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# COMPLEX COMPOUNDS OF TI (IV), Fe (III), Ni (II), Cu (II) and Zn (II) WITH SEVERAL AROMATIC AND HETEROAROMATIC HYDROXY ACIDS AND THEIR APPLICATION AS PRECURSORS OF NANOSIZED OXIDE PHASES

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# КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ Ті(IV), Fe(III), Co(II), Ni(II), Cu(II) И Zn(II) С НЕКОТОРЫМИ АРОМАТИЧЕСКИМИ И ГЕТЕРОАРОМАТИЧЕСКИМИ ГИДРОКСИКИСЛОТАМИ И ИХ ПРИМЕНЕНИЕ КАК ПРЕКУРСОРОВ НАНОРАЗМЕРНЫХ ОКСИДНЫХ ФАЗ

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#### **INTRODUCTION**

#### **Relevance of the work**

Modern science is characterized by the ongoing miniaturization of technological processes, leading to the formation of a fundamental novel area - nanotechnology. It is defined as the design, characterization and application of structures, devices and systems by controlling shape and size at the nanometer scale (1 to 100 nm) and finds practical applications in various fields of everyday life, for instance electronics and materials science, chemistry, biology and medicine [1]. Industrial applications of nanoparticles are associated with their use as magnetic seals in motors, information carriers, catalysts of various processes, and other areas.

Heterogeneous catalysts based on individual and modified transition metal oxides find application in different fields of science and technology (in systems for purification of wastewater and polluted air from anthropogenic contaminants). In contrast to homogeneous systems, they can be separated easily from the reaction mixture, without contaminating it and have a wide pH range of catalytic action. Reducing the size of catalysts to the nanometer scale (1 to 100 nm) increases the active surface area and thus increases their activity.

A promising method for obtaining nanosized oxide particles is the hydrothermal method, in which precursors (hydroxides, nitrates, carbonates, oxalates) are precipitated from aqueous solutions with subsequent calcination. The use of organic metal complexes is much more efficient [2]. The decomposition of complex compounds of metals with organic ligands releases a large amount of gaseous decomposition products (mainly  $CO_2$  and  $H_2O$ ), which prevent oxide particles from sticking together into large agglomerates, resulting in a significant reduction in the size of oxide catalyst grains and improvement of their surface properties. From the economic standpoint, it is important to reduce the temperature and processing time of precursors while maintaining the physical and chemical characteristics of the resulting catalyst; therefore, finding optimal precursors based

on low-cost raw materials and optimizing the routes for obtaining nanoscale catalysts are highly relevant.

### The degree of development of the topic

The analysis of the published literature on the topic of the study shows that inorganic salts or freshly precipitated metal hydroxides are usually used for the synthesis of nanosized metal oxides by the hydrothermal method. In previous studies conducted at the Department of General Chemistry, Peoples' Friendship University of Russia, the possibilities of using complex compounds of N-nitrosohydroxylamine derivatives [3] and some dihydroxyaromatic compounds [4] for these purposes were studied. The use of  $\alpha$ -hydroxyaromatic acids for the synthesis of metal complexes and their further thermal decomposition to isolate nanosized metal oxides is an appropriate direction of research. Carboxyl group and hydroxyl group in the neighboring position form chelate complexes with most metal cations, and low temperatures of decarboxylation and further decomposition of organic ligands lead to the release of a large number of gaseous products (carbon dioxide and water), without polluting the environment and without introducing additional impurities in the thermal decomposition of their metal complexes. As a result, the precursor processing temperatures for obtaining nanoscale oxide materials are significantly reduced.

 $\alpha$ -Hydroxyaromatic and heteroaromatic acids are commercially available, thus their use is economically and environmentally beneficial. However, additional studies are required to optimize the processes of metal complexes isolation (determination of optimal metal:ligand ratio and synthesis pH, identification of stability of isolated complexes and their thermal stability regions).

#### Statement of the task and aims of the study

The goal of this study is the synthesis of new coordination compounds of Ti(IV), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with a number of  $\alpha$ -hydroxyaromatic and heteroaromatic acids on the basis of benzene and pyridine rings, the study of their physicochemical properties and regions of thermal stability, as well as the use

of these complex compounds and their mixtures for the preparation of nanoscale oxide materials and identifying areas of possible use.

In order to achieve the goal, the following task were solved in this framework:

a) Investigate the processes of complexation in solutions, determine the composition of complexes and their formation constants, reveal the dependence of complexation on the physicochemical characteristics of the central ion and organic ligands;

b) Optimize synthesis methods and isolate individual complex compounds, characterize them using modern physicochemical methods of analysis, including spectral methods and X-ray phase analysis;

c) Establish the conditions for the formation of nanosized metal oxides of different morphologies;

d) Study the catalytic activity of certain isolated compounds.

In this study, the following chemical and physicochemical methods were used: elemental, potentiometric, thermogravimetric, X-ray analysis methods; IR and electron spectroscopy; electron microscopy.

#### **Scientific novelty**

Using the modified methods, 31 complex compounds of Fe(II), Co(II), Ni(II), Zn(II), Cu(II) and Ti(IV) with 2-hydroxynicotinic acid, 3-hydroxypicolinic acid, 2-hydroxy-6-methylnicotinic acid, 3-methoxysalicylic acid, 3,5-diisopropylsalicylic acid, 2-hydroxy-1-naphthoic acid, 2,3-dihydroxybenzoic acid and 3,5-dinitrosalicylic acid were isolated and identified, 20 of which were discovered for the first time and their compositions and structures were determined. The molecular and crystal structures of four complex compounds and two organic ligands were identified. The composition and formation constants of the complex compounds in water-ethanol solutions were determined. The conditions for the formation of metal oxide nanoparticles of different morphology were evaluated, their catalytic activity in the reactions of photodegradation of phenol-containing compounds was proved,

and it was demonstrated by in silico modeling methods that the introduction of hydroxyaromatic acids into the composition of metal complexes does not change their biological activity.

#### Scientific and practical significance

Theoretical and experimental results together with conclusions contribute to the coordination chemistry of transition metals and metal complexes with hydroxyaromatic carboxylic acids. They can be used in the study of related organic molecules. Structural and spectral characterizations of organic ligands and their metal complexes will be included in the corresponding reference books, reviews and monographs. The results obtained on the thermal decomposition of metal complexes would be useful for modification of synthesis methods for nanoscale metal-oxide catalysts.

#### Methodology and methods of research

The methodology of this study is determined by the solution of the tasks and fulfillment of the research objectives: literature search on the issue and justification of the research objects selection, synthesis methods of coordination compounds and their analysis methods. The oxide phases obtained from thermal treatment of precursors were studied by a combination of research methods to determine their composition, homogeneity and potential photocatalytic properties.

## **Provisions for the defense**

1. Investigation of complexation processes of certain 3d-metals with  $\alpha$ hydroxyaromatic and heteroaromatic acids, determination of the metal complexes composition in solutions, their formation constants, revealing the dependence of metal complexes stability on the physicochemical characteristics of the complexing agent and organic ligands.

2. Optimization of synthesis methods for metal complexes, isolation of crystalline phases, spectral characteristics of metal complexes.

3. Crystal and molecular structures of four metal complexes and three organic ligands.

4. Assessment of the possibility of using the isolated compounds as precursors for the synthesis of nanoscale metal-oxide phases and their further application as efficient catalysts and UV filters.

5. Evaluation of sorption activity of oxide phases obtained from inorganic precursors.

## **Reliability of the results**

The confidence level of the results is evaluated by using a combination of independent research methods and certified instrumentation, application of mathematical methods of statistics to analyze the results obtained, the experiment reproducibility and conclusions consistency with existing scientific ideas.

## **Approbation of the study**

The principal results of this study were reported and discussed at the conference "Modern trends in the development of chemical technology, industrial ecology and environmental safety" (St. Petersburg, April 07-08, 2022), All-Russian scientific conference of young researchers with international participation "Innovative development of techniques and technologies in industry (INTEX-2023)" (Moscow, April 17-20, 2023), II International scientific conference "Catalysis for a Sustainable World" (Moscow, December 12-15, 2023), Fourteenth All-Russian scientific conference with international participation "Chemical thermodynamics" (Moscow, December 12-15, 2023), Fourteenth All-Russian scientific conference with international participation "Chemical thermodynamics" (Moscow, December 12-15, 2023), Fourteenth All-Russian scientific conference with international participation "Chemical thermodynamics" (Moscow, December 12-15, 2023), All-Russian scientific conference with international participation "Chemical thermodynamics" (St. Petersburg, April 12-15, 2023), All-Russian scientific conference with international participation "Chemical thermodynamics" (Moscow, April 17-20, 2023).

There are 9 published works on the subject of the thesis, 5 of them in scientific journals indexed in international databases and in editions from the VAK List recommended by the Academic Council of PFUR.

# Compliance with the passport of specialty

The dissertation research corresponds to the passport of specialty 1.4.1 Inorganic chemistry, namely item 3 Chemical bonding and structure of inorganic compounds; item. 7 Complexation processes and reactivity of coordination compounds, reactions of coordinated ligands.

# Structure and scope of the dissertation.

The thesis consists of an introduction, literature review, experimental part, discussion of results, conclusions and a list of references containing 136 titles. It is set out on 129 pages and includes 58 figures and 15 tables.

## LITERATURE REVIEW

# 1.1 Characteristics of hydroxyaromatic acids of carbocyclic and heterocyclic series

#### 1.1.1 General information

1

Hydroxy acids refer to organic chemical compounds containing one or more hydroxyl groups and a carboxylic acid group [5]. These compounds are widely distributed in nature. Hydroxy acids in particular can be classified according to the position of the hydroxyl substituent on the carbon skeleton, for example,  $\alpha$ ,  $\beta$ ,  $\gamma$ hydroxy acids; the number of hydroxyl groups, including mono- or polyhydroxy acids; and the nature of the carbon skeleton, specifically hydrocarbon, aromatic, or heterocyclic [6]. Among them, hydroxyaromatic carboxylic acid and heterocyclic rings - in particular hydroxypyridine carboxylic acid, are two groups of hydroxyacids that have attracted considerable attention of researchers due to their special optical properties and biological activity. Therefore, they are studied and applied in innumerable areas of life.

## A. Hydroxypyridine carboxylic acids

Hydroxypyridine carboxylic acids are hydroxy derivatives of pyridine carboxylic acids which include the following three isomers: Picolinic acid, Nicotinic acid and Isonicotinic acid (Table 1)[7].

Pyridine carboxylic acids and their derivatives are members of a highly interesting family of biological compounds [8], being among the most basic organic compounds of extraterrestrial origin that reached the early Earth from meteorites [9]. They are important for synthesizing larger complex coenzymes, in particular nicotinamide adenine dinucleotide, an important coenzyme in living organisms [10].

Hydroxypyridine carboxylic acids has attracted the attention of scientists because of its presence in many natural products for instance alkaloids, vitamins, coenzymes, they exhibit diverse biological activities, low toxicity and play an important role in physiological functions of living organisms [10–12]. In addition, hydroxypyridine carboxylic acids likewise are also aromatic ligands containing three types of functional groups, including: oxygen of the carbonyl group, nitrogen of the amide group and oxygen of the carboxylic group [13]. They possess the ability to coordinate a number of different metal ions, along with the enol-keto tautomerization phenomenon of some hydroxypyridine carboxylic acids, which is also an interesting feature that attracts the attention of researchers [14].

Common name	Picolinic acid	Nicotinic acid/Niacin	Isonicotinic acid
IUPAC name	Pyridine-2- carboxylic acid	Pyridine-3- carboxylic acid	Pyridine-4- carboxylic acid
Structure formula	OH OH O	OH OH	HOOO

Table 1. Isomers of pyridinecarboxylic acid

Currently, there are numerous publications on the potential applications of transition metal complexes with hydroxypyridinecarboxylic acid in various fields. In agriculture, various hydroxypyridine carboxylic acid derivatives act similarly to natural auxins, stimulating root and stem growth and promoting flowering and fruiting. Certain derivatives are capable of suppressing weed growth without harming crops [15,16]. Nicotinic acid (vitamin B3) is essential for energy metabolism in the body [10]. Many of its derivatives have anti-inflammatory and analgesic properties, which is used in the treatment of arthritis and ulcerative colitis [17]. Several studies have demonstrated the potential of these compounds in inhibiting the growth of cancer cells [18,19]. In addition, their ability to form

complexes with heavy metal ions has been proven, which promotes the excretion of heavy metals from the body [20].

In the industrial sector, there are a large number of hydroxypyridine carboxylic acid derivatives that are starting materials for the synthesis of many organic compounds, including dyes, pesticides, and fine chemicals [21,22]. Several derivatives are used as stabilizers or additives in the manufacture of plastics.

In the food industry, certain derivatives of hydroxypyridine carboxylic acid have antibacterial and antifungal properties on their own and are used as preservatives [23]. On the other hand, a number of other derivatives display characteristic aromas which are used in the food and perfume industries [24,25].

Thus, hydroxypyridine carboxylic acids represent a diverse group of compounds known to have important applications in various fields. The diversity of structure and chemical properties of these compounds provided abundant opportunities to investigate and develop novel applications.

### B. Hydroxyaromatic carboxylic acids

Hydroxyaromatic carboxylic acids represent an extremely important group of organic compounds that play a role in a wide range of processes, both natural and industrial. They are commonly found in nature, especially in plants [26]. The majority of hydroxyaromatic carboxylic acids are biologically active [27,28] widely used in medicine, pharmacology [29], biology [30], cosmetics and food technology [31,32]. In the chemical industry, hydroxyaromatic carboxylic acids serve as important synthetic chemicals [33], while in the materials field they are utilized to create materials having special properties that include conductive materials, polymers, biomaterials, and nanomaterials [31,34].

Similar to hydroxypyridinecarboxylic acid, hydroxyaromatic carboxylic acids show the ability to form complexes to various other metal ions due to the presence of -OH and -COOH functional groups that readily form bonds with metals, especially transition metals, and their complexes have been investigated extensively because of properties including color caused by electromagnetic transitions in the molecule, higher biological activity compared to free ligands, and optical and magnetic properties. Therefore, their metal complexes have attracted the attention of researchers from numerous fields including pharmaceuticals, analytical chemistry, sensor materials, optical materials, catalysis [35,36].

Among the aromatic hydroxycarboxylic acids, salicylic acid and its derivatives are the most studied and well understood. Salicylates have been in use for approximately 4,000 years and are found in abundance in willow bark [37], which is probably where their name comes from the Latin word "salix" meaning willow. Salicylic acid was synthesized and commercially produced in the early 19th century. In 1897, its derivative, acetylsalicylic acid, was registered by Bayer under the trade name aspirin, which is the most commonly used non-steroidal anti-inflammatory medicine in the world nowadays [38]. Salicylic acid is an organic compound characterized by many biological effects and diverse applications. It is not only an important plant hormone involved in plant growth and development, but also widely used in medicine and pharmaceuticals [38]. In the field of medicine, salicylic acid and its derivatives are known for their analgesic, antipyretic, anti-inflammatory effects and especially for their ability to eliminate dead cells and soften the skin. Therefore, they are often used for the treatment of skin conditions that include acne, psoriasis, and dermatitis. In addition, salicylic acid provides antibacterial, antifungal action, helping to heal wounds [6].

In the pharmaceutical industry, salicylic acid appears to be the precursor for the production of aspirin, one of the world's most commonly used pain relievers. Aspirin not only relieves pain and reduces fever, but also has the ability to prevent blood clots, reducing the risk of cardiovascular disease. In addition, salicylic acid used in cosmetics act as a chemical exfoliant that helps open pores and improve skin texture [6,37].

1.1.2 Isomerism and tautomeric transformations of hydroxyaromatic acids

Tautomerism refers to the dynamic equilibrium among two or more structural forms that differ only in the position of hydrogen atoms and double bonds while preserving the carbon skeleton of the compound [39]. The earliest scientist to develop tautomerism rules was Emil Erlenmeyer in the 1880s [40]. There are four different types of tautomerism, including prototropy, ring-chain tautomerism, ring tautomerism, and valence tautomerism [41]. Tautomerization is capable of creating novel coordination sites for metal ions, therefore impacting the shape and stability of the generated complex. In enzyme catalysis, this process has the potential to create or change functional groups in the active site of enzymes, affecting their catalytic activity. During DNA replication, uncommon tautomeric forms of bases could lead to mispairing, causing genetic mutations in nature. During organic synthesis, tautomerism may affect the process of organic reactions, especially reactions involving carbonyl compounds [39,42].

Concerning tautomerization processes, the enol-keto process is the widespread and significant one. This tautomerization process is frequently found in carbonyl compounds (ketones or aldehydes), where a proton moves from the carbon atom beside the carbonyl group ( $\alpha$ -carbon) onto the oxygen atom of the carbonyl group, forming a C=C double bond and a hydroxyl group. Therefore, the phenomenon of enol-keto tautomerism is significant in the chemistry of heterocyclic compounds and a wide variety of groups of substances, playing an important role in numerous chemical and biological processes [13,43].

2-hydroxynicotinic acid undergoes Enol-keto tautomerism either in solution or in the solid state due to the unstable H atom of the OH group in position 2 being very close to the nitrogen atom of the pyridine. In structural terms, 2-hydroxynicotinic can be considered as an enol form. In the keto form, the hydrogen atom moves from the hydroxyl group to the nitrogen atom, the oxygen of the hydroxyl group becomes carbonyl oxygen. Consequently, 2-hydroxynicotinic acid exhibits various modes of coordination, including monodentate (via one oxygen or nitrogen atom) or bidentate via pyridyl nitrogen atoms and phenolic oxygen atoms, forming a four-membered chelate ring, and salicylate type O,O-chelating through carboxylate group and phenolic oxygen, forming a six-membered chelate ring [44,45]. The tautomerization process induces high flexibility in the formation of complexes with metal ions in 2hydroxynicotinic acid. Depending on the environmental conditions and the type of metal ion, 2-hydroxynicotinic acid can be present in the enol or keto form, or in both forms, forming various complex compounds. The tautomerization process increases the diversity of metal complexes that could be formed from 2-hydroxynicotinic acid, offering a multitude of potential applications [46]. For these reasons, 2hydroxynicotinic acid is considered to be one of the most interesting and investigated hydroxypyridine carboxylic acids.

2-Hydroxy-6-methylpyridin-3-carboxylic acid, alternatively known as 2hydroxy-6-methylnicotinic acid, likewise is a biologically active derivative of pyridinecarboxylic acid. It also undergoes isomerization in solution, similar to 2hydroxynicotinic acid, as illustrated in Figure 1, thereby promising the ability to form a variety of complexes with many metals [12].



**Figure 1** Enol-keto tautomerism of 2-Hydroxynicotinic acid and 2-hydroxy-6methylpyridine carboxylic acid molecules

#### **1.1.3** Crystal structure

Hydroxypyridinecarboxylic acids are polydentate ligands widely studied and used in coordination chemistry owing to the thermodynamic stability of their complexes compared to monodentate ligands. This comes with a variety of their ligand types: neutral, anionic or cationic depending on the pH of the media [47]. In addition, due to the presence of multiple functional groups, they can act as monodentate or bidentate ligands, providing the ability to form stable five- or sixmembered chelate rings with metal ions [43,48]. Therefore, the crystal structure of hydroxypyridine derivatives of carboxylic acids is an interesting subject for a large number of researchers and has been studied since a long time.

Figure 2 shows the molecular [49]. The molecule contains intramolecular hydrogen bonding between hydroxyl and carboxyl groups. The molecules in the crystal are stabilized by intermolecular hydrogen bonds involving nitrogen atoms of heterocycle and carboxyl group. Stabilization also occurs due to stacking (the C-C distance of adjacent parallel aromatic rings is 3,362 Å, indicating the overlap of their  $\pi$ -orbitals.



**Figure 2 a)** The molecular structure and hydrogen bonding of 3hydroxypicolinic acid are drawn at the 50% probability level; **b)** Molecular packing of 3-hydroxypicolinic acid [49]

2-Hydroxynicotinic acid exhibits a planar structure. The Fourier map results indicate the keto form of the molecule. The strong intramolecular hydrogen bonding [50], O---H–O has a distance of 2,504 Å, the hydrogen bond network in the crystal structure is formed by the intermolecular bond N–H---O with distance of 2,810 Å, creating a unidirectional chain of hydrogen bonds [51]. Similarly, the structure of 2-hydroxy-6-methylnicotinic acid demonstrates the keto form of the molecule either. An intramolecular connection is established from the proton of the carboxyl group to the oxygen atom of the nearby phenolate group with an O-H---O bond angle of 157° and a distance of 2,512 Å. Meanwhile, an intermolecular hydrogen bond is formed over the oxygen center of the carbonyl group linked to the proton of the N-H bond of the surrounding molecule, wherein the N-H---O bond angle is 171° and the distance reaches 2,847 Å [52].

Crystal structure studies of hydroxyaromatic carboxylic acids have significant importance in numerous fields that include pharmaceuticals, materials science, and crystal chemistry. Similarly to hydroxypyridine carboxylic acids, their crystals are formed on the basis of intramolecular hydrogen bonds and intermolecular hydrogen bonds which form dimers, chains or three-dimensional networks, together with weak van der Waals interactions between benzene rings which form stack-like structures [53].

The asymmetric unit of 3-methoxysalicylic acid monohydrate contains two organic molecules connected by two water molecules via O–H---O hydrogen bonds forming rings  $R_4^4(12)$  [54] (Figure 3a), the O---O distances between 3-methoxysalicylic acid molecule and water molecule are 2,5634 Å to 3,1930 Å, and the intramolecular O---O distances are 2,6142 Å and 2,5946 Å, respectively. These rings are further connected to each other by O–H---O hydrogen bonds forming rings  $R_6^6(18)$  [54], thus creating helical chains arranged around the b-axis (as shown in Figure 3b). These helices are assembled through  $\pi$ - $\pi$  stacking interactions among the aromatic rings of the chains, producing a supramolecular network (center-center distance 3,6432 Å), interplanar distance 3,44 Å [55].



**Figure 3 a)** Molecular structure of 3-methoxysalycilic acid monohydrate. Displaced ellipses are drawn at the 50% probability level. **b)** Crystal packing of 3methoxysalycilic acid monohydrate (hydrogen bonds are shown by dashed lines) [55]

3,5-diisopropylsalicylic acid crystallizes from three independent molecules in an asymmetric unit (Figure 4). Two of them form a dimer due to hydrogen bonding. The geometries of the three molecules are almost identical and are stabilized by intramolecular O–H---O bonding with distances: O2–H2---O12 2,6162 Å; O11– H11---O12 2,6374 Å and O2–H2---O12 2,6417 Å, respectively. Whereas the O–H-

--O intermolecular bonds have O---O distances in the range of 2,6420 Å to 2,6891 Å [56].



**Figure 4 a)** Independent molecule of 3,5-diisopropylsalicylic acid; **b)** Packing of molecules in the crystal [56]

Two polymorphic forms of 2,3-dihydroxybenzoic acid have been reported in the literature. One of them crystallizes in the form of two independent molecules in an asymmetric cell and creates a two-dimensional structure in the solid state. Two types of bonds exist between these planar molecules (Figure 5a). The carboxyl group of the other polymorphic form (Figure 5b) interacts with the hydroxyl groups of the surrounding molecules. In both shapes, the molecules have similar intramolecular hydrogen bonds, between nearby hydroxyl groups and the hydrogen bond established by the hydroxyl group and the carbonyl oxygen atom of the carboxyl group [53].



**Figure 5** Crystal structures of two polymorphic forms of 2,3-dihydroxybenzoic acid. Ellipsoids for non-H atoms correspond to the probability level of 50 % [57]

R. Mathammal et al. have grown crystals of 3,5-dinitrosalicylic acid monohydrate by the slow evaporation method at room temperature employing water as a solvent, the crystals obtained were analyzed by single crystal X-ray diffraction to identify their crystal structure. The molecular structure is shown in Figure 6a, the packing diagram of 3,5-dinitrosalicylic acid monohydrate is shown in Figure 6b. Single crystal data indicate that the grown crystal crystallizes in a monoclinic crystal system with non-centrosymmetric C2 space group. Single crystal data indicate that the grown crystal crystallizes in a monoclinic crystal system with noncentrosymmetric C2 space group. In the crystal structure, water molecules are the binding components owing to the fact that they assist in anchoring the 3,5-dinitrosalicylic acid molecules through intermolecular hydrogen bonds. Five types of hydrogen bonds are present in the asymmetric unit, including O(5)-H(5)--O(8), O(7)-H(7)--O(3), O(7)-H(7)--O(6), O(8)-H(8A)--O(6), and O(8)-H(8B)--O(2) [58].



**Figure 6** Structure of 3,5-dinitrosalicylic acid (a) and its packing in the crystal (b). Hydrogen bonds are shown by dashed lines

Regarding 2-hydroxy-1-naphthoic acid, there are numerous researches on the synthesis and structure of their complexes with metals for example: Zn<sup>2+</sup>, Mo<sup>4+</sup>, Ag<sup>+</sup>, Pd<sup>2+</sup> and Pt<sup>2+</sup> [59], and co-crystalline structures involving other organic compounds

as follows: caffeine [59], 1,2,4,5-tetracyanobenzene [60],... However, until now, there have been no published studies on the crystal structure of 2-hydroxy-1-naphthoic acid.

#### 1.1.4 Acid-base properties

Hydroxyaromatic acids are organic compounds where both the hydroxyl group (-OH) and the carboxylic acid group (-COOH) are attached to the aromatic hydrocarbon skeleton. The carboxylic acid group is the principal acidic functional group in these compounds. It readily gives up a proton  $(H^+)$  to form carboxylate ion. The carboxylic acid group is the principal acidic functional group in these compounds. It readily gives up a proton (H<sup>+</sup>) to form carboxylate ion. The phenolic hydroxyl group also is weakly acidic. Deprotonation of this group leads to the formation of phenoxide ion. The acidity of the phenolic group is typically lower than the acidity of the carboxyl group [61]. In acidic media, the compounds exist mainly in the protonated form, generally preferable to solubility in organic solvents. In basic media, their existence is in the form of deprotonated salts, that are better soluble in polar solvents. Meanwhile, hydroxypyridine carboxylic acids are a group of organic compounds that exhibit unique acid-base properties due to the interaction between the pyridine ring, the hydroxyl group and the carboxylic acid group. Similar to hydroxyaromatic carboxylic acids, they also contain acidic functional groups: carboxylic and hydroxyl, however, in particular, they exhibit basic properties due to the fact that the nitrogen atom in the pyridine ring has a lone pair of electrons, giving it a weak base. This can accept a proton to form a pyridinium ion [62].

The acid-base properties of these compounds depend on numerous factors including substituents, resonance, and conjugation effects. Specifically, the nature of the substituents: electron-withdrawing substituents (-NO<sub>2</sub>, -Cl, -Br) increase the acidity, while electron-donating substituents (-CH<sub>3</sub>, -OCH<sub>3</sub>) decrease the acidity of the compound. In addition, the position of the substituents also considerably affects their acid-base properties. The ability of these compounds giving or receiving

protons is important for their biological activity, especially their ability to interact with enzymes, receptors and DNA [63]. The Table 2 below provides the acidity constants of certain hydroxyaromatic carboxylic acids and hydroxypyridinecarboxylic acids that have been studied and published.

 Table 2 Acidity constants of some aromatic hydroxy carboxylic acids and hydroxypyridine carboxylic acids have been studied and published

No	Name of substances (Common name/IUPAC name)	Structure	рКа
1	2-hydroxynitcotinic acid (2-oxo-1H-pyridine-3-carboxylic acid)	OH OH OH OH	pKa (1) = 6,2 ± 0,02 pKa (2) = 9,65 ± 0,01 Kamal A. Idriss et al [64]
2	3-hydroxypicolinic acid (3-hydroxypyridine-2-carboxylic acid)	OH OH OH	pKa(1) = 1,14 pKa (2) = 5,19 pKa (3) = 12,01 Małgorzata Szabłowicz and Ewa Kita [62]
3	3,5-diisopropylsalicylic acid (2-hydroxy-3,5-di(propan-2-yl) benzoic acid)	ОН	pKa = 4,63 J.S. Preston [65]



# **1.1.5** Complex compounds of metals with hydroxyaromatic carboxylic acids and hydroxypyridine carboxylic acids

Complexes of hydroxyaromatic carboxylic acids, hydroxypyridinecarboxylic acids and metals represent a class of coordination compounds with diverse structures and great potential towards a wide range of applications. These compounds are composed by one or more metal ions linked together with one or more ligands, including hydroxyaromatic carboxyaromatic carboxylic acids or hydroxypyridine carboxylic acids. Hydroxyaromatic carboxylic acids and hydroxypyridinecarboxylic acids act as complexing agents by binding to metal ions via the carboxylate and hydroxyl groups of the hydroxyaromatic carboxylic acid and the carboxylate groups, hydroxyl groups or nitrogen atoms of the pyridine ring. Their properties and applications depend on the central metal ion and the nature of the ligand. A large number of metallocomplexes of hydroxyaromatic carboxylic acids and hydroxylic acids and hydroxypyridinecarboxylic acids have been synthesized, structurally characterized

and studied for applications in many areas. On the basis of the central group of metal ions, along with the differences in structure, characteristics, and field of application, they are divided into three groups namely as follows:

1) Transition metal complexes: Which are the earliest and most widely studied coordination compounds. Metals of this group namely iron, copper, nickel, cobalt and zinc easily form complexes together with aromatic hydroxycarboxycarboxylic acids and hydroxypyridinecarboxylic acids due to their ability to accept electron pairs from the ligands. Therefore, in addition to the biochemical properties of the ligands, these complexes also exhibit characteristic transition metal properties that include magnetic properties and the ability to catalyze selective oxidation reactions [68–70].

2) Lanthanide and actinide (rare earth elements) complexes: This group of metals has recently attracted much attention of scientists because of its characteristically large ionic radius and high coordination number. Consequently, complexes of this family of metals with hydroxyaromatic carboxycarboxylic acids and hydroxypyridine carboxylic acids frequently possess unique optical properties and are being studied for applications as luminescent materials and contrast agents in medical imaging [71,72].

3) *Alkali and alkaline earth metal complexes:* These metals, for example sodium, potassium, calcium and magnesium, form complexes with aromatic hydroxycarboxylic acids and hydroxypyridinecarboxylic acids through ionic-dipole interactions. These complexes show low cytotoxicity and facile synthesis methods, thus those complexes are commonly investigated for application in drug carriers and precursors for metal oxide nanoparticle synthesis [73].

Table 3 summarizes the published crystal structures of several of their metalcomplex compounds.

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 Table 3 Certain published crystal structures of metal complexes with aromatic

 hydroxycarboxylic acids and hydroxypyridine carboxylic acids

N o	Molecular formula	Crystal structure	
1	[Cu(L) <sub>2</sub> ] HL: 2- Hydroxynicotinic acid [14]		
2	[Mn(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] HL: 2- Hydroxynicotinic acid [45]		
3	[Cd(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] HL: 3- Hydroxypicolinic acid [74]		
4	[Mn(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] HL: 3- Hydroxypicolinic acid [75]	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	





# 1.2 Complex compounds of metals with organic ligands as precursors of nanosized metal oxides

Nanotechnology is the field of research, characterization, and utilization of microscopic structures and systems of extremely small size (typically less than 100 nm). Nanoparticles are the most basic building blocks in the fabrication of nanostructures and are much smaller than the world of everyday objects described

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by Newton's laws of motion, but larger than a simple atom or molecule governed by quantum mechanics. As a result, their properties are special compared to larger materials, due to quantum effects manifested at the nanoscale, such as mechanical, electrical, optical and magnetic properties that are significantly different from conventional materials [81]. For comparison, the diameter of an atom ranges from 0.1-0.6 nm, DNA chain are about 2 nm in diameter, most viruses are 20-500 nm in size, while a bacterial cell is about 1000 nm in size. Therefore, nanoscale materials are a promising area of research, with the potential to change many industries and improve human life [82]. Nobel Prize-winning American physicist Richard Feynman first described nanotechnology in 1959, and the terminology "nanotechnology" was used and defined by scientist Norio Taniguchi 15 years later. Up to now, many research projects have been carried out in this revolutionary field of research, especially after the 2000s, with significant financial and human resources, at the same time as commercial applications of nanomaterials emerged [82].

Nanotechnology is considered the most promising technology of the 21st century, and numerous studies show its potential for widespread application in many fields including: electronics, materials, biomedicine, agriculture and the environment. In the field of nanomaterials, metal oxide nanoparticles are one of the most studied and produced nanomaterials due to their unique properties. Metal oxides are a group of materials exhibiting a wide range of unique physical and chemical properties, including optoelectronic, magnetic, mechanical, optical, electrical, thermal and catalytic properties [83]. High biocompatibility, strong interaction on molecules and outstanding electro-optical properties are the distinct advantages of metal oxide nanoparticles. Because of these properties, metal oxide nanoparticles are expected to make breakthroughs in diverse fields, from materials technology to medicine and energy. In more than three decades since their appearance, plenty of oxide nanoparticles have been synthesized and studied, the most common of them include Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub> and ZnO [83].

# **1.2.1** Main methods of synthesis of nanosized metal oxides

There are numerous and diverse methods for synthesizing nanomaterials, each one having its own advantages and disadvantages. Therefore, depending on the purpose of use, when synthesizing nanomaterials, a suitable method is chosen to be applied to fulfill the technical requirements (particle size, homogeneity, etc.), economic requirements (product cost), and suitable for the available technical equipment conditions. Based on the size of the starting material compared to the size of the nanomaterial, the synthesis of nanomaterials is approached by two methods, is illustrated in Figure 7, including:

*A.* **Top-down approach:** Based on the method of creating nanomaterials by breaking down larger particles [84].

*B.* **Bottom-up approach:** On the contrary to the top-down approach, the principle of this approach is to create nanoscale materials from atoms or ions (smaller than the size of the nanomaterial) [84].



Figure 7 Two different approaches to nanoparticle synthesis

Methods for synthesizing metal oxide nanoparticles are classified into three main categories: chemical methods, physical methods, and biological methods [85].

According to these methods, the chemical method is the most widely used method, certain remarkable methods can be mentioned, listed below:

- Sol-gel method [86]: This is a popular and widely applied method due to the well controlled size, high purity and homogeneity of the obtained products, along with low reaction temperature. The synthesis procedure of this method is based on the hydrolysis of precursors (typically metal alkoxides) to the colloidal state (sol), followed by dehydration leading to the formation of gels. These gels are then dried to remove solvent, forming xerogels or aerogels, followed by calcination to remove organic components. Finally, metal oxide nanocrystals are obtained. This method, however, has the disadvantages of using toxic organic solvents and long reaction times.
- 2) Hydrothermal method [86]: The principle of this method is to dropwise add a precipitating agent (commonly NaOH or KOH) into an aqueous solution of metal precursors before transferring into a Teflon-lined stainless-steel autoclave. Heating the reaction mixture at high temperature and high pressure accelerates the reaction and promotes the formation of nanoparticles. By adjusting the reaction conditions as temperature, pressure and reaction time, the size, shape and crystalline phase of the resulting metal oxide nanoparticles can be controlled. This method is widely used to synthesize crystalline materials, having the advantages of good size control, purity, synthesis efficiency and simple process. This method, however, requires long reaction time, multiple process steps and chemical reagents.
- 3) Microwave assisted synthesis method [83]: This method has been developed over the last three decades, along with advances in microwave generator design, synthesis of metal oxide nanoparticles by microwave assisted synthesis is becoming increasingly attractive to researchers. Metal salt or metal alkoxide is dissolved in a suitable solvent, then the mixture is irradiated under microwave irradiation at selected power and

time, during this irradiation, metal oxide nanoparticles are formed. Since the heating process in the reaction system is carried out under the exposure to microwave radiation, the entire reaction system is heated simultaneously in a rapid time, increasing the reaction rate significantly. Advantages of this method include high speed and uniform heating, so the resulting products have homogeneity, good purity and narrow size distribution. In addition, the advantages of this method include fast synthesis time and eco-friendly. In the present scientific and technical conditions, this method can only be performed on a limited scale, and the temperature and pressure conditions are difficult to control.

Among the top-down methods for the synthesis of nanomaterials, thermal decomposition has become a very promising technology for the synthesis of metal oxide nanoparticles. Compared with traditional methods, this method has many outstanding advantages. First, the thermal decomposition process is frequently simpler, more controllable, and less expensive. Second, this method provides precise control over the size, shape and size distribution of nanoparticles, meeting the growing demand for nanomaterials with unique properties. Finally, thermal decomposition typically occurs under easier conditions that do not require extreme temperatures or high pressures, reducing production costs and improving environmental friendliness. In this field, the synthesis of metal oxide nanoparticles by solid-phase thermal decomposition of their complexes is one of the simplest and most cost-effective methods to obtain pure and nanosized transition metal oxides having relatively high specific surface area at low temperature. This method use complexes of metals and organic ligands, which have a low decomposition temperature, therefore without the need for high temperatures during calcination. There are many advantages of this method: there is no need for salts, surfactants and complicated equipment, high productivity, low energy consumption and simple reaction technology. In this regard, a large number of simple nanoparticles and metal oxide compounds have been prepared by solid-phase thermal decomposition of their corresponding complexes [83,87,88].

#### **1.2.2 Main classes of organic precursors**

The morphology of nanomaterials, in particular the shape, particle size and surface area, is especially important in specifying the physical and chemical properties of the material and potential uses. For the synthesis of metal oxide nanoparticles by thermal decomposition, the morphology of the material is affected by various factors including precursor type, decomposition conditions, and postdecomposition treatment. Specifically, precursor selection is the beginning step in the thermal decomposition synthesis process and plays a significant role in the final morphological characteristics of the resulting oxide nanoparticles. They are classified according to the origin of the components: inorganic and organic precursors. Inorganic precursors are typically salts and hydroxides of metals, which are widespread and inexpensive substances used for the synthesis of nanomaterials from the earliest times. Nevertheless, synthesis of metal oxide nanoparticles from inorganic precursors has numerous limitations: the morphology and particle size are difficult to control; inorganic precursors require extremely high decomposition temperatures, consume much energy and are unsuitable for temperature-sensitive materials; nanomaterials are lacking plenty of functional groups on the surface, restricting their application. Owing to these reasons, scientists are currently interested in synthesizing metal oxide nanoparticles from organic precursors. The group of organic precursors that scientists are interested in investigating includes: metal-organic frameworks (MOFs), organometallic compounds, polymeric precursors, etc., which are useful to better control the morphology, size and surface properties of the material [89–92]. Comparisons between organic precursor forms are summarized in Table 4.

Features	Metal–organic	Organometallic or	Polymeric precursors
	frameworks (MOFs)	metal-organic complex	
		compound	
Structure	Crystalline porous network, expanded, consisting of metal ions or clusters connected via organic linkers [93].	Discrete molecules or complexes which are composed of a metal center bonded to one or more organic ligands [94].	Amorphous or semi- crystalline polymers consist of a polymer chain with functional groups able to interact with metal ions [95].
Metal-ligand bonds	Strong coordination bonds between metal ion and organic linker (primarily coordinate covalent bonds) [93].	Mainly covalent bonding of metal-carbon or metal ions and electron-rich donor atoms of organic ligands [94].	Weaker interaction between metal ion and polymer chain [96].
Advantages	Quality control of the size, shape and porosity of the produced metal oxide nanoparticles. High surface area of nanoparticles, homogeneous dispersion of particles. Opportunity to design and synthesize a variety of metal oxides with accurate composition ratio. [97]	Product size and shape can be controlled. The synthesis process is not complicated [90]. Neither large quantities of chemicals nor expensive equipment are required. Available to be produced on a large scale [98].	Excellent control of material morphology: nanoparticles, nanofibers, nanorods. Material has numerous special properties: porous structure, homogeneous size, multiple functional groups on the surface. Several biopolymeric precursors available from renewable resources make the synthesis process more

# Table 4 Characteristics of several common organic precursors

			environmentally
			friendly [99].
	Synthesis process is	Not appropriate for the	Synthesis of metal-
	complicated and time	synthesis of other types	polymer compounds
Discharge	consuming.	of nanostructures like	can be complicated and
Disadvantages	High cost, challenging to	nanofiber, nanotubes or	time-consuming.
	implement in large scale	nanorods [101].	Large scale production
	production [100].		is challenging [95].

## **1.3** Conclusions from the literature review

Derivatives of hydroxypyridine carboxylic acids and hydroxyaromatic carboxylic acids and their metal complexes have attracted considerable research attention in recent years due to their potential in many fields. The application of their complexes and metals as precursors for the synthesis of oxide nanoparticles offers numerous advantages, in particular, a simple synthesis process that does not require high temperature and pressure compared to traditional methods. Meanwhile, by changing the reaction conditions, the size and shape of nanoparticles can be controlled, adjusting their physical and chemical properties. The hydroxyl and carboxyl functional groups in these compounds can form chemical bonds on the surface of nanoparticles, improving their stability and surface properties. However, there are few studies and publications on this specialized area of research concerning metal complexes with hydroxypyridine carboxylic acid derivatives and hydroxyaromatic carboxylic acids.

The synthesis of transition metal oxide nanoparticles based on complexes of their metals and derivatives of hydroxypyridine carboxylic acids and hydroxyaromatic carboxylic acids is a promising area of research. Possessing advantages including stability, controllability and diverse applications, these nanoparticles promise to play an important role in many aspects of life. However,
further studies on their formation mechanism, structure, properties and applications are necessary to realize the full potential of these materials.

### 2 EXPERIMENTAL PART

#### 2.1 Initial substances

The initial substances for the synthesis of complex compounds were inorganic salts of 3d-metals: FeCl<sub>3</sub>.6H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, ZnCl<sub>2</sub>.6H<sub>2</sub>O; titanium (IV) tetrabutoxide Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, besides organic ligands - aromatic and heteroaromatic hydroxy acids (Figure 8) and 9,10-phenanthrene chloride monohydrate.



Figure 8. Organic ligands used in this study

All compounds used in this work are commercially available, have a purity of 99% and were used without further purification.

#### 2.2 Research Methods

*Elemental C, H, N analysis* was performed on a Varian 735-OES analyzer at the shared equipment center "Instrumental Chemical Analysis and Complex Investigation of Substances and Materials" at the Russian Technological University MIREA.

*Metal analysis* was performed on AAnalyst atomic absorption spectrometer model 200 in shared equipment center "Instrumental chemical analysis and complex research of substances and materials" at the Russian Technological University MIREA.

*Electronic absorption spectra* of ethanol solutions of organic molecules in different pH intervals and spectra of their titration with aqueous solutions of metal salts were recorded on a Cary-50 spectrophotometer at  $22 \pm 1^{\circ}$ C and zero ionic strength in the wavelength range 200 - 450 nm in 1 cm wide cuvettes. The concentrations of the solutions were selected for each titration individually. Ionization constants of organic molecules and constants of metal complexes formation in solutions were determined by the saturation method using the following calculation formulas:

$$pK = -lg K = pH \pm lg \frac{Aion - A}{A - Amolec}$$
(1)  
$$\beta = \frac{(A / A_{max}) \times c_{M}}{(c_{M} - (A / A_{max}) \times c_{M}) \times (c_{L} - (A / A_{max}) \times c_{M})^{n}}$$
(2)

Statistical processing of the obtained results was performed for 95% confidence level.

*The pH measurements* at potentiometric titration of ligand solutions  $(10^{-2} \text{ mol/L})$  and equimolar mixtures of metal-ligand mixtures with NaOH solution  $(10^{-1} \text{ mol/L})$  were carried out on a universal ionometer Expert-001 at room temperature in the pH range from 2 to 13.5. The accuracy of the instrument readings was controlled using standard buffer solutions.

*IR absorption spectra* of organic molecules, complex compounds and oxide phases were recorded on a Perkin Elmer FT-IR 1650 spectrophotometer in KBr pellets in the frequency range 4000-400 cm<sup>-1</sup>.

*X-ray diffraction analysis* of organic molecules and complex compounds was performed on a Bruker XSCANS automatic diffractometer at the Federal Research Center for Problems of Chemical Physics and Medical Chemistry of the Russian Academy of Sciences (Chernogolovka city). The structures were determined by the direct method, the positions of non-hydrogen atoms were refined by the least-squares method in the anisotropic approximation. Hydrogen atoms were placed in the calculated positions and refined using the rider model with fixed isotropic parameters, Uiso(H) = 1.2 Ueq(C). Calculations were performed using the SHELXTL computer programs. The main crystallographic parameters of the refinement of crystal structures are given in the Appendix (Tables 5).

**Table 5** Structure decoding parameters of  $Cu(L^2)_2$ ,  $Zn(L^2)_2 \cdot 2H_2O$ , $[Cu(Phen)_2Cl]L^8$ ,  $[Zn(Phen)_2Cl]L^8$ ,  $L^7$ ,  $L^8 \cdot H_2O$ ,  $L^8 \cdot Phen$ 

$Cu(L^2)_2$				
T (K)	100(2)			
$\lambda$ (Å)	0,71073			
Crystal system	monoclinic			
Space group	P 21/c			
Crystal cell parameters				
<i>a</i> , Á	6,31760(18)			
<i>b</i> , Å	11,3753(4)			
<i>c</i> , Å	7,9723(2)			
α, (°)	90			
β, (°)	92,979(3)			
γ, (°)	90			
$V, Å^3$	572,15(3)			
Z	2			
$D_{calc} (g \ cm^{-3})$	1,972			
$\mu, mm^{-1}$	1,943			
F (000)	342			

θ range (°)	3,123-29,344
Index ranges	$-8 \le h \le 7;$
	$-14 \le k \le 6;$
	-10≤ <i>l</i> ≤ 10
Reflections collected	2564
Independent reflections	1322
Criterion for observed reflections $I > 2\sigma(I)$	1322
GOOF	1,053
$R_1 \left[ I > 2\sigma(I) \right]$	0,0307
wR <sub>2</sub>	0,0769
$Zn(L^2)_2 \cdot 2H_2O$	
T (K)	100(2)
$\lambda$ (Å)	0,71073
Crystal system	monoclinic
Space group	P 21/n
Crystal cell parameters	
<i>a</i> , Å	5,0626(4)
<i>b</i> , Å	22,6761(13)
<i>c</i> , Å	6,6184(5)
α, (°)	90
β, (°)	111,743(9)
γ, (°)	90
$V, Å^3$	705,74(9)
Ζ	2
$D_{calc} (g \ cm^{-3})$	1,777
$\mu$ , mm <sup>-1</sup>	1,787
F (000)	384
θ range (°)	3,434-31,950
Index ranges	$-7 \le h \le 6;$
	$-33 \le k \le 33;$
	$-9 \le l \le 9$
Reflections collected	6756
Independent reflections	2168
Criterion for observed reflections $I > 2\sigma(I)$	2168
GOOF	1,122

$R_1 \left[ I > 2\sigma(I) \right]$	0,0407					
wR <sub>2</sub>	0,0822					
[Cu(Phen) <sub>2</sub> Cl]L <sup>8</sup>						
T (K)	150(2)					
$\lambda$ (Å)	0,71073					
Crystal system	triclinic					
Space group	P-1					
Crystal cell parameters						
<i>a</i> , Á	7,5150(3)					
b, Á	11,5529(7)					
<i>c</i> , Å	15,8796(9)					
$\alpha, (^{\circ})$	90,042(5)					
β, (°)	90,869(4)					
γ, (°)	102,331(4)					
$V, Å^3$	1346,70(13)					
Ζ	2					
$D_{calc} (g \ cm^{-3})$	1,693					
$\mu$ , mm <sup>-1</sup>	0,976					
F (000)	698					
θ range (°)	3,6020-29,0050					
Index ranges	-10≤ <i>h</i> ≤10;					
	$-15 \le k \le 15;$					
	-21≤ <i>l</i> ≤21					
Reflections collected	6198					
Independent reflections	5183					
Criterion for observed reflections $I > 2\sigma(I)$	5183					
GOOF	1,110					
$R_1 \left[ I > 2\sigma(I) \right]$	0,1249					
$wR_2$	0,1123					
[Zn(Phen) <sub>2</sub> Cl]L <sup>8</sup>						
T (K)	150(2)					
$\lambda$ (Å)	0,71073					
Crystal system	triclinic					
Space group	P-1					
Crystal cell parameters						

<i>a</i> , Å	10,5871(4)
b, Å	11,5934(4)
<i>c</i> , Å	12,1825(4)
$\alpha, (^{\circ})$	78,365(3)
β, (°)	78,276(3)
γ, (°)	74,875(3)
$V, Å^3$	1395,79(9)
Ζ	2
$D_{calc} (g \ cm^{-3})$	1,638
$\mu$ , mm <sup>-1</sup>	1,039
F (000)	700
θ range (°)	3,287-32,644
Index ranges	-16≤ <i>h</i> ≤ 14;
	-17≤ <i>k</i> ≤16;
	-14≤ <i>l</i> ≤ 18
Reflections collected	9775
Independent reflections	7045
Criterion for observed reflections $I > 2\sigma(I)$	7045
GOOF	0,0856
$R_1 \left[ I > 2\sigma(I) \right]$	0,0537
$\mathbf{L}^7$	
T (K)	100(2)
$\lambda$ (Å)	0,71073
Crystal system	triclinic
Space group	P-1
Crystal cell parameters	
<i>a</i> , Å	8,2765(3)
b, Å	9,3810(3)
<i>c</i> , Å	10,0542(3)
$\alpha, (^{\circ})$	67,1703(9)
β, (°)	69,0140(10)
γ, (°)	65,9465(9)
$V, \text{\AA}^3$	638,18(4)
Ζ	4
$D_{calc} (g \ cm^{-3})$	1,604

$\mu$ , mm <sup>-1</sup>	0,134			
F (000)	320			
θ range (°)	2,48-32,52			
Index ranges	$-12 \le h \le 12;$			
	$-14 \le k \le 14;$			
	-15≤ <i>l</i> ≤15			
Reflections collected	4654			
Independent reflections	3471			
Criterion for observed reflections $I > 2\sigma(I)$	3471			
GOOF	1,016			
$R_1 \left[ I > 2\sigma(I) \right]$	0,0688			
wR <sub>2</sub>	0,1190			
L <sup>8</sup> ·H <sub>2</sub> O				
T (K)	100,01(10)			
λ (Å)	0,71073			
Crystal system	monoclinic			
Space group	C 2/c			
Crystal cell parameters				
<i>a</i> , Å	25,3545(13)			
<i>b</i> , Å	6,3324(3)			
<i>c</i> , Å	12,4181(6)			
α, (°)	90			
β, (°)	111,7900(10)			
γ, (°)	90			
$V, \text{\AA}^3$	1851,33(16)			
Ζ	8			
$D_{calc} (g \ cm^{-3})$	1,766			
$\mu$ , mm <sup>-1</sup>	0,166			
F (000)	1008			
θ range (°)	3,31-32,40			
Index ranges	-38≤ <i>h</i> ≤ 38;			
	$-9 \le k \le 9;$			
	-18≤ <i>l</i> ≤18			
Reflections collected	3397			
Independent reflections	2524			

Criterion for observed reflections $I > 2\sigma(I)$	2524			
GOOF	1,052			
$R_1 [I > 2\sigma(I)]$	0,0655			
wR <sub>2</sub>	0,1036			
L <sup>8</sup> ·Phen				
Т(К)	200(2)			
λ (Å)	0,71073			
Crystal system	monoclinic			
Space group	P 21			
Crystal cell parameters				
<i>a</i> , Å	7,8497(9)			
b, Å	7,1980(8)			
<i>c</i> , Å	14,97889(18)			
$\alpha, (^{\circ})$	90			
β, (°)	97,542(11)			
γ, (°)	90			
V, Å <sup>3</sup>	839,02(14)			
Z	2			
$D_{calc} (g \ cm^{-3})$	1,616			
$\mu$ , mm <sup>-1</sup>	0,127			
F (000)	420			
θ range (°)	2,8-26,2			
Index ranges	$-10 \le h \le 8;$			
	$-9 \le k \le 9;$			
	-18≤ <i>l</i> ≤ 20			
Reflections collected	2571			
Independent reflections	2094			
Criterion for observed reflections $I > 2\sigma(I)$	2094			
GOOF	1,038			
$R_1 \left[ I > 2\sigma(I) \right]$	0,0662			
wR <sub>2</sub>	0,1088			

*X-ray phase analysis* of oxide phases obtained after thermal decomposition of complex precursors was carried out on X-ray diffractometer Dron-7. The

measurements were carried out in the scientific laboratory of the Scientific Laboratory of the Center for Chemical Engineering of PFUR.

Thermal decomposition processes of complex precursors were studied on a NETZSCH STA 449F5 derivatograph in the temperature range of 20-1000°C in a platinum crucible in argon atmosphere with a sample heating rate of 10 °C /min. at the Department of Physical and Colloidal Chemistry of PFUR.

*Microphotographs and EDX analysis* of the composition of oxide phases were obtained using a TESCAN BRNO-Mira 3 LMU electron microscope at Tver State University.

*Adsorption-desorption isotherms* and surface area characteristics were obtained on a Brunauer-Emmett-Teller instrument (Micromeritics Tristar II 3020) at the Joint Russian-Vietnamese Tropical Scientific and Technological Research Center (Vietnam).

*The magnetic properties* were measured at room temperature using a VSM magnetometer at the Joint Russian-Vietnamese Tropical Scientific and Technological Research Center (Vietnam).

Computer prognostics of the potential biological activity of organic ligands and complex compounds were performed using freely available programs: SwissADME (<u>https://www.swissadme.ch/;</u> AdmetSar (<u>https://lmmd.ecust.edu.cn/admetsar2;</u> ADMETlab 2.; Toxtree v2.5.1 (<u>https://toxtree.sourceforge.net/</u>); Prediction of Biological Activity Spectra (PASS); PharmMapper and SwissTargetPrediction.

# 2.3 Synthesis methods and characterization of metal complex compounds containing aromatic and heteroaromatic hydroxy acids

Synthesis of complex compounds was carried out according to the following methods.

1. Aqueous solution containing 0.5 mmol of the corresponding inorganic metal salt or  $TiO(C_4H_9)_4$  was slowly added to 10 mL of ethanolic solution containing 1 mmol of heteroaromatic hydroxy acid (L<sup>1</sup> to L<sup>3</sup>). The resulting solutions were

heated with vigorous stirring on a water bath (60°C) for 1 h and kept at room temperature till crystallization started. The precipitates were filtrated, washed using a small amount of cold ethanol and dried at 100°C to constant weight. The yield was 70-80%.

2. Aqueous solution containing 0.5 mmol of the corresponding inorganic metal salt or  $TiO(C_4H_9)_4$  was slowly added to 10 mL of ethanolic solution containing 1 mmol of aromatic hydroxy acid (L<sup>4</sup> - L<sup>8</sup>). The obtained solutions were heated with vigorous stirring on a water bath (60°C) for 1 hour, with the addition of dilute aqueous sodium hydroxide solution the pH of the solutions was adjusted to 7 (control by universal indicator) and kept at room temperature until crystallization began. The precipitates were filtrated, washed with a small amount of cold ethanol and dried at 100°C to constant weight. The yield is 50-65%.

3. An ethanol solution containing 0.5 mmol of 1,10-phenanthroline chloride monohydrate (0.1173 g) was neutralized by aqueous NaOH solution (molar ratio 1:1). To the obtained solution was added 5 mL of an ethanolic solution containing 0.5 mmol of the corresponding hydroxyaromatic acid ( $L^7$  or  $L^8$ ). The resulting solution was slowly added to 5 mL of an aqueous solution containing 0.5 mmol of the corresponding solution containing 0.5 mmol of the corresponding to 5 mL of an aqueous solution containing 0.5 mmol of the corresponding inorganic salt (CuCl<sub>2</sub>, ZnCl<sub>2</sub> or FeCl<sub>3</sub>). The resulting solution was heated on a water bath to 60°C, stirred vigorously at this temperature for 1 h and kept at room temperature until the beginning of crystallization. The precipitate was filtrated, purified using a small amount of cold ethanol and dried at 100°C to constant weight. The yield is 80-85%.

Chemical analysis results: experiment/theory, %.

Cu(L<sup>1</sup>)<sub>2</sub>\* (I), M 339,75; C 41,85/42,42; N 8,04/8,25; H 2,69/2,37; Cu 19,13/18,70;

Co(L<sup>1</sup>)<sub>2</sub>·2H<sub>2</sub>O\* (**II**), M 371,17; C 39,15/38,83; N 7,94/7,55; H 3,48/3,26; Co 15,49/15,88;

Zn(L<sup>1</sup>)<sub>2</sub>·2H<sub>2</sub>O\* (III), M 363,61: Zn 18,08/18,23; C 40,28/40,09; N 3,05/3,46; H 4,33/4,12;

TiO(L<sup>1</sup>)<sub>2</sub>\*\* (**IV**), M 340,08; C 42,18/ 42,38; N 8,65/8,24; H 2,00/2,37; Ti 14,54/14,08;

Ni(L<sup>2</sup>)<sub>2</sub>\* (V), M 334,90; C 43,52/43,04; N 8,43/8,36; H 2,80/2,41; Ni 17,87/17,52;

Cu(L<sup>2</sup>)<sub>2</sub> \*\*\* (VI), M 339,75; C 42,10/42,42; N 8,53/8,25; H 2,77/2,37; Cu 18,92/18,70;

Zn(L<sup>2</sup>)<sub>2</sub>·2H<sub>2</sub>O \*\*\* (VII), M 363,61: Zn 17,98/18,23; C 39,64/40,09; N 3,85/3,46; H 3,33/4,12;

TiO(L<sup>2</sup>)<sub>2</sub> \*\* (VIII), M 340,08; C 42,27/42,38; N 8,35/8,24; H 2,64/2,37; Ti 14,38/14,08;

Cu(L<sup>3</sup>)<sub>2</sub>·2H<sub>2</sub>O \*\* (IX), M 339,75; C 42,10/42,42; N 8,53/8,25; H 2,77/2,37; Cu 18,92/18,70;

Ni(L<sup>3</sup>)<sub>2</sub>·2H<sub>2</sub>O \*\* (**X**), M 334,90; C 43,52/43,04; N 8,43/8,36; H 2,80/2,41; Ni 17,87/17,52;

Fe(L<sup>3</sup>)<sub>2</sub>Cl·6H<sub>2</sub>O \*\* (**XI**), M 339,75; C 42,10/42,42; N 8,53/8,25; H 2,77/2,37; Cu 18,92/18,70;

Ni(L<sup>4</sup>)<sub>2</sub> \* (**XII**), M 392,97; C 49,21/48,90; H 4,02/3,59; Ni 15,00/14,93;

Cu(L<sup>4</sup>)<sub>2</sub> \*\* (**XIII**), M 397,83; C 48,54/48,31; H 4,24/3,55; Cu 16,11/15,97; Zn(L<sup>4</sup>)<sub>2</sub> \*\* (**XIV**), M 399,66; C 48,28/48,08; H 4,15/3,53; Zn 15,81/16,36; TiO(L<sup>4</sup>)<sub>2</sub> \*\* (**XV**), M 398,16; C 48,53/48,27; H 3,98/3,54; Ti 11,78/12,03; Ni(L<sup>5</sup>)<sub>2</sub> \*\* (**XVI**), M 501,24; C 62,46/62,30; H 7,51/6,84; Ni 12,05/11,71; Cu(L<sup>5</sup>)<sub>2</sub> \* (**XVII**), M 506,10; C 61,38/61,70; H 7,11/6,77; Cu 12,95/12,56; Ni(L<sup>6</sup>)<sub>2</sub> \*\* (**XVIII**), M 433,04; C 61,88/61,02; H 3,78/3,26; Ni 13,47/13,55; TiO(L<sup>6</sup>)<sub>2</sub> \*\* (**XIX**), M 438,23; C 59,76/60,30; H 3,85/3,22; Ti 11,28/10,93; Cu(L<sup>7</sup>)<sub>2</sub> \* (**XXI**), M 369,77; C 45,82/45,47; H 3,01/2,73; Cu 17,87/17,19; Ni(L<sup>7</sup>)<sub>2</sub> \*\* (**XXII**), M 364,92; C 46,23/ 46,08; H 3,03/2,76; Ni 15,85/16,08; Co(L<sup>7</sup>)<sub>2</sub> \*\* (**XXII**), M 352,09; C 47,61/47,76; H 2,13/2,29; Ti 14,04/13,60; Cu(Phen)<sub>2</sub>(L<sup>7</sup>)<sub>2</sub> \*\* (**XXIV**), M 730,19; C 62,38/62,51; N 7,43/7,67; H 4,80/3,59; Cu 8,87/8,70;

Cu(L<sup>8</sup>)<sub>2</sub> \* (**XXV**), M 517,77; C 32,06/32,48; N 10,88/10,82; H 1,05/1,17; Cu 12,99/12,27;

Ni(L<sup>8</sup>)<sub>2</sub> \* (**XXVI**), M 512,91; C 32,45/32,78; N 10,98/10,92; H 1,03/1,18; Ni 11,83/11,44;

Zn(L<sup>8</sup>)<sub>2</sub>·2H<sub>2</sub>O **\*\*** (**XXVII**), M 555,63; C 30,54/30,26; N 9,87/10,08; H 2,04/1/81; Zn 11,43/11,77;

TiO(L<sup>8</sup>)<sub>2</sub> \*\* (**XXVIII**), M 518,10; C 33,46/32,46; N 10,96/10,81; H 1,15/1,17; Ti 9,51/9,24;

 $[Cu(Phen)_2Cl]L^8 *** (XXIX);$ 

[Zn(Phen)<sub>2</sub>Cl]L<sup>8</sup> \*\*\* (XXX);

[Fe(Phen)<sub>2</sub>Cl<sub>2</sub>]L<sup>8</sup> \*\*\* (**XXXI**), M 714,28; C 52,16/52,13; N 11,25/11,77; H 2,76/2,68; Fe 8,34/7,82.

\* synthesized by modified method

\*\* synthesized for the first time

\*\*\* compounds were isolated as single crystals, the composition was determined by single-crystal X-ray Diffraction.

#### **3 RESULTS AND DISCUSSION**

## 3.1 Study of complexation processes of aromatic and heteroaromatic hydroxy acids with metal cations

The literature data analysis allowed us to conclude that metal complexes of derivatives of hydroxypyridinecarboxylic acids and hydroxyaromatic carboxylic acids have a number of advantages in the preparation of nanosized metal oxide precursors. These organic ligands are commercially available, their thermal decomposition is performed at sufficiently low temperatures and leads to the release of a large amount of gaseous products per 1 mol of complex compound. The presence in molecules of several coordination centers in neighboring positions (carboxyl and hydroxyl group, nitrogen atom in pyridine cycle) leads to the fact that these compounds are capable of complexation with metals of different nature and form metal chelate compounds of considerable stability. The drawback is a rather high solubility of organic molecules and their metal complexes, which makes it difficult to isolate the complexes in the crystalline state. In this regard, it is important to determine the conditions for the existence of complex compounds in solution, investigate their composition and stability, and optimize methods for the isolation of these compounds from solution.

Optimization of metal complexes isolation processes involves a detailed study of the interaction of organic molecules together with metal cations in solution under synthetic conditions. However, despite the large number of publications on the isolation and study of the structure, properties and applications of aromatic and heteroaromatic hydroxycarboxycarboxylic acid coordination compounds, available data on the composition and stability of metal complexes with these ligands in solution remains very limited. In this respect, the first stage of our research included the study of complexation processes in solution, determination of the composition of compounds, calculation of their formation constants, determination of the pH range of stability of complexes in solution, and determination of the dependence of complexation processes on some physical and physicochemical characteristics of ligands and the complexing metal. Optimization of metal complexes isolation processes involved a detailed study of the interaction of organic molecules with metal cations in solution under synthetic conditions. Eight organic ligands - derivatives of hydroxypyridinecarboxylic acids and hydroxyaromatic carboxylic acids (Figure 8) and a number of 3d-metal cations were selected as objects of study.

#### **3.1.1** Study of complexation processes by spectrophotometric method.

To study the processes of ligand ionization and complexation in solutions, spectrophotometric titration of ethanol solutions of hydroxy-substituted aromatic and pyridine carboxylic acids with NaOH, HCl and inorganic metal salts was carried out. Due to the fact that in aqueous solutions titanium (IV) compounds undergo hydrolysis with the formation of oxocations TiO<sup>2+</sup>. Therefore, it can be said that this work studies the interaction of hydroxyaromatic acid with two- and three-charged metal cations.

The electronic absorption spectra of ethanol solutions of pyridine hydroxyaromatic acids L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup> are characterized by three main absorption bands in the region of 326 (lg $\epsilon_1$  3. 89); 234 (lg $\epsilon_2$  3.83); 204 (lg $\epsilon_3$  4.01) nm for L<sup>1</sup>; 330 (lg $\epsilon_1$  4.03); 236 (lg $\epsilon_2$  3.86); 203 (lg $\epsilon_3$  4.08) nm for L<sup>2</sup> and 304 (lg $\epsilon_1$  3.83); 227 (shoulder); 205 (lg $\epsilon_3$  4.12) nm for L<sup>3</sup>, respectively.



Figure 9 Changes in the electronic absorption spectra of ethanol solutions  $L^1$  (1)  $L^2$  (2) and  $L^3$  (3) by gradual addition of aqueous NaOH solution

During titration of ethanol solutions  $L^1-L^3$  with NaOH solution, there is a hypsochromic shift of the main absorption bands ( $\Delta\lambda = 34$ , 35 and 9 nm for  $L^1$ ,  $L^2$  and  $L^3$ , respectively) and a significant decrease in their intensity (Figure 9).

Addition of HCl solution to 50% water-ethanol solutions of  $L^1-L^3$  up to pH = 2 does not lead to changes in their electronic absorption spectra. This can probably be explained by the fact that organic molecules exist in the solutions in the zwitterionic form, in which one of the mobile hydrogen atoms is localized on the pyridine nitrogen atom.

The electronic absorption spectra of ethanol solutions of hydroxyaromatic acids of the carbocyclic series L<sup>4</sup>, L<sup>5</sup> and L<sup>6</sup> are characterized by principal absorption bands in the regions of 315 and 245 nm (lg $\epsilon_1$  3,64; lg $\epsilon_2$  3,81) for L<sup>4</sup>; 317 and 244 nm (lg $\epsilon_1$  3,65, lg $\epsilon_2$  3,82) for L<sup>5</sup>, 337; 303; 291(shoulder) nm (lg $\epsilon_1$  3,57; lg $\epsilon_2$  3,52) for L<sup>6</sup>, respectively. When ethanol solutions of L<sup>4</sup> and L<sup>5</sup> are titrated with NaOH solution, there is a hypsochromic shift of the main absorption bands at 8 and 10 nm with a minor decrease in their intensity. Deprotonation at spectrophotometric titration of hydroxynaphthoic acid L<sup>6</sup> by sodium hydroxide solution is characterized by a bathochromic shift of the long-wavelength band L<sup>6</sup> 336 nm to the region 342 nm and an increase in its intensity, as well as by a hypsochromic shift of the characteristic band 303 nm to the region 298 nm and of the shoulder 291 nm to the region 286 nm, in addition to the formation of the shoulder in the region 276 nm (Figure 10). The calculated acid type dissociation constants are pKa (L<sup>4</sup>) 5,42 ± 0,06; pKa (L<sup>5</sup>) 5,71 ± 0,31; pKa (L<sup>6</sup>) 6,06 ± 0,25.



Figure 10 Changes in the electronic absorption spectra of ethanol solutions  $L^4$  (1)  $L^5$  (2) and  $L^6$  (3) upon gradual addition of aqueous NaOH solution

The character of the change in the electronic absorption spectra of ethanol solutions of  $L^{1}-L^{8}$  upon gradual addition of metal salts (Figure 11) corresponds to the change in their spectra upon deprotonation, which is consistent with the fact that the process of complexation is accompanied by ionization of ligands. It should be noted that the shift of long-wavelength absorption bands in the case of pyridine hydroxycarboxylic acid derivatives  $L^{1}-L^{3}$  (7-26 nm depending on the nature of the metal and organic molecule) is larger than in the case of their carbocyclic analogs  $L^{4}-L^{8}$  (2-7 nm).





**Figure 11** Changes in the electronic absorption spectra of  $L^2$  (1) and  $L^5$  (2) upon gradual addition of CuCl<sub>2</sub> (a), CoCl<sub>2</sub> (b), NiCl<sub>2</sub> (c), Zn(NO<sub>3</sub>)<sub>2</sub> (d) and Ti(BuO)<sub>4</sub> (e) solutions

Based on the results of spectrophotometric titration, saturation curves were plotted and the compositions of complexes in solutions ( $ML_n$ ) and their formation constants ( $lg_\beta$ ) were calculated. The results of calculations are summarized in Table 6.

M <sup>n+</sup>	n (ML <sub>n</sub> )	lgβ	M <sup>n+</sup>	n (ML <sub>n</sub> )	lgβ
		L	1		
Cu <sup>2+</sup>	2	$10,\!74\pm0,\!12$	Ni <sup>2+</sup>	1	$6,\!46 \pm 0,\!15$
Co <sup>2+</sup>	2	9,71 ± 0,21	Fe <sup>3+</sup>	1	$7,21 \pm 0,52$
Zn <sup>2+</sup>	2	10,59 ± 0,03			
		L	2		
Cu <sup>2+</sup>	2	$14,\!29\pm0,\!12$	Ni <sup>2+</sup>	2	19,16 ± 0,41
Co <sup>2+</sup>	2	$14,59 \pm 0,22$	Fe <sup>3+</sup>	1,5	$9,28 \pm 0,14$
Zn <sup>2+</sup>	2	$13,61 \pm 0,05$			

Table 6 Compositions and formation constants of metal complex compounds with  $L^1$ - $L^8$ 

$M^{n^+}$	n (ML <sub>n</sub> )	lgβ	M <sup>n+</sup>	n (ML <sub>n</sub> )	lgβ			
$L^3$								
Cu <sup>2+</sup>	2	8,45 ± 0,11	Ni <sup>2+</sup>	2	$17,57 \pm 0,95$			
Co <sup>2+</sup>	2	$8,71\pm0,09$	Fe <sup>3+</sup>	1,5	$9{,}79\pm0{,}07$			
Zn <sup>2+</sup>	2	13,61 ± 0,13						
	·	l	L <sup>4</sup>					
Cu <sup>2+</sup>	2	$15,03 \pm 0,03$	Ni <sup>2+</sup>	1	$10,\!61 \pm 0,\!09$			
Co <sup>2+</sup>	1	$7,30 \pm 0,24$						
$Zn^{2+}$	2	$18,73 \pm 0,09$						
		]	L <sup>5</sup>					
$Cu^{2+}$	2	$14{,}28\pm0{,}06$	Ni <sup>2+</sup>	2	$8,\!76\pm0,\!05$			
Co <sup>2+</sup>	1	$6,34 \pm 0,12$	6,34 ± 0,12					
Zn <sup>2+</sup>	2	17,48 ± 0,25						
	·		L <u>6</u>	·				
Cu <sup>2+</sup>	2	$16,59 \pm 0,06$	Ni <sup>2+</sup>	2	$18,93 \pm 0,08$			
Co <sup>2+</sup>	1	$10,18 \pm 0,45$	Fe <sup>3+</sup>	1	$6,\!17\pm0,\!09$			
Zn <sup>2+</sup>	2	$15,46 \pm 0,28$	15,46 ± 0,28					
			L <sup>7</sup>					
Cu <sup>2+</sup>	2	$10,\!48 \pm 0,\!20$	Ni <sup>2+</sup>	1	$7,24 \pm 0,09$			
Co <sup>2+</sup>	2	$10,64 \pm 0,37$	Fe <sup>3+</sup>	1	$4,30 \pm 0,06$			
$Zn^{2+}$	2	$12,23 \pm 0,03$						
		l	L <sup>8</sup>					
$Cu^{2+}$	1	$6{,}47\pm0{,}10$	Ni <sup>2+</sup>	1	$8,\!47\pm0,\!15$			
Co <sup>2+</sup>	1	$7,\!81 \pm 0,\!25$	Fe <sup>3+</sup>	1	$7,\!12 \pm 0,\!34$			
$Zn^{2+}$	2	$17,06 \pm 0,27$						

The results of Table 6 show that in the case of divalent metals of the first transition series, complex compounds of composition ML ( $\lg\beta = 6,34 - 10,18$ ) and

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ML<sub>2</sub> ( $\lg\beta = 7,30 - 19,82$ ) are formed. The calculated values of the formation constants indicate their medium and high stability. In the case of trivalent metal cations additionally in solutions there are complexes of composition M<sub>2</sub>L<sub>3</sub> ( $\lg\beta = 7,60 - 11,36$ ).

#### 3.1.2 Potentiometric titration

In order to determine the pH intervals at which complexation takes place in solution, potentiometric titration of organic molecules, including mixtures of them with metal salts, with sodium hydroxide solution was carried out.

The titration curves of ligands are characterized by two titration jumps, which corresponds to the alternate detachment of two mobile protons (Figure 12).



Figure 12. Potentiometric titration curves  $L^{1}(1)$  and  $L^{4}(2)$ 

The acidity constants of organic molecules calculated from the results of potentiometric titration are: L1 – pKa1 2,52; pKa2 7,25; L2 – pKa1 3,22; pKa2 8,04; L3 – pKa1 2,50; pKa2 6,23; L4 – pKa1 3,04; pKa2 6,81; L5 – pKa1 2,56; pKa2 5,86; L6 – pKa1 2,86; pKa2 6,16.

It should be mentioned that there are rather contradictory data on the values of dissociation constants of  $\beta$ -hydroxyaromatic acids in the literature. Probably, it can be related to the peculiarities of their structure and ionization, in particular, the strong intra- and intermolecular hydrogen bonding, which is significantly influenced by the nature of the solvent, concentration of solutions, temperature, method of determination, etc. For comparison, Table 7 shows certain literature values of dissociation constants of compounds L<sup>1</sup>, L<sup>3</sup> and L<sup>4</sup>, as well as the results obtained in the present work.

Ligand	Study method	Solvent	Ionic strength of the solution, mol/L	Т, °С	рКа	Ref
	Spectrophotometry	50% H <sub>2</sub> O/EtOH	0,10 M NaClO4	20	$6,2 \pm 0,02$ $9,65 \pm 0,01$	[64]
L <sup>1</sup>	Potentiometry	H <sub>2</sub> O	0,2 M KCl	25	$\begin{array}{c} 4,905 \pm 0,006 \\ 11,94 \pm 0,08 \end{array}$	[102]
	Spectrophotometry	50% H <sub>2</sub> O/EtOH	-	22	$7,\!27 \pm 0,\!05$	*
	Potentiometry	50% H <sub>2</sub> O-EtOH	-	22	2,52 7,25	*
	Potentiometry	H <sub>2</sub> O	0,6 M NaCl	25	$\begin{array}{c} 4,997 \pm 0,001 \\ 10,87 \pm 0,01 \end{array}$	[103]
- 2	Spectrophotometry	40% EtOH/H <sub>2</sub> O	0,10 M NaClO4	25	$\begin{array}{c} 3,91 \pm 0,02 \\ 9,22 \pm 0,04 \end{array}$	[104]
L	Spectrophotometry	50% H <sub>2</sub> O/EtOH	-	22	$7,50 \pm 0,28$	*
	Potentiometry	50% H <sub>2</sub> O-EtOH	-	22	2,50 6,23	*
т 4	Spectrophotometry	H <sub>2</sub> O	-	25	7,4	[105]
L	Spectrophotometry	50%		22	$5,\!42 \pm 0,\!06$	*

**Table 7.** Some of known values of dissociation constants  $L^1$ ,  $L^3$  and  $L^4$  obtained by different experimental methods

		H <sub>2</sub> O/EtOH	-			
Potentiometry	Dotontionatmy	50%		22	3,04	*
	H <sub>2</sub> O-EtOH	-		6,81		

\* - present study

In the case of mixtures of solutions of organic ligands and metal salts, the titration curves lie below the titration curves of individual ligands, indicating complexation. The increase in the acidity of the medium indicates the replacement of mobile hydrogen atoms in the ligand molecules by metal cations (Figure 13).



**Figure 13** Potentiometric titration curves of  $L^3$  and  $L^5$  and their equimolar mixtures with metal salt solutions by NaOH solution

It is demonstrated that for pyridinecarboxylic acids the process of complex formation begins in acidic medium, and for aromatic acids in neutral or slightly alkaline medium, which can be explained by the presence of an additional coordination center on the nitrogen atom of the ligands of the pyridine family.

### **3.1.3** Correlation of metal compound formation constant and properties of central atom and ligands

To establish coordination compound formation models, correlations were built between the properties of the central atom and the ligand with the formation constant of the metal complexes.

The dependence of stability of complex compounds on the degree of filling of valence degrees is considered in this study on the example of compounds of delements from the first transition series. The doubly charged ions of these elements are practically indistinguishable from each other in ionic radius and form high-spin octahedral complexes.

As can be seen from Figure 14, in the case of the formation of complex compounds  $L^1$ ,  $L^2$  and  $L^3$  with cations Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, the maximum stabilization is specific for copper (II) complexes, which corresponds to the Irving-Williams stability series [106], the arrangement depends on the split energies of the d sub-level in the octahedral field, and additional stabilization of Cu<sup>2+</sup> complexes is achieved due to the Jahn-Teller effect occurring due to the distortion of the octahedral polyhedron.

In the case of hydroxyaromatic acids of the carbocyclic series (L<sup>4</sup>-L<sup>6</sup>) with similar metal cations, the dependence does not correspond to the stability series of doubly charged ions of transition elements of the fourth period. Most probably, this can be explained by the fact that the influence of the electrostatic effect on the value of the metal complex formation constant is less significant than the specific steric effects of organic molecules L<sup>4</sup>, L<sup>5</sup>, and L<sup>6</sup>.



**Figure 14** Dependence between the formation constants of metal complexes and the atomic number of the 3d-element

The influence of the organic molecules' nature on the stability of metal complexes formed by them is considered on the example of the dependence between the formation constant of the similar metal complexes and the acid dissociation constant of aromatic and pyridine carboxylic acids hydroxy derivatives (Figure 15).

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**Figure 15** Dependence of the formation constants of copper (1), cobalt (2), nickel (3) and zinc (4) metal complexes on the acid dissociation constants of organic ligands

As can be seen, a decrease in the value of the acid dissociation constant of the organic molecule is accompanied by an increase in the stability of the corresponding metal complexes formed by ligands of the pyridine series  $L^1-L^3$ .

The same is true for complexes formed by aromatic ligands of carboxylic acids  $(L^4-L^8)$ . The stability of metal complex compounds increases as the pKa value decreases. The exception is nickel complex compounds, where an increase in the constant of the hydroxyaromatic acid leads to a decrease in the stability of the formed metal complex compounds.

3.2 Characterization of metal complexes isolated in the crystalline state

#### **3.2.1** Optimization of synthesis methods

The study of complexation processes in solutions made it possible to optimize methods for the synthesis of complex compounds. As has been shown above, complexation processes of pyridine hydroxycarboxycarboxylic acids take place in all pH intervals, therefore, the isolation of complex compounds from solutions is possible without changing the pH of the reaction medium (due to the fact that pyridine hydroxycarboxylic acids have a fairly high acidity, and the process of complexation is associated with the release of free hydrogen ions through its substitution for the metal cation, reaction mixtures generated after mixing solutions of organic ligands and metal salts solutions, has a slightly acidic environment (pH 5-5,5). At the same time, complexation of hydroxyaromatic carboxylic acids initiates at pH > 8 (potentiometric titration curves of mixtures of solutions of organic ligands and metal salts are under the titration curves of ligand solutions). In this respect, synthesis of complex compounds is appropriate to be carried out in a slightly alkaline medium (pH around 8). Higher pH values of the reaction medium may cause a competitive reaction to form precipitates of the corresponding metal hydroxides, which will reduce the yield of the target product. An attempt to carry out the synthesis without changing the pH of the reaction medium led to the precipitation of the corresponding organic ligands, which in several cases were 62btainned in the form of monocrystals.

According to the spectrophotometric titration results, the metal : ligand optimum ratios are 1:1 and 1:2.

In the experimental process it was shown that the desired complex compounds have high solubility in water and are isolated in crystalline form only in the form of finely dispersed powders. In order to reduce the solubility, the synthesis was conducted by using ethanol solutions of organic ligands and concentrated aqueous solutions of inorganic metal salts. However, it was observed that even in this case complex compounds are isolated only at significant removal of solvent (more than two-thirds), single crystals of compounds could not be obtained. Therefore, a further modification of the methodology was performed and part of the synthesis was carried out in the presence of an additional ligand -1,10-phenanthroline.

More details on the methods of synthesis of complex compounds are given in the experimental part.

As the result, 30 complex compounds were isolated during the study, to which the following formulas were assigned on the basis of elemental analysis (in several cases – X-ray diffraction studies):

Cu(L<sup>1</sup>)<sub>2</sub> (**I**), Co(L<sup>1</sup>)<sub>2</sub>·2H<sub>2</sub>O (**II**), Zn(L<sup>1</sup>)<sub>2</sub>·2H<sub>2</sub>O (**III**), TiO(L<sup>1</sup>)<sub>2</sub> (**IV**), Ni(L<sup>2</sup>)<sub>2</sub> (**V**), Cu(L<sup>2</sup>)<sub>2</sub> (**VI**), Zn(L<sup>2</sup>)<sub>2</sub>·2H<sub>2</sub>O (**VII**), TiO(L<sup>2</sup>)<sub>2</sub> (**VIII**), Cu(L<sup>3</sup>)<sub>2</sub>·2H<sub>2</sub>O (**IX**), Ni(L<sup>3</sup>)<sub>2</sub>·2H<sub>2</sub>O (**X**), Fe(L<sup>3</sup>)<sub>2</sub>Cl·6H<sub>2</sub>O (**XI**), Ni(L<sup>4</sup>)<sub>2</sub> (**XII**), Cu(L<sup>4</sup>)<sub>2</sub> (**XIII**), Zn(L<sup>4</sup>)<sub>2</sub> (**XIV**), TiO(L<sup>4</sup>)<sub>2</sub> (**XV**), Ni(L<sup>5</sup>)<sub>2</sub> (**XVI**), Cu(L<sup>5</sup>)<sub>2</sub> (**XVII**), Ni(L<sup>6</sup>)<sub>2</sub> (**XVIII**), TiO(L<sup>6</sup>)<sub>2</sub> (**XIX**), Cu(L<sup>7</sup>)<sub>2</sub> (**XX**), Ni(L<sup>7</sup>)<sub>2</sub> (**XXI**), Co(L<sup>7</sup>)<sub>2</sub> (**XXII**), TiO(L<sup>7</sup>)<sub>2</sub> (**XXIII**), Cu(Phen)<sub>2</sub>(L<sup>7</sup>)<sub>2</sub> (**XXIV**), Cu(L<sup>8</sup>)<sub>2</sub> (**XXV**), Ni(L<sup>8</sup>)<sub>2</sub> (**XXVI**), TiO(L<sup>8</sup>)<sub>2</sub> (**XXVII**), [Cu(Phen)<sub>2</sub>Cl]L<sup>8</sup> (**XXVIII**), [Zn(Phen)<sub>2</sub>Cl]L<sup>8</sup> (**XXIX**), [Fe(Phen)<sub>2</sub>Cl<sub>2</sub>]L<sup>8</sup> (**XXX**).

## **3.2.2** Crystal and molecular structures of complex compounds and initial organic ligands

The molecular structure of the compound  $Cu(L^2)_2$  is illustrated in Figure 16.



**Figure 16** Molecular structure of  $Cu(L^2)_2$ . Elipsoids are given for 50% probability. Intramolecular hydrogen bonding is shown by a dashed line

The copper ion forms coordination bonds with two monodeprotonated ligands. Bond lengths Cu - O(1) = 1,9533(18) Å, Cu - N(1) = 1,9684(19) Å, O(1)CuN(1) = 83,93(8) degrees. The coordination polyhedron is almost a regular square, the mean square deviation of the position of atoms from the plane does not exceed 0,076 Å. The molecule contains an intramolecular hydrogen bond to the carbonyl oxygen atom of the carboxyl group: O(3)-HO(3) = 0,724(1), O(3)...O(2A) = 2,601 (2) Å, O(3)HO(3) O(2A) = 155,1 deg (2).

In the crystallization, the Cu atom establishes two additional intermolecular contacts to the oxygen atoms O(3B) and O(3C) (Figure17) to form a pseudo-octahedral structure. The distances of Cu to O(3B) and Cu to O(3C) are 2,707(1) Å.

In structure VII, water molecules enter the inner sphere of the coordination compound  $[Zn(L^2)_2(H_2O)_2]$  (Figure 18).



Figure 17 Intermolecular interactions in  $Cu(L^2)_2$  crystal (shown by dashed lines)



**Figure 18.** Molecular structure of  $[Zn(L^2)_2(H_2O)_2]$ . The elipsoids are given for 50% probability. Intramolecular hydrogen bonding is displayed by a dashed line

 $L^2$  ligands are dissociated at the carboxyl group and coordinated by zinc (II) cation through the oxygen atoms of the COO-group and nitrogen atoms of the pyridine cycle. The coordination number of the complexing agent is 6, the coordination polyhedron is almost a regular octahedron. The bond lengths of Zn-O

of the organic ligand are 2,1067(15) Å, Zn-N 2,1155(17) and 2,1156(17) Å, Zn-O(W) 2,1266(16) Å, the angles in the O1 Zn N1 plane are 100,62(6) and 79,38(6) degrees, and the angles of O1 Zn OW and N1 Zn OW lie between 87,06(7) and 92,94(7) degrees. No intermolecular bonds were found in the crystal (Figure 19).



Figure 19 The packing of  $[Zn(L^2)_2(H_2O)_2]$  molecules in the crystal

It should be noted that the crystal structures of the compounds  $Cu(L^2)_2$  (VI) and  $[Zn(L^2)_2(H_2O)_2]$  (VII) were described previously [75]. However, in contrast to the literature results, which were obtained at 293(2) K, our experiments were carried out at 100(2) K. Due to this, the crystal cell parameters and bond lengths in the molecules are not identical.

Comparison of certain results obtained by our experiments with the literature data is given in Table 8.

 Table 8 Comparison of certain crystallographic parameters of compounds VI

 and VII with literature data [75]

Parameter	Our results		Our results Previous studies by Cha	
			Sun et al. [75]	
Compound	$Cu(L^2)_2$	$[Zn(L^2)_2(H_2O)_2]$	$Cu(L^2)_2$	$[Zn(L^2)_2(H_2O)_2]$
Т, К	100(2)	100(2)	293(2)	293(2)

Crystal system	monoclinic				
Space group	P2(1)/c	P2(1)/n	P2(1)/c	P2(1)/n	
a, Å	6,3176(18)	5,0626(4)	6,394(2)	5,124(2)	
b, Å	11,3753(4)	22,6761(13)	11,458(4)	22,716(9)	
c, Å	7,9723(2)	6,6184(5)	8,085(3)	6,640(3)	
β, °	92,979(3)	111,743(9)	91,926(6)	110,599(6)	
Certain bond					
lengths, Å:					
М-О	1,9533(18)	2,1067(15)	1,9560(19)	2,100(4)	
M-O(W)	-	2,1266(16)	-	2,129(5)	
M-N	1,9684(19)	2,1155(17)	1,973(2)	2,109(5)	

Since single crystals of complex compounds with hydroxyaromatic acids could not be isolated, a modified synthesis using the second ligand, 1,10-phenanthroline (Phen), was carried out. From aqueous-ethanol solutions containing equimolar amounts of copper or zinc chlorides, 3,5-dinitrosalicylic acid (L<sup>8</sup>) and 1,10phenanthroline (Phen), green needle-shaped crystals [Cu(Phen)<sub>2</sub>Cl]L<sup>8</sup> (**XXVIII**) and yellowish needle-shaped crystals [Zn(Phen)<sub>2</sub>Cl]L<sup>8</sup> (**XXIX**), which were investigated by PCA, were obtained during partial evaporation of the solvent.

The molecular structure of compound XXVIII is illustrated in Figure 20.



**Figure 20** Molecular structure of [Cu(Phen)<sub>2</sub>Cl]L<sup>8</sup>. Elipsoids are given for 50% probability. Intramolecular hydrogen bonding is shown by a dashed line

As can be seen from Figure 20, the coordination sphere of copper cation is formed by four nitrogen atoms of two phenanthroline molecules and one chloride anion. The coordination number of copper is 5, and the coordination polyhedron is a square pyramid. This coordination is characteristic of copper(II) complements with organic and inorganic ligands. The Cu-N(Phen) bond lengths are 2,005(7); 2,019(6); 2,079(7) and 2,079(7) Å, respectively, and practically coincide with the bond lengths of other known Cu(II) complexes with phenanthroline [107–116]. The length of the axial Cu-Cl bond is slightly longer than the Cu-N bond and equals 2,352(2) Å. The monoanion of 3.5-dinitrosalicylic acid plays the role of an outer-sphere ligand; its electron-donor fragments do not participate in the formation of coordination or hydrogen bonds with the complex cation. However, the distance between the copper atom and one of the oxygen atoms of the nitro group of the organic anion in position 3 (3,808 Å) could with a certain degree of probability indicate the existence of a very weak axial interaction, which leads the Cu(II) coordination polyhedron to a strongly distorted octahedron with one elongated axial bond. The 3,5-Dinitrosalicylate anion is deprotonated at the hydroxyl group. This leads to the fact that the corresponding C-O bond is strongly shortened (1,269(3) Å) and approaches a double C=O bond in

character, i.e., one unshared pair of oxygen atom electrons is conjugated to the benzene ring. In the L<sup>8</sup> anion, there is also a strong hydrogen bond involving the hydrogen atom of the carboxyl group and the oxygen atom of the deprotonated hydroxyl group. This interaction probably hinders the formation of coordination bonds with the copper(II) cation. In the crystal, intermolecular hydrogen bonds are absent, but there are several short contacts O...H and Cl...H with participation of hydrogen atoms of C-H bonds of phenanthroline fragments (Table 9).

**Table 9** Characterization of intramolecular hydrogen bonding in the counterion of the complex compound  $[Cu(Phen)_2Cl]L^8$  and intermolecular close contacts

D-H	d(D-H)	d(HA)	<dha< td=""><td>d(DA)</td><td>А</td></dha<>	d(DA)	А
O2-H2A	0,840	1,798	152,15	2,571	03
C8-H8A	0,950	2,378	134,47	3,118	O7 [ -x, -y, -z ]
С17-Н17А	0,950	2,800	148,36	3,643	Cl [ -x+1, -y+1, -z-1 ]
С20-Н20А	0,950	2,900	121,26	3,489	Cl [ x+1, y, z ]
C21-H21A	0,950	2,918	119,94	3,490	Cl [ x+1, y, z ]
C28-H28A	0,950	2,656	162,11	3,572	O5 [ x-1, y, z ]

Especially interesting is the crystal structure  $[Zn(Phen)_2Cl]L^8$  (XXIX), in which the zinc atom exhibits an unusual coordination number 5 and forms a square pyramid coordination polyhedron (Figure 21).



**Figure 21** Molecular structure of [Zn(Phen)<sub>2</sub>Cl]L<sup>8</sup>. Elipsoids are given for 50% probability. Intramolecular hydrogen bonding is shown by a dashed line

As can be seen from Figure 21, the unit cell consists of one mono-charged complex  $[Zn(Phen)_2Cl]^+$  and the monoanion of 3,5-dinitrosalicylic acid (L<sup>8</sup>) as a counterion. There is no coordination or hydrogen bonding between the organic anion and the complex cation. The central ion has a coordination number of 5 and forms a polyhedron square pyramid. The basic plane contains a zinc atom, three nitrogen atoms of two phenanthroline ligands and a chloride anion. The Zn-N distances are 2,0037(19); 2,0056(19); 2,071(2) Å, the Zn-Cl bond length is slightly longer (2,2698(7) Å). The azimuthal Zn-N bond (2,188(2) Å) is almost 0,2 Å longer. This bond distribution indicates a significant distortion of the polyhedron in contrast to the copper complex [Cu(Phen)\_2Cl]L<sup>8</sup> described above. As a result, the two phenanthroline fragments do not lie in the same plane, and are nearly perpendicular to each other.

The mobile hydrogen atom of the organic monoanion is localized on the carboxyl group and forms a strong intramolecular hydrogen bond with the adjacent ionized hydroxyl group (d(O-H) 0,840; d(H...O) 1,688; d(O...O) 2,476 Å; <OHO 155,17 deg). The C-O bonds in the carboxyl fragment are non-equivalent and equal to 1,314(3) Å (C-OH) and 1,213(3) Å (C=O). The length of the C-O bond in the

ionized hydroxyl group (1,269(3) Å) indicates a strong pairing of one unshared pair of oxygen electrons with the benzene ring. No intermolecular hydrogen bonds and short contacts were found in the crystal (Figure 22).



Figure 22 Packing of [Zn(Phen)<sub>2</sub>Cl]L<sup>8</sup> molecules in the crystal

It should be emphasized that there is nearly no information on complex compounds incorporating pentacoordinated zinc atoms in the literature. As an example, crystal structures of bis-o-semiquinone complexes of zinc together with some bidentate N-donor ligands like phenazine and 4,4'-bipyridyl [117].

As mentioned above, the complexation of hydroxyaromatic carboxylic acids with the studied metals cannot take place in weakly acidic solutions. From the reaction mixtures without pH change, single crystals of 2,3-dihydroxybenzoic acid ( $L^7$ ), 3,5-dinitrosalicylic acid ( $L^8$ ) and the co-crystallizate of 3,5-ditnitrosalicylic acid with 1,10-phenanthroline were isolated and the crystal structures of their polymorphic forms which were not described in the previously published literature.

Compound L<sup>7</sup> crystallizes in triclinic syngony, space group P-1 with two independent molecules in the unit cell (Figure 23). Bond lengths are standard and do not differ from those known for other hydroxyaromatic acids. Stabilization of crystal

packing proceeds with the participation of intra- and intermolecular hydrogen bonds (Table 10).



Figure 23 Molecular structure of L<sup>7</sup> (ellipsoids are shown for 50% probability)

D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>А</th></dha<>	d(DA)	А
O2 H2O	0,86(2)	1,80(2)	175,0(18)	2,6608(13)	01
O3 H3O	0,85(2)	1,90(2)	145,2(17)	2,6429(13)	01
O4 H4O	0,80(2)	2,243(19)	116,7(16)	2,7006(13)	03
O4 H4O	0,80(2)	2,09(2)	144,0(18)	2,7814(12)	05
O6 H6O	0,88(2)	1,76(2)	174,8(19)	2,6287(13)	08
O7 H7O	0,886(19)	1,821(19)	148,9(17)	2,6202(12)	05
O8 H8O	0,825(19)	1,92(2)	146,7(18)	2,6484(13)	04

**Table 10.** Hydrogen bonds in  $L^7$ 

3,5-Dinitrosalicylic acid ( $L^8$ ) crystallizes as a monohydrate and its crystal structure is shown in Figure 24.


Figure 24 Molecular structure of  $L^8 \cdot H_2O$  (ellipsoids are shown for 50% probability

The bond lengths in the molecule are typical and correlate with the corresponding bond lengths of other  $\beta$ -hydroxyaromatic acids. In the crystal, the molecules are stabilized by a system of intra- and intermolecular hydrogen bonds (Table 11).

D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>Α</th></dha<>	d(DA)	Α
01-H1	0,90(2)	1,71(2)	175,5(17)	2,6092(13)	08
О3-Н3	0,876(19)	1,759(19)	151,0(18)	2,5602(13)	O2
08-H8A	0,81(2)	2,21(2)	157,0(18)	2,9664(14)	03
O8-H8B	0,86(2)	2,00(2)	169,9(17)	2,8526(12)	05

Table 11 Hydrogen bonding parameters in L<sup>8</sup>·H<sub>2</sub>O

In the structure of  $L^8$ ·Phen, one of the mobile protons of 3,5-dinitrosalicylic acid is localized close to the nitrogen atom of the phenanthroline fragment, forming an ion pair of the composition (HPhene)<sup>+</sup>( $L^8$ )<sup>-</sup> (Figure 25).



Figure 25 Molecular structure of  $(HPhenn)^+(L^8)^-$  (ellipsoids are given for 50% probability

The ionization of the hydroxyl group in the 3,5-dinitrosalicylate anion causes a significant shortening of the corresponding C-O bond, as observed above for complex compounds **XXVIII** and **XXIX**, from 1,3289(14) Å in the non-ionized molecule to 1,296(5) Å in its anionic form. The hydrogen bonding features are provided in Table 12.

D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>А</th></dha<>	d(DA)	А
O2 H2	1,09(5)	1,38(5)	153(4)	2,413(4)	03
N3 H3	0,91(4)	2,00(4)	143(4)	2,785(4)	01

**Table 12** Characteristics of hydrogen bonds in  $(HPhen)^+(L^8)^-$ 

The main characteristic band in the IR absorption spectra are the valence vibration bands of carboxyl groups. The frequencies of the bands of their valence vibrations in the IR spectra of  $L^1$  -  $L^8$  and their complexes with metals are given in Table 13.

**Table 13** The position of the valence vibration bands of the carbonyl group (cm-1) in the IR spectra of organic ligands  $L^1 - L^8$  and their metal complexes (KBr tablets)

Ligands	Compounds	VC=O	Ligands	Compounds	VC=O
	L <sup>1</sup>	1695,		L <sup>5</sup>	1647
		1750	ОН		
	$Cu(L^1)_2$	1637	ОН	$Ni(L^5)_2$	1647
И ОН	$Co(L^1)_2 \cdot 2H_2O$	1644	$\sim$	$Cu(L^5)_2$	1645
	$Zn(L^1)_2 \cdot 2H_2O$	1653	ON OH	L <sup>6</sup>	1634
	$TiO(L^1)_2$	1625	ОН	$Ni(L^6)_2$	1628
	L <sup>2</sup>	1656		$TiO(L^6)_2$	1618
0		1700	~ ~		
N OH	$Ni(L^2)_2$	1653	HO	L <sup>7</sup>	1676
ОН	$Cu(L^2)_2$	1645	ОН	$Co(L^7)_2$	1575
- On	$Zn(L^2)_2 \cdot 2H_2O$	1653	ОН	$Cu(Phen)_2(L^7)_2$	1581
	$TiO(L^2)_2$	1675		L <sup>8</sup>	1620
	$Cu(L^3)_2 \cdot 2H_2O$	1683	HO	$TiO(L^8)_2$	1587
		1606	ОН		
	$Ni(L^3)_2 \cdot 2H_2O$	1588	O2N NO2	$[Cu(Phen)_2Cl] \cdot L^8$	1615
	$Fe(L^3)_2Cl\cdot 6H_2O$	1614		[Fe(Phen) <sub>2</sub> Cl <sub>2</sub> ]L <sup>8</sup>	1608
	L <sup>4</sup>	1647			
	$Ni(L^4)_2$	1645			

Ligands	Compounds	VC=O	Ligands	Compounds	VC=O
	$Cu(L^4)_2$	1645			
UH UH	$Zn(L^4)_2$	1640			
	$TiO(L^4)_2$	1645			

The IR spectra of organic molecules containing 2-hydroxypyridine moieties ( $L^1$  and  $L^3$ ) have a broad asymmetric band in the spectra with a maximum at 1694-1695 cm<sup>-1</sup> and a shoulder at 1750/1730 cm<sup>-1</sup> (Figure 26).



**Figure 26** IR absorption spectrum of  $L^1$ 

It is known that 2-hydroxypyridines usually exist in the  $\alpha$ -pyridone form, thus it can be assumed that the hydrogen atom of the hydroxyl group can transfer to the pyridine nitrogen atom, and the C-O bond length of the deprotonated hydroxyl group shortens, as has been shown in the analysis of crystal structures of metal complexes, and acquire a significant double character. The carboxyl group is not protonated, the C-O fragment is not involved in hydrogen bond formation and appears in the IR spectra in the region of 1750 and 1730 cm<sup>-1</sup> for L<sup>1</sup> and L<sup>3</sup>,

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respectively. At coordination with metals, most probably, a metal-chelate ring with participation of hydroxyl and carboxyl groups is formed, and in IR spectra a shift of the valence vibration band of the carbonyl group to the low-frequency region is observed (Figure 27).



**Figure 27** The IR absorption spectrum of  $Co(L^1)_2 \cdot 2H_2O$ 

In the case of compound  $L^2$ , in which the hydroxyl group is in position 3 relative to the pyridine ring, the formation of a pyridone structure most probably does not occur. The transfer of the proton of the carboxyl group to the nitrogen atom of the ring is not excepted. In this situation the carboxyl group is deprotonated and in IR spectra there are bands of valence symmetric and antisymmetric vibrations of carboxylate anion: 1656 and 1700 cm<sup>-1</sup>. X-ray diffraction analysis of the complex compounds Cu(L<sup>2</sup>)<sub>2</sub> and Zn(L<sup>2</sup>)<sub>2</sub>·2H<sub>2</sub>O indicates that the coordination is realized through the oxygen atom of the carboxyl group and the pyridine nitrogen atom. One absorption band remains in the IR absorption spectra of the metal complexes (1645 and 1653 cm<sup>-1</sup> for Cu(L<sup>2</sup>)<sub>2</sub> and Zn(L<sup>2</sup>)<sub>2</sub>·2H<sub>2</sub>O, respectively. The similar character of the IR spectra of other L<sup>2</sup> complexes indicates the same nature of coordination.

According to the results of X-ray diffraction analysis known in the literature and our data,  $\beta$ -hydroxyaromatic acids of the carbocyclic series are characterized by strong intramolecular hydrogen bonding of adjacent carboxyl and hydroxyl groups. In this context, the valence vibration bands of the C=O groups of these molecules are shifted to the low-frequency region. In the process of complexation, the hydrogen atom is replaced by a metal atom while maintaining the general character of the ring, and the shift of the absorption bands of the carbonyl group practically does not occur.

### **3.3** Characterization of oxide phases produced using organic metal complex precursors and alternative methods

As it was shown in the literature review part, complex compounds of metals with organic ligands are promising precursors for the preparation of micro- and nanoscale oxides that exhibit catalytic and other useful properties. During their thermal decomposition, a large amount of gaseous substances is released, which contributes to the grinding of the resulting oxide phases to nanoscale. The initial complex compounds have a constant composition and are stable during storage, which makes it possible to use them when necessary to obtain phases (nanoscale particles are prone to stick together in larger agglomerates and require the addition of stabilizers).

In order to prepare metal oxide nanoparticles and study their characteristics and catalytic and other activities, we used the following approaches:

- Decomposition of individual complex compounds (holding at T 700°C, for 5 h).
- Decomposition mixtures of Ti (IV) and M(II) complexes (M = Co, Zn, Ni); (incubation at T 700°C, for 5 h).
- From inorganic salts (Hydrothermal synthesis and modification with graphene oxide, GO):

$$Fe^{2+} + 2Fe^{3+} + 80H^- \rightarrow Fe_3O_4 + 4H_2O_4$$

Thermal treatment of the natural mineral vermiculite (Mg, Ca, K, Fe<sup>+2</sup>)<sub>3</sub>(Si, Al, Fe<sup>+3</sup>)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O.

### 3.3.1 Investigation of thermal stability of complex compounds - precursors of nanosized metal oxides

For determination the optimal conditions to thermal decomposition of complex compounds - precursors of nanosized metal oxides, it was necessary to first determine the intervals of their thermal stability. For this purpose, the method of thermogravimetric analysis was applied. A number of complex compounds of zinc and titanium were studied as objects of research. Thermal decomposition curves are shown in Figure 28, and the results of calculations based on TG curves are given in Table 14.

As can be observed, thermal decomposition of complex compounds begins with the process of decarboxylation in the temperature ranges 125-360°C, which in some cases is overlapped with the process of organic mass burnout (up to 775°C). The final products of decomposition are oxides ZnO and TiO<sub>2</sub>.





Figure 28 Thermogravigrams of certain complex compounds of zinc and titanium with hydroxyaromatic and heteroaromatic acids

 Table 14 Thermal analysis processes of several complex compounds of zinc

 and titanium

Compounds	Decarboxylation		Combustion	Residue ZnO/TiO <sub>2</sub> , %		
	t, °C	Δm <sub>cal.</sub> , %	Δm <sub>exp</sub> ., %	of organic matter (t),°C	Theory	Experiment
$Zn(L^4)_2$	125 - 155	10,55	6,48	175 - 500	19,42	15,20
$Zn(L^6)_2$	90 - 125	7,00	21,49	175 - 650	12,89	12,04
$TiO(L^2)_2$	160 - 275	23,53	15,17	350 - 700	42,78	43,12
$\operatorname{TiO}(L^5)_2$	125 - 350	17,46	13,14	400 - 775	31,75	33,05
$TiO(L^6)_2$	110 - 250	18,64	12,10	325 - 775	33,90	37,13
$TiO(L^1)_2$	190 - 260	23,53	7,78	300 - 750	42,78	35,66

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The results of thermogravimetric analysis allowed us to propose using the decomposition temperature of complex precursors 500°C (middle of the decomposition temperature range) to obtain oxide phases. The holding time at this temperature of 5 h was used for complete completion of the process.

# **3.3.2** Characterization of oxide phases isolated during thermal decomposition of precursors obtained by decomposition of individual complex precursors

X-ray phase analysis (XRD) of thermal decomposition products of zinc complex compounds has shown that the obtained phases are identical and correspond to zinc oxide ZnO (Figure 29). On the basis of microphotographs (Figure 30) it was determined that the particle size is  $3-13 \mu m$ .







 $Zn(L^3)_2$ 



**Figure 29** XRD analysis of thermal decomposition products of certain zinc (II) complex compounds



Figure 30 SEM image of zinc oxide obtained by calcination of the complex compound  $Zn(L^4)_2$ 

During decomposition of complex compounds of titanium (IV), according to XRD results, all obtained phases correspond to titanium oxide TiO<sub>2</sub> in the form of allotropic modification of anatase with admixture of rutile (Figure 31).



Figure 31 X-ray diffraction of TiO(L<sup>5</sup>)<sub>2</sub> thermal decomposition product

It is evident from the experiment that the phase composition and crystal size do not depend on the selected organic precursor; therefore, when selecting the precursor for further laboratory experiments, it was chosen to focus mainly on commercial availability and ecological safety. The size of the resulting particles after calcination does not meet the definition of "nanomaterial". In this regard, we decided to change from decomposition of individual complex compounds to decomposition of mixtures of complexes of titanium and divalent metals in different molar ratios.

## 3.3.3 Characterization of oxide phases isolated during thermal decomposition of precursor mixtures based on complex compounds of titanium (IV) and divalent 3d-metals

L<sup>8</sup> ligand (3,5-dinitrosalicylic acid) was selected as an experimental sample for the preparation of mixtures in the various molar ratios of titanium and zinc complex compounds and in the role of a precursor for its preparation. The mixtures were prepared by grinding different molar ratios of titanium and zinc complex compounds in agate mortar (Figure 32).



**Figure 32** Mixtures of zinc and titanium complex compounds (precursor L<sup>8</sup>) grinded in an agate mortar before incineration

During sample calcination, it was found that the use of 3,5-dinitrosalicylic acid as a precursor for obtaining complex compounds of titanium and zinc with the consequent separation of their nanosized oxides is not reasonable, because detonation occurs during heating - decomposition with explosion. However, despite this, it was possible to study the powders obtained during calcination. On the basis of electron-probe microanalysis and microphotographs (Figure 33) the compositions, shape and sizes of the obtained particles were revealed. It was determined that titanium oxide TiO<sub>2</sub> was formed in the form of rods about 30  $\mu$ m long with a diameter cross section of roughly 0,3  $\mu$ m (300 nm). It was found that zinc titanate ZnTiO<sub>3</sub>, produced by calcination of a mixture of precursors in a molar ratio of 1:1, is generated in the form of finely dispersed needle-like formations with a length of about 200 nm and a cross-sectional diameter of approximately 20 nm, with a tendency to form spherical agglomerates with a diameter of 2-10  $\mu$ m. Zinc oxide in samples with prevalence of zinc complex compounds is formed in the form of branched rods with an average length of 50  $\mu$ m and a cross section of 0,35  $\mu$ m (350 nm). Titanium oxide is present in all samples irrespective of the molar ratio of the initial mixtures. According to XRD data, the main modification of titanium oxide is rutile. Zinc titanate has the crystalline structure of perovskite.





Figure 33 Microphotographs of powders obtained by thermal decomposition of zinc and titanium ( $L^5$ ) complex compound mixtures in different molar ratios



**Figure 34** X-ray diffraction patterns of oxide phases obtained by thermal treatment (700°C, 5 h) of equimolar mixtures of the following precursors:  $1 - \text{Ni}(\text{L}^7)_2$ : TiO(L<sup>7</sup>)<sub>2</sub>;  $2 - \text{Ni}(\text{L}^2)_2$ : TiO(L<sup>2</sup>)<sub>2</sub>;  $3 - \text{Ni}(\text{L}^8)_2$ : TiO(L<sup>8</sup>)<sub>2</sub>;  $4 - \text{Cu}(\text{L}^2)_2$ : TiO(L<sup>2</sup>)<sub>2</sub>

As shown in Figure 34, samples 1-3 contain a phase of perovskite-like nickel titanate (33-0960, IDD PDF-2). The X-ray amorphous diffractogram with blurred broad peaks of sample 3 (precursor  $L^8$ ) may indicate high dispersion compared to samples 1 and 2 (precursors  $L^2$  and  $L^7$ ).

Samples 1 and 2 also show reflections characteristic of anatase modified TiO<sub>2</sub> (21-1272, IDD PDF-2). The anatase impurity is maximum in sample 1 and absent in sample 3. The impurity modification of titanium dioxide in samples 1 and 2 is rutile (21-1276, IDD PDF-2). Anatase, rutile and CuO oxide phases are found in sample 4 (48-1548, IDD PDF-2).

Adsorption-desorption isotherms of some of the obtained oxide phases are shown in Figure 35.



**Figure 35** Nitrogen adsorption-desorption isotherms for oxide phases obtained by thermal treatment (700°C, 5 h) of mixtures of equimolar amounts of the following precursors:  $1 - Cu(L^2)_2$ : TiO(L<sup>2</sup>)<sub>2</sub>;  $2 - Ni(L^2)_2$ : TiO(L<sup>2</sup>)<sub>2</sub>;  $3 - Ni(L^8)_2$ : TiO(L<sup>8</sup>)<sub>2</sub>.

Based on adsorption-desorption isotherms, the surface areas of oxide particles were calculated, which were 17,13; 18,63 and 22,69 m<sup>2</sup>/g for samples 1, 2 and 3, respectively. According to the results, the largest surface area is observed for nickel titanate obtained by decomposition of the complex precursor based on 3,5-dinitrosalicylic acid.

### **3.3.4** Characterization of Fe3O4 oxide particles modified with graphene oxide obtained from inorganic precursors

Due to the fact that we have not succeeded in obtaining certain results when trying to isolate nanosized iron oxides using metal complex precursors, we have synthesized  $Fe_3O_4$  oxide particles modified with graphene oxide (oxidized surface graphene, GO) obtained from inorganic precursors (a mixture of iron(II) and iron(III) chlorides) by their thermal decomposition in the presence of conc. H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> (the detailed methodology is described in the experimental part). The separated oxide phase was characterized by a combination of methods.

FTIR spectra of the isolated oxide materials are shown in Figure 36.



**Figure 36** FTIR spectra of Fe<sub>3</sub>O<sub>4</sub> oxide, graphene oxide (GO) and iron oxide modified with graphene oxide

The 582 cm<sup>-1</sup> absorption band present both in the spectrum of Fe<sub>3</sub>O<sub>4</sub> oxide and in the spectrum of this oxide modified by graphene oxide can be attributed to Fe-O

valence vibrations based on literature data [118,119]. The 1384 and 1052 cm<sup>-1</sup> absorption in the GO spectrum can be assigned to the valence vibrations of C-O(H) and C-O(OH) bonds, respectively. Hydroxyl and carboxyl groups are formed on the surface of graphene during its partial oxidation. The C=O bond vibrations appear in the GO spectrum in the region of 1717 cm<sup>-1</sup>, while the OH bond vibrations show up as a broad asymmetric band with the center of gravity at 3423 cm<sup>-1</sup> [120,121]. The presence of these absorption bands in the modified Fe<sub>3</sub>O<sub>4</sub>-GO iron oxide indicates that the GO surface was successfully modified with Fe<sub>3</sub>O<sub>4</sub> iron oxide to increase its sorption activity towards organic pollutants.

The X-ray diffraction patterns of the initial Fe<sub>3</sub>O<sub>4</sub>, GO and GO-modified iron oxide are shown in Figure 37.



**Figure 37** X-ray diffraction analysis results of Fe<sub>3</sub>O<sub>4</sub>, GO and GO-modified iron oxide

As is evident from Figure 37, the reflections characteristic of  $Fe_3O_4$  oxide (JCPDS No. 190629) are also observed in the  $Fe_3O_4$ -GO sample. The presence of amorphous GO in the modified sample results in the appearance of noise background in the X-ray diffraction pattern.

As can be seen from the micrographs, the average size of oxide particles localized on the GO surface (Figure 38) is 30-100 nm.



Figure 38 Microphotographs of the Fe<sub>3</sub>O<sub>4</sub>-GO sample

The nitrogen adsorption-desorption isotherm for the Fe<sub>3</sub>O<sub>4</sub>-GO sample is shown in Figure 39. The surface area of the nanocomposite calculated on its basis is  $604,57 \text{ m}^2/\text{g}$ , which is greater than the results obtained in [122,123].



Figure 39 Nitrogen adsorption-desorption isotherm for the Fe<sub>3</sub>O<sub>4</sub>-GO sample

The magnetic hysteresis loops of  $Fe_3O_4$  sample and  $Fe_3O_4$ -GO nanocomposite is shown in Figure 40. The saturation magnetization of  $Fe_3O_4$ -GO is 15,91 emu/g

(electromagnetic units per gram), which is much lower than the same value for  $Fe_3O_4$  (73,5 emu/g). This can be explained as a considerably lower concentration of oxide particles on the surface of nonmagnetic GO.

The presence of paramagnetism of the  $Fe_3O_4$ -GO composite suggests that it can be easily removed from the solution at the end of sorption under the action of a magnetic field.



Figure 40 Magnetic hysteresis loops of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-GO nanocomposite

#### 3.3.5 Characterization of modified natural mineral vermiculite

To compare the efficiency of metal oxide nanoparticles and their nanocomposites isolated by us, a natural oxide mineral, vermiculite, whose composition corresponds to the formula  $(Mg^{+2},Fe^{+2},Fe^{+3})_3[(Al,Si)_4O_{10}]\cdot(OH)_2\cdot4H_2O$ , was modified. It is a mineral from the hydrous mica group, having a layered lamellar structure. When heated, the plates form worm-like columns or threads of golden or silvery color with transverse division into the finest scales (so-called expanded

vermiculite with high porosity). In addition, vermiculite is a low-cost raw material, it is environmentally friendly and non-toxic for humans.

In the current work, we compared the surface properties of the original vermiculite mineral (RV) and its modified sample (EV), which was prepared according to the scheme shown in Figure 41.



Figure 41 Scheme for the preparation of modified vermiculite

Several physical characteristics of the original vermiculite (RV) and its modified sample (EV) are shown in Figure 42. The X-ray phase analysis (Figure 42a) shows the preservation of the main peaks of RV in the X-ray pattern of EV, indicating the preservation of the morphology of the samples. The decrease in the intensity of reflections in the modified sample can be explained by the partial loss of crystallinity due to the rapid removal of interlayer water molecules under the action of microwave radiation and the destruction of the layer structure of the mineral.

Figure 42b shows the TGA curves of the original and modified vermiculite. It can be seen that the untreated vermiculite, when heated to 700°C, loses more than 15% of mass due to the elimination of interlayer water, whereas for the modified vermiculite, there is almost no mass loss, which may indicate the removal of interlayer water during the modification process.

According to the analysis of adsorption-desorption isotherms (Figure 42c), the modification of vermiculite leads to a significant increase in its surface area (73,953 m<sup>2</sup>/g for EV compared to 17,718 m<sup>2</sup>/g for RV). The EDX spectrum of the modified vermiculite (Figure 42d) confirms its composition: SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, K<sub>2</sub>O, and TiO<sub>2</sub>, which is consistent with literature data.



**Figure 42** Several characteristics of the original (RV) and modified (EV) vermiculite: (a) - XRD analysis; (b) - thermogravigrams; (c) - nitrogen adsorption-desorption isotherms; (d) - EDX analysis of the sample composition

Microphotographs of RV and EV samples (Figure 43) demonstrate the preservation of a layered structure with particle thickness at the nanoscale.



Figure 43 SEM images of RV (a and b) and EV (c and d)

#### **3.4** Several applications of isolated oxide phases and nanocomposites

It is well-known that nanosized metal oxides are used for sorption of organic pollutants from solutions. Nanocatalysts based on metal titanates are effective in reactions of photocatalytic decomposition of organic substances, and zinc and titanium(IV) oxides are used in the cosmetic industry as inorganic UV filters. In this regard, we conducted preliminary tests to determine the possible applications of oxide phases and composites obtained using complex precursors or alternative methods.

### 3.4.1 Nanoscale 3d-metal titanates as photocatalysts for bromophenol blue decomposition

We studied the catalytic activity of the isolated sample in the reaction of photodegradation of bromophenol blue, a model environmental pollutant with

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organic colored compounds, by the example of nickel titanate obtained by calcination of an equimolar mixture of complex compounds  $Ni(L^8)_2$  and  $TiO(L^8)_2$ . The experiment was carried out according to the method developed earlier in [4]. For this purpose, 500 ml of bromophenol blue solution in water (C = 0,001 mol/l) was prepared in a flask. 3,86 g of catalyst was added to the solution and kept in a dark place for 30 min under vigorous stirring and bubbling of oxygen. The flask was placed under a sunlight lamp at room temperature. Keep vigorously stirring the solution with the catalyst. The change in the concentration of bromophenol blue was evaluated by the change in the intensity of the absorption band at 432 nm in the electronic absorption spectrum (Figure 44). The experiment was conducted for 2 hours.



**Figure 44** The variation in the electronic absorption spectrum of the bromophenol blue solution during time (1) and the calculation of the apparent reaction rate constant (2)

According to the results of the experiment, we calculated the apparent rate constant of the reaction (first-order reaction), ka = 0.04.

When the solution of bromophenol blue was kept in the experimental conditions without a catalyst, no change in the color of the solution was observed (Figure 45).



**Figure 45** Changes in color of bromophenol blue solution during time: 1 - freshly prepared solution; 2 - solution maintained in the light for 2 days without catalyst; 3 - solution kept in the light for 2 days in the presence of catalyst (NiTiO<sub>3</sub>)

Therefore, it was shown that metal complex compounds with hydroxyaromatic acids are suitable for obtaining efficient photocatalysts in the decomposition reactions of organic pollutants.

### **3.4.2** Application of zinc titanate as an inorganic UV filter in cosmetic products

In spite of the internal mechanisms for protecting the body from the harmful effects of UV radiation, in current conditions they are not enough, thus we need additional protection, one type of which is the use of sunscreen cosmetics. This type of cosmetic products contains active ingredients - ultraviolet filters (UV filters), which prevent the penetration of UV rays into the skin. Typical representatives of inorganic UV filters are zinc oxides ZnO and titanium oxides TiO<sub>2</sub> [124]. They have a wide spectrum of action, their principal advantages include excellent photostability and low risk of allergic reaction during use, are suitable for sensitive skin and have a lower potential for irritation than organic filters. However, cosmetics with a high proportion of inorganic UV filters in their composition tend to be translucent and white on the skin, besides being rather "heavy" in feeling [125,126]. Reducing the particle sizes of zinc (II) and titanium (IV) oxides to the nanoscale allows

eliminating undesirable effects like whiteness and a "heavy" feeling, and the combination of organic and inorganic filters increases the effectiveness of UV protection [127].

A sample of nickel titanate, obtained by thermal decomposition of equimolar mixtures of  $Zn(L^8)_2$  and  $TiO(L^8)_2$ , has been used as objects for the study of photoprotective properties. It should be noted that in the literature there is information about the use of titanium and nickel oxides or their mixtures separately, but nickel titanate was not used.

The absorption capacity of cosmetic compositions with the addition of zinc titanate samples was determined in ethanol solutions according to the method described by Mansour et al [128]. An attempt to put nanosized inorganic particles into the cream substrate without pre-treatment of the particle surface did not achieve a homogeneous mass with a uniform texture, therefore, treatment of the particle surface by grinding the powder with glycerol in a mortar before creating the cosmetic form was performed. A comparison of the absorption capacity of powders (4% wt. % addition to the cream base) with different molar ratios of  $Zn(L^8)_2 \cdot 2H_2O$  and  $TiO(L^8)_2$  is demonstrated in Figure 46.



Figure 46 Comparison of UV absorption ability of powders obtained by calcination of mixtures with different molar ratio of  $Zn(L^8)_2 \cdot 2H_2O$  and  $TiO(L^8)_2$ : 1 - 1:1; 2 - 4:1; 3 - 3:2; 4 - 1:0; 5 - 0:1

It can be seen that the highest UV absorption ability is characteristic of the powder with molar ratio Ti:Zn 1:1, which corresponds to nanoscale ZnTiO<sub>3</sub>, and the lowest is for TiO<sub>2</sub>. A synergistic effect is also observed when the powders are mixed: the absorption capacity of the mixtures is higher than that of pure oxides.

Since organic and inorganic UV filters are widely used together in cosmetic formulations, we investigated the ability of the obtained inorganic filters to enhance the effect of the most common organic filter in cosmetic practice - ethylhexyl methoxycinnamate (EHMC). Powders with molar ratio Ti:Zn=1:1, the precursors of which were complex compounds of zinc(II) and titanium(IV) with L<sup>1</sup> and L<sup>8</sup>, were incorporated in an amount of 4% by weight to the cream base containing EHMC additive in an amount of 8% by weight (Figure 47).



**Figure 47** The synergistic effect when organic and inorganic UV filters are used in combination: 1 - EHMC; 2 - ZnTiO<sub>3</sub> - added ENMC (precursors -  $Zn(L^1)_2 \cdot 2H_2O$  and TiO( $L^1$ )<sub>2</sub> at a molar ratio of 1:1); 3 - ZnTiO<sub>3</sub> - added ENMC (precursors -  $Zn(L^8)_2 \cdot 2H_2O$  and TiO( $L^8$ )<sub>2</sub> at a molar ratio of 1:1)

It appears that both inorganic filters enhance the influence of the organic UV filter, with the powder whose precursor was complex compounds of the aromatic ligand  $L^8$  having a greater synergistic effect compared to the powders obtained from the decomposition of complex compounds based on the heteroaromatic ligand  $L^1$ .

### **3.4.3** The adsorption activity of Fe<sub>3</sub>O<sub>4</sub>-GO nanocomposite and modified natural mineral vermiculite towards organic dyes

Considering that the Fe<sub>3</sub>O<sub>4</sub>-GO nanocomposite and modified natural mineral vermiculite obtained by our alternative methods are characterized by a large surface area comparable to known sorbents, it was interesting to study their adsorption activity towards organic dyed compounds - methylene blue (MB), congo red (CR) and alizarin red (AR).

The study of adsorption processes of MB and CR on Fe<sub>3</sub>O<sub>4</sub>-GO composite in the pH range of 3-8 (Figure 48) showed that the adsorption maximum for MB is approximately at pH 5, and for CR - at about pH 6. This fact can be explained by the following. From the literature [123,129], the pH of the zero charge point of the Fe<sub>3</sub>O<sub>4</sub>-GO surface is known to be 6,2. The acid dissociation constants pKa for MB and CR are 3,8 and 4,5, respectively. The maximum adsorption at pH 5 and 6 can be related to the electrostatic interaction between the positively charged adsorbent surface and the negatively charged analytes (MB and CR). At higher pH, the adsorbent surface becomes negatively charged and adsorption decreases.



**Figure 48** Dependence of MB and CR adsorption on Fe<sub>3</sub>O<sub>4</sub>-GO composite on pH value

In the case of AR, a significant decrease in adsorption on vermiculite with increasing pH was observed (Figure 49).



Figure 49 Dependence of AR adsorption on modified vermiculite on pH value

The adsorption mechanism in this case can be represented as electrostatic interaction of functional groups of adsorbent and adsorbate. The composition of alizarin red includes sulfo groups -SO<sub>3</sub>H, which have high acidity and, consequently, ionized even at low pH values, while the surface of vermiculite under these conditions is positively charged, the pH of the point of zero charge is 7. An increase in pH decreases the charge of the adsorbent surface and adsorption decreases.

The dependence of the adsorption ability on the amount of adsorbent added is shown in Figure 50. As can be seen, the optimal amount of adsorbent added to 1 liter of solution is 50 mg.



**Figure 50** The influence of adsorbent (Fe<sub>3</sub>O<sub>4</sub>-GO) mass on the adsorption ability of MB and CR

In the case of vermiculite this value is significantly higher and reaches 2 g/l (Figure 51).



Figure 51 The effect of vermiculite mass on the adsorption efficiency of AR

According to the results shown in Figure 52, the adsorption of MB and CR on the Fe<sub>3</sub>O<sub>4</sub>-GO surface proceeds rapidly and practically completed within 10 min (the efficiency of organic substances extraction from solutions is 90%).



Figure 52 Time dependence of MB and CR adsorption on Fe<sub>3</sub>O<sub>4</sub>-GO surface

In order to determine the possibility of recycling the Fe<sub>3</sub>O<sub>4</sub>-GO composite, desorbing agents were examined that satisfy the following conditions: low cost, environmentally friendly, ensuring the efficiency of adsorbate leaching and not changing the structure of the adsorbent.

Consequently, the following methodology was proposed. The adsorbent used was placed in a weakly acidic solution containing 20 mL of water and a several drops of concentrated acetic acid. The suspension was kept in a ultrasonic bath for 5 min, then the adsorbent was separated using a magnet and washed with distilled water. The procedure was repeated two times. The adsorbent was then washed twice with distilled water at 40°C and ethanol at the same temperature. The regenerated adsorbent was dried at 60°C for 12 hours. The test results of regenerated Fe<sub>3</sub>O<sub>4</sub>-GO (Figure 53) show that it maintains its adsorption properties towards methylene blue and congo red after at least 5 cycles of use.



Figure 53 Reusability study of  $Fe_3O_4$ -GO adsorbent towards methylene blue and congo red ( adsorption time 10 min, pH 6, amount of adsorbent 50 mg/L)

Comparison of the results obtained in the current work with the results known in the literature (Table 15) suggest the possibility of using Fe<sub>3</sub>O<sub>4</sub>-GO nanocomposite as an effective sorbent of methylene blue and congo red from neutral solutions.

Table 15 Comparison of adsorption properties of  $Fe_3O_4$ -GO composite with other known sorbents

		Maximum		
N⁰	Sorbent	capacity	References	
		MB	CR	
1.	Wheat husk	1656		(Bulut & Aydin
		10,30	-	2006) [130]
2.	Halloysite nanotubes	84.22		(Zhao & Liu
	(HNTs)	04,32	-	2008) [131]
3.	Graphene	152.85		(Liu et al. 2012)
		155,65	-	[122]
4.	Activated biochar	161		(Franciski et al.
	(CO <sub>2</sub> -biochar)	101	-	2018) [132]
5.	Zn-Fe <sub>2</sub> O <sub>4</sub> Nanospheres		16.58	(Rahimi et al.
		-	10,58	2011) [133]
6.	Maghemite nanoparticles			(Afkhami &
	$(\gamma - Fe_2O_3)$	-	208,33	Moosavi 2010)
				[134]
7.	Anilinepropylsilica xerogel		22 62	(Pavan et al.
	(SiAn)	-	22,02	2008) [135]
8.	Unmodifide fly ash		22.12	(Hajar et al.
		-	22,12	2022) [136]
9.	Fe <sub>3</sub> O <sub>4</sub> -GO	135,1	285,7	This work

### 3.5 Potential biological activity of 3d metal complex compounds with aromatic and heteroaromatic hydroxy acids

Due to the fact that aromatic and heteroaromatic acids used in this work as ligands exhibit a wide range of biological activity and are used as medicines, it was interesting to evaluate how their biological activity will change when they are transferred to complex compounds and assessment possibilities for the entry of these substances into the human body. For this purpose, we used *in silico* method (computer prognostics) on the example of ligands L<sup>4</sup>, L<sup>7</sup>, L<sup>8</sup> and their metal complexes using freely available programs: SwissADME (https://www.swissadme.ch/;, AdmetSar (https://lmmd.ecust.edu.cn/admetsar2; ADMETlab 2.; Toxtree v2.5.1 (https://toxtree.sourceforge.net/); Prediction of Biological Activity Spectra (PASS); PharmMapper and SwissTargetPrediction.

As demonstrated by modeling in the PASS program, the main biological activities of the uncoordinated ligands are associated with their antimicrobial activity, which is maintained when switching to metallocomplexes (Figure 54).



**Figure 54** Probability of displaying inhibition of the multiprotein complex in the respiratory electron transfer chain:  $1 - L^8$ ;  $2 - Co(L^8)_2$ ;  $3 - Cu(L^8)_2$ ;  $4 - Zn(L^8)_2$ ;  $5 - Fe(L^8)_3$ 

The development of novel pharmacological medicines usually starts with the study of their physicochemical properties, biocompatibility, lipophilicity, absorption

and distribution in the body, metabolism, excretion and toxicity. Figure 55 provides information on important properties of ligands and their complexes related to biocompatibility according to the five Lipinski rule:

- molecular weight  $\leq$  500;

- no more than 10 acceptor hydrogen bonds (total number of nitrogen or oxygen atoms);

- no more than 5 donor hydrogen bonds (total number of nitrogen-hydrogen and oxygen-hydrogen bonds);

- octanol-water distribution coefficient (lg P), less than 5.

In the case that all or most of these rules are fulfilled, it can be said that the compound under study can be considered as a potential medicine.



**Figure 55** Bioavailability radars of organic ligands and their metal complexes. The pink area represents the optimal range of physicochemical properties (lipophilicity: XLOGP3 between -0,7 and +5,0, size: MW (molecular weight) between 150 and 500 g/mol, polarity: TPSA (topological polar surface area) between 20 and 130 Å2, solubility: lgS not higher than 6, saturation: carbon fraction in Csp<sup>3</sup> hybridization not smaller than 0,25 and flexibility: less than 9 rotatable bonds): 1-L<sup>7</sup>; 2 - L<sup>4</sup>; 3 - L<sup>8</sup>; 4 - Zn(L<sup>7</sup>)<sub>2</sub>; 5 - Fe(L<sup>7</sup>)<sub>3</sub>; 6 - Zn(L<sup>8</sup>)<sub>2</sub>

According to Figure 55, the examined organic ligands, based on the calculated radars, have bioavailability and only deviated from the optimal values by the degree of saturation of molecules (Csp<sup>3</sup> fraction), which is less than the minimum value of 0,22. In the case of complex compounds, at least two or three parameters do not satisfy Lipinski's rule. The largest deviations are observed for trivalent iron complexes.

The probable pathways of adsorption of potential pharmacologic medicines into the body through the gastrointestinal tract can be evaluated from the diagrams shown in Figures 56-58. When the point corresponding to a given sample is placed in the white part of the diagram, the compound is more likely to be able to penetrate into the body through oral intake. A point in the yellow area indicates a high probability of the compound being able to penetrate into the brain. A dot in the gray part of the diagram suggests that the compound is not able to be absorbed into the body.



**Figure 56** Simulations of potential pathways for organic molecules to enter the body:  $1 - L^7$ ;  $2 - L^8$ ;  $3 - L^4$ 



**Figure 57** Modeling of possible pathways for organic molecules to enter the body:  $1 - L^4$ ;  $2 - Fe(L^4)_3$ 



**Figure 58.** Modeling of possible pathways for organic molecules to enter the body:  $1 - L^7$ ;  $2 - Co(L^7)_2$ 

As is evident from Figure 56, compound  $L^8$  (3,5-dinitrosalicylic acid) is not able to adsorb through the gastrointestinal tract in comparison with compounds

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$L^4$  and  $L^7$ . The adsorption capacity of metal complexes decreases compared to the original organic molecules. To the lowest extent this ability is displayed for complex compounds of iron (III) and all complex compounds of 3,5-dinitrosalicylic acid ( $L^8$ ).

## CONCLUSIONS

1. 31 complex compounds of Ti(IV), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with three pyridine hydroxycarboxycarboxylic acids and five hydroxyaromatic carboxylic acids, of which 20 compounds were isolated for the first time. It was found that, depending on the synthesis conditions, organic ligands can enter the inner sphere of the complexes in the form of bidentate-chelate ligands or play the role of outer-sphere anions.

2. By methods of spectrophotometric and potentiometric titration the processes of complexation in solutions were studied and it was shown that pyridine carboxylic acids are capable of complexation with metal cations in the range of pH 3 - 11, and hydroxyaromatic acids only at pH >7. In this case, complex compounds of the composition ML, ML<sub>2</sub> and M<sub>2</sub>L<sub>3</sub> of medium and high stability are formed in solutions.

**3.** The molecular and crystal structures of three polymorphic forms of organic ligands, one co-crystallizate and four complex compounds not described earlier have been determined. The existence of an unconventional type of coordination of zinc complex compound with 9,10-phenanthroline and 3,5-dinitrosalicylic acid was proved: the coordination number is 5, the polyhedron is a tetragonal pyramid, 3,5-dinitrosalicylic acid acts as a counterion.

4. It was found that the processes of thermal decomposition of synthesized complex compounds begin at 125-360 °C, which in some cases overlap with the process of degradation of organic components (up to 775 °C). The final products of thermal decomposition are micro-sized oxides of the corresponding metals (3-13  $\mu$ m). In the case of calcination of equimolar mixtures of complex compounds of divalent metals and corresponding titanium (IV) complexes, it was shown that the final products of decomposition are the corresponding nanoscale perovskite-like titanates (20-200 nm) with a small admixture of titanium oxide TiO<sub>2</sub> in the form of anatase. The specific surface area was determined for a number of nanoscale samples.

5. The possibility of using nickel titanate as an effective photocatalyst for the decomposition of bromophenol blue has been proved. It was found that zinc titanate, when introduced into cosmetic compositions, enhances the effect of organic UV filter, and the powder, the precursor of which was complex compounds of aromatic ligand  $L^8$ , has a greater synergistic effect compared to the powders obtained by decomposition of complex compounds based on heteroaromatic ligand  $L^1$ .

6. It is shown that the composite representing graphene oxide and natural mineral vermiculite modified by the developed technique with nanosized  $Fe_3O_4$  particles exhibit good adsorption properties towards methylene blue, congo red and alizarin red, which are not inferior to the known literature analogs.

7. In silico studies of biological activity have shown that 2,3dihydroxybenzoic acid and 3-methoxysalicylic acid, as well as their complexes with divalent metals can be considered as potential pharmacological drugs with the most probable route of penetration into the body through the gastrointestinal tract.

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