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СОСТАВ И АНТИРАДИАЦИОННАЯ АКТИВНОСТЬ ХЛОРИДНОГО КОМПЛЕКСА МАРГАНЦА (II) С САЛИЦИЛОВОЙ КИСЛОТОЙ

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COMPOSITION AND ANTIRADIATION ACTIVITY OF THE MANGANESE (II) CHLORIDE COMPLEX WITH SALICYLIC ACID

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В результате реакции салициловой кислоты с хлоридом марганца (II) был получен комплекс марганцево-салициловой кислоты $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, L – салициловая кислота. Состав комплекса изучен методами элементного анализа, термического анализа, ЭПР-спектрального, рентгенофазового анализа, ИК-и УФ-спектроскопии. Методом ИК-спектроскопии показано, что лиганд в комплексе металла (II) переходит в нейтральную форму. Результат термогравиметрических исследований показал, что конечным продуктом соединения является оксид металла. Антирадикальную активность комплекса изучали на облученных семенах пшеницы. Выявлено, что обработка семян пшеницы перед облучением водным раствором комплекса приводит к нормализации биосинтеза фотосинтетических пигментов

Ключевые слова: антирадиация; ИК-спектроскопия; комплекс; марганец; оксид металла; салициловая кислота; спектр ЭПР; термогравиметрия; фотосинтетические пигменты.

As a result of the reaction of salicylic acid with manganese (II) chloride, a complex of manganese salicylic acid was obtained $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, L – salicylic acid. The composition of the complex was studied by elemental, thermal, EPR spectrum, X-ray phase analysis, IR, and UV spectroscopy. The method of IR spectroscopy showed that the ligand in the complex of the metal (II) complexes enter the neutral form. The result of thermogravimetric studies have shown that the final product of the compound is metal oxide. 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.

Key words: antiradiation; complex; EPR spectrum; IR spectroscopy; manganese; metal oxide; photosynthetic pigments; salicylic acid; thermogravimetry.

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 as medicines ^{3–10}.

The aim of this work was the synthesis of a complex of salicylic acid with manganese (II) chloride, the study of structures, and anti-radiation properties. In this paper, we present methods of synthesis and study of the properties of manganese (II) complexes with salicylic acid, and their biological effects.

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).

Experimental part

Synthesis of $[MnL_2(H_2O)_2] \cdot 2H_2O$, L – salicylic acid

2.760 g of the salicylic acid was dissolved in 20 ml of ethanol. The resulting solution was added to 1.259 g of manganese (II) chloride in 20 ml of distilled water and then refluxed for 2 hours. The precipitate formed was filtered off, washed with ethanol and dried in a desiccator over anhydrous calcium chloride for one week.

Results and conclusion

Differential Scanning Calorimetry

With the definition of the thermic stability and the composition of synthesized complexes $[MnL_2(H_2O)_2] \cdot 2H_2O$ the thermographic analysis was carried out (Fig. 1).

Thermocouples were used to determine the composition and durability of the synthesized complex compound and it was established that the complex is resistant to a temperature 160 °C. At higher temperatures, the complex gradually breaks down, and this process ends in several stages, and in all cases the final product of the thermolysis process consists of metal oxides

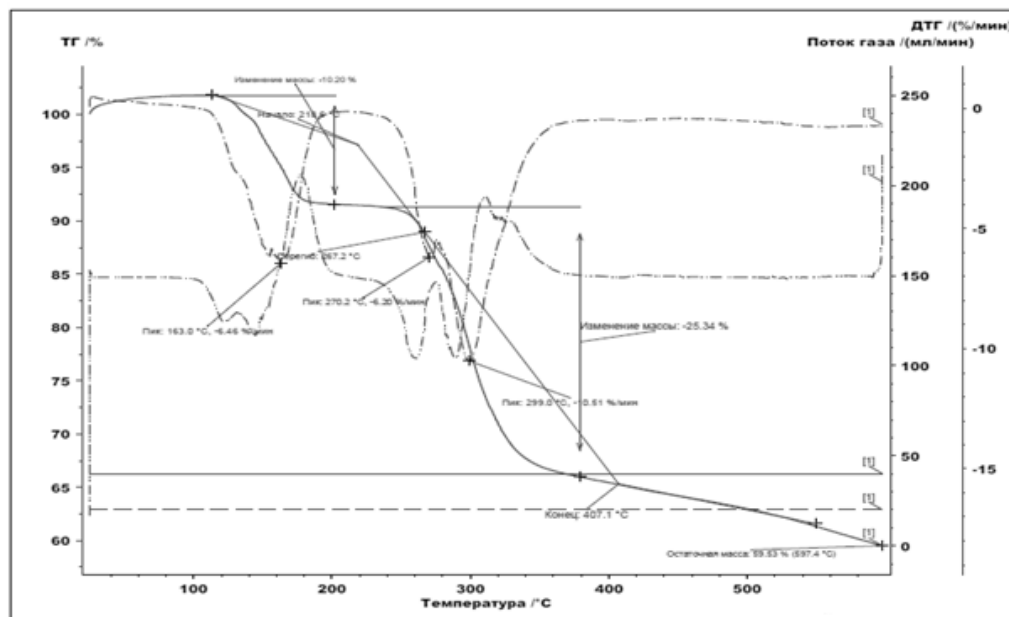


Fig. 1. Thermogravigram complex $[MnL_2(H_2O)_2] \cdot 2H_2O$, L – salicylic acid

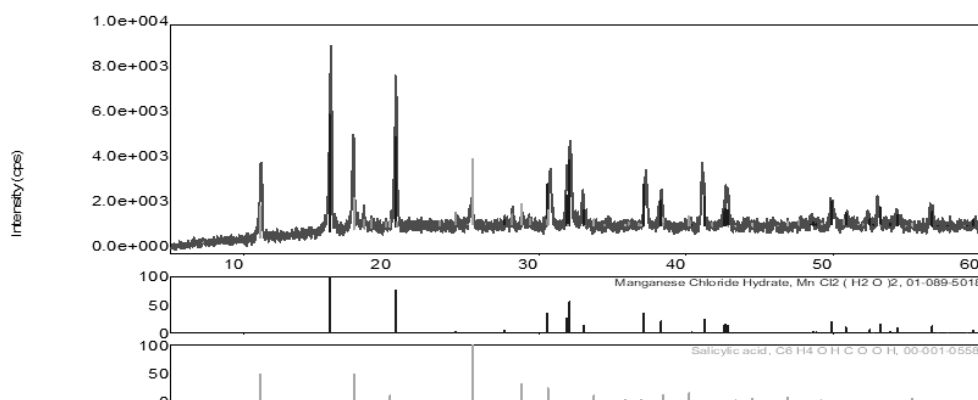


Fig. 2. Diffractogram of the complex $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, L – salicylic acid

X-ray phase analysis

Fig. 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 $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complex.

Since the parameters of the crystalline cell differ from each other, a coordination complex Mn- salicylic acid was created. Salicylic acid peaks did not appear in Mn- salicylic acid, but almost all complexes were created

UV-VIS spectroscopy

The UV-VIS spectroscopy analysis of 0.01 M of $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complex in water was made. It is clear from the specimen that the d-d passage is 480–560 nm wavelength (Fig. 3).

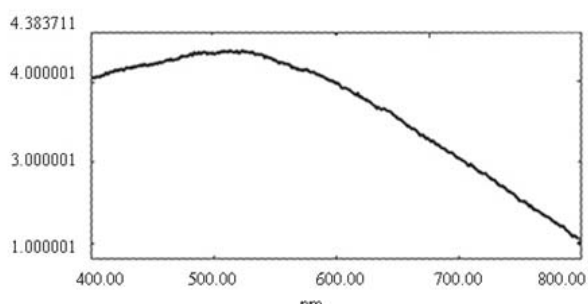


Fig. 3. $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, ultraviolet absorption spectrum of 0.01 M solution of complex

The X-band EPR spectrum of Mn (II) complex is obtained at room temperature for the polycrystalline sample and is shown in the EPR spectrum exhibits a broad signal without fine or hyperfine structure the effective g value is found to be 2.04. This signal suggests that dipolar interactions between manganese ions exist. Mn (II) ions belongs to 3d5 electron configuration for 55Mn nucleus, the nuclear spin $I = 5/2$ and hence EPR spectrum of Mn (II) complex at room temperature exhibits a characteristic six line hyperfine splitting. If the symmetry around Mn (II) is distorted due to complexation, the

resonances become anisotropic and a randomly oriented sample may exhibit a broad line. The observed broad signal in the present work suggests that the symmetry around Mn (II) ion in the complex is distorted one.

The results of the investigations showed that in all cases the final product of the thermal decomposition of the complexes is metal oxide. 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 depends on the ratio of the initial products To determine the composition and thermal stability of the complexes under study, we performed elemental analysis, X-ray phase analysis, IR spectral and thermogravimetric analysis

The antiradiation activity of complex Mn(II) with salicylic acid

The antiradiation activity of the complex was checked on irradiated seeds of wheat (Tab. 1). The content of photosynthetic pigments was determined in seedlings.

As can be seen from Tab. 1, seeds treated with MnCl_2 –salicylic acid, 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.

Treatment of wheat seeds before irradiation (250 Gy 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.

Influence of $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complex with salicylic acid 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	85	2.04	1.34	0.65
0.001% – $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$				
	94	2.15	1.37	0.75
Irradiated 250 Gy				
Irradiated control	45	1.33	0.54	0.44
Irradiated +0.005% – $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$	90	1.97	1.01	0.71
Irradiated +0.001% – $[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$	87	1.85	0.97	0.63

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