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СИНТЕЗ И ИССЛЕДОВАНИЕ АНТИРАДИАЦИОННОЙ АКТИВНОСТИ КОМПЛЕКСОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ С САЛИЦИЛОВО-РЕЗОРЦИНОВЫМ СПИРТОМ

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SYNTHESIS AND STUDY OF THE ANTI-RADIATION ACTIVITY OF TRANSITION METAL COMPLEXES WITH SALICYLIC-RESORCINOL ALCOHOL

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В нейтральной среде синтезированы комплексные соединения переходных металлов марганца (II) и цинка (II)) с салицилово-резорциновым спиртом $[MnL_2Cl_2]$, $[ZnL_2(H_2O)_2]_2(H_2O)$. Идентификация синтезированных комплексов проводилась с помощью элементного, рентгенофазового анализа, УФ-спектроскопии, ИК спектрального и термогравиметрического методов анализа. Кристаллическая структура комплексов была определена методом монокристаллической рентгеновской дифракции. Согласно УФ- спектроскопии в комплексах наблюдается *d–d* переход, соответствующий длине волны для Mn (II) 480–560 нм, для комплекса Zn (II) 238 нм. Результаты термогравиметрических исследований показали, что конечным продуктом термического разложения всех соединений является оксид металла соответственно. Изучена антирадиационная активность комплексов марганца (II) и цинка (II) на облученных семенах пшеницы. Обнаружено, что обработка семян пшеницы перед облучением водным раствором комплексов приводит к нормализации биосинтеза фотосинтетических пигментов.

Ключевые слова: антирадиационная активность; ИК-спектроскопия; комплекс; марганец; рентгенофазовый анализ; салицилово-резорциновый спирт; термогравиметрический анализ; цинк.

Transition metal manganese (II) and zinc (II)) complexes with salicylic resorcinol alcohol $[MnL_2Cl_2]$, $[ZnL_2(H_2O)_2]\cdot 2(H_2O)$ were synthesized in neutral medium. Identification of the synthesized complexes was carried out using elemental, X-ray phase analysis, UV spectroscopy, IR spectral and thermogravimetric methods of analysis. The crystal structure of the complexes was determined by single crystal X-ray diffraction. According to UV spectroscopy, *d–d* transition was observed in the complexes corresponding to the wavelength for Mn (II) 480–560 nm, for Zn (II) complex 238 nm. The results of thermogravimetric studies showed that the final product of thermal decomposition of all compounds is metal oxide, respectively. The anti-radiation activity of manganese (II) and zinc (II) complexes on irradiated wheat seeds was studied. It was found that treatment of wheat seeds before irradiation with an aqueous solution of the complexes leads to normalization of photosynthetic pigments biosynthesis.

Key words: anti-radiation activity; complex; IR spectroscopy; manganese; salicylic-resorcinol alcohol; thermogravimetric analyzes; X-ray phase analysis; zinc.

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Coordination compounds of most transition metals with organic ligands such as benzoic acid, salicylic acid, resorcinol, bipyridine, polyaminopolyphosphonic acids exhibit biological activity, since they are donors of vital trace elements and biomolecules and can also exhibit high cytotoxic activity against tumor cells, therefore and are widely used in the production of various drugs [1–4]. The biological activity of the complexes is determined not only by the nature of the metal ion and ligands, but also by the conditions of the synthesis, the composition of the external and internal coordination spheres, and the structure of the compounds obtained [5=8].

In this paper, we present methods of synthesis and study of the properties of manganese (II) with salicylic-resorcinol alcohol and salicylic acid.

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_2Cl_2 (L – salicylic-resorcinol alcohol). A sample of 0.6 g (0.03 mol) of $MnCl_2$ was dissolved in 30 ml of ethyl alcohol at 60 °C, 40 ml of salicylic resorcinol was added to the solution and then boiled under reflux for 2 hours. The resulting precipitate was filtered off, washed with ethanol, and dried in a desiccator over sulfuric acid for one week.

Synthesis $[ZnL_2(H_2O)_2]\cdot 2H_2O$, L – salicylic-resorcinol alcohol. The synthesis of a zinc (II) complex with salicylic-resorcinol alcohol was obtained by the method described above.

Results and conclusion

IR- spectroscopy. We have synthesized complex compounds of manganese (II) and zinc (II) with salicylic-resorcinol alcohol $[MnL_2Cl_2]$, $[ZnL_2(H_2O)_2]\cdot 2H_2O$ in a neutral medium. To determine the nature of the coordination of the ligand with the complexing agent, an IR spectral analysis of the obtained complexes was carried out, which showed that the complexation is accompanied by significant spectral changes in comparison with the spectrum of the free ligand.

Comparison of the IR spectra of the obtained complex compounds and the initial one showed that the absorption bands of the carbonyl group in the complex are in an ionized form, since absorption bands of asymmetric and symmetric vibrations of the deprotonated carboxyl group appear in the region of 1659-1510 and 1445-1377 cm^{-1}, respectively, and the bands disappear absorption in the range 1665-1700 cm^{-1} (Fig. 1).

Related to the stretching vibrations of the C=O bond of the unionized carboxyl group. The difference between asymmetric and symmetric stretching vibrations of the ionized carboxyl group $\Delta\nu(COO^-)$ is less than 220 cm^{-1}, which suggests its bidentate coordination with the manganese ion in the resulting

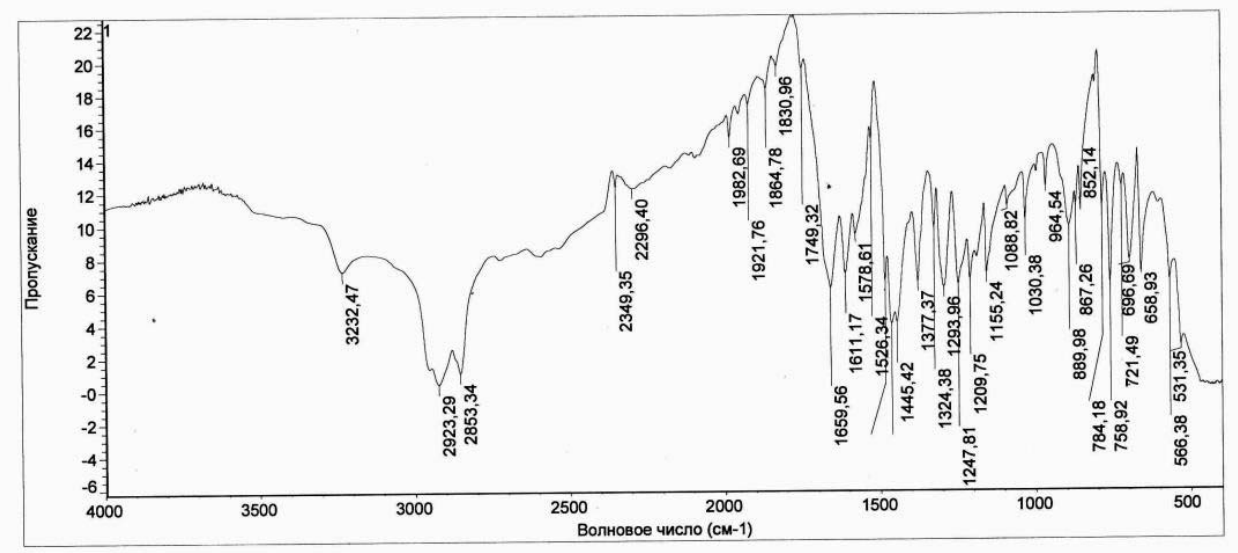

Fig. 1. IR spectrum of the Mn (II) complex with salicylic-resorcinol alcohol

complex compound. For the same reason, it can be concluded that the type of bond between the carboxylate oxygen atom of the ligand with the manganese (II) ion is predominantly ionic. Interpretation of the obtained data also confirms the formation of complexes $[MnL_2Cl_2]$, $[ZnL_2\cdot(H_2O)2]\cdot2H_2O$ *L*-(salicylic-resorcinol alcohol).

Differential Scanning Calorimetry. With the definition of the thermic stability and the composition of synthesized complexes $[MnL_2Cl_2]$ the thermographic analysis was carried out.

Using thermocouples, the composition and strength of the synthesized complex compound was determined, and it was found that the complex is stable up to 160 °C. (Fig 2.)

At higher temperatures, the complex gradually disintegrates, and this process ends in several stages, and in all cases the result is that Me^{+2} is converted to Me^{+3}. Thus, according to the results of the physicochemical methods used in this work, it was found that the composition and structure of the obtained complexes directly depend on the ratio of the initial products (Fig 3.)

X-ray phase analysis. Fig. 4. shows the result of X-ray phase analysis of the synthesis product. The interpretation of the obtained data also confirms the formation of the $[MnL_2Cl_2]$ complex.

Since the parameters of the crystalline cell differ from each other, a coordination complex Mn-

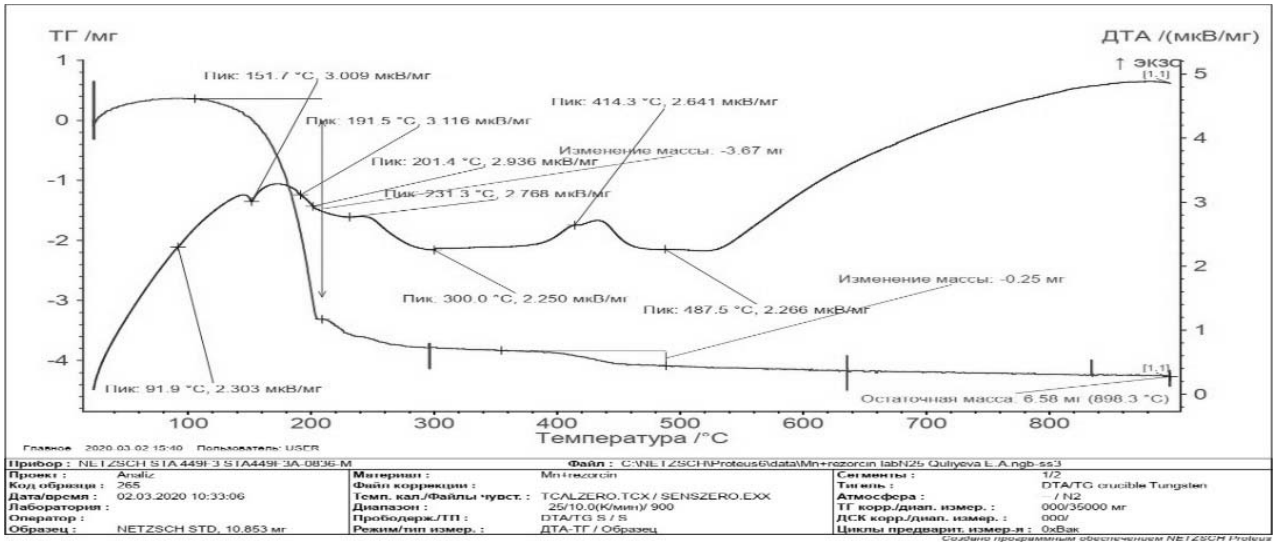

Fig.2 .Thermogravigram complex MnL_2Cl_2 (L – salicylic-resorcinol alcohol)

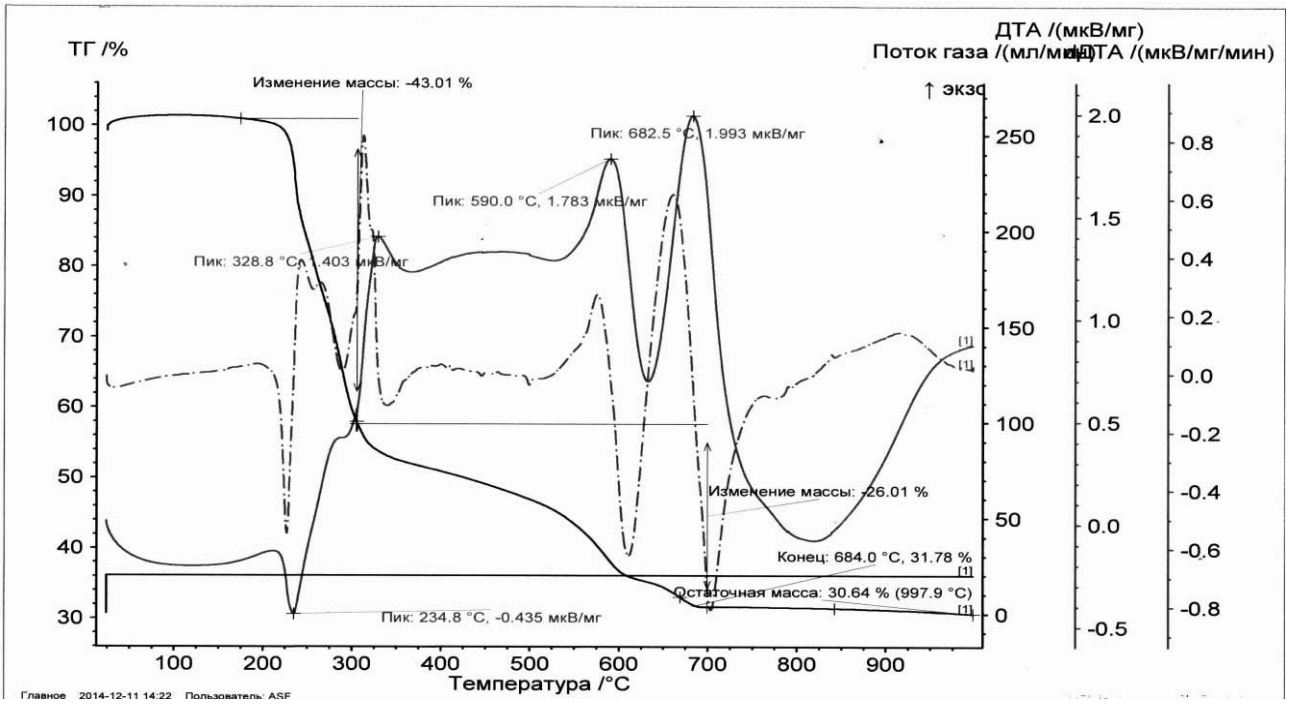

Fig.3. Thermogravigram of the complex $[ZnL_2(H_2O)_2]\cdot2(H_2O)$ (L – salicyl-resorcinol alcohol)

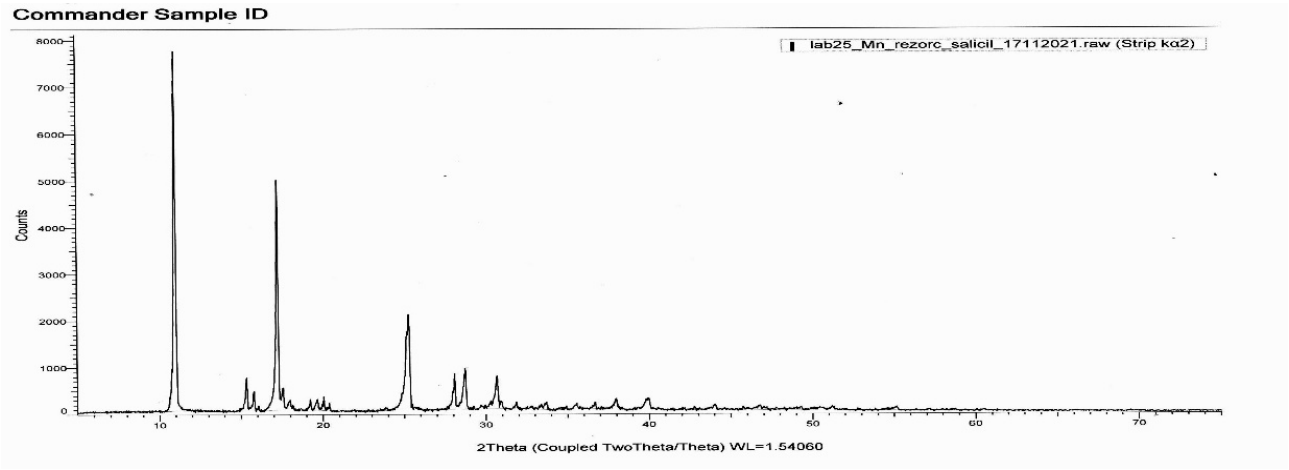

Fig. 4. Diffractogram of the complex $[MnL_2Cl_2]$ (L – salicylic-resorcinol alcohol)

salicylic-resorcinol alcohol was created. salicylic-resorcinol alcohol peaks did not appear in Mn-salicylic-resorcinol alcohol, but almost all complexes were created

UV-VIS spectroscopy. The UV-VIS spectroscopu analysis of 0.01 M of manganese (II) and zinc (II), complex is water was made. It is clear from the specimen that the d-d passage is 480-560 nm wavelength Mn (II). The complex with Zn^{2+} is characterized by the appearance of one maximum at 238 nm. The maximum at 238 nm characterizes the formation of a metal-ligand coordination bond.

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.

Study of anti-radiation activity of manganese (II) and zinc (II) complexes with salicylic resorcinol alcohol

In the manganese (II) and zinc (II) complexes obtained, the anti-radiation activity was tested on irradiated wheat seeds. Photosynthetic pigment content was determined in seedlings. Seeds treated with $MnCl_2$-salicyl-resorcinol had high germination rate and high photosystem activity. The complexes also had a positive effect on chlorophyll content as well as on the chlorophyll /A chlorophyll/ B ratio. It was found that low concentrations of complexes positively affect chlorophyll and carotenoids synthesis and increase functional activity of chloroplasts. Treatment of wheat seeds before irradiation (irradiation dose 300 Gy) with aqueous solutions of complexes (solution concentration 0.001%) leads to normalization of photosynthetic pigments biosynthesis, promotes elimination of mitotic division anomaly in root hair cells and stimulates reparative mechanisms.

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