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SYNTHESIS AND BIOLOGICAL ACTIVITY OF MANGANESE (II) COMPLEXES WITH LEUCINE AND TRYPTOPHAN

Sh.I. Gahramanova[1], F.F. Jalaladdinov[1], R.A. Samadova[1],A.S. Abdullayev[2], G.E. Gasimova[2], A.S. Aghayeva[2], E.N. Shamilov[2], N.M. Rashydov[3]

[1]Institute of Catalysis and Inorganic Chemistry of ANAS
[2]Institute of Radiation Problems of ANAS
[3]Institute of Genetics Inceenering and Cell Biology Ukrainian NAS
sahnaz.gahramanova@gmail.com

Abstract: Synthesized complexes of manganese (II) with ligands leucine and tryptophane $[MnLCl_2(H_2O)_2]H_2O$,$[MnL_2Cl_2].2H_2O$,$[MnCl_2L_2]$ were synthesized. It is shown that the composition of the complexes obtained depends on the ratio of the initial components. The composition and structure of the complexes were studied by elemental and thermogravimetric analysis, IR and EPR. The results of thermogravimetric studies have shown that the final product of the thermal decomposition of all compounds is a metal oxide, respectively. 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 activity of the complexes was tested on a wheat seedling. It was revealed that the complexes had a positive effect on the content of chlorophylls and carotenoids, increasing the functional activity of the chloroplasts. Treatment of wheat seeds before irradiation (250Gy irradiation dose) with aqueous solutions of the complexes (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.

Keywords: manganese, leucine, tryptophan, metal oxide complex, amino groups, thermogravimetry, IR spectroscopy, irradiation, photosynthetic pigments, chloroplasts

Amino acids and their derivatives were studied extensively by the researchers and were presented in a variety of different ways. It is important to use them as ligands with the transitional and nontransitional element, through its association with the NH_2, and COO^- electron donors. The study of the complex formation of transition metals with amino acids is of both theoretical and practical interest for both modern bioinorganic chemistry and the chemistry of coordination compounds. It is known that the complexes of many metals, mainly with amino acids, are widely used in medicine as medicines [1-2].

In addition, they can serve as a model of processes occurring in living organisms]. There is enough information in the literature on the synthesis and properties of complex compounds of many metals with various amino acids [3-7].

However, information about complex compounds of Mn with amino acids is poorly understood and is limited to only a few papers.

The purpose of this work was the synthesis and study of the biological properties of Mn (II) complexes with the amino acids leucine and tryptophan.

1. Experimental part

The composition and chemical structure of the synthesis products obtained are studied by physical-chemical analysis methods: elemental analysis (ICP-MS); X-ray phase analysis

(diffractometer (Germany) D-2 Phaser firm Bruker); IR spectroscopy ("Specord M-80" brand Carl Zeiss). Differential thermogravimetric analysis was performed on a derivative (NETZSCH STA 449F3 STA449FSA-0622-M)

Synthesis –[MnL_2Cl_2]

A weighed 0.5 g (0.004 mol) of $MnCl_2$ was dissolved in 30 ml of hydrochloric acid at a temperature of 600°C, and 1g (0.008 mol) of leucine previously dissolved in acetic acid was added to the solution obtained. After about 30 minutes, white, needle crystals began to precipitate out of the solution, which separated, washed with mother liquor, then several times with ether and dried in a desiccator over sulfuric acid until a permanent compound was established.

Synthesis [$MnCl_2L(H_2O)_2$]. H_2O

A portion of 0.5 g (0.004 mol) of $MnCl_2$ was dissolved in 10 ml of acetic acid at a temperature of 450°C and 0.5 g (0.004 mol) of leucine was added. The resulting colorless solution was heated at 45–50°C for 2 hours with constant stirring. -h hours. The solution was cooled to room temperature and left to crystallize. The precipitated white needle-like crystals were filtered, washed with the mother liquor, then several times with acetone and dried in a desiccator over sulfuric acid to constant weight.

Synthesis -[$MnCl_2L_2$]2H_2O

According to the above procedures, 2.04 g (0.01 mol) of ligand L- tryptophan(molar ratio 1: 1), previously dissolved in 20 ml of ethyl alcohol, was added to 1.62 g (0.01 mole) $MnCl_2$ X2H_2O 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.

The results of the elemental analysis of the complexes are shown in table 1

Symbolic formula	Molecular weight	%Cl		%C		%N		%Metal	
		Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
[MnL_2Cl_2]	388	18.56	18.5	18.55	18.45	7.22	7.2	14.18	14.16
[$MnCl_2L(H_2O)_2$]· H_2O	311	22.83	22.69	23.15	23.00	9.03	9.0	17.68	17.6
[$MnCl_2L_2$]2H_2O	570	12.46	12.4	46.32	46.3	9.82	9,8	9.65	9.6

2. Results and conclusion

To determine the nature of the coordination of the ligand with the complexing agent, IR spectral analysis of the obtained complexes was carried out, which showed that the complexation is accompanied by significant spectral changes compared with the spectrum of the free ligand. So, in the spectra of the [MnL_2Cl_2] ·H_2O complexes, there is an intense broad absorption band with a maximum at 1700 cm-1, which is characteristic of stretching vibrations of the non-ionized (protonated) carboxyl group. Note that the absorption band in the amino acid spectrum observed at 1600 cm-1. which is characteristic of an ionized carboxyl group. Such a high-frequency shift of the bands, characteristic of carboxyl groups, indicates that the amino acid with the metal is coordinated through the nitrogen atom, and the carboxyl group remains in the protonated form. In addition, absorption bands at 1325 and 1260 cm-1 are observed in the spectrum of the free

ligand; for deprotonated carboxyl groups. These absorption bands show that the amino acid molecules are bipolar in which there are strong intra- or intermolecular hydrogen bonds. In the spectrum of compounds of the composition $[MnCl_2L\ (H_2O)_2]$. H_2O, an intense absorption band is observed at 1660 cm^{-1}, related to the stretching vibrations of ionized (deprotonated) carboxyl groups. The absorption band characteristic of the valence vibrations of the NH_2 groups appears as a broad band of medium intensity in the region of 3350-3450 cm-^{1}. This band relative to the spectrum of the free ligand is shifted to the high-frequency region of the spectrum, approximately 200 cm^{-1}, which indicates the amine group in coordination with the complexing agent.

To determine the composition and thermal stability of the complexes under study, we performed a thermogravimetric analysis. The general form of the derivatograms of the complexes are similar, but they differ significantly from each other in the nature of thermal decomposition.

The research results showed that in all cases the final product of the thermal decomposition of the complexes is a metal oxide.

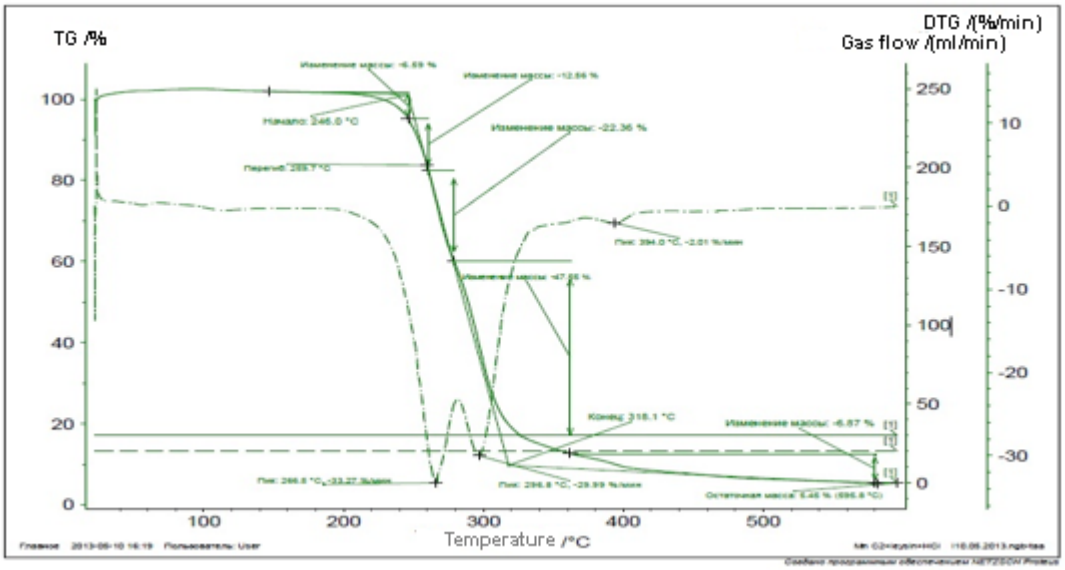

Fig.1. Thermogram of the complex $[MnCl_2L_2]$; L- leucine

From the thermograms, it can be seen that the complex is stable at a temperature of 245°C. At higher temperatures, the complex is gradually destroyed, and this process ends in several stages. The final product of the thermolysis process consists of metal oxides.

Figure 2 shows the result of X-ray phase analysis of the synthesis product. The interpretation of the obtained data also confirms the formation of the $[MnL_2(H_2O)_2]$ complex.

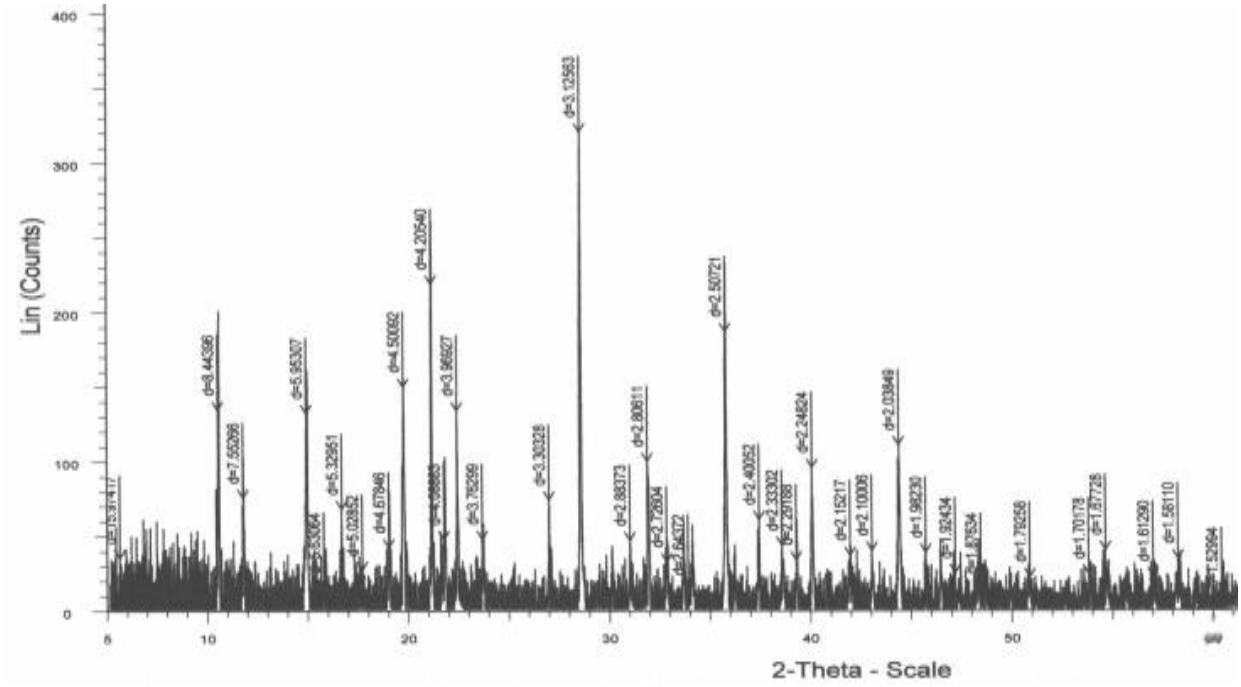

Fig.2. Diffractogram of the complex $[MnL_2(H_2O)_2]$;L- tryptophan

The spectrum of electron paramagnetic resonance (EPR)

The EPR spectrum of Mn(II) complex is obtained at room temperature for the polycrystalline sample and is shown in Fig.3. The EPR spectrum exhibits a broad signal without a fine or hyperfine structure.

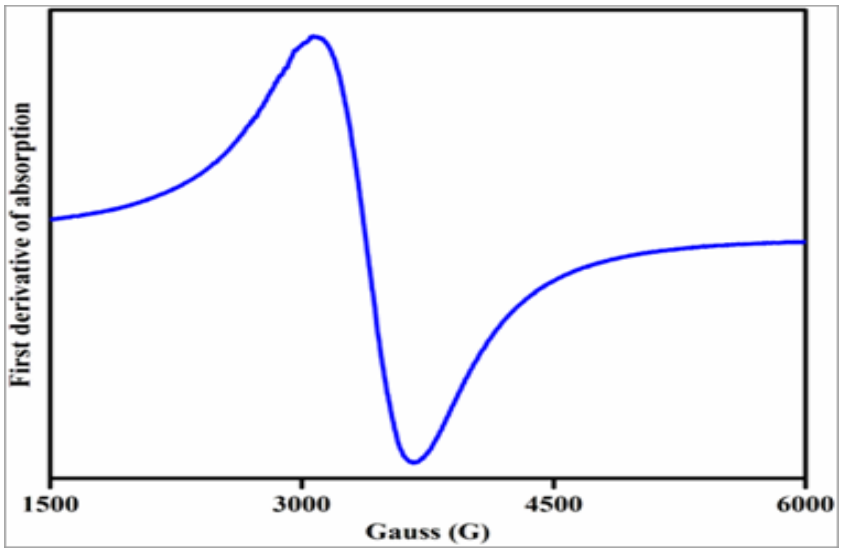

Fig.3. EPR spectrum of $[MnL_2(H_2O)_2]$ complex; L- tryptophan

The effective g value is found to be 2.04. This signal suggests that dipolar interactions between manganese ions exist. Mn(II) ions belong to $3d^5$ electron configuration for 55Mn nucleus, the nuclear spin I = 5/2 and hence the EPR spectrum of Mn(II) complex at room

temperature exhibits a characteristic six-line hyperfine splitting. During complexation the symmetry around Mn (II) is distorted. The observed broad signal suggests that the symmetry around the Mn (II) ion in the complex is changed.

Thus, according to the results of the physicochemical methods used in the work, it is established that the composition and structure of the obtained complexes directly depend on the ratio of the initial products.

Biological activity of complexes

The activity of the complexes was tested on wheat seedlings. For comparison, the seeds were treated with manganese chloride and complexes. The seedlings determined the content of photosynthetic pigments.

Table 2. The effect of tryptophan $MnCl_2$ complexes on seed germination, chlorophyll content and photosystem activity (PSI, PSII) in wheat leaves

Variants	Germination, %	Chlorophyll a+b (mg/g leaf)	Chlorophyll a/b	Activity of PS II mkmol O_2/mg chl. hour	Activity of PS I mkmol O_2/mg chl. hour
Control $MnCl_2$ $X2H_2O$	85	6.75±0.2	2,5	72±2	125±4
$MnCl_2$ - tryptophan	96	8,95±0.2	2,8	90±3	150±6

As can be seen from table 2, seeds treated with $MnCl_2$ - tryptophan, have a high germination rate and high activity of photosystems. These complexes also had a positive effect on the content of chlorophyll, as well as on the ratio of chlorophyll a / chlorophyll b.

Earlier, we noted the stimulating effect of low concentrations of a solution of manganese chloride on the germination energy and growth of seedlings [3-4]. It was indicated that low concentrations of manganese chloride positively affect the synthesis of chlorophyll and carotenoids, increase the functional activity of chloroplasts.

Thus, the tryptophan complexes with manganese 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 complexes (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.

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References

1. 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, Copper, Cobalt and Zinc with Tryptophan and their Biological Activity International Journal of Chemical Sciences**,** 2018,p.138-144
2. G.E. Gasimova , A.S. Aghayeva , A.S. Abdullayev , E.N. Shamilov, Sh.I. Qahramanova, F.F. Jalaladdinov, R.H. Hamidov, I.V. Azizov. Journal of Radiation Researches, vol.5, №2, 2018, pp.241-246.
3. Gahramanova Sh. I., Kulieva.E.A., Azizov. I.V. The effect of newly synthesized zinc complexes with amino acids on the morphophysiological indicators of wheat seedlings. // Academic Journal of Western Siberia №5. Tom 10. 2014. c 94-952.
4. Gahramanova Sh. İ., Guliyeva.E.A., Suleymanov G.Z., Azizov.I.V. Influence Newly Syntesized Manganese Complexes with Amino Asids on Morphophysiological Chracteristics Wheat Germ. American International Journal of Contemporary Research Vol.4, No. 12; December 2014.P.58-60
5. Mahmudov K.T., Sutradhar M., Martins L., Silva F.C, Ribera A., Nunes V.M., Marchetti F., Pombeiroa A.L., Gahramanova Sh.I., Mn(II) and Cu(II) complexes with arylhydrazones of active methylene compounds as effective heterogeneous catalysts for solvent and additive-free microwave-assisted peroxidative oxidation of alcohols. // RSC Advances An international journal to further the chemical sciences. The Royal Society of Chemistry. 2015. 5, P. 25979–25987.
6. Gahramanova Sh. I., Gulieva E.A, Suleimanov G.Z, Karimova U.A, Asgarova T. Y. Interaction of manganese (II) with valine and ß-alanine // International Youth Scientific and Practical Conference of Students, graduate students and young "Fundamental and applied research in the field of chemistry and ecology", (Kursk September 23 - September 26, 2015). Pp. 29-31.
7. Gahramanova Sh.I., Osmanov N.S., Gulieva E.A., Khudaverdiev R.A., Asgarova T.Y.. Synthesis and study of manganese (II) complexes with leucine. Chemical Problems, Baku.2010, №3,p. 469-471

СИНТЕЗ И БИОЛОГИЧЕСКАЯ АКТИВНОСТЬ КОМПЛЕКСОВ МАРГАНЦА (II) С ЛЕЙЦИНОМ И ТРИПТОФАНОМ

Ш.И. Гахраманова, Ф.Ф. Джалаладдинов, Р.А. Самадова, А.С. Абдуллаев, Г.Е. Гасымова, А.С. Агаева, Э.Н. Шамилов, Н.М. Рашидов

Резюме: Синтезированы комплексы марганца (II) с лигандами лейцином и триптофаном [$MnLCl_2$ (H_2O) $_2$] H_2O, [MnL_2Cl_2] .H_2O [$MnCl_2L_2$].

Показано, что состав полученных комплексов зависит от соотношения исходных компонентов. Состав и строение комплексов изучали методом элементного и термогравиметрического анализа, ИК и ЭПР. Результаты термогравиметрических исследований показали, что конечным продуктом термического разложения всех соединений является оксид металла соответственно. ИК-спектроскопия показала, что лиганды в составе комплексов металла (II) переходят в нейтральную форму и координируются с комплексообразующим агентом через атом азота. Активность комплексов проверяли на проростках семян пшеницы. Выявлено, что комплексы положительно влияют на содержание хлорофиллов и каротиноидов, повышая функциональную активность хлоропластов.Обработка семян пшеницы перед облучением (доза облучения 250 Гр) водными растворами комплексов (концентрация раствора 0,001%) приводит к нормализации биосинтеза фотосинтетических пигментов, помогает устранить аномалии митотического деления в клетках корневых волосков, стимулирует репаративные механизмы.

Ключевые слова: марганец, лейцин, триптофан, оксид металла, комплекс, аминогруппы, термогравиметрия, ИК-спектроскопия, облучение, фотосинтетические пигменты, хлоропласты

LEYSİN VƏ TRİPTOFANIN MANQAN (II) KOMPLEKSLƏRİNİN SİNTEZİ VƏ BİOLOJİ AKTİVLİKLƏRİ

Ş.İ. Qəhrəmanova, F.F. Cəlaləddinov, R.A. Səmədova, A.S. Abdullayev, G.E. Gasımova, Ə.S. Ağayeva, E.N. Şamilov, N.M. Rəşidov

Xülasə: Manqan(II)-nin leysin və triptofanla kompleksləri $[MnLCl_2(H_2O)_2]H_2O$, $[MnL_2Cl_2]\cdot H_2O$,$[MnCl_2L_2]$sintez edilmişdir. Alınmış komplekslərin tərkiblərinin ilkin maddələrin nisbətindən asılılığı müəyyənləşdirilmişdir. Komplekslərin tərkibi və koordinasiyanın xarakteri element və termoqravimetrik analizlə, İQ, EPR spektroskopiyası ilə müəyyənləşdirilmişdir. Termoqravimetrik analizin nəticələri göstərmişdir ki, son parçalanma məhsullarını metal oksidi təşkil edir. İQ spektrlərə əsasən ikivalentli metalın azot atomları ilə koordinasiyası müəyyənləşdirilmişdir.

Komplekslərin aktivlikləri buğda toxumlarında və onlardan əmələ gələn cücərtilərdə yoxlanılmışdır. Müəyyən edilmişdir ki, komplekslər xloroplastların funksional aktivliklərini qaldırmaqla xlorofillərin və karotinoidlərin miqdarına müsbət təsir göstərir. Şüalanmadan əvvəl (şülanma dozası 250 Qr) toxumların 0,001%-li məhlulları ilə işlənməsi fotosintez piqmentlərinin biosintezini normallaşdırır, kök hüceyrələri tükcüklərində mitotik bölünmələr zaman yaranan anomaliyaların aradan qalxmasına kömək edir, reparasiya proseslərini normallaşdırır.

Açar sözlər: manqan, leysin, triptofan, metal oksidi, kompleks, aminqruplar, termoqravimetrik analiz, İQ-spektroskopiya, şüalanma, fotosintez piqmentləti, xloroplastlar