SYNTHESIS AND INVESTIGATION OF A Zn(II) COMPLEX COMPOUND WITH INDOLE-3-ACETIC ACID AND ACETAMIDE

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Abstract

The article describes the synthesis of a new mixed-ligand coordination compound of zinc(II) ion with indole-3-acetic acid (heteroauxin) and acetamide. The composition and structure of the obtained complex compound were investigated using elemental analysis and IR spectroscopy. Analysis of the IR spectra allowed determining the coordination modes of the ligands to the metal ion. In the second part of the study, the electronic structure and thermodynamic characteristics of the complex were analyzed using quantum-chemical calculations (DFT method). The results show a high correlation between theoretical and experimental data, providing a basis for the potential biological activity of the synthesized complex.

Keywords: zinc(II), indole-3-acetic acid, acetamide, coordination compound, synthesis, IR spectroscopy, quantum-chemical analysis, DFT, HOMO-LUMO.

Annotatsiya. Ushbu maqolada rux(II) ionining indol-3-sirka kislotasi (geteroauksin) va atsetamid bilan yangi aralash ligandli koordinatsion birikmasining sintezi bayon etilgan. Olingan kompleks birikmaning tarkibi va tuzilishi elementar tahlil hamda IK-spektroskopiya usullari yordamida o‘rganildi. IK-spektrlarni tahlil qilish ligandlarning metall ioniga koordinatsiyalanish usullarini aniqlash imkonini berdi. Tadqiqotning ikkinchi qismida kompleksning elektron tuzilishi va termodinamik xususiyatlari kvant-kimyoviy hisoblashlar (DFT usuli) yordamida tahlil qilindi. Natijalar nazariy va eksperimental ma’lumotlar o‘rtasida yuqori moslik mavjudligini ko‘rsatdi hamda sintez qilingan kompleksning potensial biologik faolligi uchun asos yaratadi.

Kalit so‘zlar: rux(II), indol-3-sirka kislotasi, atsetamid, koordinatsion birikma, sintez, IK-spektroskopiya, kvant-kimyoviy tahlil, DFT, HOMO–LUMO.

Аннотация. В данной статье описан синтез нового смешанно-лигандного координационного соединения иона цинка(II) с индол-3-уксусной кислотой (гетероауксином) и ацетамидом. Состав и структура полученного комплексного соединения исследованы с использованием элементного анализа и ИК-спектроскопии. Анализ ИК-спектров позволил определить способы координации лигандов к иону металла. Во второй части исследования электронная структура и термодинамические характеристики комплекса были проанализированы с применением квантово-химических расчётов (метод DFT). Полученные результаты показывают высокую корреляцию между теоретическими и экспериментальными данными, что служит основой для предположения о потенциальной биологической активности синтезированного комплекса.

Ключевые слова: цинк(II), индол-3-уксусная кислота, ацетамид, координационное соединение, синтез, ИК-спектроскопия, квантово-химический анализ, DFT, HOMO–LUMO.

Introduction. One of the priority directions of modern coordination chemistry is the synthesis of new complex compounds of transition metals based on biologically active ligands and the fundamental study of their properties. Among transition metals, zinc (Zn(II)) stands out due to its low toxicity, its important role in biological processes, and its versatile coordination capabilities. Zinc ions are components of many enzymes and participate in regulating metabolic processes in the organism. In this study, indole-3-acetic acid (IAA), selected as a ligand, is one of the most important natural plant growth regulators (belonging to the auxin group). Due to the presence of donor atoms in its structure (the nitrogen in the indole ring and the oxygen in the carboxyl group), IAA is capable of forming stable and biologically active complexes with metal ions. The second ligand, acetamide, is a simple yet effective amide that exhibits high selectivity in coordination with d-metals and is frequently found in pharmaceutical compounds. The synthesis of mixed-ligand complexes is relevant not only for obtaining new substances but also from the perspective of studying intermolecular interactions. The investigation of the structure and properties of complex compounds formed by the simultaneous coordination of both a hormonal ligand (IAA) and an amido ligand around a zinc ion opens new prospects for agriculture and pharmaceutical applications. Modern chemical research is inconceivable without quantum-chemical analysis. The initially selected main ligand, indole-3-acetic acid (heteroauxin, IAA), and the newly synthesized coordination compound $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$ were studied using the Gaussian program with the CAM-B3LYP basis set. The aim of this article is to synthesize a mixed-ligand complex compound of the Zn(II) ion with indole-3-acetic acid and acetamide, to confirm its composition using modern physicochemical methods, and

to theoretically substantiate the stable structure and electronic properties of the complex through quantum-chemical calculations.

Research methodology. The mixed-ligand coordination compound of zinc(II) chloride with indole-3-acetic acid and acetamide was synthesized using the following procedure. First, 0.01 mol (1.75 g) of indole-3-acetic acid (IAA) was dissolved in 50 mL of ethanol. To ensure deprotonation of the ligand's carboxyl group, 0.01 mol of potassium hydroxide (KOH) was added to the resulting solution. In a separate beaker, 0.005 mol (0.85 g) of zinc(II) chloride dihydrate ($ZnCl_2 \cdot 2H_2O$) was completely dissolved in 20 mL of distilled water. The metal salt solution was then added dropwise to the indole-3-acetic acid solution under constant stirring and mixed on a magnetic stirrer for 25–30 minutes. Afterwards, in order to form the mixed-ligand complex, a solution of 0.01 mol (0.59 g) of acetamide (AA) was added dropwise (5–10 mL) to the reaction mixture, followed by further stirring for 25–30 minutes. The reaction mixture was then continuously stirred at 50–55 °C for 1–1.5 hours using a magnetic stirrer [1]. At the end of the reaction, a clear, colorless solution was obtained. The resulting solution was purified by filtration, washed several times with a mixture of distilled water and ethanol, and dried in a vacuum desiccator (over P_2O_5) until constant mass was achieved [2,3].

As a result of the synthesis process, a clear colorless crystalline powder was obtained. The overall yield of the synthesis reaction was 82%, which confirms the high efficiency of the selected synthetic method. Based on the compositional analysis of the complex compound, it can be represented by the formula $[Zn(IAA)_2(AA)_2] \cdot 2H_2O$ [4]. The reaction equation can be expressed as follows.

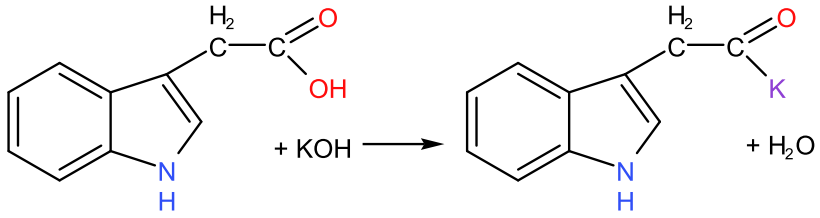


Figure 1. The reaction for obtaining the potassium salt of indole-3-acetic acid

In solution, the selected ligands lose their protons and are converted into IAA^- and AA^- anions. The Zn^{2+} ion possesses vacant coordination orbitals and forms coordination bonds with the IAA^- and AA^- ligands through the oxygen atoms of the carboxylate groups.

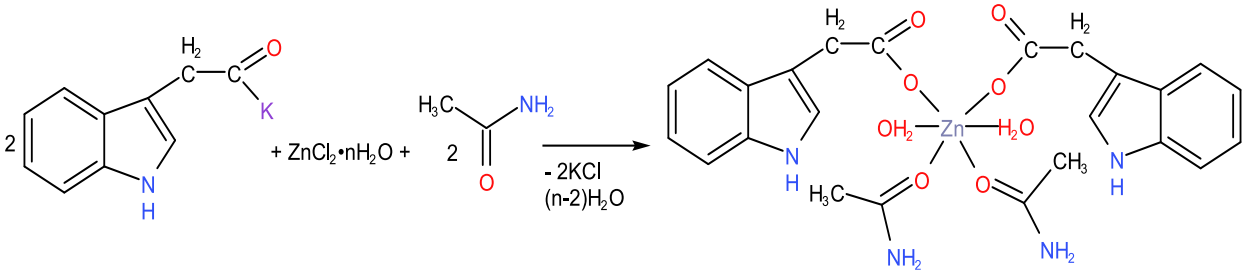


Figure 2. The reaction equation for the formation of the complex compound $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$

As a result, a coordination compound with six coordination and octahedral geometry is formed. During crystallization, the resulting complex incorporates two water molecules, which are considered water of crystallization: $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$.

Analysis and results. In this study, the electronic structure, geometric parameters, and stability of the synthesized complex $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$ were investigated using quantum chemical calculations. All computations were carried out using the Gaussian program package. The geometry optimization and subsequent analyses were performed within the framework of Density Functional Theory (DFT) employing the range-separated hybrid functional CAM-B3LYP, which is known for its improved description of long-range electron interactions and charge-transfer systems. The initial molecular structure of the complex was constructed based on experimental

coordination assumptions, where Zn(II) is coordinated by two indole-3-acetate (IAA^-) and two acetate (AA^-) ligands through oxygen donor atoms. Full geometry optimization was performed without any symmetry constraints, and the nature of the stationary points was confirmed by vibrational frequency analysis, ensuring the absence of imaginary frequencies.

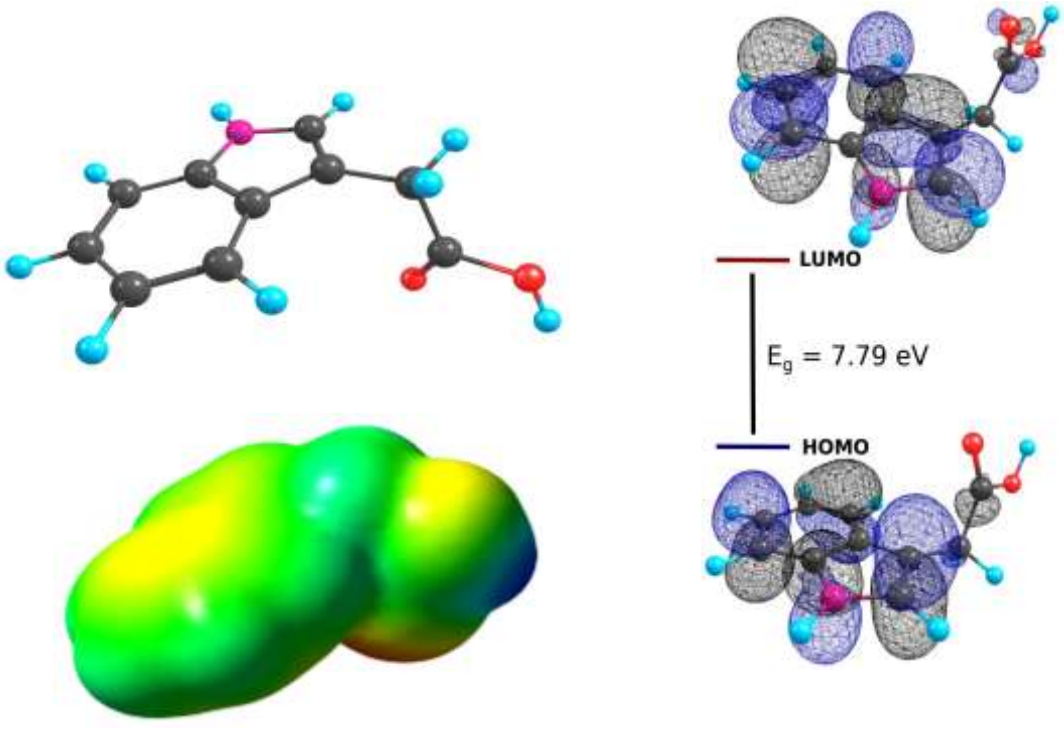
The optimized structure reveals that the Zn(II) center adopts a distorted octahedral coordination environment, where the ligand molecules form stable coordination bonds via carboxylate oxygen atoms. The presence of crystallization water molecules plays an important role in stabilizing the supramolecular structure through hydrogen bonding interactions. Furthermore, frontier molecular orbital (FMO) analysis was carried out to evaluate the electronic properties of the complex. The energies and spatial distributions of HOMO and LUMO orbitals provide insight into the chemical reactivity, kinetic stability, and possible charge-transfer pathways within the complex. The HOMO–LUMO energy gap indicates the relative stability of the system and its potential reactivity. Additionally, charge distribution analysis and electron density mapping were used to better understand the coordination behavior and electron delocalization within the complex system. These results provide a theoretical basis for interpreting the stability and physicochemical properties of the synthesized zinc complex.

Quantum chemical study of ligands and transition metal complex.

All quantum chemical calculations were carried out using the Gaussian 16 software package [5]. The molecular geometry was fully optimized in the gas phase without symmetry constraints using the range-separated hybrid functional CAM-B3LYP [6], which incorporates the Coulomb-attenuating method to improve the description of long-range exchange interactions. The LANL2DZ basis set [7] was employed throughout: it applies the Los Alamos National Laboratory double-zeta ECP basis for zinc, treating the inner core electrons through relativistic effective core potentials, while the ligand atoms

(C, N, O, H) are described with the standard Dunning/Huzinaga full double-zeta basis. Frequency calculations were performed on the optimized structure to confirm that the geometry corresponds to a true energy minimum on the potential energy surface (absence of imaginary frequencies). Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program interfaced with Gaussian-16 [8] to obtain natural atomic charges, orbital hybridizations, and donor-acceptor interactions via second-order perturbation theory. Frontier molecular orbitals (HOMO, LUMO) and their energy eigenvalues were extracted from the converged DFT wavefunction. The electrostatic potential was computed on the 0.001 a.u. electron density isosurface and mapped with a color scale ranging from electron-rich (red) to electron-poor (blue) regions.

Electronic structure analysis of ligands.



Conclusion. The present study reports a quantum chemical investigation of the zinc(II) complex $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$ using Density Functional Theory calculations performed with the Gaussian program package. Geometry optimizations and electronic

structure analyses were carried out at the CAM-B3LYP/LANL2DZ level of theory, confirming a stable optimized structure without imaginary frequencies. The results show that Zn(II) forms a six-coordinate distorted octahedral geometry with oxygen donor atoms. NBO analysis indicates predominantly ionic Zn–O interactions with partial covalent character due to ligand-to-metal charge transfer. Frontier molecular orbital analysis reveals a ligand-centered electronic structure with a large HOMO–LUMO gap (7.6 eV), indicating high kinetic stability and low reactivity. Electrostatic potential mapping further identifies oxygen atoms as the main reactive sites in the complex. Overall, the obtained theoretical results provide a consistent description of the structural stability and electronic properties of the synthesized zinc(II) complex, supporting its potential relevance in coordination and bioinorganic chemistry.

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