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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS AND PROPERTIES OF RHENIUM O- AND N-  
DONOR LIGAND COMPLEXES**

Speciality: 2303.01 - “Inorganic chemistry”

Field of science: Chemistry

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The work was performed at Azerbaijan State Oil and Industry University, laboratory of the "Chemistry and Technology of Inorganic Substances" department and SRL "New chemical materials and technologies".

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## GENERAL CHARACTERISTICS OF WORK

### **Relevance and degree of development of the topic:**

Inorganic chemistry is the basis for the creation of many important substances and materials that determine the future scientific and technological progress and functioning of our society. One of the main directions in the development of inorganic chemistry is the chemistry of coordination compounds. In the last decade characteristic trend in the development of inorganic chemistry is the intensive involvement of all elements of Mendeleev's periodic table in to the scientific and technical progress sphere. The coordination chemistry of rare elements has been specially developed. These elements are also related to rhenium. The level of knowledge in the rhenium chemistry has increased many times, although only 80 years have passed since the discovery of rhenium. New types of rhenium compounds with unusual chemical structures, new reactions that lead to the formation of chemical bonds - there are fundamental achievements in all these areas. This is explained by the fact that it is obtained in quantities in non-ferrous metallurgy which was previously difficult to get. The main areas of consumption of rhenium are the production of catalysts for the petrochemical industry, as well as the production of filter-neutralizers for exhaust gases from cars. Rhenium-promoted catalysts are widely used in various technological processes.

The unique valence potentials of rhenium are of interest from the point of chemical structure and bond theory view. All possible oxidation states for rhenium from +7 to -1 are realized, which provides a rich experimental material for a comprehensive study of the chemistry of this element. Rhenium itself is not necessarily toxic, but it has an important physiological effect in its compounds, which can be used for therapeutic purposes. Against the background of research in the field of complex compounds of rhenium with S- and P-containing ligands, there are certain gaps in the study of N- and O-containing ligand compounds. The current situation has played an important role in this research.

Another situation is the need for a comprehensive study of an important class of rhenium complex compounds - its compounds with nitrogen and oxygen-containing organic ligands. Despite the growing interest in the chemistry of rhenium in general, there are still many questions in the chemistry of this metal: regularities in the change of physical and chemical properties of its compounds, depending on the nature of the ligands, have not yet been studied.

In recent years, the coordination chemistry of rhenium has developed significantly due to the great interest in the development of radiopharmaceuticals. It has been determined that its complex compounds can be successfully used for the diagnosis and treatment of cancers of various human organs. In this case, the radiotherapeutic drug can be delivered directly to the human body in the form of certain types of ligands and structurally coordinated compounds with the help of specific molecular transmitters.

The problem of studying the scientific basis for the synthesis and practical use of rhenium (V) complexes remains relevant. Rhenium (V) complexes are of interest in the study of electron transfer and oxygen transport reactions, electroanalysis and photophysical properties. Most of the rhenium complexes used in radiotherapy are oxocomplexes, and therefore compounds containing the  $\text{Re} = \text{O}$  polar group are of great interest. For the chemistry of complex compounds among organic ligands, o-phenanthroline, nicotinamide, imidazole, benzimidazole and their derivatives, phthalocyanine are of greater interest. This is due to the presence of donor atoms of different nature in their composition. Their pharmacological properties allow their use in medicine, agriculture and some sectors of the economy.

**Object and subject of the research:** The object of the current research is the complex compounds of rhenium (V) with nitrogen and oxygen-containing organic ligands. The development of new principles and specific ways of their synthesis, as well as the study of some characteristic features of the chemical activity and structure of these compounds in order to identify more promising

substances than directed physiological activity are considered purposeful.

All these necessitates condition the search for new, convenient and purposeful methods of synthesis of rhenium (V) complexes with N- and O- containing ligands and a deeper study of the obtained compounds.

**Aim and objectives of the research:** development of optimal conditions and effective methods for the synthesis of new complexes with a number of organic ligands containing N- and O-donor atoms of rhenium in the presented dissertation and their composition, structure and physicochemical properties using physico-chemical methods are study of the nature of chemical bonds and types of coordination.

**Research methods:** A number of chemical and physicochemical analysis methods - IR and UV-spectroscopy, element analysis, EPR, thermogravimetry, etc. have been used for the identification of complexing reagents, the study of the composition and properties of complex compounds.

**The main provisions of the defense:** The following issues are included in the defense:

1. Development of methods for the synthesis of complex compounds of Re(V) with phenanthroline, nicotinamide, imidazole, benzimidazole and phthalocyanine;
2. Determination of the degree of oxidation of rhenium in the obtained complexes;
3. Study of the composition, structure and properties of compounds obtained by element analysis, IR spectroscopy, RSA thermal analysis methods;
4. Study of the laws of formation of the obtained complexes depending on the ratio of primary reagents, pH, concentration of hydrogen-halide acids;
5. Determination of electrolyte type in various organic solvents by conductometry of synthesized compounds and study of catalytic properties in oxidation reactions.

**Scientific novelty of the research:** Methods of synthesis of 19 previously undescribed complexes of rhenium (V) with a number of organic nitrogen and oxygen donor ligands, o-phenanthroline, nicotinamide, imidazole, benzimidazole and phthalocyanine have been developed and their structure and properties have been studied. All synthesized compounds have been characterized by infrared (IR spectroscopy), thermogravimetry, conductometry, EAS and element analysis methods. The electrochemical properties of some synthesized compounds have been studied. The structure has been characterized by X-ray structural analysis method. Depending on the type of ligands, their reversible individual electron oxidation or reduction ability has been determined. The concentration of hydrogen-halogen acids, which provide the formation of oxo- or oxohydroxycomplexes, and the thermal resistance of the synthesized complexes have been determined; The catalytic properties of the synthesized Re (V) complexes in oxidation reactions have been studied and the possibility of using these compounds as catalysts has been shown. The catalytic activity of the synthesized Re (V) complexes in the oxidation reactions of benzylphenylsulfide and cyclohexene has been studied and their possibility as a catalyst has been shown. Thermodynamic calculations have been carried out for some Re complexes and the thermodynamic properties have been determined. The oxidation state of rhenium in all the obtained complexes has been defined by potentiometric titration analysis method. The transfer of rhenium phenanthroline complexes from the outer sphere of the ligand to the inner sphere, the monodentate coordination of the nicotinamide complex by the heterocyclic nitrogen atom and the dimer structure have been determined by physicochemical methods. The monodentate coordination of rhenium imidazole complexes and the presence of the Re=O polar group in all compounds have been confirmed. The dependence of the composition of benzimidazole complexes on the concentration of HCl and HBr acids, the ratio of reagents and monodentate coordination by the nitrogen atom of the ligand has been found. A new method of synthesis of rhenium phthalocyanine complex has

been proposed. As a result of the synthesis, only one form of rhenium phthalocyanine complex has been obtained and the structure of PcReO has been determined. Methods for the synthesis of cluster compounds of rhenium with carbonyl- and amine-containing organic bifunctional ligands have been developed. The tetrahedral structure of the synthesized cluster complexes has been confirmed by physicochemical methods.

**Theoretical and practical significance of the research:**

- The developed synthesis schemes of coordinated compounds of rhenium (V) can be used for purposeful synthesis of complexes with other classes of organic ligands. Isolated rhenium (V) complexes can be used as biologically active substances;
- Theoretical and experimental evidence obtained from physicochemical studies of synthesized complex compounds is considered a contribution to the development of modern bioinorganic chemistry and can be used in scientific research.

**Approbation and application:** The main results of the dissertation have been presented and discussed at the following Republican and International conferences. Scientific conference dedicated to the 90th anniversary of T.N. Shakhtakhtinsky (Baku 2015), XXIX Scientific and technical conference "Chemical reagents, reagents and processes of low-tonnage chemistry" - Abstracts of reports. «REACTIVE-2015», (Novosibirsk 2015), XIX and XX Republican scientific conference of doctoral students and young researchers, (Baku 2015,2016), VI Republican scientific conference dedicated to the 80th anniversary of the "Analytical Chemistry" department, (Baku, 2015), XI All-Russian scientific - technical conference "Actual problems of development of the oil and gas complex of Russia", (Moscow 2016), XXIV International scientific-practical conference "Actual problems in modern science and their solutions", (Moscow 2016), IX International Conference XXI century, (Moscow 2016), II All-Russian scientific-practical conference with international participation" Science in motion: reflection on the creation of reality "(Almetyevsk 2017) Turkic World Conference On Chemical Sciences and Technologies (Baku

2017), “Natural disasters and human life safety” International scientific-technical conference (Baku 2017), “Oil and Gas 2018,2019” 72nd and 73th International Youth Scientific Conference (Moscow 2018,2019), International Scientific Conference “Actual Problems of Modern Natural and Economic Sciences” (Ganja 2018,2019), “Actual Chemistry problems” XII and XIII International scientific conference (Baku 2018,2019),“Innovative perspectives of development of oil refining and petrochemistry”(Baku 2018), Scientific conference “Nagiyev readings”dedicated to the 110th anniversary of Academician M. Nagiyev (Baku 2018), "Innovative materials and technologies-2019" (Minsk 2019), “Radiation and chemical safety problems” International scientific-technical conference(Baku 2019), “Prospects for Innovative Development of Chemical Technology and Engineering” (Sumgayit 2019), XVIII International Scientific-Practical Conference “Natural and Intellectual Resources of Siberia (Siberia 2020), Actual Problems of Chemical Engineering. International Conference dedicated to the 100th Anniversary of Azerbaijan State Oil and Industry University (Baku 2020).

**Name of the organization where the dissertation work has been carried out:** The dissertation work has been carried out in the laboratory of the "Technology of Chemistry and Inorganic Compounds" department and SRL “New chemical materials and technologies” of the Azerbaijan State University of Oil and Industry.

**Total volume of the thesis with symbols taking into account it's structural sections individually:** Introduction- 10294, I chapter- 55719, II chapter- 26301, III chapter- 87274, total-211102symbols.

**Structure and volume of the thesis:** The thesis consists of the introduction, 3 chapters, literature sources review, experimental part, discussion and results. The thesis consists of 154 pages of computer text, 43 figures and 25 tables.

**The author's contribution:** in carrying out experimental researches, working out literature sources information, preparing of articles and thesis was significant.



## MAIN CONTENT OF THE WORK

**The introductory part of the dissertation** shows the relevance of the topic, the specific purpose of the work, the scientific novelty of the work, its practical significance, the structure and scope of the work, approbation.

### **In the first chapter**

The first chapter, consisting of six sections, presents a review of the references on research in the field of synthesis, structural properties and properties of complex compounds of rhenium with nitrogen- and oxygen-containing ligands. Particular attention has been paid to cluster compounds of rhenium, which are of interest in terms of structure and biological activity.

An analysis of the references has shown that there are some gaps in the study of rhenium compounds with N- and O-ligands against the background of studies of complex compounds with S- and P-ligands. The current situation has played an important role in the current research.

### **In the second chapter**

Information has been provided on the initial reagents, their properties, experimental techniques, research methods used (element analysis, IR-, UV-, electron absorption spectroscopy EAS, EPR, thermogravimetry, RSA and molar electrical conductivity).

It summarizes the experimental evidence, which shows the methodology for the synthesis of complex compounds of rhenium (V) with phenanthroline of different composition and different structure, amide of nicotinic acid, imidazole, benzimidazole and phthalocyanine. Selection of the mentioned ligands is connected with the presence of N- and O- donor atoms in their composition and their biological activity. Considering structural properties of ligands, their chemical and physiological activity have been forecasted in advance.

### **In the third chapter**

#### **Renium complex compounds with phenanthroline.**

The interest in the use of phenanthroline as a ligand is due to the fact that it contains two donor nitrogen atoms and is coordinated with

metals as a bidentate ligand. 8 complex combinations of Re (V) with phenanthroline have been obtained.

The synthesis is resulted in obtaining of three types - oxo-, hydroxo- and aqua complexes. IR spectrum of the synthesized complexes have been taken. In the IR spectrum of [Re(Phen)(Ph<sub>3</sub>P)OCl], the absorption bands disappear at 3336 cm<sup>-1</sup>, which is related to the ν (N - H) vibration of the nitrogen atom protonated in the primary ligand. When Phen enters the inner sphere of the rhenium metal, the absorption bands at 840 cm<sup>-1</sup> slide into the high-frequency field with a decrease in intensity, which is evidence of the entry of phenanthroline into the inner coordination sphere of the metal. Absorption bands of coordinated triphenylphosphine in the spectrum of the complex maintain their position relative to the spectrum of the original [ReO(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>]. The band belonging to ν (Re = O) also maintains its position at 968 cm<sup>-1</sup> by reducing its intensity only to a certain extent.

The IR frequencies of the primary reagents and the rhenium phenanthrol [ReO(Phen)(PPh<sub>3</sub>)Cl<sub>2</sub>]Cl complex are compared in Table 1.

**Table 1**

**Characteristic IR frequencies of [ReO(Phen)(PPh<sub>3</sub>)Cl<sub>2</sub>]Cl complex**

Complex	ν(N-H) (cm <sup>-1</sup> )	ν(C-H) (cm <sup>-1</sup> )	ν(Re=O) (cm <sup>-1</sup> )
Phen	3336	840, 775, 715	-
[ReO(PPh <sub>3</sub> )Cl <sub>3</sub> ]	-	-	968
[ReO(Phen)(PPh <sub>3</sub> )Cl <sub>2</sub> ]Cl	-	848	968

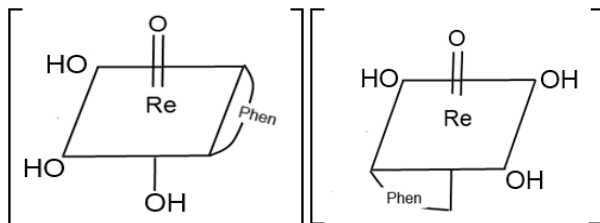
IR spectra of rhenium complex with phenanthroline [ReO(Phen)(OH)<sub>3</sub>] are also given. The presence of hydroxyl groups around rhenium is confirmed by the formation of ν(OH<sup>-</sup>) valence oscillations at 3300 cm<sup>-1</sup> and ν(OH<sup>-</sup>) deformation oscillations at 1044 cm<sup>-1</sup>. At 720, 780, 848 cm<sup>-1</sup>, and so on, absorption bands belonging to π(C-H) coordinated phenanthroline are observed. In this complex, ν(Re = O) valence oscillations occur at 912 cm<sup>-1</sup> (Table 2).

**Table 2**

**Characteristic IR frequencies of Phen and [ReO(Phen)(OH)<sub>3</sub>] complex**

Compound	$\nu(\text{OH}^-)$ ( $\text{cm}^{-1}$ )	$\sigma(\text{OH}^-)$ ( $\text{cm}^{-1}$ )	$\nu(\text{C-H})$ ( $\text{cm}^{-1}$ )	$\nu(\text{Re=O})$ ( $\text{cm}^{-1}$ )
Phen			840, 775, 715	
[ReO(Phen)(OH) <sub>3</sub> ]	3300	1044	848, 780, 720	912

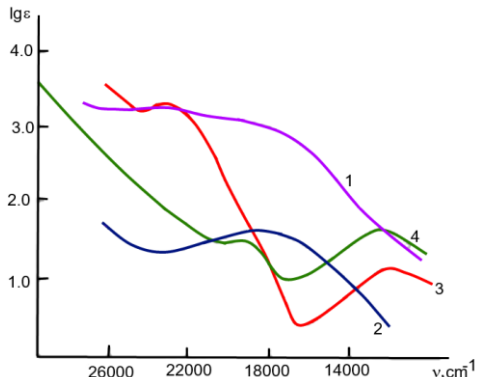
Such a very large displacement of the absorption band Re = O compared to the original [ReO(PPh<sub>3</sub>)Cl<sub>3</sub>] with the same band can be explained by the change in the ligand coverage of the rhenium atom. The following two structural formulas for this compound can be proposed on the basis of elemental analysis and measurements of electrical conductivity of the phenol-containing [ReO(Phen)(OH)<sub>3</sub>] complex obtained as a result of synthesis.



The general nature of the EAS of acetonitrile solutions of synthesized compounds is the presence of three absorption bands (48200-49600, 45200-45500, 36880-37560  $\text{cm}^{-1}$ ) characterizing the chromophore system of phenanthrol in the UV field, which proves the fact of its inclusion in the studied complexes. However, the distinguishing feature of each of the studied compounds is the individuality of the formation of absorption bands in the visible field due to the electronic transition in the metal-ligand system, depending on the nature and spatial structure of groups in the sphere of ligand coverage, which can be used to identify the obtained complexes.

The transition of phenanthroline from the inner sphere to the ligand sphere of rhenium (V) is proved by the change in the nature of EAS [PhenH<sub>2</sub>][ReOBr<sub>5</sub>] → [ReOPhenBr<sub>3</sub>] (Figure 1). In this case, a

slight hypochromic displacement ( $600\text{ cm}^{-1}$ ) is observed for longitudinal bands ( $[\text{PhenH}_2][\text{ReOBr}_5]$  combination) at approximately  $12,000\text{ cm}^{-1}$ , so that at  $19,000\text{ cm}^{-1}$  instead of a strip at  $19,000\text{ cm}^{-1}$ , a maximum consisting of hyperchrome effect expressed two stripes ( $23560$  and  $22400\text{ cm}^{-1}$ ) occurs.

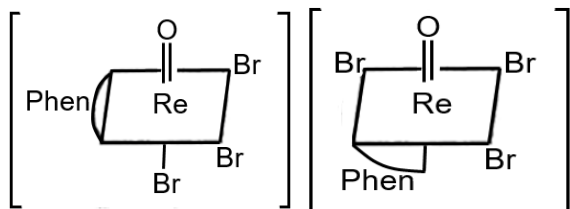


**Fig.1. Electron absorption spectra of complex compounds of rhenium (V) with o-phenanthroline.**

- 1 -  $[\text{ReO}(\text{Phen})(\text{Ph}_3\text{P})\text{Cl}_2]\text{Cl}$ ; 2 -  $[\text{ReO}(\text{Phen})(\text{OH})_3]$ ;  
3 -  $[\text{PhenH}_2][\text{ReOBr}_5]\cdot\text{H}_2\text{O}$ ; 4 -  $[\text{ReO}(\text{Phen})\text{Br}_3]$**

A derivatogram of the  $[\text{PhenH}_2][\text{ReOBr}_5]\cdot\text{H}_2\text{O}$  complex has been drawn and two endothermic effects have been observed. One corresponds to the separation of water of crystallization water at  $87^\circ\text{C}$ , the other – to the Andersen grouping at  $187^\circ\text{C}$ .

In view of the above, for the structure  $[\text{ReO}(\text{Phen})\text{Br}_3]$  complex the following structure has been proposed.



**The structure of the  $[\text{ReO}(\text{Phen})\text{Br}_3]$  compound**

Compounds containing  $\text{PhenH}_2[\text{ReOHal}_5]$  have been obtained, and as a result of their thermal decomposition, compounds containing  $[\text{ReOHal}_3\text{Phen}]$  have been synthesized. It has been found that thermal decomposition continues with the release of the corresponding hydrogen halide and the displacement of the phenanthroline molecule from the outer sphere to the inner sphere. The study of the complex formation of rhenium (V) with phenanthroline in HCl at different temperatures showed that the process of adding  $\text{H}_2[\text{ReOCl}_5]$  to a system consisting of phenanthroline and its oxidized form increases the potential, which in turn with rhenium (V). proves the presence of phenanthroline, not its oxidized form, in the process of complex formation.

After the addition of a small amount of  $\text{H}_2[\text{ReOCl}_5]$ , the solution turns brown during the titration process, which gradually changes to dark purple, blue, and green as the concentration of rhenium (V) increases. When phenanthrol is added to a green solution, the color of the solution changes in the opposite direction. Determining the value of  $\Delta E$  at each titration point, we calculate the equilibrium concentration of phenanthroline, using which we calculate the value of  $\bar{n}$ .

Experimental results have been obtained to determine the function of the formation of oxychlorophenanthroline complexes of rhenium (V) in the temperature range 273-338 K in an environment of 4-6 mol/l HCl.

Based on potentiometric titration data, curves for the formation of oxychlorophenanthroline complexes of rhenium (V) at different temperatures have been constructed, which proves the similarity of the process of complex formation in the temperature range 273-338 K. Regardless of temperature, five consecutive complex forms of rhenium (V) with phenanthroline have been formed. The formation curves of oxychlorophenanthroline complexes of rhenium (V) at different temperatures in 6 mol/l HCl medium have been determined and the  $\text{pK}_i$  value is shown in Table 3.

**Table 3****PK<sub>i</sub> value for rhenium (V) oxochlorophenanthroline complexes in 6 mol/l HCl medium at 273-338 K**

T, K	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>	pK <sub>4</sub>	pK <sub>5</sub>
273	3.98	3.6	3.22	2.85	2.35
288	3.75	3.3	2.9	2.5	2.14
298	3.59	3.13	2.72	2.33	2.02
308	3.47	2.96	2.52	2.08	1.8
318	3.38	2.86	2.41	2.00	1.76
328	3.2	2.68	2.26	1.92	1.7
338	3.00	2.47	2.01	1.77	1.66

It can be seen from Table 3 that all stepwise formation constants of rhenium (V) oxochlorophenanthroline complexes in 6 mol/l HCl medium decrease with increasing temperature, which proves the exothermicity of the complex formation process.

The value of the resistance constant has been used to evaluate the thermodynamic characteristics of the complex formation process by the temperature coefficient method. Analysis of thermodynamic properties indicates the values of  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ; for monosubstituted complexes increase with the raise of HCl concentration.

**Complex compounds of Re (V) with nicotinic acid amide (NAA).**

It is known from the literature that the amide group does not tend to coordinate through the nitrogen atom. The presence of two other donor atoms in the amide molecule of nicotinic acid suggests the possibility of both monodentate and bidentate coordination. 1 complex compound of Re (V) with nicotinic acid amide has been obtained and its composition has been determined by elemental analysis.

The IR spectrum of this complex remains virtually unchanged at 1680 cm<sup>-1</sup> (as in the free ligand spectrum), while the other slides into a longer wavelength range up to 1650 cm<sup>-1</sup>. This separation may

be due to the interaction of *sis*-located nicotinamide molecules and the unequal value of the carbonyl groups of the two ligands due to the possible formation of intramolecular hydrogen bonds. At 1620  $\text{cm}^{-1}$ , the absorption band associated with the deformation vibration of the  $\text{NH}_2$  group does not change in the spectrum of the complex, which allows us to assume the lack of coordination of nicotinamide with carbonyl oxygen or amino group nitrogen. The separation of the absorption bands of the free ligand into 1010  $\text{cm}^{-1}$  and 1020  $\text{cm}^{-1}$  components in the spectrum of the complex at 1030  $\text{cm}^{-1}$  pertaining to the vibration of the heterocyclic ring indicates NTA coordination in the central rhenium atom by the heterocyclic nitrogen atom. Absorption bands corresponding to the vibration of the Re-O-Re bond are accompanied. However, there is a vibration of the Re-P bond, so it is not possible to accurately assign the sector in this area. (925  $\text{cm}^{-1}$ ) slipped. Such a very small value of  $\nu$  (Re = O) is observed in a dimer with a linear grouping  $\text{O} = \text{Re} - \text{O} - \text{Re} = \text{O}$  (Table 4).

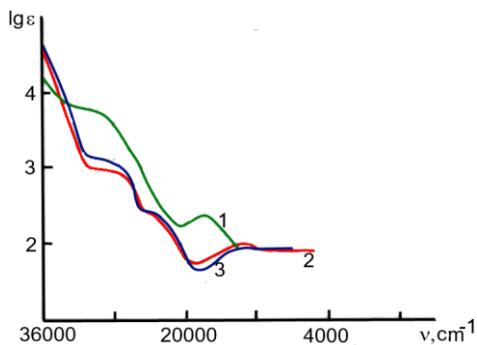
**Table 4**  
**Characteristic IR frequencies of NAA and its complex**

Compound	$\nu(\text{C}=\text{O})$ ( $\text{cm}^{-1}$ ) “amid I”	$\nu(\text{NH}_2)$ ( $\text{cm}^{-1}$ ) “amid II”	$\nu(\text{circle})$ ( $\text{cm}^{-1}$ )	$\nu(\text{Re}=\text{O})$ ( $\text{cm}^{-1}$ )
NAA	1680	1620	1030	
$[\text{Re}_2\text{O}_5(\text{NAA})_2(\text{Ph}_3\text{P})_2\text{Cl}_4]$	1680, 1650	1620	1050, 1020	925

The study of EUS of complex compounds in different solvents shows that the spectral picture in the visible field changes over time. For the study, have been used complex solutions in solvents such as dimethylformamide, acetonitrile and chloroform. The density of the solution is  $C = 2.07\text{-}3.21 \text{ mol/l}$ .

It has been found that the spectral picture in the visible field changes over time. Thus, the rate of change depends on the nature of the solvent: the more the solvent is considered a donor, the higher the

rate of change. Thus, the spectrum taken immediately after the solution of the complex in DMFA gives three detectable maximums in the visible field ( $13500$ ,  $17880$  and  $29160\text{ cm}^{-1}$ ), chloroform ( $23000\text{ cm}^{-1}$ ) and maximum in the UV field (acetonitrile)  $38260\text{ cm}^{-1}$ . The position of the last two maxima does not change over time, but at  $17880\text{ cm}^{-1}$  in the visible area the strip disappears completely within 6 hours. In acetonitrile, such an event is observed after two days, while in chloroform, the spectral picture does not change. According to the literature, the absorption bands at  $13500\text{ cm}^{-1}$  and  $17880\text{ cm}^{-1}$  can be attributed to the oxychloride complexes of rhenium (V). Also, the strips at  $23,000\text{ cm}^{-1}$  prove once again the dimer structure of the complex. The disappearance of the bands over time at  $17880\text{ cm}^{-1}$  can be explained by the replacement of the acidoligand solvent with donor molecules, the interaction with which is not detected in this area of the spectrum. The invariant retention of the bands characterizing the chromophore system of nicotinamide ( $29160$  and  $38260\text{ cm}^{-1}$ ) indicates that nicotinamide is more strongly bound to the complex than to the chloride ion (Figure 2).



**Fig.2 EUS of  $[\text{Re}_2\text{O}_3(\text{NAA})_2(\text{Ph}_3\text{P})_2\text{Cl}_4]$  solution  
When  $C = 6 \cdot 10^{-4}\text{ mol/l}$  immediately after preparation (1);  
6 hours later (2); 18 hours later (3).**

In DMFA, the molar electrical conductivity changes over time at a concentration of  $C = 1 \cdot 10^{-3}\text{ mol/l}$  of the complex solution. After the solution of the complex sample, the value of molar

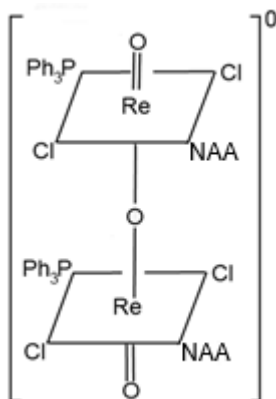


electrical conductivity corresponds to a non-electrolytic type compound ( $25000 \text{ m}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ), then gradually increases and in 1 hour it reaches to a value corresponding to 1: 1 electrolyte ( $65100 \text{ m}^{-1}\cdot\text{cm}^2$ ).

Subsequently, the increase in the cost of molar conductivity weakens. In 4 hours, it reaches  $80050 \text{ m}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ . One day later the start of the experiment, measurements show that stabilization occurs and the value of molar electrical conductivity ( $65\text{-}900 \text{ m}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ) did not go beyond the value corresponding to a 1: 1 type electrolyte ( $83760 \text{ m}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ).

The research allows to give the structure of the following complexes.

### Structure of the complex $[\text{Re}_2\text{O}_3(\text{NAA})_2(\text{Ph}_3\text{P})_2\text{Cl}_4]$



Thermodynamic parameters of the process of complex formation of rhenium (V) with NAA in anhydrous and mixed (water-ethanol and water-DMSO) solvents have been studied. Stability indicators of the complexes have been determined.

Based on the results obtained, the monodentate coordination of nicotinamide through the heterocyclic nitrogen atom has been determined and the two-nucleated structure was confirmed.

### Complex compounds of rhenium (V) with imidazole.

The next ligand we studied, imidazole, is important for biochemical processes. The imidazole system is based on essential

amino acids histidine, which play an important role in enzymatic proton exchange processes. 6 complex combinations of Re (V) with imidazole have been synthesized and the composition of the complexes has been determined by the element analysis method.

It is known that rhenium in different compounds has a degree of oxidation from +1 to +7. Such an estimate of the degree of oxidation suggests that the rate of oxidation of rhenium +5 may change as a result of disproportionation in the interaction of primary compounds containing  $H_2[ReOHa_5]$  with ligands, oxidation by air, redox reactions in the presence of organic ligands.

In this regard, it is important to determine the degree of oxidation of rhenium in the synthesized complex compounds. For this purpose, potentiometric titration method has been used in the study. Evidence for determining the degree of oxidation of rhenium for some of the synthesized complexes is shown in Table 5.

**Table 5**

**Evidence for the determination of the degree of oxidation of rhenium in complex compounds by potentiometric methods**

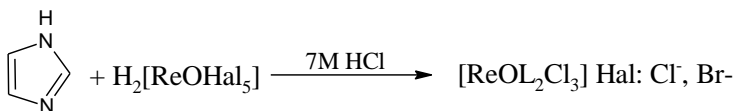
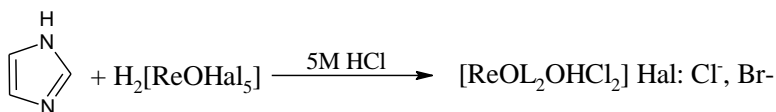
№	Compound	Volume of oxidizer at equivalent point, ml	Mass of complex	Number of electrons	Oxidation rate
1	$[ReO(H_2O)OHLCl_2]$	0,70	0,0203	2	5,0
2	$[ReO(H_2O)OHLBr_2]$	0,74	0,0285	2	5,1
3	$[ReO(OH)L_2Cl_2]H_2O$	0,77	0,0302	2	5,1
4	$[ReO(OH)L_2Br_2]H_2O$	0,68	0,0296	2	5,03

As it can be seen from the data in Table 5, rhenium retains five oxidation states in all synthesized complex compounds. This means that the rate of oxidation of rhenium does not change and remains constant as a result of the synthesis of complex compounds of Re (V) with imidazole.

The interaction of  $H_2[ReOHal_5]$  (Hal = Cl, Br) in different media of hydrogen-halogen acids and different proportions of primary reagents leads to the formation of oxo-, oxohydroxycomplexes according to the following scheme.

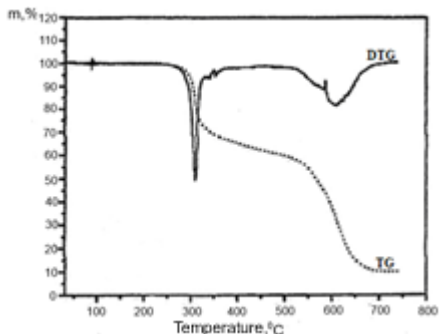
It was found that depending on the concentration of hydrogen-halide acids, complexes with different ligand coverage are formed. Oxocomplexes containing  $[ReOHal_3L_2]$  are formed when the acid concentration is high, and  $[ReOHal_2(OH)L_2]$  when the acid concentration is low.

### Interaction of $H_2[ReOHal_5]$ (Hal = Cl, Br) with hydrogen-halogenic acids in different media



In the IR spectra of these compounds, the valence band of renin groups is found at  $980\text{ cm}^{-1}$ , which indicates the formation of oxocomplexes and proves their octahedral structure.

Purposeful studies have been conducted to study the process of thermal decomposition of rhenium (V) complex compounds. The study of the thermal properties of complexes containing  $[ReOBr_3L_2]$  proves the absence of coordinated molecules and water of crystallization. The thermogram of the complex containing  $[ReOBr_3L_2]$  is shown (Figure 3).

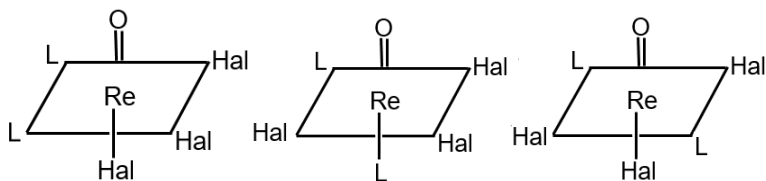


**Fig.3. Thermogram of a complex containing  $[\text{ReOBr}_3\text{L}_2]$**

The compound containing  $[\text{ReOBr}_3\text{L}_2]$  begins to decompose at high speed with an exo-effect, starting at  $300^\circ\text{C}$ , the mass of the complex is reduced by 65%, which corresponds to the separation of two molecules of hydrogen bromide or rhenium oxide. The process of thermolysis of this complex is completed at  $560\text{--}600^\circ\text{C}$ .

Based on the evidence of X-ray structural analysis, crystallographic data and values of valence angles and main bond lengths have been obtained for 2 types of rhenium complexes containing imidazole.

Based on the results of all research methods, the following structures can be proposed for the complex.



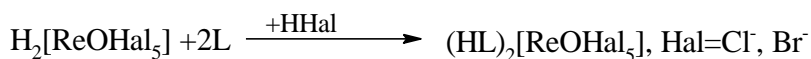
New coordinated compounds of Re (V) with imidazole have been synthesized and characterized. It has been determined by IR spectroscopic method that all ligands in the obtained complexes have been monodentate coordinated. Strips characteristic of  $\nu(\text{Re}=\text{O})$  valence oscillations have been found in the IR spectra of all complexes.

### Complex compounds of Re (V) with benzimidazole.

Compounds synthesized to determine the method and composition of rhenium (V) coordination with benzimidazole have been studied by IR spectroscopy, thermogravimetry, conductometry. New complexes of rhenium with benzimidazole ligand have been synthesized and studied by the method of approximate element analysis.

Complexes of benzimidazole with transition metals d have a molecular nature. In addition, benzimidazole and its derivatives present themselves as Lewis bases, and metal ions precipitate in aqueous solution in the form of hydroxides, so the formation is carried out in a strongly acidic environment, not in an aqueous medium. The location of ligands is determined by spectral characteristics or by other images (eg, -derivatographic).

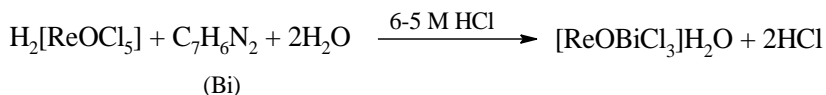
In the production of the studied complexes, 1-8 mol/l hydrogen chloride and hydrogen bromide acid medium have been used. Protonated molecules of ligands are released in the form of complex ions from a strongly acidic environment (7-8 mol/l acid solution).



Comparison of IR spectra of these complexes with IR spectra of free ligands allows to say the following results: first, it consists of an absorption band  $\nu$  (Re = O) in the area of  $1000 \text{ cm}^{-1}$ , the oscillations of Re-Hal bonds occur in the lower  $400 \text{ cm}^{-1}$ . The second characteristic for similar molecular complexes shows the coordination of ligands in the area of  $1400\text{-}1900 \text{ cm}^{-1}$ .

As a result of lowering the concentration of hydrogen-halogen acids to 5-6 mol/l, the complex, which passes into the inner sphere of benzimidazole rhenium (V) ion, is separated with the removal of halogen ions from there, as a rule, excess ligand leads to the formation. These are fundamentally different from the complexes of rare earth elements with benzimidazole. In addition, the water molecule replaces the halogen ions in the sphere of internal

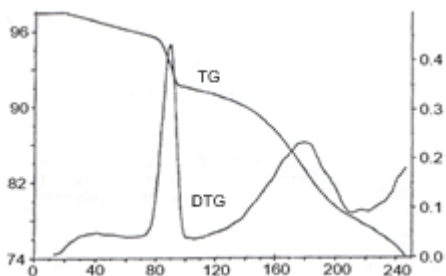
coordination. Thus, the reaction of formation of molecular complexes of rhenium (V) with benzimidazole can be described as follows.



As it can be seen from the spectra, the distribution of intensive doublet bands in complexes at 800-900  $\text{cm}^{-1}$  occurs at a maximum of 740 and 710  $\text{cm}^{-1}$ , and the displacement of absorption bands in ligands occurs. The difference in the ratio of external and internal spherical waters is clearly visible in the derivatograms.

Thus, for complexes without coordinated water, the reduction in mass is due to the decomposition of the ligand, which begins at 220-280°C, while the water of the outer sphere decomposes at 65-80°C. The water of the inner sphere begins to decompose at 120-130°C. The loss of mass corresponds to the number of moles of coordination water.

[ReOLHal<sub>3</sub>(H<sub>2</sub>O)] for H<sub>2</sub>O-containing complexes, there are two stages in the separation of the H<sub>2</sub>O molecule. Crystalline water separates at 65-90°C, a second endo effect is observed with increasing temperature (Fig.4). This occurs as a result of its dimerization with the removal of HCl and coordinated water molecules from the complex.



**Fig.4. Absolute and relative curves of the complex mass with [ReOLCl<sub>3</sub>(H<sub>2</sub>O)]H<sub>2</sub>O composition.**

The collapse of the complex begins at 250°C. In the IR spectrum of the heated product at 910-990 cm<sup>-1</sup>  $\nu_{as}(\text{Re} = \text{O})$  at 725 cm<sup>-1</sup> characteristic bands for was (Re-O-Re) oxygen-bridged dual-core rhenium complexes are visible. As the temperature rises to 160°C, mononuclear complexes form bipolar compounds, which are bridged ligands in the benzimidazole molecule. The composition and properties of compounds coordinated with conductometry, one of the electrochemical methods, have been studied.

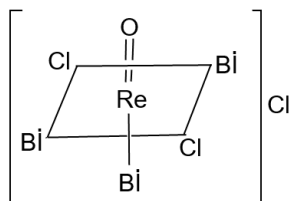
**Table 6**

**Values of molar electrical conductivity of rhenium (V) with benzimidazole**

№	Compounds	Solvents	$\mu, \text{Om}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$			
			20°C	30°C	40°C	50°C
1	(HL) <sub>2</sub> [ReOCl <sub>5</sub> ]	Acetone	180,60	168,00	154,20	144,70
		Methanol	200,47	198,60	196,30	192,44
		DMFA	159,96	132,21	119,68	89,34
2	(HL) <sub>2</sub> [ReOBr <sub>5</sub> ]	Acetone	198,74	190,02	186,55	170,21
		Methanol	206,45	202,93	198,23	196,66
		DMFA	167,54	144,17	128,96	90,09
3	[ReOLCl <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	Acetone	43,61	46,96	49,96	52,31
		Methanol	59,45	69,26	69,26	74,38
		DMFA	20,22	44,52	44,52	67,96
4	[ReOLBr <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	Acetone	46,64	48,73	50,09	53,95
		Methanol	62,25	67,33	71,64	77,56
		DMFA	21,26	38,48	49,71	71,42
5	[ReOLCl <sub>3</sub> ]·2H <sub>2</sub> O	Acetone	30,62	31,16	32,21	35,39
		Methanol	52,92	56,28	61,88	69,24
		DMFA	32,64	42,05	48,96	62,51
6	[ReOLBr <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	Acetone	42,54	46,91	50,50	54,64
		Methanol	66,62	68,91	72,26	74,09
		DMFA	36,36	49,72	56,68	64,84
7	[Re <sub>2</sub> O <sub>3</sub> L <sub>2</sub> Br <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]·2H <sub>2</sub> O	Acetone	8,18	8,24	8,71	8,80
		Methanol	10,69	14,49	20,06	30,21
		DMFA	40,69	56,24	72,82	116,93

In the outer sphere, coordinated compounds consisting of ions of one or another sign are usually electrolytes, and their solutions, like those of simple salts, are carried out in the same way as themselves. However, the molar value of the electrical conductivity of solutions of complex compounds characterizes the durability of the solvent (Table 6). As it can be seen from Table 6, a complex containing  $(HL)_2[ReOHal_5]$  has a molar value of electrical conductivity according to type 2: 1 electrolytes. The molar value of the electrical conductivity of methanol does not change significantly with increasing temperature. Respectively, in acetone and DMFA, as the temperature rises to  $50^\circ\text{C}$ , the value of  $\mu$  decreases to the value of a 1: 1 type electrolyte.

Taking into account all of the above, the resulting complex can be described as follows.



The dependence of the composition of the synthesized benzimidazole complexes on the concentration of HCl and HBr, the ratio of reagents and the coordination of the monodentate by the ligand nitrogen atom have been determined.

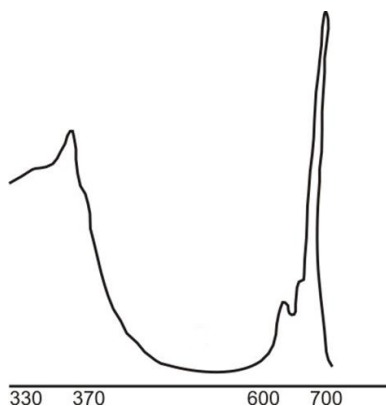
### **Complex combination of rhenium (V) with phthalocyanine**

Research in the field of metal phthalocyanine complexes (PcM) has developed rapidly over the last decade. The interest in this class of compounds is due to the fact that phthalocyanines, which are widely used in nature as synthetic analogues of porphyrins, exhibit unique physicochemical properties, semiconducting and catalytic properties, and are considered promising for use as catalysts in hydrocarbon oxidation reactions.



Figure 5 shows the EAS of the solutions, with the peak height ratio of the main bands (368–370 and 651–697 nm) being 45%; 625-630 and 668 nm satellites do not dissolve well, which is typical for monomeric forms of phthalocyanines. Looking at the spectra, it appears that only one form of rhenium phthalocyanine and ruthenium phthalocyanine is formed as a result of synthesis.

In the IR spectrum of the complexes there is a band at 940-945  $\text{cm}^{-1}$ , which corresponds to the  $\text{Re} = \text{O}$ , bond. The absence of any band in the range 3100-3700  $\text{cm}^{-1}$  indicates that neither the ligand nor the metal atom contains an OH group.



**Fig.5. Electron absorption spectrum of rhenium complex with phthalocyanine**

The synthesis of rhenium phthalocyanines has been carried out by the reaction of triple-butylphthalodinitrile with ammonium perrenate, and the structural properties of the obtained complexes have been studied using IR, UB/Vis and EPR spectra. It has been shown that the obtained complexes contain high-covalent  $\text{Re} = \text{O}$  groups and do not show the EPR spectra characteristic of paramagnetic rhenium complexes with rhenyl bonds. It has been found that the formation of bands at 945  $\text{cm}^{-1}$  in the IR spectra of

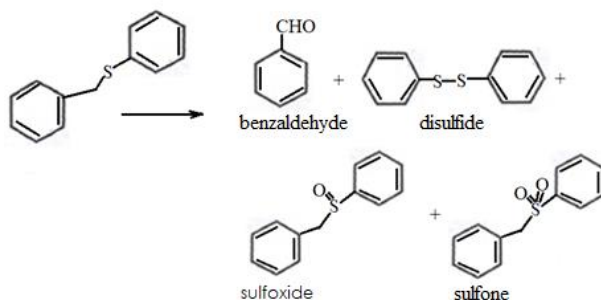
rhenium phthalocyanine complexes is associated with renin binding in the complex.

A new method of synthesis of rhenium phthalocyanins, characterized by availability and high yield, has been proposed. It has been found that only one form of rhenium phthalocyanine is formed as a result of synthesis, which can also be written as  $\text{PcReO}$  on the basis of physicochemical studies. The catalytic properties of the synthesized  $\text{Re (V)}$  complexes in oxidation reactions have been studied and the possibility of using these compounds as catalysts has been shown.

### Study of catalytic properties of rhenium complexes

Two types of N- and O-containing ligands of the synthesized complex compounds: 1) amide of nicotinic acid, 2) imidazole have been studied in catalytic oxidation reactions.

Oxidation of benzylphenyl sulfide has been carried out at room temperature using catalysts  $[\text{ReOL}^2_2\text{Cl}_3]$ ,  $[\text{ReOL}^2_2\text{Br}_3]$ ,  $[\text{ReOL}^3_2\text{Cl}_3]$ ,  $[\text{ReOL}^3_2\text{Br}_3]$ . For this purpose, hydroxide peroxide and a catalyst were added to the acetonitrile solution of benzylphenylsulfide. The reaction lasted 3 hours and the course of the reaction has been monitored by high-performance liquid chromatography. The oxidation reaction of benzylphenylsulfide is shown in the following diagram.



As a result of oxidation of benzylphenylsulfide, the composition of benzylphenylsulfoxide and benzylphenylsulfone

[ReOL<sub>2</sub>Cl<sub>3</sub>] has been mixed with a maximum conversion of 91% for the complex. For a complex containing [ReOL<sub>2</sub>Br<sub>3</sub>], the reaction is selective for 81% complexes. In addition to improving conversion, the complexes also provide selectivity in the sulfoxide reaction.

According to the results of the study, the reaction rate for the [ReOL<sub>2</sub>Cl<sub>3</sub>] complex (mol product/mol.cat.hours) is 28, and for [ReOL<sub>2</sub>Br<sub>3</sub>] it is 30.

The second test substrate was cyclohexene, which also allows the differentiation of hetero- and homolytic oxidation mechanisms, such as benzylphenylsulfide. The synthesized rhenium metal complexes produce products typical of heterolytic oxidation mechanisms (epoxy and trans-cyclohexene-1, 2-diol) along with products typical of homolytic oxidation mechanisms (2-cyclohexene-1-ol and 2-cyclohexene-1-on).

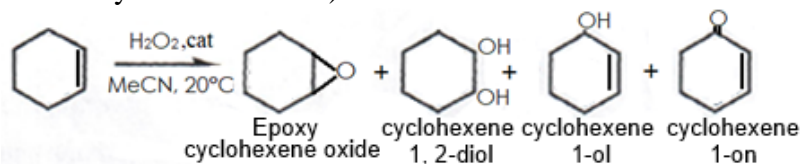


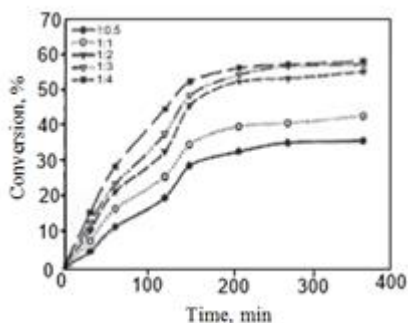
Table 7 shows the results obtained for the conversion of cyclohexene and the selectivity of various oxidation products 6 hours after the start of the reaction.

**Table 7**

**Oxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub> in the presence of rhenium catalysts**

	Catalyst	Oxidative	Conversion, %	Selectivity, %			
				Epoxy	SH-diol	SH-ol	SH-on
1	[ReOL <sub>2</sub> <sup>2</sup> Cl <sub>3</sub> ]	H <sub>2</sub> O <sub>2</sub>	35	37	8	-	53
2	[ReOL <sub>2</sub> <sup>2</sup> Br <sub>3</sub> ]	H <sub>2</sub> O <sub>2</sub>	31	43	5	-	50
3	[ReOL <sub>2</sub> <sup>3</sup> Cl <sub>3</sub> ]	H <sub>2</sub> O <sub>2</sub>	43	32	6	-	51
4	[ReOL <sub>2</sub> <sup>3</sup> Br <sub>3</sub> ]	H <sub>2</sub> O <sub>2</sub>	39	37	9	-	48

As it can be seen in Table 7, the highest selectivity is in the use of a complex containing  $[\text{ReOL}_2\text{Cl}_3]$ . The conversion dependence is given by the reaction time shown in Figure 6 and the different ratios of  $\text{H}_2\text{O}_2$  cyclohexene. As the proportion of  $\text{H}_2\text{O}_2$  cyclohexene increases, the conversion decreases from 55% to 30% when using the  $[\text{ReOL}_2\text{Br}_3]$  complex.

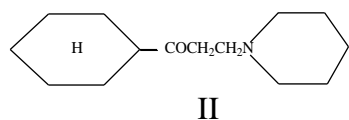
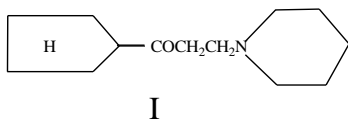


**Figure 6. Time dependence of the conversion of cyclohexene to different ratios. Reaction conditions: (0.51 g, 5mmol) catalyst  $[\text{ReOL}_2\text{Cl}_3]$  (20 mg., 5mol%), temperature  $70^\circ\text{C}$ ,  $\text{CH}_3\text{CN}$  (25ml).**

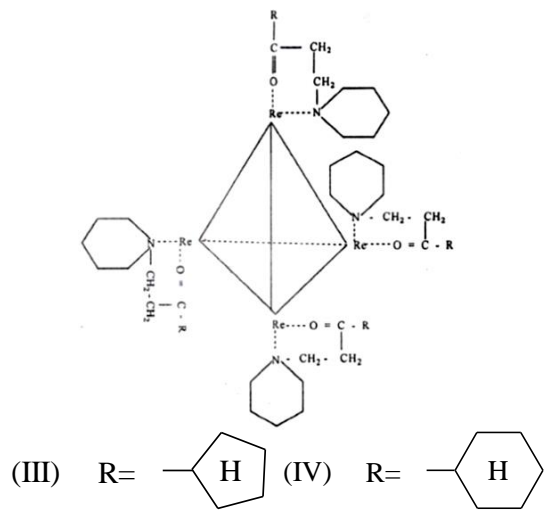
Thus, studies show that renimun complexes stereoselectively catalyze the oxidation of cyclohexene to oxide.

### **Rhenium cluster complexes.**

Scientists working in the field of inorganic chemistry began to pay more attention to complex compounds with several metal ions in their molecules, called multinucleated coordination compounds, in which the bond length between metals is significantly shorter than that of compact metals. Unlike classical single-centered coordination compounds, in these compounds, the ligands are surrounded by several metal atoms (ions) that are in close contact with each other. In this regard, it is interesting to obtain polyunsaturated metal complexes with rhenium carbonyl group and organic bifunctional ligands (I and II), which are amine fractions in the B-position of the chlorine atom.



When ligands I and II are added, clusters III and IV, which gradually dissolve in water within 30 minutes, are formed respectively.



The obtained dark brown precipitate is washed in distilled water and dried in a nitrogen medium at a temperature of 35-40°C. The melting temperatures of clusters III and IV are 195°C and 212°C (decomposition), respectively. Thermogravimetric method determined that compounds III and IV are resistant to temperatures of 187°C and 201°C, but above these temperatures in the range of 177°C to 229°C the process of separation of amino ketones I and II, accompanied by an endothermic effect occurs. Methods for the synthesis of rhenium cluster complexes based on carbonyl and amine containing organic bifunctional ligands have been developed. The structure of the obtained cluster combinations were determined on the basis of IR spectroscopy data, methods of thermogravimetry and elemental analysis.

## MAIN RESULTS

1. Methods of synthesis of rhenium complex compounds with a number of N- and O-retaining donor organic ligands (phenanthroline, nicotinamide, imidazole, benzimidazole, phthalocyanine) have been developed. A total of 19 associations have been separated, 11 of which have been obtained for the first time.
2. The composition and structure of the synthesized compounds, the nature and type of coordination of chemical bonds, element analysis and various physicochemical methods: IR-spectroscopy, EUS, thermogravimetry, evidence of molar electrical conductivity have been determined.
3.  $\text{PhenH}_2[\text{ReOHal}_5]$  compounds have been obtained,  $[\text{ReOHal}_3\text{Phen}]$  compounds have been synthesized as a result of their thermal decomposition. It has been found that thermal decomposition continues with the release of the corresponding hydrogen halide and the displacement of the phenanthroline molecule from the outer sphere to the inner sphere.
  - Based on the results obtained, the monodentate coordination of nicotinamide through the heterocyclic nitrogen atom has been determined and the two-nucleated structure has been confirmed.
  - Imidazole-coordinated compounds of Re (V) have been synthesized. It has been determined by IR spectroscopic method that all ligands in the obtained complexes have been coordinated monodentate. Strips characteristic of  $\nu(\text{Re} = \text{O})$  valence oscillations have been found in the IR spectra of all complexes.
  - The composition of the synthesized benzimidazole complexes depends on the concentration of HCl and HBr in an acidic environment, while in all cases the ligand is monodentate coordinated by a non-substituted nitrogen atom. The composition of the synthesized benzimidazole complexes depends on both the environment and the ratio of reagents, and the ligand is always bidentate coordinated.

- A new method of synthesis of rhenium phthalocyanins, characterized by affordability and high yield, has been proposed. It has been found that only one form of rhenium phthalocyanine is formed as a result of synthesis, which can also be written as  $\text{PcReO}$  on the basis of physicochemical studies.
4. The catalytic effects of the synthesized  $\text{Re (V)}$  complexes in benzylphenylsulfide and cyclohexane oxidation reactions have been studied and their possibility as a catalyst has been shown.
  5. By conductometry in media of various organic solvents, the type of electrolyte, which includes the studied complex compounds, was determined.
  6. Thermodynamic calculations have been done for some  $\text{Re}$  complexes and thermodynamic properties have been determined.
  7. Methods for synthesis of cluster compounds of rhenium with carbonyl- and amine-containing organic bifunctional ligands have been developed. It has been found that the reduction of rhenium salt in the water molecule forms ultradispersive nanoparticles of metallic rhenium, and their interaction forms cluster compounds. Tetrahedral coordination of rhenium has been confirmed in the synthesized cluster compounds.

**The main results of the dissertation are reflected in the following publications.**

1. Aghaguseynova M.M., Amanullayeva G.I., Gudratova F.D. Synthesis of cluster complexes of rhenium with N-donor organic ligands // Scientific conference dedicated to the 90th anniversary of T.N. Shakhtakhtinsky, Acad. Institute of Catalysis and Inorganic Chemistry named after M.F. Nagiyev, Baku, October 22-23, 2015, p. 139.
2. Gudratova F.D., Mamedova L.N. Complex rhenium compounds (V) with nitrogen-containing heterocyclic ligands // XXIX Scientific and Technical Conference "Chemical reagents, reagents and processes of low-tonnage chemistry". - Abstracts of

- reports. «REACTIVE-2015», - Academgorodok Novosibirsk, September 28 - October 1, 2015, - p. 94.
3. Gudratova F.D. Synthesis and research of rhenium benzimidazole complexes // XIX Republican scientific conference of doctoral students and young researchers, Baku, April 7-8, 2015, p.61-62.
  4. Aghaguseynova M.M., Gudratova F.D. Synthesis and research of rhenium complexes with N-donor organic ligands // VI Republican scientific conference dedicated to the 80th anniversary of the Department of Analytical Chemistry, Baku, December 16-17, 2015, pp.76-77.
  5. Aghaguseynova M.M., Gudratova F.D., Mikailova M.R. Development of new Re and Ru complex compounds - perspective drugs for radiodiagnostics of oncological diseases // XI All-Russian Scientific and Technical Conference "Actual Problems of Development of the Oil and Gas Complex", February 8, Russia p. 187.
  6. Aghaguseynova M.M., Adygezalova M.B., Gudratova F.D. Complex compounds of rhenium with benzimidazole: synthesis and properties // XXIV International scientific-practical conference "Actual problems in modern science and their solutions", ockMoscow, March 25-26, 2016, pp. 98-100.
  7. Aghaguseynova M.M., Gudratova F.D. Properties of complex compounds of rhenium (V) with phenanthroline // IX International scientific-practical conference "Actual problems of science of the XXI century", Moscow, 2016, 4 parts, p.5-7.
  8. Aghaguseynova M.M. Synthesis and properties of re and phthalocyanine complexes / M.M. Aghaguseynova, F.D. Gudratova, M.R. Mikayilova // Journal of News of Azerbaijan Higher Technical Schools, Baku, 2016, №3 (103), p.67-70.
  9. Gudratova F.D. Study of catalytic properties of rhenium organic ligand complexes // XX Republican scientific conference of doctoral students and young researchers, Baku, May 24-25, 2016, p.78-81.
  10. Gudratova, F.D. Synthesis and physico-chemical properties of coordination compounds of rhenium (V) with imidazole and its



- derivatives // II All-Russian scientific-practical conference with the international participation "Science in motion: reflection on the creation of reality", A., 2017, p. 385-387.
11. Aghaguseynova M.M., Cluster complexes of rhenium / M.M. Aghaguseynova, F.D. Gudratova // Norwegian Journal of development of the International Science, 2017, p.9-11.
  12. Aghaguseynova M.M., Synthesis and study of Re (v) complex compounds with benzimidazole / Aghaguseynova M.M., Gudratova F.D. // Azerbaijan Chemical Journal, 2017, №3. p.39-42.
  13. Aghaguseynova, M.M., Gudratova F.D. "Rhenium (V) complex compounds with phenantroline" // 3rd International Turkic World Conference on Chemical Sciences and Technologies –2017, – p.182.
  14. Aghaguseynova, M.M., Gudratova F.D. Development of new methods for the synthesis of cluster rhenium catalysts // International scientific-technical conference. Azerbaijan University of Architecture and Construction, 2017, p.322-323.
  15. Gudratova F.D. "Complex connections Re (V)" "Oil and Gas 2018" 72nd International Youth Scientific Conference, Moscow, April 23-26, 2018, Volume 2, p.312.
  16. Gudratova F.D. Synthesis and research of complex compounds with rhenium (V) 1,10-phenanthroline // International scientific conference "Actual problems of modern natural and economic sciences". Ganja, 04-05 May, 2018, p.63-64.
  17. Gudratova F.D. "Synthesis and study of rhenium (V) complex compounds" "Actual problems of chemistry" // XII International scientific conference, Baku, 2018, 03-04 May, p.221-222.
  18. Gudratova F.D. Obtaining complexes of rhenium // "Innovative prospects for the development of oil refining and petrochemistry", dedicated to the 110th anniversary of Academician VS Aliyeva, Baku, 2018, October 9-10, 58.
  19. Gudratova F.D. Complex compounds of rhenium (V) with imidazole and methylimidazole // Scientific conference "Nagiyev

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