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SYNTHESIS, STRUCTURE AND PROPERTIES OF MIXED-LIGAND COMPLEX COMPOUNDS OF Co^{2+} WITH 2-AMINO-1-METHYLBENZIMIDAZOLE AND SALICYLIC ACID

Annotation

For the first time, mixed-ligand complex compounds of Co(II) with 2-amino-1-methylbenzimidazole (MAB) and salicylic acid (SA) were synthesized. The structures of the synthesized complexes were investigated using elemental analysis, SEM-EDS, IR and Raman spectroscopy, as well as thermogravimetric analysis. The results showed that the complexes' composition, structural features, and physicochemical properties are influenced by both the type of complexing agent involved and the specific coordination behavior of the ligands.

Key words: Co(II), complex, ligands, MAB, SA, IR, DTA, SEM-EDS, morphology, synthesis, mapping.

Co(II) NING 2-AMINO-1-METILBENZIMIDAZOL VA SALISIL KISLOTA BILAN ARALASH LIGANDLI KOMPLEKS BIRIKMALARI SINTEZI, TUZILISHI VA XOSSASI

Annotatsiya

Ilk bor Co(II) ionining 2-amino-1-metilbenzimidazol (MAB) va salitsil kislotasi (SA) bilan aralash linadli kompleks birikmalari sintez qilindi. Sintez qilingan kompleks birikmalarning tuzilishi element, SEM-EDS, IQ-, Raman-spektroskopiyasi, termogravimetrik analiz usullari bilan o'rganildi. Tadqiqot natijalari shuni ko‘rsatdiki, komplekslarning tarkibi, strukturaviy xususiyatlari va fizik-kimyoviy xossalari ularda ishtirok etayotgan kompleks hosil qiluvchi moddaning tabiati hamda ligandlarning aniq koordinatsion holatlariga bog‘liqdir.

Kalit so‘zlar*:* Co(II), kompleks, ligand, MAB, SA, IQ, DTA, SEM-EDS, morfologiya, sintez, xaritalash.

СИНТЕЗ, СТРОЕНИЕ И СВОЙСТВА СМЕШАННОЛИГАНДНЫХ КОМПЛЕКСНЫХ СОЕДИНЕНИЙ Co^{2+} С 2-АМИНО-1-МЕТИЛБЕНЗИМИДАЗОЛОМ И САЛИЦИЛОВОЙ КИСЛОТОЙ

Аннотация

Впервые синтезированы смешаннолигандные комплексные соединения ионов Co(II) с 2-амино-1-метилбензимидазолом (MAB) и салициловой кислотой (SA). Строение синтезированных комплексных соединений изучено методами элементного, SEM-EDS, ИК-, раман-спектроскопии, термогравиметрического анализа. Результаты показали, что состав, структурные особенности и физико-химические свойства комплексов зависят как от природы комплексообразующего агента, так и от специфики координационного поведения лигандов.

Ключевые слова:. Co(II), комплекс, лиганд, MAB, SA, IK, DTA, SEM-EDS, морфология, синтез, картирование.

Introduction. Today, cobalt plays an important role in the production of lithium-ion batteries, one of the most advanced technologies, as cobalt is used as a lithium cobalt oxide cathode material. This, in turn, helps improve the efficiency of modern electronics and energy storage systems [1]. Cobalt is also of significant biological importance as it serves as the active center of the Vitamin B12 group, which is one of the eight B vitamins essential for life and produced by the body [2]. Three new transition metal complexes, Cu(II) 1, Co(II) 2, and Zn(II) 3 with ligand 'bimnap' derived from 1-methyl-2-aminobenzimidazole and 2-hydroxynapthaldehyde were synthesized and characterized [3]. A series of cobalt–alkyne complexes, especially a derivative of aspirin known as Co-ASS, have shown significant cytotoxic effects. Structural modifications of the alkyne ligand revealed insights into their biological behavior, including COX enzyme inhibition, cellular uptake, and DNA interaction. The findings suggest these organometallic compounds function as potential anticancer agents, likely through mechanisms involving COX suppression [4]. The complexation behavior of Co(II), Ni(II), and Cu(II) with 5-sulfosalicylic acid and 5-hydroxysalicylic acid was analyzed in varying urea–water mixtures at constant ionic strength and temperature. Several ternary species were identified, with enhanced stability attributed to factors like chelation, hydrogen bonding, and charge neutralization. The study also detailed species distribution profiles across different pH levels [5].The interaction of 2-aminobenzimidazole — specifically its benzimidazole nitrogen atoms and the exocyclic amino group — with carbon disulfide in an alkaline NaOH medium, followed by methylation using methyl iodide, was investigated. With careful control of the stoichiometric quantities and addition sequences, this set of reactions allows the selective functionalization of the benzimidazole ring with N-dithiocarbamate, S-methyldithiocarbamate or dimethyl-dithiocarboimidate groups [6]. A newly developed organic single crystal, 2-amino-4-methylpyridinium 5-sulfosalicylate

(2A4MP5SSA), shows strong third-order nonlinear optical (NLO) activity, thermal stability, and wide optical transparency. Grown via slow evaporation, the crystal crystallizes in the centrosymmetric triclinic system (P1) and demonstrates excellent features such as high laser damage threshold and consistent morphology. These characteristics highlight its potential for future applications in photonic and optoelectronic technologies [7]. Simple phenolic acids, including hydroxybenzoic and hydroxycinnamic derivatives, are important plant secondary metabolites known for their diverse biological activities such as antioxidant, anticancer, and antimicrobial effects. Due to their wide-ranging benefits, these compounds hold strong potential for applications in food, pharmaceutical, and cosmetic industries [8]. Salicylic acid is a naturally occurring monohydroxybenzoic acid, originally isolated from the bark of the white willow tree (Salix alba). It is an important active metabolite of aspirin and is converted into a prodrug of salicylic acid (which generates biological activity). Salicylic acid is also widely used in the treatment of skin diseases due to its keratolytic, antifungal, antibacterial, and photoprotective properties [9]. In microorganisms and plants, salicylic acid (SA) is produced from chorismate via the shikimate pathway and serves as a bioactive secondary metabolite involved in various physiological processes. SA is an essential phytohormone in plants that regulates growth, environmental stress responses, and defense mechanisms against diseases. Additionally, salicylates are also synthesized by bacteria, such as Pseudomonas, Bacillus, and other bacterial species [10].

The aim of the study is the synthesis of new coordination compounds with mixed ligands, which are the complexes of some 3D metal ions with hydroxybenzoic acid derivatives and benzimidazole derivatives, and the study of their composition, structure, and properties using physicochemical analysis methods.

Research Method. *Materials and Methods:* Cobalt (II) sulfate $Co(SO_4)_2$, 1-methyl 2-aminobenzimidazole ($C_8H_9N_3$), and salicylic acid ($C_7H_6O_3$) (Sigma-Aldrich) were used in this study. Chemically pure reagents were used throughout the experiments, with no further purification performed. SEM-EDS data were obtained using a scanning electron microscope with an energy-dispersive detector for elemental analysis and mapping (JEOL JSM-IT200LA, Japan). Thermogravimetric analysis was conducted using a Thermogravimetric Analyzer (Discovery SDT 650 TGA, USA).

Synthesis reaction: Initially, a 0.1 molar solution of $Co(SO_4)_2$, was prepared by dissolving its salt in distilled water to obtain 10 ml of the solution. Then, 10 ml of a 0.05 molar solution of 1-methyl 2-aminobenzimidazole (MAB) in ethanol was added to this solution and stirred for 4 hours using a magnetic stirrer. In the next step, 10 ml of a 0.05 molar solution of salicylic acid (SA) in ethanol was added, and the reaction continued for another 4 hours under magnetic stirring. The resulting solution was left at room temperature, in a place protected from external influences, for 2 weeks to allow crystallization. The formed crystals were washed several times with ethanol to remove impurities and filtered. As a result, pink-colored crystals were obtained. The obtained complex [Co(MAB)2(SA)2] is insoluble in water, poorly soluble in alcohol, acetone, benzene, and well soluble in DMSO and DMFA.

Results and Discussion. *EDS analysis*: Energy-dispersive X-ray spectroscopy (EDS) analysis results for the prepared complex are illustrated in Figure 1. The EDS spectrum shows intense peaks for carbon (C), nitrogen (N), oxygen (O), cobalt (Co), and sulfur (S), confirming their presence on the analyzed surface. The elements C, N, O, Co, and S were found to be evenly dispersed over the sample surface, as shown by elemental mapping analysis. The identification of C-K, N-K, O-K, and Co-K spectral lines confirms that these elements are part of the cobalt-containing complex structure. Additionally, the presence of S-K spectral lines suggests that a small amount of sulfate salts remains as a residue.

SEM analysis: In Figure 2, SEM images of the newly synthesized $Co(MAB)_2(SA)_2$ complex compound are presented. The images were taken at magnifications of ×250 and ×500, with sizes corresponding to 100 micrometers and 50 micrometers, respectively.

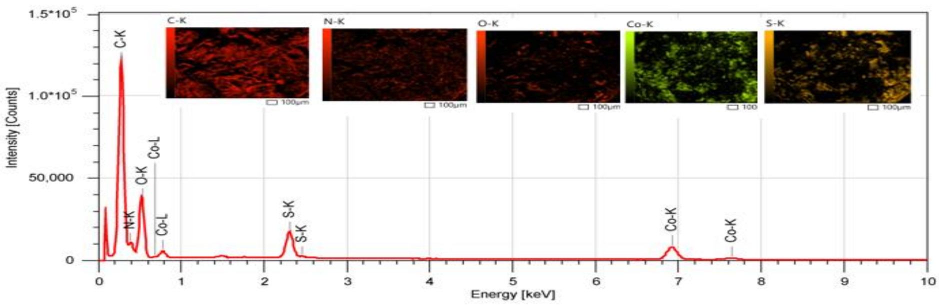
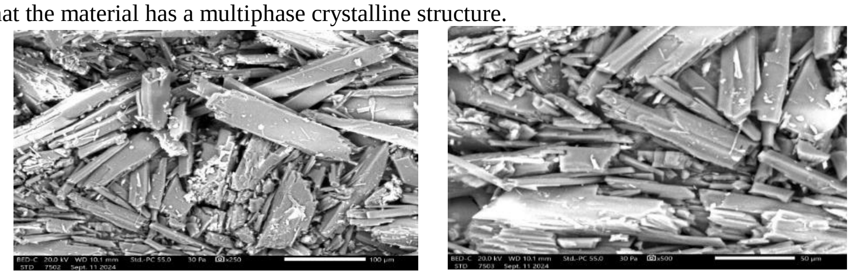


Fig. 1. EDS spectra of [$Co(MAB)_2(SA)_2$].

In both images, flat and plate-like particles are observed. The particles are densely packed and randomly arranged, indicating a large surface area of the material. At higher magnification (×500), the gaps and microcracks between the particles are more clearly visible, confirming the presence of high porosity. Such plate-like structures are typically characteristic of crystalline materials. The presence of voids between the particles may enhance the material's adsorption or catalytic activity. Since this is a cobalt complex, it can be assumed that the material has a multiphase crystalline structure.



a) **b)**

Fig. 2. SEM images of [$Co(MAB)_2(SA)_2$]. a) ×250 100 micrometers and b) ×500 50 micrometers.

Infrared analysis. In Figure 3 the IR spectrum of free 1-methyl-2-amino benzimidazole exhibits characteristic bands around ~3400 cm⁻¹ for ν(N–H), ~1600 cm⁻¹ for ν(C=N), and ~1500 cm⁻¹ for aromatic ring vibrations. Upon coordination to the Co(II) ion through the ring nitrogen, the ν(C=N) band is shifted to lower wavenumbers, indicating coordination via the imine nitrogen atom. The IR spectrum of uncoordinated salicylic acid displays a broad, intense absorption band in the 3200–2500 cm⁻¹ range, corresponding to O–H stretching, and a sharp peak near 1700 cm⁻¹, assigned to the C=O stretching vibration of the carboxylic group. In the complex, the disappearance of the O–H stretching band and the shift of the ν(C=O) band to lower frequencies suggest deprotonation and coordination of the carboxylate oxygen to Co(II). Additionally, new bands observed in the region of ~500–600 cm⁻¹ and ~400–500 cm⁻¹ are assigned to ν(Co–N) and ν(Co–O) vibrations, respectively, confirming the formation of the coordination complex.

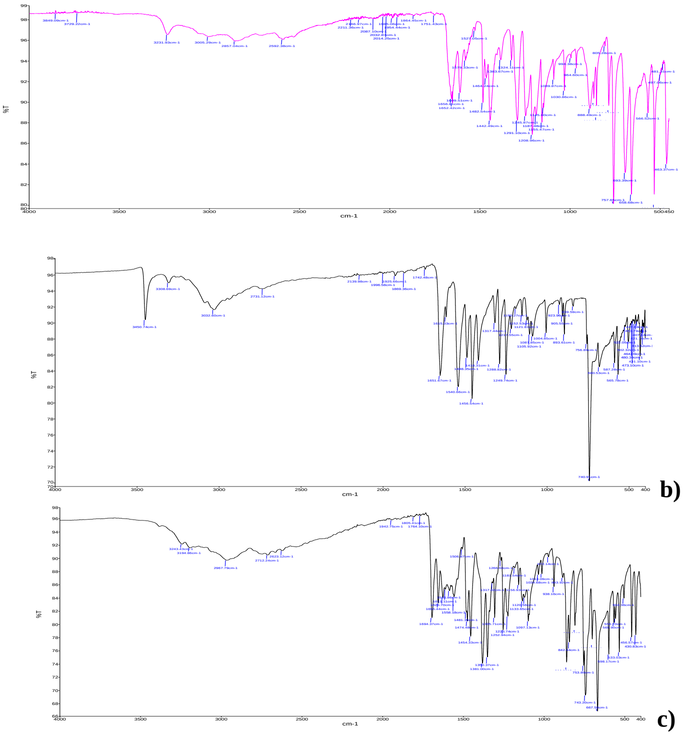

a) b) c)

Fig. 3. Infrared spectroscopy: a) L_1-SA; b) L_2-MAB; c) $[Co(MAB)_2(SA)_2]$

Thermal analysis: Differential thermal analysis (DTA) was conducted to determine the thermal stability and composition of the obtained complex compound (fig. 4). Thermal analysis (TG, DSC, DTA) is used to determine the thermal properties, decomposition stages, stability limits, and residue composition of complex compounds. From the image, we can observe that the initial weight loss occurs at 85.38°C, accounting for 12.101%. Given that there is no water present in the compound, this stage likely corresponds to the release of physically bound volatile components and the disruption of internal hydrogen bonds within the complex.

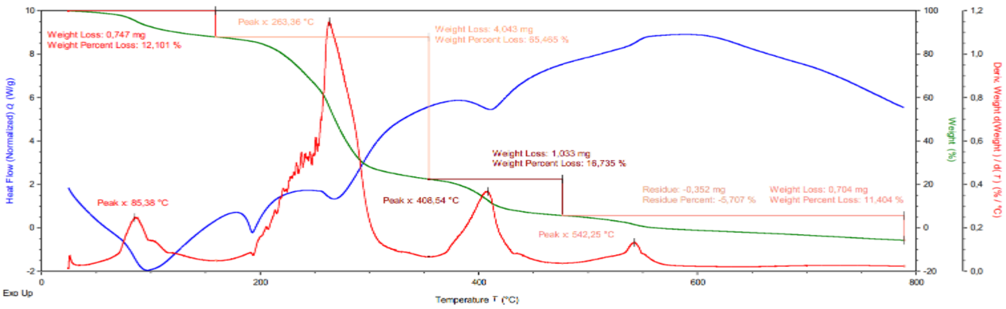


Fig.4. $[Co(MAB)_2(SA)_2]$ derivative

The major decomposition stage occurs at 263.36 °C, accompanied by the most significant weight loss of 65.46%. At this stage, the 1-methyl-2-aminobenzimidazole (MAB) ligand and a portion of salicylate (SA) decompose, with the cleavage of NH_2 and C–H bonds and the thermal degradation of the benzimidazole ring. The next decomposition step occurs at 408.54°C, where the salicylate ligand undergoes complete oxidation, leading to a 16.735% weight loss. At this temperature, the formation and release of gaseous byproducts such as CO_2 and CO are highly probable. The final decomposition stage takes place at 542.25°C, resulting in an 11.404% weight loss. The final decomposition stage occurs at 542.25°C, resulting in a weight loss of 11.404%. This suggests that Co(II) complexes undergo thermal decomposition at elevated temperatures, resulting in the formation of CoO or Co_3O_4. Furthermore, if sulfate residues persist, thermal decomposition may also lead to the formation of cobalt sulfide (CoS) or cobalt sulfate ($CoSO_4$). At the end of the analysis, a residual value of -5.707% is recorded, which can be attributed to instrumental error.

Conclusion. In this study, a mixed-ligand complex compound involving 3d transition metals was synthesized. Its structural and physicochemical properties were investigated using three analytical techniques. Crystallographic parameters of the complex, as well as the solubility characteristics of the ligands and the complex in various solvents, were also reported. Further studies will involve the application of additional analytical methods for more in-depth characterization.

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