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STUDY OF THE STRUCTURE OF COMPLEX COMPOUNDS BASED ON 2-AMINO-1,3,4-THIADIZOLE AND ADIPIC ACID OF SALTS OF CO(LL), NI(LL), CU(LL), ZN(LL) USING PHYSICAL MEANS

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Abstract

Complex compounds with heteroligands were synthesized based on 2-amino-1,3,4-thiadiazole, adipic acid and salts of Co(II), Ni(II), Cu(II), Zn(II). The physicochemical properties of the synthesized complex compounds were studied using IR-spectrum, SEM-EDA and thermal analysis. The results are presented in tables. The chemical structure of complex compounds was determined based on the above results.

Keywords: Coordination compounds, ligands, metal-complex formers, IR-spectrum, thermal analysis, endothermic and exothermic effects

Introduction

Five-membered heterocyclic compounds have high biological properties, of which 2-amino-1,3,4-thiadiazole is significant for its biological activity. Therefore, thiadiazol and its derivatives are used as anti-parasitic, anti-coagulant, anti-microbial, anti-cancer, anti-inflammatory and anti-tuberculosis agents (Atmaram, U. A., Roopan, S. M. 2022). According to the results of various studies, 2-amino-1,3,4-thiadiazole has excellent pharmacological value as an anti-fungal, diuretic, and anthelmintic activity, and several methods of synthesis of this substance have been created. Recently, the synthesis of heteroligand metal complexes based on 2-amino-1,3,4-thiadiazole and its derivatives has

attracted interest because these substances are widely used in medicine and material science. The 2-amino-5-methyl-1,3,4-thiadiazole (amtz) ligand containing one S and three N coordination sites has been recognized as a potential multidentate ligand to form some interesting compounds. In this literature, the following complex compound $\text{CoCl}_2(\text{C}_3\text{H}_5\text{N}_3\text{S})_2$ was synthesized with CoCl_2 salt and 2-amino-5-methyl-1,3,4-thiadiazole. In this complex, Co(II) is tetracoordinated from two monodentate 2-amino-5-methyl-1,3,4-thiadiazole ligands by two chlorine anions and two nitrogen atoms and forms a monoclinic syngonia (Ye Song, Yu-Fei Ji, Min-Yan Kang and Zhi-Liang Liu, 2012). The authors presented the synthesis

and crystal structure of the tetramis (I) complex connected with the 2-amino-1,3,4-thiadiazole ligand. Another structural feature is that two different hydrogen bonds are formed between the ClO_4^- anions and the NH_2 group of the 2-amino-1,3,4-thiadiazole ligand. Two new tetracopper(I) and tetrasilver(I) complexes $\text{Cu}_4(\text{atdz})_6(\text{ClO}_4)_4 \cdot 2\text{CH}_3\text{OH}$ (1) and $[\text{Ag}_4(\text{atdz})_6](\text{ClO}_4)_4$ (2) formed a tetranuclear structure (Masahiko Maekawa, Megumu Munakata, Takayoshi Kuroda-Sowa, Yusaku Suenaga, Kunihiisa Sugimoto, 1999).

Two new mixed ligand complexes $[\text{M}(\text{atdz})(\text{DCA})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, ($\text{M} = \text{Co(II)}, \text{Zn(II)}$; $\text{atdz} = 2\text{-amino-1,3,4-thiadiazole}$, $\text{C}_2\text{H}_3\text{N}_3\text{S}$; $\text{DCA} = \text{demethylcanthate}$, 7-oxabicyclo[2,2,1]heptane-2,3-dicarboxylate, $\text{C}_8\text{H}_8\text{O}_5$) was prepared and characterized by elemental analysis. The structure of the complexes was determined by X-ray diffraction. The crystals have the empirical formulas $\text{CoC}_{10}\text{H}_{19}\text{N}_3\text{O}_9\text{S}$ (1) and $\text{ZnC}_{10}\text{H}_{19}\text{N}_3\text{O}_9\text{S}$ (2) respectively. Syngonia of complexes 1 and 2 showed a monoclinic structure (Na Wang, Qiu-Yue Lin, Jie Feng, Yu-Ling Zhao, Yan-Jun Wang, Shi-Kun Li, 2010).

The literature analysis shows that much scientific research has been carried out on the synthesis, structure, and properties of complexes of dicarboxylic acids, including adipic acid with intermediate metals. This shows the need to carry out tasks such as synthesizing complex compounds with the same and mixed ligands with heterocyclic compounds of intermediate metals, analyzing their composition and structure, determining relevant laws from the analysis of the obtained results, and defining the fields of application of complex compounds according to the identified properties.

Research methodology

Salts of metals in crystalline hydrate form: zinc(II), nickel(II), cobalt(II) and copper(II) chloride, acetate, sulfate and nitrate salts were used to synthesize complex compounds.

Carbon, sulfur and metals in complex compounds were determined using elemental analysis in an atomic absorption “Bruker” (Germany) spectrophotometer.

Absorption IR-spectra of the compounds in the range of $400\text{--}4000\text{ cm}^{-1}$ were recorded on Avatar System 360 FT-IR and Rrotege

460 Magna-IR technology spectrophotometers from “Bruker” (Germany) using a KBr tablet sample with a diameter of 7 mm and an accuracy of 4 cm^{-1} . was studied.

Thermal analysis was carried out with a thermodynamic apparatus — DTG-60 SMILTANEOUS DTA-TG APPARATUS (Japan), K-type (Shimadzu) thermo steam and porcelain crucible. All measurements were carried out in an inert argon atmosphere with an argon flow rate of 80 ml/min. The temperature range of the analysis was $20\text{ }^\circ\text{C}$, the heating rate was 5 K/min. The amount of sample in one measurement is 6–10 mg. The measuring system vibrates using a set of standard substances KNO_3 , In, Bi, Sn, Zn, CsCl.

Experiment

Complex compounds were synthesized according to a specific methodology (Wu Q. et al., 2015). According to it (0.001 mol) 0.101 g 2-amino-1,3,4-thiadiazole (LT), (0.001 mol) 0.146 g adipic acid (LA), (0.001 mol) 0.04 g sodium hydroxide, (0.001 mol) 0.295 g of Co(II) nitrate crystal hydrate was obtained. Initially, adipic acid, Co(II) nitrate and sodium hydroxide were dissolved in 5 ml of distilled water. Subsequently, 2-amino-1,3,4-thiadiazole was dissolved in methanol. To neutralize adipic acid, sodium hydroxide solution was poured over it and heated at $65\text{ }^\circ\text{C}$ for 30 minutes. Sodium adipinate was added to the dissolved salt with stirring. A solution of 2-amino-1,3,4-thiadiazole in methanol was poured onto the resulting mixture and heated at $60\text{ }^\circ\text{C}$ for 2 hours. As a result, the color of the solution turned pink. The mixture was removed for crystallization. After 10 days, pink crystals began to fall. They were filtered and washed several times in ethanol. Yield 81%.

Result and discussion

Complex compounds of Co(II), Ni(II), Cu(II), Zn(II) chloride, nitrate and acetate salts with 2-amino-1,3,4-thiadiazole and adipic acid were synthesized in the same way.

Co(II), Cu(II), Ni(II) and Zn(II) chloride, nitrate, acetate and sulfate salts of complex compounds synthesized in the presence of adipic acid and 2-amino-1,3,4-thiadiazole IR-spectroscopic were analyzed based on the analysis (Table 1) and compared with the IR-spectra of the original ligands (Fig. 1).

Table 1 shows the results of the IR spectra of the synthesized mixed-ligand complexes. Symmetric and asymmetric valence vibrations of the = N-N= bond in the 2-amino-1,3,4-thiadiazole ring are manifested in the low-frequency region in the area of 1011–1040 cm⁻¹. The valence vibrations of the amino group give vibrations in the ν(NH₂) 3277 cm⁻¹ region and the deformation vibrations in the δ(NH₂)1524 cm⁻¹ region. Absorption lines of characteristic valence vibrations of C-S-C bonds of medium intensity were recorded in the region of C=N bond 1614 cm⁻¹, 664–783 cm⁻¹ (Nuralieva G.A., Xayrullayev G.U., Kadirova Sh.A., 2020). Also, the characteristic valence vibrations of the CH bond in the heteroring were manifested in the high-frequency region at 3099–3162 cm⁻¹ (Tarasevich B. N., 2012).

- In the IR-spectra of adipic acid, the absorption spectra of the valence vibrations of the ν(C=O) bond are in the 1694 cm⁻¹ region, δ(OH) is in the

1280 cm⁻¹ region, and δ(CH) is in the 737 cm⁻¹ region (Kazitsyna L. A., Kupletskaya N. B., 1971);

- When the IR spectra of complex compounds were analyzed, new wavelengths were observed, unlike the ligands;
- Valence vibrations of C=N bonds in complex compounds gave an intense signal in the range of 1654–1686 cm⁻¹. Valence vibrations of -N-N- bonds appeared in the range of 1020–1098 cm⁻¹, with absorption lines of the NH₂ group around 3090–3107 cm⁻¹.

In the IR spectra of coordination compounds, absorption areas appear in the region of 1620–1525 cm⁻¹, which is characteristic of asymmetric stretching vibrations of the carboxylate anion. In the spectra of the synthesized compounds, symmetric stretching vibrations of the anion appear in the region of 1440–1340 cm⁻¹.

Table 1. The main vibrational frequencies of IR-spectra

Compound	ν _s (C=N)	δ (NH ₂)	ν(COO ⁻)	ν (-N-N)	ν (C-S)	ν (M-N)	ν (M-O)
[Zn(L)(Adp)(H ₂ O)] ₂	1691	3279	1505	1044	613	554	491
[Cu(L)(Adp)(H ₂ O)] ₂	1686	3277	1507	1086	611	557	511
[Co(L) ₂ (Adp) ₂ (H ₂ O) ₂]	1654	3291	1508	1098	616	506	455
[Ni(L) ₂ (Adp) ₂ (H ₂ O) ₂]	1684	3281	1552	1060	637	511	458

The difference in the wavelengths of the asymmetric and symmetric stretching vibrations of the carboxylate anion ranges from 86 cm⁻¹ to 255 cm⁻¹. Such values of ν indicate that in coordination compounds, both monodentate and bidentate, as well as bidentate-bridge methods of coordination of the carboxylate anion are implemented. It should be noted that for polymeric carboxylates, a combination of different modes of ligand coordination is often observed. In the IR spectrum, it was confirmed that the valence vibrations of M ← N, and M ← O bonds appeared at frequencies of 407–491 and 511–554 cm⁻¹.

The thermal decomposition process is a complex multi-step process with the release of intermediate products. Thermal decomposition of complexes is significantly affected

by the presence of metal and components of complex compounds (Nakanishi K., 2013; Wendlandt W. 1978).

The results of thermal analysis, the nature of thermal effects, observation of thermal decomposition of compounds, temperature intervals of effects and their nature, as well as mass loss in percentages in the same effect interval are presented in Table 2.

Analysis of the dynamic thermogravimetric curve (DTGA) of [Ni(L)₂(adi)₂(H₂O)₂] shows that the DTGA curve mainly takes place in the 2 intense decomposition temperature ranges, and one mass loss process that goes with absorption occurs. Decomposition range 1 corresponds to the temperature of 186–222 °C, decomposition range 2 corresponds to the temperature of 222–353 °C, and the mass absorption

range corresponds to the temperature of 353–800 °C.

The analysis shows that an intensive decay process took place during the 2nd decay

interval. In this interval, 32% of the decomposition has taken place. A detailed analysis of dynamic thermogravimetric analysis curve and DSK curve is shown in Table 2–3.

Table 2. DTGA and DSK curve results of $[Ni(L)_2(Adp)_2(H_2O)_2]$

No.	Temperature, °C	Mas Loss mg	Mass Loss, %	The amount of energy consumed, J	Time, min.
1	100	0.271	4.77	1.23	7.33
2	200	0.726	12.79	7.76	16.97
3	300	3.434	60.48	16.22	27.35
4	400	3.701	65.18	13.66	37.52
5	500	3.771	66.41	3.56	47.77
6	600	3.914	68.93	15.57	58.07
7	700	4.340	76.43	54.83	68.38
8	800	4.633	81.60	118.06	78.83

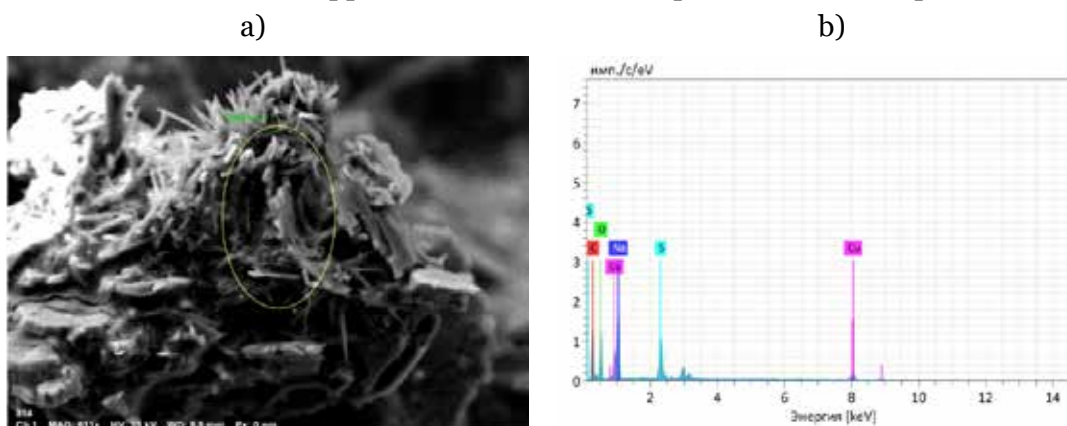
Table 3. DTGA and DSK curve results of $[Cu(L)(Adp)(H_2O)]_2$

No.	Temperature °C	Mass Loss, mg	Mass Loss, %	The amount of energy consumed, J	Time, min.
1	100	0.067	1.56	2.39	7.70
2	200	0.349	8.10	6.81	17.77
3	300	1.332	30.95	12.28	27.83
4	400	1.698	39.45	11.09	38.02
5	500	2.297	53.37	3.65	42.27
6	600	2.342	54.41	18.19	58.57
7	700	2.475	57.50	41.85	68.9
8	800	2.946	68.45	81.57	79.35

Element analysis SEM-EDA – With the help of electron beams (in electron microscopes) or X-rays (in X-ray fluorescence analyzers), the atoms of the studied sample are stimulated and emit X-ray radiation characteristic of each

chemical element. By studying the energy spectrum of such radiation, it is possible to draw a conclusion about the qualitative and quantitative composition of the sample (Nuralieva G. A., Aliyeva M., 2023; Marshall J. L. 1991).

Figure 1. a) microstructure and b) EDA diagrams of $[Cu(L)(Adp)(H_2O)]_2$
From the SEM-EDA data of complex compounds formed with ligands, it was determined that copper and nickel ions were present in the complex

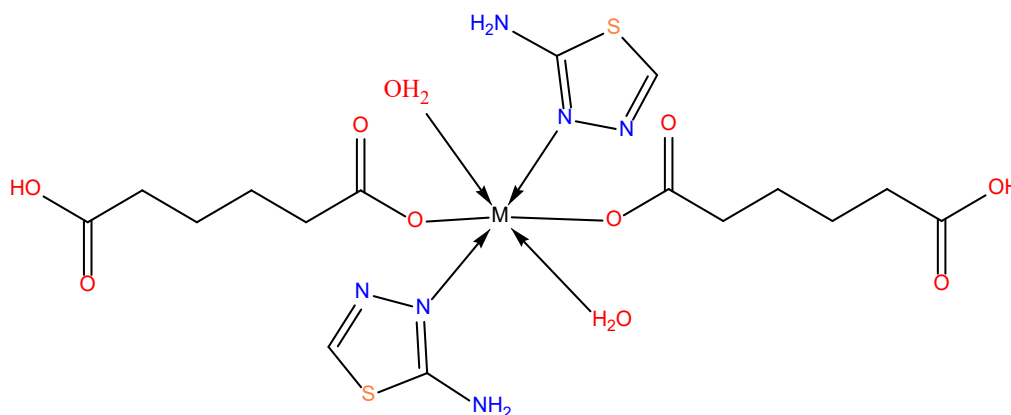


The amounts of elements (carbon, nitrogen, sulfur, oxygen, metal elements) in the synthesized mixed ligand complexes were analyzed using the SEM-EDA method. The microstructure and EDA diagrams of the obtained complexes are presented in (Fig. 1). The amount of nitrogen, sulfur and metal in the obtained complex compounds was determined using energy-dispersive analysis (SEM-EDA) by scanning energy microscopy. Based on the SEM and EDA data, it can be concluded that the complex formation of metal ions with organic ligands leads to changes in the microstructure of the ligands, in particular, many metal peaks are recorded, which is confirmed by EDA analysis.

Conclusion

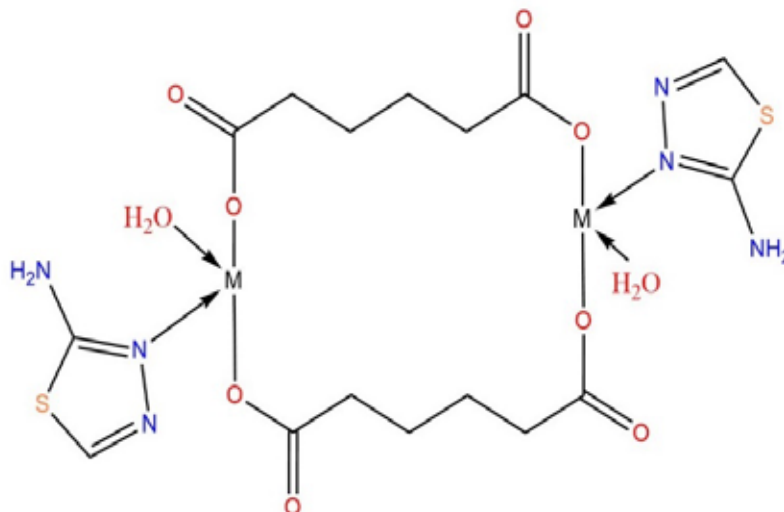
The composition, structure and properties of the synthesized complex compounds were analyzed using physico-chemical methods: elemental analysis, IR-spectroscopy, thermal analysis and SEM-EDA methods. It was found that in complex compounds with synthesized Co(II) and Ni(II) metal salts, the nitrogen atom in the 2-amino-1,3,4-thiadiazole molecule is coordinated to the central atom, and adipic acid is coordinated to the oxygen atoms of the carboxyl group.

Based on physical and chemical studies, it was concluded that the structure of the complex compound is composed of 2-amino-1,3,4-thiadiazole – metal-adipine in a ratio of 2:1:2, and the structure of the complex compounds synthesized with Ni(II), Co(II) metal salts recommended as follows:



It was found that with Cu(II) and Zn(II) salts, the nitrogen atom in the 2-amino-1,3,4-thiadiazole molecule was coordinated to the central atom through the atom, and adipic acid was coordinated to the oxy-

gen atoms of the carboxyl group in the bridge position, forming a binuclear complex compound. The structure of complex compounds synthesized with Cu(II), Zn(II) metal salts was suggested as follows.



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