SYNTHESIS, STRUCTURE AND ELECTRONIC PROPERTIES OF A NEW $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$ COORDINATION COMPLEX: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

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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. Maqolada rux(II) ioni bilan indol-3-sirka kislotasi (geteroauksin) va atsetamid asosidagi yangi aralash ligandli koordinatsion birikmaning sintezi tavsiflangan. Olingan kompleks birikmaning tarkibi va tuzilishi element tahlili hamda IQ-spektroskopiya usullari yordamida tadqiq etildi. IQ-spektrlar tahlili ligandlarning metal ioniga koordinatsiyalanish usullarini aniqlash imkonini berdi. Tadqiqotning ikkinchi qismida kompleksning elektron tuzilishi va termodinamik xarakteristikalari kvant-kimyoviy hisoblashlar (DFT usuli) yordamida tahlil qilindi. Natijalar nazariy va tajribaviy ma'lumotlar o‘rtasida yuqori korrelyatsiya mavjudligini ko‘rsatdi, bu esa sintez qilingan kompleksning potentsial biologik faolligi uchun asos bo‘lib xizmat qiladi.

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

Аннотация. В статье описан синтез нового смешаннолигандного координационного соединения иона цинка(II) с индол-3-уксусной кислотой (гетероауксином) и ацетамидом. Состав и структура полученного комплексного соединения были исследованы с помощью элементного анализа и ИК-спектроскопии. Анализ ИК-спектров позволил определить способы координации лигандов к иону металла. Во второй части исследования с помощью квантово-химических расчетов (метод DFT) были проанализированы электронное строение и термодинамические характеристики комплекса. Результаты демонстрируют высокую корреляцию между теоретическими и экспериментальными данными, что дает основание для прогнозирования потенциальной биологической активности синтезированного комплекса.

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

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].

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 $[Zn(IAA)_2(AA)_2] \cdot 2H_2O$ [3]. The reaction equation can be expressed as follows.

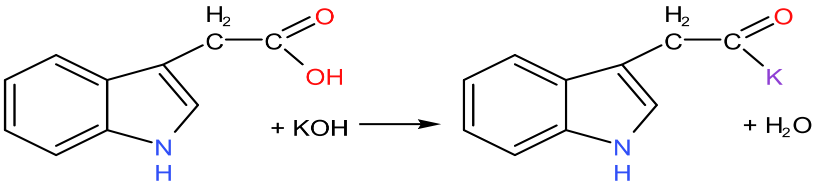

Figure 1. The reaction for obtaining the potassium salt of indole-3-acetic acid

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.

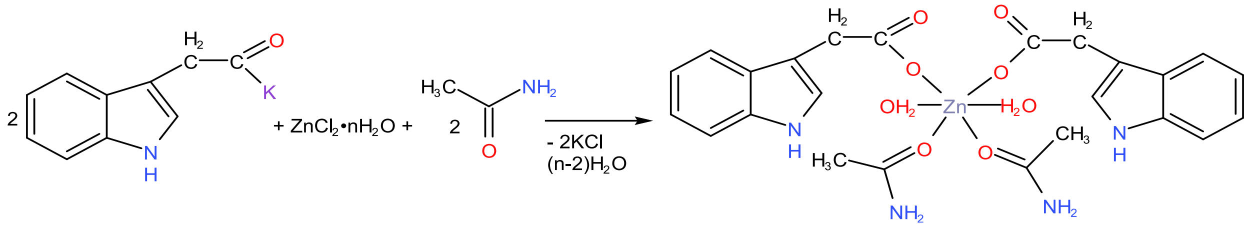

Figure 2. The reaction equation for the formation of the complex compound $[Zn(IAA)_2(AA)_2]\cdot 2H_2O$

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.

Electronic structure analysis of Zn(II) complex.

Zinc(II) coordination complexes occupy a prominent position in bioinorganic chemistry, materials science, and medicinal chemistry owing to the unique electronic properties of the d^{10} metal center, which confers high thermodynamic stability, Lewis acidity, and favorable luminescence behavior [4]. Unlike transition metals with partially filled d-orbitals, Zn(II) exhibits no d–d transitions, directing all photophysical activity toward ligand-based or ligand-to-metal charge-transfer (LMCT) processes [5]. Indole and its derivatives are biologically privileged scaffolds that appear as constituents of the essential amino acid tryptophan and a broad spectrum of natural products and pharmaceuticals [6]. Their aromatic nitrogen and electron-rich π-system make them excellent candidates for chelation of transition metals, offering both σ-donor N-coordination and π-stacking stabilization [7]. The incorporation of carboxylate and amide functionalities alongside the indole moiety creates multidentate ligand platforms capable of saturating the coordination sphere of Zn(II) while imparting solubility and hydrogen-bonding capacity relevant to aqueous biological environments. Density functional theory (DFT) has become the standard computational methodology for characterizing the structure, bonding, and reactivity of metal complexes [8]. The range-separated CAM-B3LYP functional is particularly well-suited to zinc coordination compounds, accurately describing charge-transfer excitations and long-range electron correlation effects that are poorly treated by conventional hybrid functionals [9]. The LANL2DZ effective core potential (ECP) basis set provides a computationally efficient treatment of the zinc core electrons while maintaining accuracy for valence-shell properties [10].

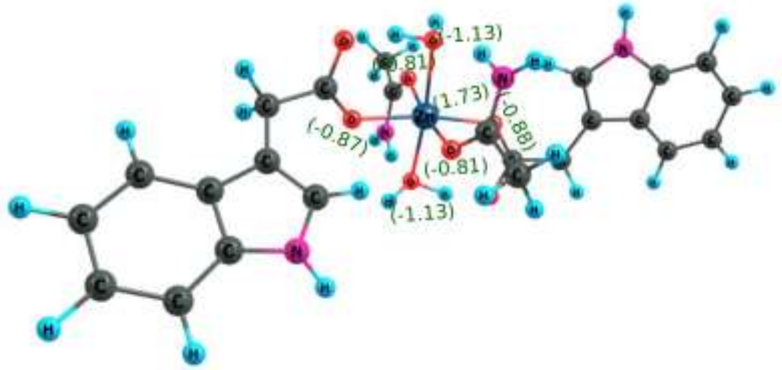

Figure 3. Optimized geometry of the Zn(II) complex at the CAM-B3LYP/LANL2DZ level with NBO partial charges (in parentheses, green text) shown for key donor atoms. Color code: Zn (dark blue), O (red), N (magenta), C (dark gray), H (cyan).

The optimized structure (Figure 3) reveals that the Zn(II) center is hexacoordinate with a strictly oxygen-donor O_6 coordination sphere, adopting a distorted octahedral geometry. The six donor oxygens originate from three chemically distinct sources: two carboxylate oxygens from *indole-2-carboxylic acid* (Zn–O: 2.05 and 2.07 Å), two acetamide carbonyl oxygens from the acetamide-indole ligand (Zn–O: 2.12 and 2.13 Å), and two terminal aqua oxygens (Zn–O: 2.15 and 2.13 Å).

Table 1.

Zn–O Bond lengths and NBO charges

Donor Type	Bond 1 (Å)	Bond 2 (Å)	NBO Charge 1 (e)	NBO Charge 2 (e)
Carboxylate O (indole-2-carboxylic acid)	2.05	2.07	−0.87	−0.88
Acetamide O	2.12	2.13	−0.81	−0.81
Terminal O (aqua)	2.15	2.13	−1.13	−1.13
Zn center (NBO)	—	—	+1.73	*(formal: +2.0)*

The NBO charge on zinc (+1.73 e) is reduced by 0.27 e relative to the formal +2 oxidation state, reflecting net ligand-to-metal charge transfer distributed across all six Zn–O bonds. This reduction confirms that the Zn–O bonds are predominantly ionic with a meaningful covalent component, consistent with Zn(II) acting as a borderline hard Lewis acid with a strong preference for oxygen donors over nitrogen. The carboxylate oxygens of indole-2-carboxylic acid form the shortest bonds in the complex (2.05 and 2.07 Å) and carry moderate negative charges (−0.87 and −0.88 e), identifying them as the strongest σ-donors in the coordination sphere. Their moderate charge magnitudes, rather than extreme values, reflect a balance between inherent oxygen electronegativity, partial charge transfer to Zn, and delocalization across the O–C–O resonance system of the carboxylate. The near-identical values for both oxygens ($\Delta q = 0.01$ e, $\Delta d = 0.02$ Å) confirm near-symmetric bidentate chelation of indole-2-carboxylic acid. The acetamide carbonyl oxygens exhibit intermediate bond lengths (2.12 and 2.13 Å) and the lowest negative charges among the three oxygen types (−0.81 e each). This is a direct consequence of amide resonance: the nitrogen lone pair adjacent to the C=O group donates electron density into the π*(C=O) orbital ($n_n \rightarrow \pi^*$ interaction), reducing the electron density available on the carbonyl oxygen for metal donation. Both acetamide oxygens are fully equivalent, confirming symmetric coordination geometry. The terminal aqua oxygens present an apparently paradoxical combination of the highest negative charge (−1.13 e) yet the longest Zn–O bonds (2.13–2.15 Å). This is resolved by recognizing that water oxygen retains high negative charge because of the polarization of its two O–H bonds (each H bears ~+0.5 e in NBO), not because of strong donation to zinc.

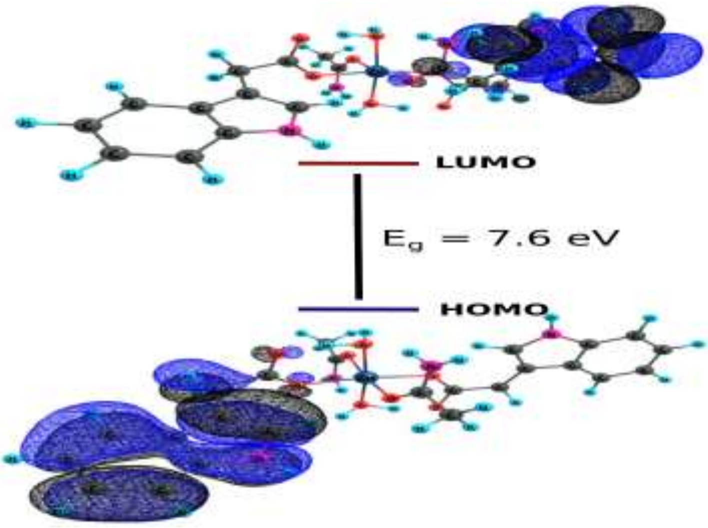

Figure 4. HOMO (bottom) and LUMO (top) of the Zn(II) complex (CAM-B3LYP/LANL2DZ, isovalue = 0.02 a.u.). Blue: positive phase; black mesh: negative phase. E^p = 7.6 eV. Both orbitals are exclusively ligand-centered.

Water is in fact the weakest donor of the three groups, forming the longest and most labile Zn–O bonds. These aqua ligands are therefore the primary sites for ligand exchange in solution and represent the most accessible substitution positions for incoming biological or pharmacological 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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