replacement of the tridetate ligand, which forms an

octahedral structure, with a mono- or two-nucleated flat square or square-pyramidal structure. The kinetics of this reaction have been studied and a mechanism has been proposed. [18,33,55].

4. New Cu(II) and Ni(II) complexes were obtained with reduced SB-(2-hydroxy-3,5-R^1, R^2-benzyl)-4-aminoantipyrins by the interaction of sodium salt of ligand sulfate in copper in aqueous solutions. However, in the alcohol solution with reduced ligands, in combination with copper 2-acetate, complexes with Schiff bases are formed. An oxidative-dehydrogenation reaction takes place in the process of complex formation.The molecular structure of the 2 Cu(II) complex, the product of the oxidation-dehydrogenation reaction was determined by the RSA method [18, 33, 34].
5. Cu(II), Ni(II), Co(II) and Pd(II) complexes with Schiff bases and derivatives of 8-aminoquinoline and salicylaldehydes were synthesized, their properties and structures were studied. It was shown that the reduced Schiff bases, derivatives of 8-aminoquinoline and salicylaldehyde depending on the type of metal and the substituents in the salicylic fragment, can either undergo an oxidative dehydrogenation reaction or form complexes with these ligands without being oxidized [27, 31, 32].
6. New Cu(II), Co(II), Ni(II) and VO(II) complexes were obtained with a reduced analogue of hydrazone obtained from the interaction of salicylic acid hydrazide and 3,5-ditretbutyl aldehyde. It has been shown that the coordination of the metal ion is formed by the enol form of the oxygen atom of the amide group, the nitrogen atom of the hydrazine group and the oxygen atom of the salicylaldiminate fragment [97].
7. Ni(II), Co(II), Cu(II), Mn(II), Fe(II) complexes of salicylhydrazone with nicotinic acid hydrazide were obtained and studied. It was found that the Cu(II) ion coordinates with 1-nicotinoil-2-salicylide hydrazone, the oxygen of the phenol fragment, the nitrogen of azomethene, and the oxygen of the amide group in the enol form, and behaves like a dianion tridentate ligand, but 1-nicotinoil-2-(2′-hydroxybenzyl) is a hydrazine monoanion tridentate [94].
8. Mn(II) and Fe(II) complexes were synthesized and studied with 3,5-ditretbutylsalicylic hydrazone of malonic acid dihydrazide.

The complex was found to be biconuclear by RSA [22, 28, 30].

9. Ni(II), Co(II), Cu(II), Mn(II), Fe(II) complexes were obtained with dihydrazones of maleic and amber acids. It has been shown that metal ions coordinate with ligands with the oxygen of the amide group in the broad form and the nitrogen atom of the azometine group. The complexes were found to be dual-nucleated [95].
10. A Ni (II) complex based on Schiff was obtained from the interaction of 3-thio-4-amino-5-hydrazino-1,2,4-triazole with salicylic aldehyde. It was found that during the formation of the complex, the triazole ring was broken down and a complex with N- (calisilidene) thiosemicarbazone was obtained. A mechanism for the breakdown of the triazole ring has been proposed [98].
11. Reduced hydrazones have been found to have high antimicrobial and fungicidal activity. Among the studied complexes, the Co (II) complex of N-3,5-ditretbutyl 2-hydroxybenzyl N-salicylloyl hydrazone showed higher activity. Its effectiveness was 3-5 times higher than the standard (8-aminoxinoline) [28, 94, 95, 97].
12. A comparison of the oxidation products of cyclohexene with hydrogen peroxide with and without a catalyst shows that the catalyst significantly increases the yield of reaction products. The H_2shzmah complex of manganese significantly increases the yield of the epoxidation reaction [30].

The main content of the dissertation is published in the following scientific publications.

1. Меджидов, А.А., Фатуллаева П.А., Редокс-свойства комплексов металлов с п-фенилендиамин-N,N.N′N′-тетрауксусной кислотой // Азербайджанский Химический Журнал,– 2000. №4, – с.29-35.
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