

COMPOSITION AND ANTIRADIATION ACTIVITY OF THE COPPER (II) CHLORIDE COMPLEX WITH TRYPTOPHANE

M.F. Farajov¹, A.S. Abdullayev¹, E.N. Shamilov¹, Sh.I. Gahramanova²,
F.F. Jalaladdinov², Z.N. Mehdiyeva²

¹*Institute of Radiation Problems of ANAS*

²*Institute of Catalysis and Inorganic Chemistry of ANAS*

sahnaz.gahramanova@gmail.com

Abstract: As a result of the reaction of tryptophan with copper (II) chloride, a complex of copper tryptophanate was obtained. The composition of the complex was studied by elemental, thermal, X-ray phase analysis, IR, and UV spectroscopy. The antiradical activity of the complex was studied on irradiated wheat seeds. It was revealed that the treatment of wheat seeds before irradiation with an aqueous solution of complex leads to normalization of the biosynthesis of photosynthetic pigments.

Keywords: copper, tryptophan, complex, metal oxide, IR spectroscopy, thermogravimetry, photosynthetic pigments, anti- radiation.

1. Introduction

Over the past decades, the number of works aimed at studying the role of biogenic macro- and microelements in biochemical processes has significantly increased. It is noted that the role of these macro- and microelements are markedly enhanced when used in combination with amino acids. Amino acids can play the role of metal- chelating ligands, which makes it possible to create, on this basis, drugs that combine amino acids with trace elements and ensure their efficient transport into the living environment [1-2]. Currently, an urgent scientific task is to elucidate the composition and structure of compositions based on macro-, microelements and amino acids at the molecular and supramolecular levels and their mechanism of action, to find ways to increase the effectiveness of these compositions.

The complexes of many metals with amino acids serve as a model of processes occurring in living organisms. Besides, many complexes are widely used in medicine as medicines [3-10].

The aim of this work was the synthesis of a complex of tryptophan with copper (II) chloride, the study of structures, and anti-radiation properties.

Materials and methods

2. Physical measurements

The composition and chemical structure of the synthesis products obtained are studied by physical-chemical analysis methods: X-ray phase analysis (diffractometer (Germany) D-2 Phaser firm Bruker); IR spectroscopy ("Specord M-80" brand Carl Zeiss). The spectra of the reaction solutions in the UV regions were recorded on the Evolution 60S spectrophotometer, by Thermo Scientific Spectronic (USA). Differential thermogravimetric analysis was performed on (NETZSCH STA 449F3 STA449FSA-0622-M).

3. Experimental part

All chemicals used for synthesis were of reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and tryptophan (Trp) (Sigma- Aldrich) were used as received.

Synthesis - $[\text{CuCl}_2\text{L}_2(\text{H}_2\text{O})]$

A sample of 0.85 g (0.005 mole)- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 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: 2) previously dissolved in 20 ml of ethyl alcohol. The resulting 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.

4. Results and conclusion

Elemental analysis

Table 1. The elemental analysis data of the metal-ligand complexes are pointed up in

Symbolic formula	Molecular weight	%Cl		%H		%N		%Metal	
		Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
$[\text{CuCl}_2\text{L}_2(\text{H}_2\text{O})]$	561.192	12.652	12.64	4.670	4.65	9.978	9.95	11.404	11.355

The difference between the diffraction patterns of the synthesized substance from the starting compounds allows us to conclude that the resulting complex is individual.

Infrared Spectroscopy

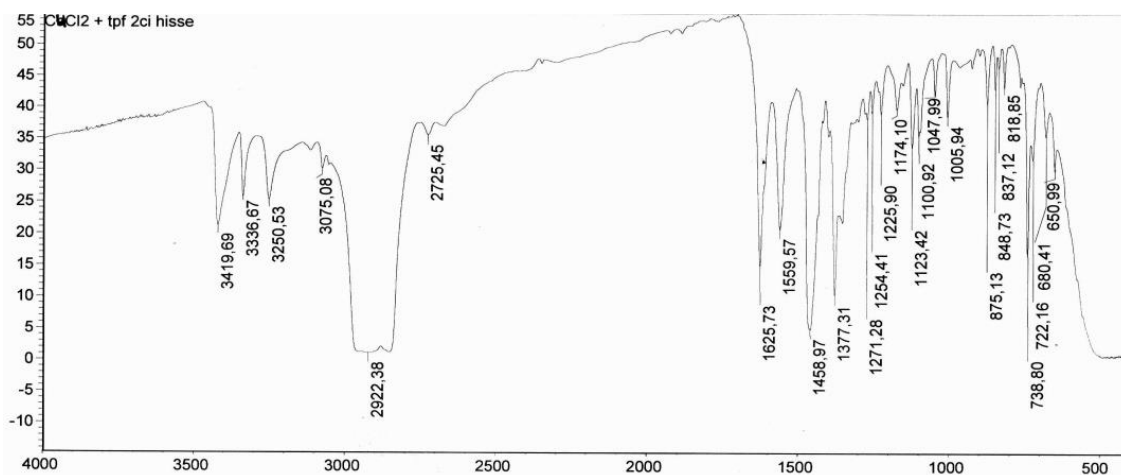


Fig. 1. IR Spectrum Trf + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

The presence in the IR spectrum of copper tryptophanate of three absorption bands in the spectral region of $3420\text{--}3075\text{ cm}^{-1}$ ($3420, 3337, 3251, 3075\text{ cm}^{-1}$), strong absorption at and weaker when related to stretching vibrations of the NH_2 group, asymmetric and symmetric vibrations of COO^- indicates that there are chelate bonds between the copper (II) ion and the tryptophan (Fig. 1).

Table 2. Characteristic IR-Fourier bands spectra of metal complex Cu(II) with tryptophan.

Groups	Cu, cm^{-1}
$\nu(\text{NH}_2)$	3420-3075
$\nu(\text{NH}_2)$	1560
$\nu(\text{C}=\text{O})$	1626
$\nu(\text{COO}^-)_{\text{sym}}$	1459
$\nu(\text{CH}_2)$	2725
$\nu(\text{C}-\text{N})$	780
$\nu(\text{M}-\text{N})$	650
$\nu(\text{M}-\text{O})$	680

The decomposition of the complex begins at a temperature of 180-220°C (Fig. 2). In the region of 450-500°C, a strong exo-effect is observed, corresponding to the burning out of the organic part of the molecule. The increase in mass on the TG curve (at 550-830°C) corresponds to the formation of copper oxide (CuO), which decomposes upon further heating. The final product of hemolysis is elemental copper.

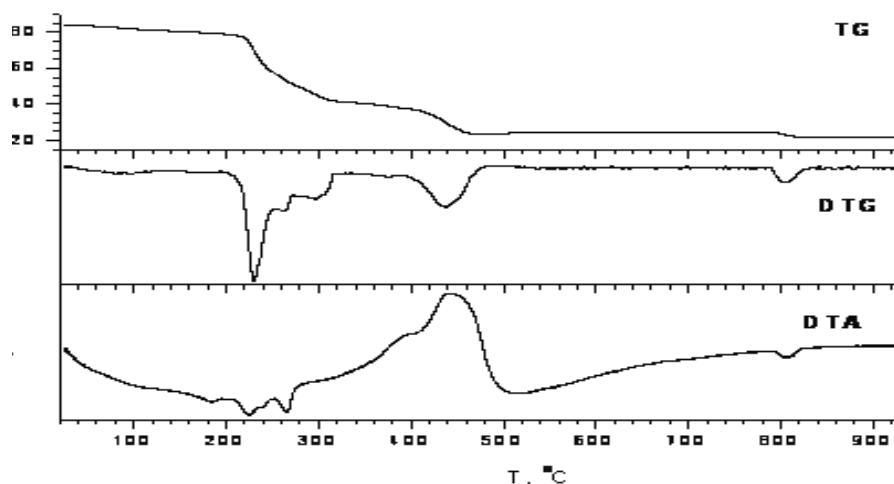


Fig. 2. Thermal analysis curves of complex Cu(II) with tryptophan.

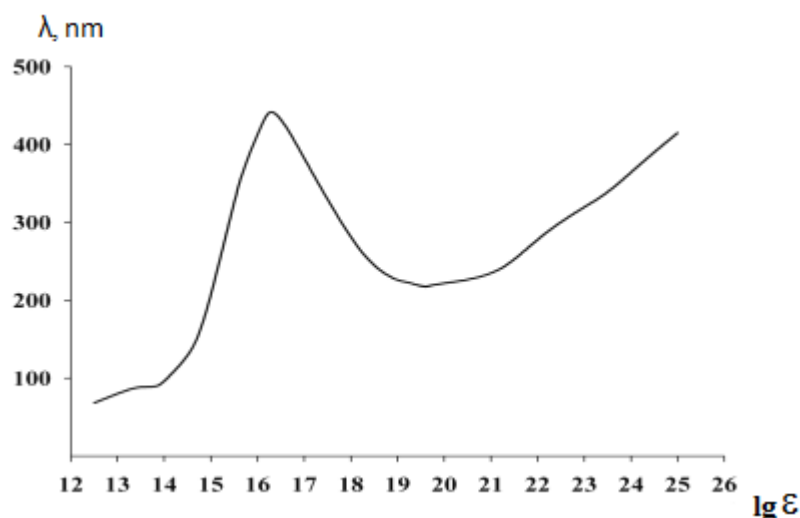


Fig. 3. Electronic absorption spectra in acetonitrile

Analysis of the data of electronic absorption spectra showed that in the visible region the absorption maximum appears at 16260 cm^{-1} , which, according to the literature, corresponds to the *d-d* transition, which gives reason to attribute the resulting compound to the same structural (pseudo-octahedral) type (Fig. 3). The results are agreeable to literature [8].

The antiradiation activity of complex Cu(II) with tryptophan.

The antiradiation activity of the complexes was checked on irradiated seeds of wheat. For comparison, the seeds were treated with copper chloride and Cu (II) complex with tryptophan. The content of photosynthetic pigments was determined in seedlings.

Table 3. Influence of $[\text{CuCl}_2\text{L}_2(\text{H}_2\text{O})]$ complex with tryptophan on the content of chlorophyll and carotenoids in leaves of wheat seedlings of irradiated wheat seeds with 250 Gy gamma radiation (mg/l)

Variants	Germination, %	Chlorophyll a (mg/ml)	Chlorophyll b (mg/ml)	Carotenoids (mg/ml)
control	86	2,01	1,31	0,68
0.001% - $[\text{CuCl}_2\text{L}_2(\text{H}_2\text{O})]$				
	95	2,17	1,39	0,73
Irradiated 250 Gy				
irradiated control	47	1,30	0,57	0,45
0.001% - $[\text{CuCl}_2\text{L}_2(\text{H}_2\text{O})]$ + irradiated	91	1,98	1,03	0,70
irradiated + 0.001% - $[\text{CuCl}_2\text{L}_2(\text{H}_2\text{O})]$	89	1,86	0,99	0,69

As can be seen from table3, seeds treated with CuCl_2 - tryptophan, have a high germination rate and high activity of photosystems. The complex also had a positive effect on the content of chlorophyll, as well as on the ratio of chlorophyll/a chlorophyll/b. It was revealed that low concentrations of complex positively affect the synthesis of chlorophyll and carotenoids, increase the functional activity of chloroplasts.

Thus, the tryptophan complex with copper chloride accelerated the germination of wheat seeds and increased the chlorophyll content in leaves, and also increased the activity of photosystems of chloroplasts.

Treatment of wheat seeds before irradiation (250Gy irradiation dose) with aqueous solutions of the complex (solution concentration 0.001%) leads to normalization of the biosynthesis of photosynthetic pigments, helps to eliminate mitotic division anomalies in root hair cells, stimulates reparative mechanisms.

References

1. E. J. Underwood, N. F. Suttle, The Mineral Nutrition of Livestock, 3rd Ed., 1999, CABI Publ., New York, USA.
2. G. Predieri, L. Elviri, M. Tegoni, I. Zagnoni, E. Cinti, G. Biagi, G. Leonardi, S. Ferruzza, J. Inorg. Biochem., 2005, 99, p.627-636
3. L.J. Bellamy. The Infra-red Spectra of Complex Molecules, Wiley, N.-Y., 1975
4. F. Albert. Cotton, David M. L. Goodgame, Margaret. Goodgame. Absorption Spectra and Electronic Structures of Some Tetrahedral Complexes // J. Am. Chem. Soc., 1962, 84 (2), p.167-172
5. Sh.I. Gahramanova, F.F. Jalaladdinov, R.A. Samadova, A.S. Abdullayev, G.E. Gasimova, A.S. Aghayeva, E.N. Shamilov, N.M. Rashydov. Synthesis and biological activity of manganese (II) complexes with leucine and tryptophan. Journal of Radiation Researches, 2019, vol.6, №1, p.53-59
6. Gahramanova S.I., Jalaladdinov F.F., Munshieva M.K., Khudaverdiev R.A., Hamidov R.H., Abdullaev A.S., Shamilov E.N., Azizov I.V., Gahramanov T.O. Synthesis and Investigation of Complex Compounds of Divalent Manganese, Cobalt and Zinc with Tryptophan and their Biological Activity International Journal of Chemical Sciences, 2018, p.138-144
7. G.E. Gasimova, A.S. Aghayeva, A.S. Abdullayev, E.N. Shamilov, Sh.I. Qahramanova, F.F. Jalaladdinov, R.H. Hamidov. I.V. Azizov. Synthesis and study of the radioprotective properties of a complex of zinc with tryptophan. Journal of Radiation Researches, 2018, vol.5, №2, p. 241-246
8. D.L. Stone, D.K. Smith, A.C. Whitwood, Copper amino-acid complexes - towards encapsulated metal centres, Polyhedron, 2004, 23, p.1709
9. Alam S.M., Shereen A. Effect of different levels of Zinc and Phosphorus on growth and chlorophyll content of wheat // Asian J. of plant sciences, 2002, № 3, p. 304-306
10. Mortvedt J.J., Giordano P.M. Availability to com of zinc applied with macro nutrient fertilizers // Soil. Sc., 1969, № 108, p. 180-187

СОСТАВ И ПРОТИВОЛУЧЕВАЯ АКТИВНОСТЬ КОМПЛЕКСА ХЛОРИДА МЕДИ(II) С ТРИПТОФАНОМ

**М.Ф. Фараджов, А.С. Абдуллаев, Э.Н. Шамилов, Ш.И. Кахраманова,
Ф.Ф. Джалаладдинов, З.Н. Мехтиева**

Резюме: В результате реакции триптофана с хлоридом меди (II) получен комплекс триптофаната меди. Состав комплекса изучали методом элементного, термического, рентгенофазового анализа, ИК и УФ-спектроскопии. Противолучевая активность комплекса изучалась на облученных семенах пшеницы. Выявлено, что обработка семян пшеницы перед облучением водным раствором комплекса приводит к нормализации биосинтеза фотосинтетических пигментов.

Ключевые слова: медь, триптофан, комплекс, оксид металла, ИК-спектроскопия, термогравиметрия, антирадикал, фотосинтетические пигменты.

MİS(II) XLORİDİN TRİPTOFANLA KOMPLEKSİNİN TƏRKİBİ VƏ ANTİRADİKAL AKTİVLİYİ

M.F. Fərəcov, A.S. Abdullayev, E.N. Şamilov, Ş.İ. Qəhrəmanova,
F.F. Cəlaləddinov, Z.N. Mehdiyeva

Xülasə: Sink-triptofan kompleksinin şüalandırılmış buğda toxumlarından əmələ gələn cücərtildə fotosintez pıqmentlərinin biosintezinə təsiri tədqiq edilmişdir..

Triptofanın mis (II) xloridlə reaksiyası nəticəsində mis triptofanat kompleksi alınmışdır. Kompleksin tərkibi element, termiki, rentgen fazalı analizləri, IQ və UB spektroskopiya üsulları ilə tədqiq edilmişdir. Kompleksin qoruyucu təsiri şüalanmış buğda toxumları üzərində tədqiq edilmişdir. Buğda toxumlarının şüalanmasından əvvəl kompleksin sulu məhlulları ilə işlənməsi fotosintez pıqmentlərin biosintezini normallaşmasına səbəb olduğu müəyyən edilmişdir.

Açar sözlər: mis, triptofan, kompleks, metal oksidi, IQ spektroskopiya, termogravimetriya, anti-radikal, fotosintez pıqmentləri.