

# ХИМИЧЕСКИЕ НАУКИ

## SYNTHESES AND STUDY OF TERNARY COMPLEXES OF RHODIUM (III) WITH PYRIMIDINE, PURINE BASICS AND SERIN

*Interaction in water solutions synthesized Coordination compounds:  
Rh(Cyt)(Ser)Cl<sub>2</sub>·H<sub>2</sub>O, Rh(Ura)(Ser)Cl<sub>2</sub>·H<sub>2</sub>O, Rh(Ade)(Ser)Cl<sub>2</sub>·H<sub>2</sub>O, Rh(Hyp)(Ser)Cl<sub>2</sub>·H<sub>2</sub>O*

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**Abstract:** The isolated compounds are characterized by the methods of IR and NMR spectroscopy. It is shown that the metal ion coordinates the amino acid through  $\alpha$ -NH<sub>2</sub>- and COO-groups. The pyrimidine bases are coordinated by the rhodium (III) ion through N<sub>3</sub> (N<sub>1</sub>) heterocycles, purine - N<sub>3</sub> (N<sub>7</sub>) and amino or carbonyl groups.

**Key words:** complexes of rhodium, complexes of pyrimidine and purine basics and serin with metal,

### 1. Introduction

The work of researchers on the study of biological activity (antitumor) complexes of rhodium (III) with derivatives of nucleobases are of great interest<sup>[1]</sup>.

It should be noted that the formation of different ligand compounds of rhodium (III) with amino acids, pyrimidine and purine bases has not been studied. At the same time, the study of the properties and structure of these compounds can regularities in the formation of homogeneously ligand and multiligand complexes and their role in biochemical processes[2-9].

### 2. Material and methods

#### 2.1. Material

In the study of complexation in aqueous solutions and in the synthesis of complex compounds, the following amino acids were used as starting materials: serine from Reanal (Hungary); adenine from Acros Organic (USA), cytosine, uracil and hypoxanthine from Fluka (Germany), RhCl<sub>3</sub>·3H<sub>2</sub>O from Aldrich (USA).

#### 2.2. methods

**Potentiometric titration:** The determination of ligand ionization constants, as well as the study of the complexation of rhodium (III) with amino acids, pyrimidine and purine bases in aqueous solutions was performed by pH-metric titration [10,11] using I-500 ionomer, using silver chloride and glass electrodes. Titration was carried out with HCl and KOH solutions with concentrations of 0.1 and 0.097 mol / l at a temperature of 20-21 ° C. The initial concentration of ligands was  $8 \cdot 10^{-3}$  mol / l. The initial volume of titratable solutions was 50.00 ml. To create the necessary ionic strength, KNO<sub>3</sub> was used with a concentration of 1 mol / l. Titration step 0.10 ml.

**Elemental analysis:** Nitrogen, carbon, hydrogen were determined on a device with a modernized CHN-analyzer EA1108 Carlo Erba instruments, Italy, with

an accuracy of 0.01-0.1%. Chlorine - argentometric titration according to the method of Mora [12]. Rhodium - thermogravimetric method.

**X-ray:** X-ray phase analysis was performed on a DRON-7 diffractometer with monochromatic CuK $\alpha$  radiation at a rate of 1/4 deg / min in the range of 50-90 $\circ$ , DRON-3 using monochromatic (graphite monochromatic CuK $\alpha$ -radiation  $\lambda$  CuK $\alpha$  = 1.5405 Å). The diffraction patterns were taken in a discrete diagram ( $\Delta\delta$  = 0.05 °, exposure time  $\tau$  = 5 sec).

**Thermogravimetric analysis:** Thermal stability Thermograms of the synthesized compounds were recorded on an IOM Q-1500D thermograph (Hungary) with heating from 20 ° C to 1000 ° C. The study used platinum crucibles, platinum - platinum-rhodium thermocouples, and as a reference - aluminum oxide. Heating rate of 10 degrees / min. Accuracy of temperature measurement  $\pm$  5 degrees.

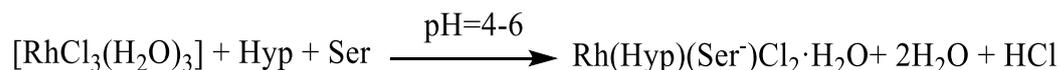
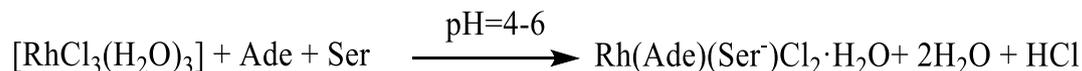
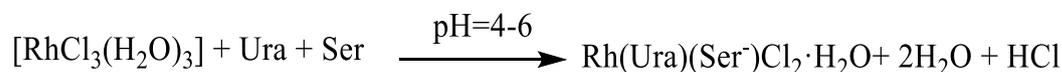
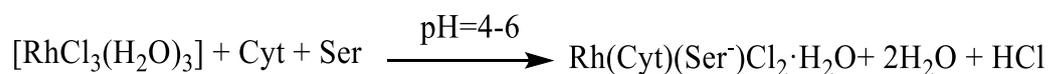
**Infrared spectroscopy:** The infrared absorption spectra of the starting materials and the resulting complex compounds were taken in liquid paraffin: on a Nexus Nicollet spectrophotometer (in the region of 200-4000 cm<sup>-1</sup>) and on a Specord M-82 spectrophotometer (in the region of 400-4000 cm<sup>-1</sup>). Interpretation of the infrared absorption spectra was carried out on the basis of literature data on the assignment of frequencies in the spectra of the initial substances and in similar compounds.

**NMR:** The <sup>13</sup>C NMR spectra were obtained on a Bruker "AVANCE-300" high resolution Fourier transform spectrometer (with a working frequency of protons 200.13 MHz) and a JNM-ECS400 spectrometer (with a working frequency of 400 MHz protons) using a single-pulse method with broadband suppression of protons. The duration of the excitation pulse was 4  $\mu$ s, with a repetition period of 1 sec., The number of accumulations was 4000-6000 scans. Tetramethylsilane was used as an external standard. The accuracy of determining chemical shifts is  $\pm$  0.5 ppm. In-

terpretation of the NMR absorption spectra of the starting materials and synthesized compounds was carried out on the basis of literature data.

### 3. EXPERIMENTAL AND DISCUSSION OF THE RESULTS

*Synthesis of complex compounds:* Synthesis of mixed ligand complexes was carried out according to the following schemes:



To isolate in the solid form of multiligand complex rhodium (III) complexes with amino acids and nucleobases with a ratio of M: L1: L2 of 1: 1: 1, two methods were used to prepare mixed ligand complexes: the displacement (or replacement) method of one of the ligands. The possibility of using the second procedure is due to fairly close values of the stability constants of the corresponding homogeneous ligand compounds [13].

In the first case, solutions of rhodium and serin of 20 ml volume were poured together and evaporated to 1/3 volume. Then, 20 ml of a hot solution of cytosine, adenine or hypoxanthine was added. It was assumed that cytosine and purine bases would replace the amino acid in the complex (since the stability constants of rhodium complexes with cytosine and purine bases are

greater than the stability constants of rhodium complexes with amino acids). The resulting mixture was evaporated to dryness. The resulting substance was repeatedly treated with a water-alcohol solution, acetone and ether and dried in a desiccator over a  $\text{P}_2\text{O}_5$  layer under vacuum.

The identification of synthesized compounds was carried out by chemical, X-ray, thermogravimetric, IR and NMR spectroscopy methods.

**Chemical analysis:** The synthesized complex compounds was carried out on the device CHNS-O EA1108 Elemental analyzer of Carlo Erbae with an accuracy of 0.01-1.1%. Rhodium - thermogravimetric method.

**Table No. 1 - Results of the chemical analysis of heteroligand complex compounds of rhodium (III).**

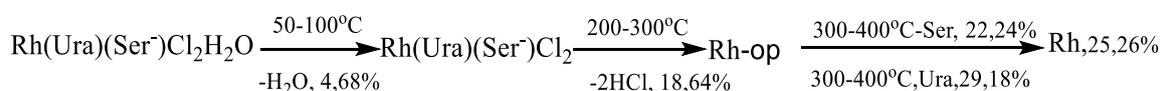
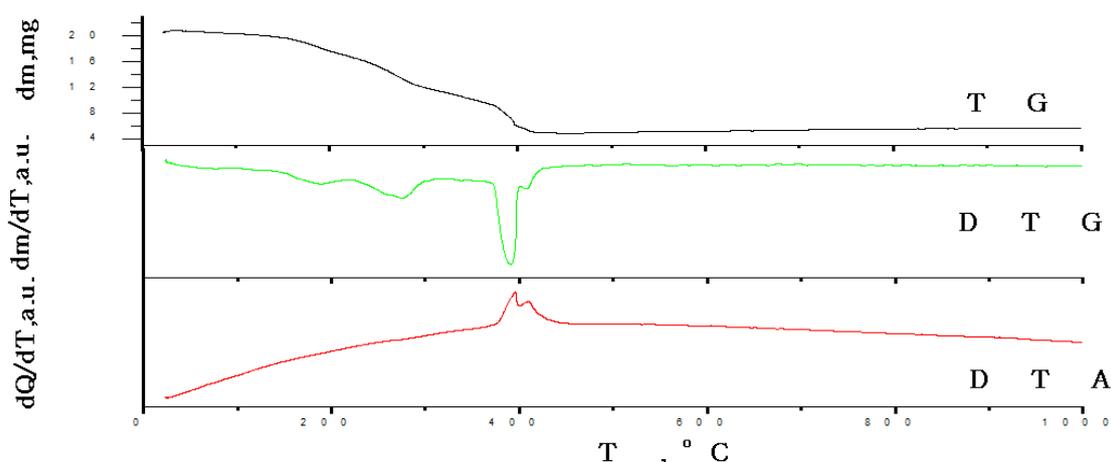
Compound	molar mass	Found / Calculated, %			
		Rh	N	C	H
Rh(Cyt)(Ser <sup>-</sup> )Cl <sub>2</sub> ·H <sub>2</sub> O	407,10	25,16	13,77	20,82	3,16
Rh(C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O)(C <sub>3</sub> H <sub>6</sub> NO <sub>3</sub> )Cl <sub>2</sub> ·H <sub>2</sub> O		25,28	13,75	20,63	3,19
Rh(Ura)(Ser <sup>-</sup> )Cl <sub>2</sub> ·H <sub>2</sub> O	408,11	26,83	9,53	19,94	2,65
Rh(C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>3</sub> H <sub>6</sub> NO <sub>3</sub> )Cl <sub>2</sub> ·H <sub>2</sub> O		25,22	10,29	20,58	2,94
Rh(Ade)(Ser <sup>-</sup> )Cl <sub>2</sub> ·H <sub>2</sub> O	431,11	23,55	19,47	21,80	2,71
Rh(C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> )(C <sub>3</sub> H <sub>6</sub> NO <sub>3</sub> )Cl <sub>2</sub> ·H <sub>2</sub> O		23,87	19,48	22,27	3,02
Rh(Hyp)(Ser <sup>-</sup> )Cl <sub>2</sub> ·H <sub>2</sub> O	432,11	23,79	16,18	22,25	2,70
Rh(C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O)(C <sub>3</sub> H <sub>6</sub> NO <sub>3</sub> )Cl <sub>2</sub> ·H <sub>2</sub> O		23,82	16,20	22,22	2,78

**Thermogravimetric analysis:** Thermograms of synthesized compounds were recorded on a thermograph "MOM Q 1500D" (Hungary) with heating from 20 °C to 1000 °C.

The analysis used platinum crucibles, platinum, platinum-rhodium thermocouples, the reference is

aluminum oxide. Heating rate 10 deg / min. The accuracy of the temperature measurement is ± 5 degrees.

Below is a diagram of the thermal destruction of the complex Rh(Ura)(Ser<sup>-</sup>)Cl<sub>2</sub>·H<sub>2</sub>O.

Drawing No. 1: The thermogram of the compound Rh(Ura)(Ser-)Cl<sub>2</sub>·H<sub>2</sub>O

The thermograms of ternary complexes are more complex in character than homogeneous ligand complex compounds. The removal of the water molecule is fixed at a temperature of about 100 °C. It should be noted that the TG curve is smooth. The mass loss is most clearly manifested in the DTG curve, where mass changes occur at temperatures of ~ 100 °C, 400 °C and in the range of 550-650 °C, which can be

attributed to the removal of water (~ 100 °C), hydrogen chloride (200 °C), the amino acid component of the complex (400 °C) burnout of cytosine (600-650 °C), the remainder is elementary rhodium.

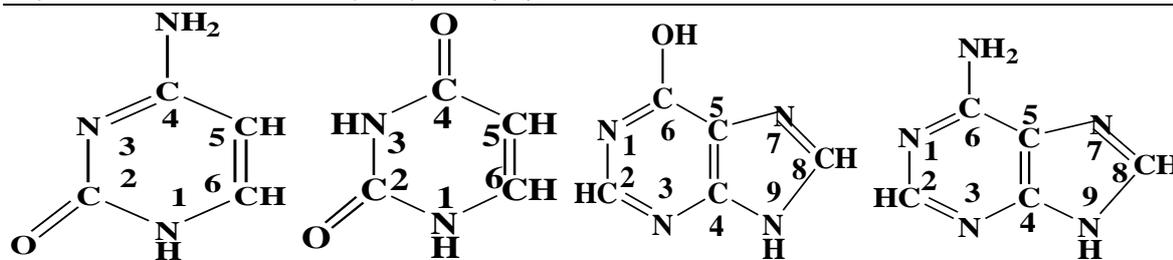
**IR:** absorption spectra of different ligand complex compounds Rh (III)<sup>[14]</sup>.

Table No.2 - Wave numbers of maxima (cm-1) of absorption bands of different ligand complex compounds Rh (III) on the basis of serine.

Compound	Rh(Cyt) (Ser-)Cl <sub>2</sub> ·H <sub>2</sub> O	Rh(Ura) (Ser-)Cl <sub>2</sub> ·H <sub>2</sub> O	Rh(Ade) (Ser-)Cl <sub>2</sub> ·H <sub>2</sub> O	Rh(Hyp) (Ser-)Cl <sub>2</sub> ·H <sub>2</sub> O
δ, α-NH <sub>2</sub> - amino acids groups	3171, 1541 (1509) 1005, 974	3417, 3104, 1455, 1461, 1122, 1112,	3395, 1600, 1115- 1117, 637	3534, 3476, 1194, 1109, 630
ν COO <sup>-</sup> related to metal group,	1674(ac) (1599), 1404 (сим.) (1469),	1651 (ac) (1599), 1417 (сим.) (1469)	1659, 1476	1626(as), 1400 (s)
ν =C=O basics groups	1722, 1725 (1717)	1651, (1657)		1718
ν and δ bonds C=C, C=N purine rings	1674 (1666)		1017 (1022), 908 (848), 779 (797)	1475, 982, 810
ν pyrimidines rings	1489, 1497 (1453, 1418, 1392).	1660, 1377		
Oscillations bonds Rh-N		544		550
Oscillations bonds Rh-Cl		326		
Oscillations bonds Rh-O		427		

**<sup>13</sup>C NMR** spectra of non-aqueous (DMSO) solutions of rhodium (III) compounds and corresponding ligands were obtained with a Bruker "AVANCE-300" high-resolution Fourier transform transformer (with an

operating frequency of 200.13 MHz) and with a JNM-ECS400 spectrometer with an operating frequency of 400 MHz protons) using a single-pulse technique with broadband proton suppression.

Table No. 3- Chemical shifts of  $^{13}\text{C}$  (ppm)  $\text{Rh}(\text{Hyp})(\text{Ser})\text{Cl}_2 \cdot \text{H}_2\text{O}$  (for example)

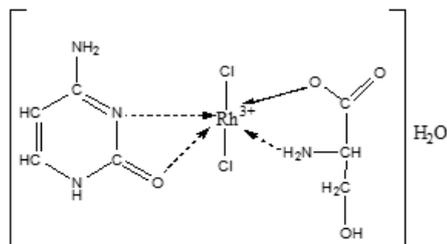
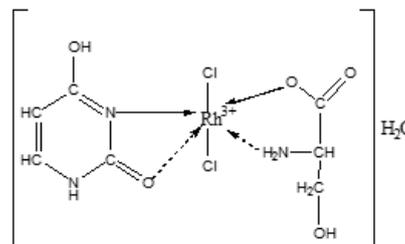
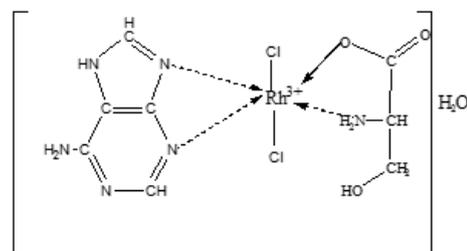
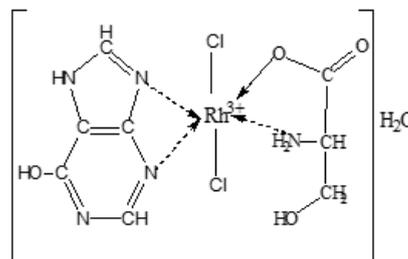
CHn-groups	Chemical shifts of $^{13}\text{C}$ (ppm)				
	Hypoxanthin	$\Delta\delta(\text{Hyp})$	$\text{Rh}(\text{Hyp})(\text{Ser})\text{Cl}_2 \cdot \text{H}_2\text{O}$	serine	$\Delta\delta(\text{Ser})$
COOH/ COO-			170,00	173,75	-3,75
C2			63,33	61,61	1,72
C3			57,95	57,63	0,32
C2-H	142,91	4,21	147,12		
C4	152,10	-0,10	152,00		
C5	117,74	-2,74	115,00		
C6	153,85	0,60	154,45		
C8-H	138,30	7,47	145,77		

The data of chemical shifts of  $^{13}\text{C}$  NMR spectra of multiligand compounds confirm the bidentate coordination of serine (COO<sup>-</sup> and NH<sub>2</sub>). Molecules of cytosine and uracil in mixed ligand complexes interact with the rhodium (III) ion through the N-3 and C=O ligand groups. since the chemical shifts of all carbon atoms of heterocycles undergo displacement with respect to the initial ligands, then the entire  $\pi$ -electron system of heterocycles reacts with the metal ion.

Adenine and hypoxanthine react as polydentate ligands, but mainly through N-3 and N-7 or N-9.

### Conclusion

Thus, based on all the studies carried out, the following structure of synthesized different ligand coordination compounds can be proposed:

Rh(Cyt)(Ser)Cl<sub>2</sub>·H<sub>2</sub>ORh(Ura)(Ser)Cl<sub>2</sub>·H<sub>2</sub>ORh(Ade)(Ser)Cl<sub>2</sub>·H<sub>2</sub>ORh(Hyp)(Ser)Cl<sub>2</sub>·H<sub>2</sub>O

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## THE NEW ENVIRONMENTALLY PURE METHOD OF OBTAINING OF SATURATED CARBONIC ACIDS OF THE CONDITIONS INTERPHASE CATALYSIS

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### SUMMARY

In the conditions of an interphase catalysis in the presence of crown-ether reactions of oxidation of primary alcohols, saturated hydrocarbons (C4 – C10) and saturated chlorhydrocarbons are investigated and easy, effective and new method for obtaining saturated organic acids is offered.

Use of crown-ether in the offered method allows to carry out process at low temperature and mild conditions, at the same time the same portions of crown-ether can be used many times without special cleaning and easily regenerated. The new simple technique is developed for cleaning and separation of crown-ether from reaction mixture after carrying out oxidation reaction. The reaction of oxidation of primary alcohols, saturated hydrocarbons (C4–C10) and saturated chlorhydrocarbons was carried out in two-phase heterogeneous system within 20-50 min. Quantity ratio of initial product: KMnO<sub>4</sub>: DB18K6A, was 0.1: 0.3-0.4: 0.003-0.004. The process is smoothly carried out at 105<sup>o</sup>C -160<sup>o</sup>C temperature interval (against 450<sup>o</sup>C -500<sup>o</sup>C in usual conditions in the lack of the interphase catalyst) without formation of chlorine containing waste and also poisonous products.

The listed data provide the maximum yield of a target product.

The interphase catalysis is one of the most interesting, perspective and developing fields of synthetic organic chemistry.

Discovery of a new method of an interphase catalysis for rather short time was generally recognized and also the widest application in all fields of organic chemistry as one of the universal methods of synthesis. IFC was taken advantage at once and took an important place in organic synthesis, having forced out many old ways. It rendered powerful impact on development of new, convenient technological ways in industrial scale [1-6].

The known ways of receiving saturated carbonic acids are based on process of oxidation of saturated hydrocarbons (C4 – C10) in steam phases at a temperature of 450-5000C and 150-200 atm. pressure and oxidation of aliphatic alcohols with aqueous KMnO<sub>4</sub> solution, and also oxidation of saturated halogenalkans [7-9]. However these ways have a number of shortcomings, of which the following is essential: 1) high temperature up to 500<sup>o</sup>C, 2) an isomerization and an molding of the reaction product under the high temperature, 3) use of rather big excess (more than 100%) of potassium permanganate, 4) obtaining of thousands tone of chlorine-containing waste, and also poisonous