

SHAMILOV E.N.^{1✉}, ABDULLAEV A.S.¹, FARAJOV M.M.¹, SHAMILI V.E.¹, GAHRAMANOVA SH.I.², JALALADDINOV F.F.²

¹ Institute of Radiation Problems of ANAS,

Azerbaijan Republic, AZ1143, Baku, B. Vahabzadeh, 9, e-mail: elshanshamil@gmail.com

² Institute of Catalysis and Inorganic Chemistry ANAS,

Azerbaijan Republic, AZ1143, Baku, Huseyn Javid ave., 113

✉ elshanshamil@gmail.com

SYNTHESIS, CHARACTERIZATION AND ANTIRADIATION PROPERTIES OF THE TRYPTOPHANATES OF COBALT (II), MANGANESE (II), COPPER (II) AND ZINC

Aim. In order to study the radioprotective activity were obtained in the tryptophanates of cobalt (II), manganese (II), copper (II) and zinc.

Methods. The composition and structure of the complexes were studied by elemental, thermogravimetric analyzes and IR infrared spectroscopy. To determine the presence of the Radioprotective Properties of the Co (II), Mn (II), Cu (II), Zn complexes with tryptophane, a test was conducted for the 30-day survival of irradiated animals. **Results.** The results of thermogravimetric studies have shown that the final product of the thermal decomposition of all compounds is metal oxide, respectively. The method of IR spectroscopy showed that the ligands in the composition of the metal (II) complexes enter the neutral form and coordinate with the complexing agent through the nitrogen atom. The results of experiments with complexes showed that they have noticeable radioprotective activity. The radioprotective activity of Co (II) complexes with tryptophan is 55%, Mn (II) with tryptophan 50%, Cu (II) with tryptophan 40%, and Zn 30%. They improve the survival and average life expectancy of lethally irradiated mice, not reaching the level of the known cystamine radioprotector, which is 80%. **Conclusions.** The data obtained by us testify to the prospects of using the complexes of Co (II), Mn (II), Cu (II), Zn with tryptophan for preventive purposes and in order to prevent local radiation injuries.

Keywords: tryptophan-metal complexes, IR spectroscopy, thermogravimetry, complex compounds, radioprotective properties.

The chemistry of complex compounds of transition metals with multidentate ligands, which simultaneously contain several donor atoms, is not only theoretical but also of practical interest, since in addition to the unusual properties of such com-

plexes, the structure and types of binding of multidentate ligands with different metals give a new impetus to the development coordination chemistry as a whole. Among the coordination compounds, the complexes obtained on the basis of biomaterials take a special place. This is due to the fact that they play an important role in many biochemical processes and therefore are widely used in plant growing, animal husbandry, and pharmacology [1-8]. In turn, the study of the properties and structure of coordination compounds of metal ions with organic ligands containing various donor centers was an important factor in the development of new approaches to their physico-chemical research.

On the other hand, complex compounds of many transition elements can possess a wide range of useful properties, for which the chemistry of complex compounds has not yet been sufficiently studied.

This article presents methods for producing complexes of manganese (II), copper (II), cobalt (II), zinc with a ligand - tryptophan, and also their anti-radiation properties are studied [10].

Material and methods

Measurement methods: The composition and structure of the complexes were studied by elemental analysis methods (ICP-MS); IR spectroscopy ("Specord M-80" by Carl Zeiss) and thermogravimetric (NETZSCH STA 449F3 STA449FSA-0622-M).

Experimental part

Synthesis -[CuCl₂L(H₂O)]

A sample of 0.85 g (0.005 mole)-CuCl₂·2H₂O was dissolved in a two-necked flask under reflux in 30 ml of ethyl alcohol at a temperature of 60 ° C, and 1.02 g (0.005 mole) of ligand L-tryptophan - (in a molar ratio of 1: 1) previously dissolved in 20 ml of ethyl alcohol. The resulting

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mixture was heated for 2 hours, then cooled to room temperature, filtered and put on crystallization. The blue-colored crystals were filtered, washed several times with the mother liquor, then 15-20 ml with acetone and dried in a desiccator over sulfuric acid until a constant weight was established.

Synthesis -[ZnL₂(H₂O)₂] 2H₂O

To a beige color solution obtained by dissolving 0.32 g (0.005 mole) –Zn powder in 20 ml of ethyl alcohol, 2.04 g (0.01 mole) of ligand L-tryptophan dissolved in 30 ml of ethyl alcohol (in a molar ratio 1: 2). The solution was heated for 2-2.5 hours at a temperature of 60 ° C. Further, the synthesis process was carried out according to the above described procedure.

Synthesis-[MnCl₂L₂]2H₂O

According to the above procedures, 2.04 g (0.01 mol) of ligand L- tryptophan (molar ratio 1: 2), previously dissolved in 20 ml of ethyl alcohol, was added to 0.85 g (0.01 mole) --MnCl₂ •2H₂O dissolved in 20 ml of ethyl alcohol. The resulting mixture was heated for 2 hours, then cooled to room temperature, filtered, washed several times with the mother liquor, then 10-15 ml with acetone and dried in a desiccator over sulfuric acid until a constant weight was established.

Synthesis-[CoCl₂L₂]2H₂O

According to the above procedures, 2.04 g (0.01 mol) of ligand L- tryptophan (molar ratio 1: 2), previously dissolved in 30 ml of ethyl alcohol, was added to 1.17 g (0.01 mole) –CoCl₂ •6H₂O dissolved in 20 ml of ethyl alcohol. The resulting mixture was heated for 2 hours, then cooled to room temperature, the purple-colored crystals were filtered, washed several times with the mother liquor, then 20-25 ml with acetone and dried in a desiccator over sulfuric acid until a constant weight was established.

Results and discussion

Elemental analysis

The elemental analysis data of the metal-ligand complexes are pointed up in table.

Differential thermal analysis

With the definition of the thermic stability and the composition of synthesized complexes [MnClL₂(H₂O)]H₂O,[CuCl₂L(H₂O)], [CoCl₂L₂]2H₂O, [ZnL₂(H₂O)₂]H₂O the thermographic analysis was made. Thermogravimetric analysis of the compounds has been conducted in the 25-850°C temperature range under nitrogen. The derivatograms of the complexes differ substantially in the nature of the thermal decomposition. Results of thermogravimetric studies have shown that the thermal decomposition of complexes occurs in three stages. The third stage of thermolysis ends with the obtaining of metal oxides.

IR spectroscopy

To determine the coordination character of the synthesized complex compounds formed between the ligand and of manganese (II), copper (II), cobalt (II) and zinc (II), IR spectroscopic analysis was carried out.

In the IR spectra of complexes the strong and broad absorption band in the range of 3600-3000 cm⁻¹ correspond to asymmetric and symmetric stretching vibrations of aqua molecules. At the range of 3392 cm⁻¹ and 3161 cm⁻¹ bands are belonging to N-H stretches of NH₂ group of tryptophan. The weak bands at the range of 2936-2906 cm⁻¹ are attributed to the CH₂ vibrations. In complexes, tryptophan ligands are coordinated to the metal ion as monodentate by carboxylic group. This claim about the products is supported by FT-IR spectra results. The (COO⁻)_{asym.} peaks are located at 1619 cm⁻¹ for Co(II), 1605 cm⁻¹ for Mn(II), 1625 cm⁻¹ for Cu(II) and 1622 cm⁻¹ for Zn complexes. (COO⁻)_{sym} peaks are observed at 1459 cm⁻¹ for Co(II), 1456 cm⁻¹ for Mn(II), 1455 cm⁻¹ for Cu(II) and 1456 cm⁻¹ for Zn complexes. The low-intensity bands in the region of 600–400 cm⁻¹ are attributed to M–N and M–O vibration [9].

Table 1. Elemental analysis results of the complexes

Symbolic formula	Molecular weight	%Cl		%H		%N		%Metal	
		Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
[CuCl ₂ L(H ₂ O)]	357	19.9	19.26	3.92	3.85	6.72	6.27	17.92	17.26
[ZnL ₂ (H ₂ O) ₂] 2H ₂ O	537	----	----	5.95	5.67	10.42	10.16	12.10	12.01
[MnCl ₂ L ₂]2H ₂ O	566	12.54	12.14	4.94	4.33	9.89	9.34	9.71	9.28
[CoCl ₂ L ₂] •6H ₂ O	646	10.99	10.36	5.57	5.75	8,66	8.18	9.13	9.02

The study of the anti-radiation properties of tryptophanates

To determine the presence of the radioprotective properties of the Co (II), Mn (II), Cu (II), Zn complexes with tryptophan, a test was conducted for the 30-day survival of irradiated animals. In experiments, mongrel mice weighing 20-25 g were used. The animals were withdrawn in accordance with the rules of the European Convention for the Protection of Vertebrates used for experimental and other scientific purposes.

Animals were irradiated with a gamma irradiation unit "RUHUND-20000" with a Co60 radiation source at a dose of 9.0 Gy; the dose rate is 0.439 Gy/s. The test complexes with tryptophane were administered to the animals in an aqueous solution 30 minutes prior to irradiation at 100 mg / kg. To compare the radioprotective activity of the complexes tryptophan studied, a radioprotector-standard cystamine (bis (β -aminoethyl) disulphide) was used in the optimal radioprotective dosage of 100 mg / kg, administered 30 min before irradiation.

Behavior monitoring and recording of animal deaths were conducted during the first hour and

then the death of the animals was recorded in the next 30 days after the injection. The test results are shown in the table.

The study of the radioprotective activity of complexes of Co (II), Mn (II), Cu (II), Zn with tryptophan showed that they have radioprotective activity. The radioprotective activity of Co (II) complexes with tryptophan is 55%, Mn (II) with tryptophan 50%, Cu (II) with tryptophan 40%, and Zn 35%. They improve the survival and average life expectancy of lethally irradiated mice, not reaching the level of the known cystamine radioprotector, which is 80%.

Conclusions

The data obtained by us testify to the prospects of using the cationic complexes of Co (II), Mn (II), Cu (II), Zn with tryptophan for preventive purposes and in order to prevent local radiation injuries.

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Table 2. Action of tryptophan complexes on the survival of irradiated animals

Options	The number of mice	Survival rate, %	Life expectancy, day
Control (distil.water)	20	20	30 and more
Irradiated control	0	0	4,32 \pm 1,21
Cystamine	16	80	18,31 \pm 0,31
Co (II) complexes with Tryptophane	11	55	16,3 \pm 2,33
Mn(II) complexes with Tryptophane	10	50	12,1 \pm 2,21
Cu(II) complexes with Tryptophane	8	40	10,53 \pm 1,5
Zn complexes with Tryptophane	7	35	8,41 \pm 1,2

Note. P <0.001.

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ШАМІЛОВ Е.Н.¹, АБДУЛЛАЄВ А.С.¹, ФАРАЖОВ М.М.¹, ШАМІЛІІ В.Е.¹, ГАГРАМАНОВА Ш.І.², ДЖАЛАЛАДДІНОВ Ф.Ф.²

¹ Інститут Радіаційних Проблем Національної Академії Наук Азербайджану, Азербайджан, AZ1143, м. Баку, вул. Б. Вагабзаде, 9, e-mail: elshanshamil@gmail.com

² Інститут Каталізу та Неорганічної Хімії ANAS, Азербайджан, AZ1143, м. Баку, проспект Гусейна Джавіда, 113

ВЛАСТИВОСТІ СИНТЕЗУ, ХАРАКТЕРИЗАЦІЇ ТА АНТРАДІАЦІЇ ТРИПТОФАНАТІВ КОБАЛЬТУ (II), МАНГАНЕЗА (II), КОФЕРА (II) І ЦИНКУ

Мета. Для вивчення радіозахисної активності були отримані триптофани кобальту (II), марганцю (II), міді (II) та цинку. **Методи.** Склад та структуру комплексів вивчали за допомогою елементарного, термогравіметричного аналізу та ІЧ-інфрачервоної спектроскопії. Для визначення наявності радіозахисних властивостей комплексів Со (II), Мп (II), Сu (II), Zn з триптофаном було проведено тест на 30-денну виживаність опромінених тварин. **Результати.** Результати термогравіметричних досліджень показали, що кінцевим продуктом термічного розпаду всіх сполук є оксид металу відповідно. Метод ІЧ-спектроскопії показав, що ліганди у складі металевих (II) комплексів входять у нейтральну форму і координують комплексоутворювач через атом азоту. Результати експериментів із комплексами показали, що вони мають помітну радіозахисну активність. Радіопротекторна активність комплексів Со (II) з триптофаном становить 55%, Мп (II) з триптофаном 50%, Сu (II) з триптофаном 40% та Zn 30%. Вони покращують виживання та середню тривалість життя смертельно опромінених мишей, не досягаючи рівня відомого радіопротектора цистаміну, який становить 80%. **Висновки.** Отримані нами дані свідчать про перспективи використання комплексів Со (II), Мп (II), Сu (II), Zn з триптофаном у профілактичних цілях для запобігання місцевих радіаційних травм.

Ключові слова: триптофанометалеві комплекси, ІЧ-спектроскопія, термогравіметрія, складні сполуки, радіозахисні властивості.