SYNTHESIS OF COMPLEX COMPOUNDS FROM SALTS OF SOME 3D-METALS.

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Аннотация: Синтез комплексных соединений солей Mn(II), Co(II), Ni(II), Cu(II) и Zn с бензойной кислотой и тиосемикарбазидом, исследование их состава, строения и свойств, а также определение законы комплексообразования. При этом разработан метод синтеза комплексных соединений хлоридов и нитратов Mn(II), Co(II), Ni(II), Cu(II) и Zn с бензойной кислотой и тиосемикарбазидом, синтезированы комплексные соединения со смешанными лигандами. с бензойной кислотой и тиосемикарбазидом. Состав, строение и свойства синтезированных комплексных соединений изучены физико-химическими методами. В частности, его изучали методами ИК-спектроскопии, рентгенофазового анализа. Путем изучения метода и условий синтеза новых комплексных соединений на основе бензойной кислоты и тиосемикарбазида предложен эффективный метод.

Ключевые слова: 3d-металлы, бензойная кислота, тиосемикарбазид, ИК-спектроскопия, рентгенофазовый анализ, лиганды, [NiCl2·ТСК·БК] и [Ni (CH3COO)2·ТСК·БК]

Abstract: Synthesis of complex compound salts Mn(II), Co(II), Ni(II), Cu(II) and Zn with benzoic acid and thiosemicarbazidom, investigation of composition, structure and properties, as well as determination of complex complex formation. Pri etom developed a method for the synthesis of complex compound chlorides and nitrates of Mn(II), Co(II), Ni(II), Cu(II) and Zn with benzoic acid and thiosemicarbazide, synthesizing complex compounds with mixed ligands. Benzoic acid and thiosemicarbazidom. Sostav, stroenie i svoystva synthezirovannyx kompleksnyx soedineniy izucheny physiko-khimicheskimi metodami. V chastnosti, ego-iruchali method IK-spectroscopy, X-ray phase analysis. Putem izuchenia method and conditional synthesis of a new complex compound and the basis of benzoic acid and thiosemicarbazide proposed effective method.

Key words: 3d metals, benzoic acid, thiosemicarbazide, IR spectroscopy, X-ray phase analysis, ligands, [NiCl2·TSA·BA] and [Ni(CH3COO)2·TSA·BA]

Annotatsiya: Benzoy kislota va tiosemikarbazid bilan Mn(II), Co(II), Ni(II), Cu(II) va Zn tuzlarining kompleks birikmalarini sintez qilish va ularning tarkibini, tuzilishini va xossalarini o‘rganish hamda kompleks hosil bo‘lish qonuniyatlarini aniqlashdan iborat. Bunda, benzoy kislota va tiosemikarbazid bilan Mn(II), Co(II), Ni(II), Cu(II) va Zn xloridlari va nitratlarining kompleks birikmalarini sintez qilish usulini ishlab chiqish, benzoy kislota va tiosemikarbazid bilan aralash ligandli kompleks birikmalar sintez

qilindi. Sintez qilingan kompleks birikmalarning tarkibi, tuzilishi va xossalari fizik-kimyoviy metodlar yordamida o‘rganildi. Xususan, IQ-spektroskopiya, rentgenofazaviy analiz usullari yordamida o‘rganildi. Benzoy kislota va tiosemikarbazid asosida olingan yangi kompleks birikmalarni sintez qilish usuli va sharoitlarini o‘rganib, samarali usul taklif qilindi.

Kalit so‘zlar: 3d-metallar, benzoy kislota, teosemikarbazid, IQ-spektroskopiya, rentgenfazaviy analiz, ligand, [$NiCl_2$· TSK ·BK] va [Ni ($CH_3COO)_2$·TSK· BK]

The aim of this scientific work is the synthesis of complex compounds of Mn(II), Co(II), Ni(II), Cu(II) and Zn salts with benzoic acid and thiosemicarbazide, as well as the study of their composition, structure and properties. as well as complex products is to determine the laws of being.

- synthesis of complex compounds of chlorides and nitrates of Mn(II), Co(II), Ni(II), Cu(II) and Zn with benzoic acid and thiosemicarbazide;

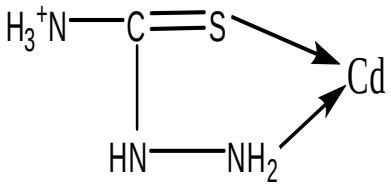
- study the composition, structure and properties of compounds obtained with the combined use of physicochemical research methods.

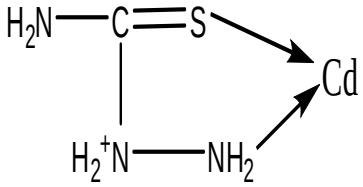
Complex compounds of chlorides, acetates and nitrates of Mn(II), Co(II), Ni(II), Cu(II) and Zn were synthesized. The composition, structure and properties of the synthesized complex compounds were analyzed using physical and chemical methods: IR spectroscopy, X-ray phase analysis and DQES analysis methods. The probability of ligand coordination is studied using quantum chemical calculations. The coordination of the ligand with the central atom and the geometric structure of new complex compounds are determined.

Complex combinations of 3d-metal salts with benzoic acid and thiosemicarbazide with mixed ligands have been practically unstudied. The study of the complex structure, composition, properties and patterns of complex compounds with mixed ligands is important for enriching the theoretical foundations of fundamental knowledge. Therefore, a lot of literature and scientific articles on the topic were carefully studied, examined and appropriate conclusions were made. Complex compounds of some 3d-metal salts synthesized with benzoic acid and thiosemicarbazide were studied using several methods of physicochemical analysis: thermal analysis, IR spectroscopy, X-ray phase analysis, DCE and semi-empirical quantum-chemical study of the reactivity of the molecule of the complex compound.

One of the main tasks of coordination compound chemistry is the study of the "composition-structure-properties" laws. The information obtained is necessary for the targeted identification and synthesis of new chemical substances with certain properties, composition and structure, as well as other important properties. This is very important for biologically active substances used in medicine[1-3]. Therefore, the synthesis of coordination compounds, the analysis of synthesized compounds using physicochemical studies, the study of their biological activity and application in life have become one of the most pressing problems facing chemists today. Thiosemicarbazide has the ability to

form coordination compounds with various ions of d-elements, where it acts as a bidentate ligand. It is known that the interaction of thiosemicarbazide containing hydrochloric acid with chlorides of some metals in aqueous solutions can form compounds of various compositions[4], for example, $3CdCl_2•2(H_2NCSNHNH_2•HCl)$, $CdCl_2•(H_2NCSNHNH_2•HCl)$, $CdCl_2•2(H_2NCSNHNH_2•HCl)$. Such compounds can have various structures. On the one hand, it can be said that they are salts containing cations $[H_2NCSNHNH_3]+$ and the corresponding complex anions. On the other hand, the following types of metallocycles can be realized:





In order to find an answer to the question of what form the chloroacid thiosemicarbazide may be in the compounds under consideration, the IR absorption spectra of complexes of the following formulas were studied: $CdCl_2•2(H_2NCSNHNH_2•HCl)$, $CdCl_2•(H_2NCSNHNH_2•HCl)$, $3CdCl_2•2(H_2NCSNHNH_2•HCl)$, $NiCl_2•2(H_2NCSNHNH_2•HCl)$, as well as the original thiosemicarbazide chlorous acid $(H_2N\text{-}CS\text{-}NH\text{-}NH_2)Cl$ and a complex of deuterated cadmium with one molecule of thiosemicarbazide chlorous acid. A review of the obtained IR spectra of the complexes and a comparison with the IR spectra of thiosemicarbazide acid chloride showed that all bands of the $(H_2NCSNHNH_3]+$ cations are present in the spectra of the complexes. It can be concluded that from[5] the studied complexes retain this cation in the form of an outer-sphere ion. It should be taken into account that cadmium(II) and nickel(II) have only a six-digit coordination number, but also have a four-digit coordination number; for the considered complexes $CdCl_2•2L$, $CdCl_2•L$ and $NiCl_2•2L$ (where L–chloride is acidic thiosemicarbazide) $[H_2NCSNHNH_2]_2•[CdCl_4]$, $[H_2NCSNHNH_2]$ The coordination formulas $2[Cd_2Cl_6]$ and $[H_2NCSNHNH_2]2[NiCl_4]$ coincide, while the second of these compounds has two chloride bridge.

Mixed-ligand complexes are also formed during the interaction of acetylacetonates with thiosemicarbazide and 3d-metals.[6] The aim of this work was to study the interaction of nickel (NH), cobalt (NH), copper (NH) and zinc acetylacetonates with thiosemicarbazide in an aqueous medium, as well as to study the composition and structure of the resulting products. To synthesize primary metal acetylacetonates, an aqueous solution of ammonia was added to a solution of a metal salt with acetylacetone and a solution of the corresponding metal salt with acetylacetone was synthesized by the interaction method.

Coordination compounds of cobalt(HH), nickel(HH), copper(HH), and zinc acetylacetonates with thiosemicarbazide were synthesized by the following methods. 0.91 g (0.01 mol) of thiosemicarbazide was dissolved in 100 ml of heated water; after cooling, 0.005 mol of the corresponding metal was added to the dry acetylacetonate. The resulting

precipitate was filtered, washed with water and alcohol, and dried in air. When the color of the precipitate and solution no longer changed, the precipitate was filtered, washed with water and alcohol, and dried. The results of chemical analysis show that for copper (HH), nickel (HH) and zinc (HH) the compounds of the metal contained in it are thiosemicarbazide - acetylacetonate 1:1:1 and for cobalt 1:2:1, both thiosemicarbazide and acetylacetonate act as single-charged anions. Analysis of IR spectra shows that "thioamide HH" increases its frequency without changing the intensity of the absorption region compared to the spectrum of free thiosemicarbazide for all the complexes obtained.

According to the literature[7], such a change in thioamide bonds corresponds to the bidentate coordination of thiosemicarbazide with sulfur and nitrogen atoms. In the spectra of all complexes in the field, a very strong absorption region is observed around 2100 cm-1, as we have shown earlier[8-10] , due to which a four-membered cycle is formed with the participation of nitrogen and sulfur atoms and thiosemicarbazide is deprotonated. Due to the absorption regions in the IR spectra, the vibrations of the acetylacetonate ion are very close to the vibrations of the original 3d-metal acetylacetonates and their complexes with thiosemicarbazide. The arrangement of wavelengths in the electronic spectra of the synthesized compounds showed that the copper (HH) complexes have a planar-square structure, and the nickel (HH) and cobalt (HH) complexes have an octahedral structure.[11] These assumptions are also confirmed by magnetic moment measurement data. These complex compounds are diamagnetic.

The complex compounds were synthesized using a known technique. According to it, (0.002 mol) 0.244 g benzoic acid (BA), (0.002 mol) 0.08 g sodium hydroxide, (0.002 mol) 0.182 g thiosemicarbazide (TSK) and nickel(II) chloride 0.165 g (0.001 mol) were obtained. Benzoic acid (BA) was dissolved in 5 ml 96% ethanol. Nickel(II) chloride, sodium hydroxide and thiosemicarbazide (TSK) were dissolved in 5 ml distilled water. First, sodium hydroxide was added to neutralize benzoic acid. Sodium benzoate was added to an aqueous solution of nickel(II) chloride with stirring. Thiosemicarbazide (TSK) was poured there and stirred. The color of the solution became dark green. The mixture was removed for crystallization. After 3 days, small dark crystals were formed, which were filtered and washed several times with ethanol. Yield = 70%. Liquid = 142-144 oC.

Complex compounds of chloride and nitrate salts of Mn(II), Co(II) and Zn with mixed ligands with benzoic acid and thiosemicarbazide were synthesized similarly.

The color, yield, melting point and elemental analysis results of the complex compounds are presented in Table 1, the solubility of the complex compounds in solvents is presented in Table 2.

The description of the physicochemical methods, analytical instruments and principles of their operation selected for the analysis of the synthesized complex compounds is given. Methods and conditions for the synthesis of new compounds based on benzoic acid and thiosemicarbazide have been developed. The synthesis of some 3d-metal salts with benzoic acid and thiosemicarbazide with new mixed-ligand complexes

has been carried out. The results of the color, yield, liquefaction temperature and elemental analysis of the synthesized complex compounds with mixed ligands are presented. The solubility of the synthesized complex compounds with mixed ligands in various solvents has been studied.

Table 1

Characteristics of the ligand and synthesized complex compounds.

Table 2

Compounds	Color	efficiency %	Cold temperature ^{0}C	found,%			Brutto - formula	Calculated , %		
				C	S	M		C	S	M
[$Co(NO_3)_2$•TSK·BK]	reddish brown	85	195 - 197	1.14	3.054	11.35	$Co_2S_6N_{24}O_{19}H_{32}C_6$	**1.13**	3.03	11.45
[$CoCl_2$•TSK·BK]	brown	82	180 - 182	**2.11**	3.085	12.20	$CoS_6N_{24}O_{16}H_{32}C_6$	**2.06**	3.06	12.50
[$ZnCl_2$•TSK·BK]	white	79	156 - 158	**1.10**	2.055	11.05	$ZnS_6N_{24}O_{19}H_{32}C_6$	**1.05**	2.095	11.28
[$MnCl_2$•TSK·BK]	light pink	78	105 - 107	**1.13**	2.095	10.28	$MnS_6N_{24}O_{19}H_{32}C_6$	**1.10**	2.08	10.35
[$NiCl_2$•TSK·BK]	Dark green	70	140 - 142	**1.98**	3.045	11.07	$NiS_6N_{24}O_{19}H_{32}C_6$	**1.11**	3.02	11.18
[$Ni(CH_3COO)_2$• TSK· BK]	Yellow	81	155 - 157	**2.12**	3.112	12.25	$NiS_6N_{24}O_{19}H_{32}C_6$	**2.11**	3.09	12.38
[$Cu(CH_3COO)_2$• TSK· BK]	Light blue	65	120 - 122	**1.10**	3.054	11.31	$CuS_6N_{24}O_{19}H_{32}C_6$	**1.08**	3.01	11.05
[$Co(CH_3COO)_2$• TSK· BK]	Dark red	60	130 - 132	**1.11**	3.025	11.40	$CoS_6N_{24}O_{19}H_{32}C_6$	**1.25**	3.05	11.70

Solubility of synthesized mixed ligand complex compounds in solvents

Compounds	Water	Ethanol	Methanol	DMFA	DMSO	Acetone
[$Co(NO_3)_2$•TSK·BK]	Oz eriydi	Eriydi	Eriydi	Oz eriydi	Erimaydi	Erimaydi
[$CoCl_2$•TSK· BK]	Oz eriydi	Oz eriydi	Eriydi	Oz eriydi	Oz eriydi	Erimaydi
[$ZnCl_2$•TSK· BK]	Eriydi	Eriydi	Eriydi	Oz eriydi	Erimaydi	Oz eriydi
[$MnCl_2$•TSK· BK]	Eriydi	Eriydi	Eriydi	Oz eriydi	Erimaydi	Erimaydi

[$NiCl_2$•TSK· BK]	Erimaydi	Eriydi	Eriydi	Erimaydi	Erimaydi	Erimaydi
[$Ni(CH_3COO)_2$•TSK· BK]	Erimaydi	Eriydi	Eriydi	Erimaydi	Erimaydi	Erimaydi
[$Cu(CH_3COO)_2$•TSK· BK]	Eriydi	Eriydi	Eriydi	Oz eriydi	Erimaydi	Oz eriydi
[$Co(CH_3COO)_2$•TSK· BK]	Oz eriydi	Eriydi	Eriydi	Oz eriydi	Erimaydi	Erimaydi

The structure of the synthesized complex compounds was studied by IR spectroscopic analysis.

Significant changes are observed in the IR spectra of complex compounds containing [Ni (CH3OO)2 ·TSK·BK] and [MnCl2 ·TSK ·BK]. If in the IR spectrum of thiosemicarbazide significant stretching vibrations of the C=S bonds are observed in a significant strong field at 800 cm-1, then a complex compound shifted to 813 cm-1 is observed. This indicates that the sulfur atom is coordinated.

The main vibration frequencies (cm-1) of the IR spectra of complex compounds based on benzoic acid and thiosemicarbazide show that, unlike the compounds [NiCl2·TSK·BK], the complex compound moves upward with symmetric and asymmetric stretching vibrations of the C=O bond. Thus, the data that the oxygen atoms of the benzoic acid molecule are bound to the metal atom are consistent with he literature. In the IR spectra of complex compounds with mixed ligands, in contrast to ligands, new vibrations are observed in the region of 796 cm-1

a) b)

Figure 1. IR spectra of ligands a) thiosemicarbazide and b) benzoic acid

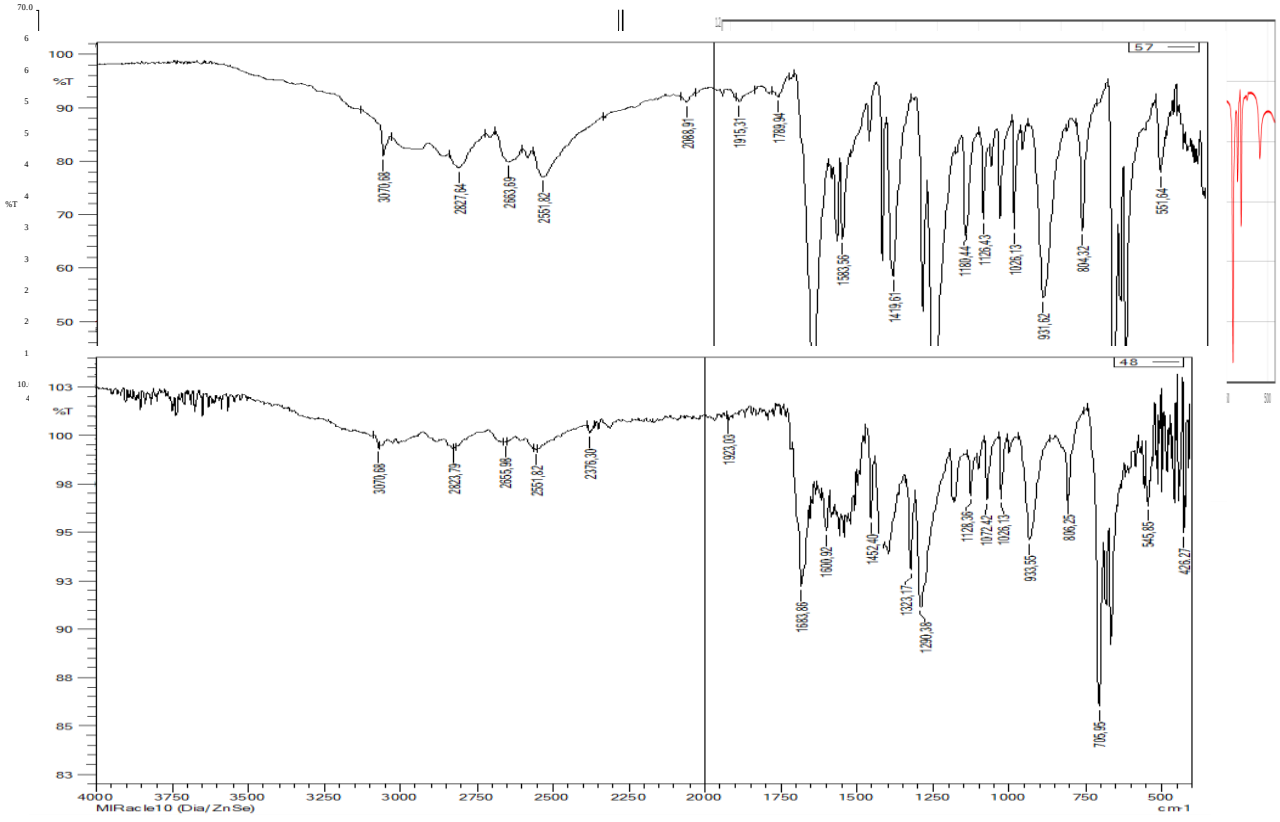


Figure 2. a) IR spectra of the complexes [NiCl2· TSK ·BK] and [Ni (CH3COO)2· TSK· BK]

In conclusion, it can be said that 8 mixed-ligand complexes of some 3d-metals with benzoic acid and thiosemicarbazide were synthesized for the first time and their composition, structure, and physicochemical properties were determined. Their structure, composition, energy, and structural parameters were determined by physicochemical analysis methods.

A Co(II) complex with thiosemicarbazide was synthesized and grown as a single crystal for the first time. The crystal structure of the Co(II) thiosemicarbazide complex was determined by X-ray diffraction analysis.

Based on X-ray phase analysis, it was proven that the coordination compounds obtained by comparing the interplanar distances and relative intensities of free ligands and synthesized compounds have an individual crystal lattice.

BIBLIOGRAPHY

1. Umadevi, P.; Deepti, K.; Srinath, I.; Vijayalakshmi, G.; Tarakaramji, M. Synthesis and in-vitro antibacterial activity of Come new urea, thiourea and thiosemicarbazide derivatives // Int. J. Pharm. Pharm. Sci. -2012. –Vol. 4. –P. 379–383.

2. Siwek, A.; Stefanska, J.; Dzitko, K.; Ruszczak, A. Antifungal effect of 4-arylthiosemicarbazides against Candida species. Search for molecular basis of antifungal activity of thiosemicarbazide derivatives // J. Mol. Model. -2012. –Vol. 18. –P. 4159–4170.

3. Wujec, M.; K˛edzierska, E.; Kusmierz, E.; Plech, T.; Wróbel, A.; Paneth, A.; Orzelska, J.; Fidecka, S.; Paneth, P. Pharmacological and structure-activity relationship evaluation of 4-aryl-1-diphenylacetyl(thio)semicarbazides // Molecules. - 2014. –Vol. 19. -P. 4745–4759.

4. Katarzyna Dziduch, Przemysław Kołodziej , Agata Paneth , Anna Bogucka-Koska and Monika Wujec. Synthesis and Anthelmintic Activity of New Thiosemicarbazide Derivatives—A Preliminary Study // Molecules.- 2020. –Vol. 25. –P. 2770-2777. doi:10.3390/molecules25122770.

5. Мурзубраимов Б., Токтомаматов А. ИК спектры поглощения соединений хлоридов никеля и кадмия с солянокислым тиосемикарбазидом // Коор. химия. - 1983. - Т.11. - Вып. 5. –С. 596-601.

6. Байрамов Г.И. Синтез и исследование азотсодержащих новых органических соединений на α-хлор-алкоксмметила // Азерб. Хим. Журн. -2008. -№3. -С.179-187.

7. Olga Khalipova, Svetlana Kuznetsova, and Vladimir Kozik Citation:The composition and structure of iron(III) complex compounds with salicylic acid in ethanol solution and in the solid thin film state // Published by the American Institute of Physics. -2016. -№ 10. - P.1063-1069.

8. Горинчой В.В., Симонов Ю.А., Шова С.Г. Кристаллические и молекулярные структуры двуядерных комплексов {Cu-M}(M=Cu, Sr, Ba) на основе салициловой кислоты // Журнал структурной химии. -2009. - Т.50. - №6. -С.1196-1202.

9. Т. В. Кокшарова координационные соединения ацетилацетонатов 3d-металлов с тиосемикарбазидом // Вісник ОНУ. Хімія. 2014. – Том. 19. -Вып. 2(50). -С.105-110.

10. Скопенко В.В., Гарновский А.Д., Кокозей В.Н. И др. Прямой синтез координационных соединений // Киев: Вентури. 2002. -178 с.

11.Сентемов В.В., Михайлов О.В. О комплекссообразовании меди с мемы и тиосемикарбазидом в сильнокислой среде // Координационная химия. - 1990. – Т.16. -Вып. 3. С.344-347.