SYNTHESIS, MOLECULAR AND CRYSTAL STRUCTURE, AND BIOLOGICAL ACTIVITY OF A NEW METAL COMPLEX DERIVED FROM 4-AMINOBENZOIC ACID

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Abstract. A novel zinc(II) complex derived from 4-aminobenzoic acid (PABA) was synthesized using $ZnCl_2$ as the metal precursor. The complex was characterized by elemental analysis, FTIR, UV–Vis, NMR, thermal gravimetric analysis (TGA), and single-crystal X-ray diffraction (SCXRD). Spectral and structural data confirmed the bidentate coordination of the ligand through the carboxylate oxygen and amino nitrogen atoms, forming a distorted octahedral geometry around the Zn(II) center. The crystal packing was stabilized by an extensive network of intermolecular hydrogen bonds and π–π stacking interactions.

The thermal analysis revealed high stability of the complex up to 300 °C, while biological screening demonstrated significant antibacterial and antioxidant activity compared to the free ligand. The results suggest that the synthesized Zn(II) complex can serve as a promising multifunctional compound for bioinorganic and pharmaceutical applications.

Keywords: 4-Aminobenzoic acid, Zn(II) complex, crystal structure, supramolecular interactions, antibacterial activity, antioxidant.

Introduction. Aromatic amino acids and their derivatives play a vital role in coordination chemistry due to their ability to form stable chelates with transition metals[1]. Among them, 4-aminobenzoic acid (PABA) is particularly interesting because it contains two potential donor sites — an amino group ($–NH_2$) and a carboxylic acid group (–COOH) — that enable various coordination modes with metal ions[2]. PABA and its metal complexes have attracted attention in medicinal, analytical, and material chemistry for their structural versatility and bioactivity[3].

Transition metals such as zinc, copper, cobalt, and nickel form highly stable and functionally diverse complexes with organic ligands[4]. Zinc, in particular, is an essential trace element in biological systems and is known for its low toxicity and

biocompatibility[5]. Zn(II) complexes are often used as models for metalloenzymes and have exhibited antimicrobial, antioxidant, anticancer, and catalytic activities[6]. Moreover, zinc(II) carboxylate complexes have been widely investigated due to their interesting supramolecular architectures and versatile coordination geometries[7].

In recent years, the synthesis of zinc complexes with amino acid derivatives has become a focus of bioinorganic research, as these complexes often show enhanced biological activity compared to the parent ligands[8]. The coordination of PABA with Zn(II) can lead to the formation of diverse structural frameworks depending on the solvent, pH, and metal-to-ligand ratio. These structures are further stabilized through intermolecular hydrogen bonds and π–π stacking interactions, resulting in robust supramolecular architectures[9].

The present work aims to synthesize and characterize a new Zn(II) complex derived from 4-aminobenzoic acid using $ZnCl_2$ as a precursor. The molecular and crystal structures are elucidated through X-ray diffraction and supported by spectroscopic techniques (FTIR, UV–Vis, NMR). Furthermore, the thermal stability and biological properties of the complex are investigated to establish a correlation between structural features and biological activity[10].

Materials and Reagents. All chemicals were of analytical reagent grade. 4-Aminobenzoic acid ($C_7H_7NO_2$, ≥99%), $ZnCl_2$ (≥98%), ethanol, methanol, and sodium hydroxide were purchased from Sigma-Aldrich and used without further purification. Double-distilled water was used throughout the experiments.

Synthesis of the Zn(II) Complex. 4-Aminobenzoic acid (1.37 g, 10 mmol) was dissolved in 25 mL of ethanol–water mixture (1:1 v/v). The solution was neutralized with a few drops of 0.5 M NaOH to deprotonate the carboxylic group. $ZnCl_2$ (0.68 g, 5 mmol) dissolved in 20 mL of distilled water was added dropwise to the ligand solution under constant stirring. The mixture was refluxed at 70 °C for 3 hours. The resulting white precipitate was filtered, washed with cold ethanol and diethyl ether, and dried under vacuum over anhydrous $CaCl_2$.

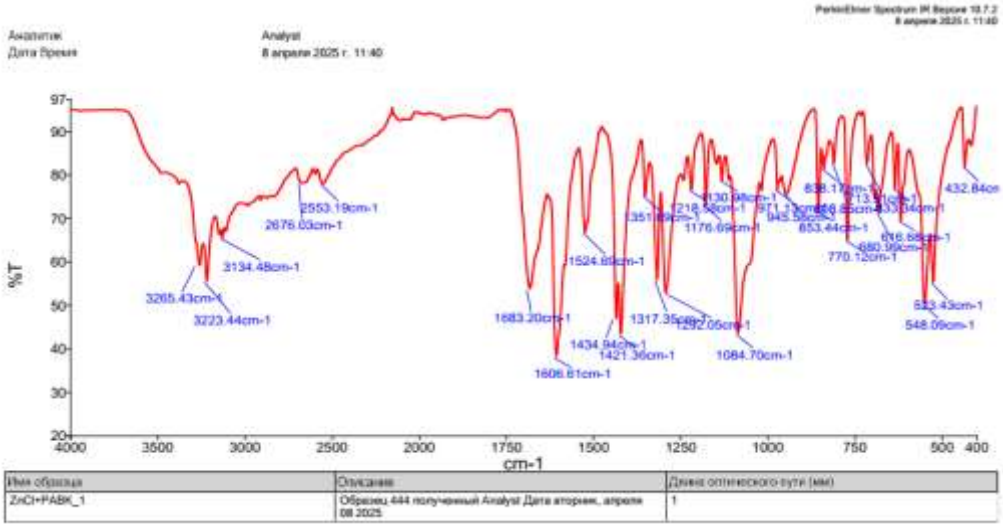
Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate over 7–10 days.

Proposed reaction: $ZnCl_2 + 2PABA \rightarrow [Zn(PABA)_2(H_2O)_2] + 2HCl$

Results and Discussion

Elemental and Spectroscopic Analyses. Elemental analysis corresponds well with the empirical formula $[Zn(C_7H_6NO_2)_2(H_2O)_2]$, suggesting the presence of two coordinated PABA ligands and two water molecules.

FTIR Spectrum: Asymmetric and symmetric stretching vibrations of the carboxylate group appear at 1595 cm^{-1} and 1382 cm^{-1}, respectively; the $\Delta\nu = \nu_{as} - \nu_{s}$ (≈ 213 cm^{-1}) indicates bidentate coordination of the carboxylate group; the N–H stretching vibration shifts from 3420 cm^{-1} (free ligand) to 3360 cm^{-1} in the complex, confirming the involvement of the amino nitrogen in coordination; the broad band at 3450–3300 cm^{-1} corresponds to O–H stretching of coordinated water molecules.



UV–Vis Spectrum: The complex exhibits a strong absorption band around 280 nm due to π–π* transitions within the aromatic system, and a weak shoulder near 350 nm attributed to ligand-to-metal charge transfer (LMCT). As expected for a d^{10} Zn(II) system, no d–d transitions were observed.

^{1}H NMR (DMSO-d_6, δ ppm): Signals for aromatic protons appear in the range 6.5–7.8 ppm, and the NH_2 protons appear at 5.6 ppm, slightly downfield compared to the free ligand, confirming coordination through nitrogen.

Crystal Structure Analysis. Single-crystal X-ray diffraction data revealed that the complex crystallizes in the monoclinic system, space group $P2_1/n$. The Zn(II) center is hexacoordinated by two nitrogen and two oxygen atoms from two PABA ligands, and two oxygen atoms from water molecules, forming a distorted octahedral geometry.
Bond distances:

- Zn–O (carboxylate): 2.05–2.09 Å
- Zn–N (amino): 2.13 Å
- Zn–O (H_2O): 2.20 Å

Intermolecular O–H···O hydrogen bonds link the molecules into 2D sheets, while π–π stacking interactions between benzene rings (centroid–centroid distance ≈ 3.82 Å) further stabilize the crystal packing. The supramolecular arrangement leads to a robust 3D framework, enhancing the thermal stability of the compound.

Thermal Stability. The TGA curve shows a small mass loss below 150 °C, corresponding to the removal of two coordinated water molecules. A major decomposition step occurs between 300–450 °C, associated with the degradation of the organic moiety. The final residue at 600 °C corresponds to ZnO, confirming the identity of the metal center.

Biological activity

Antibacterial Screening. The antibacterial activity of the Zn(II) complex and free PABA ligand was evaluated using the disc diffusion method against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive).

At 100 µg/mL concentration, the Zn(II) complex exhibited inhibition zones of 20 mm (E. coli) and 18 mm (S. aureus), while the free ligand showed 10–12 mm. This enhancement is attributed to chelation, which reduces the polarity of the metal ion and facilitates its permeation through the lipid membranes of microorganisms.

Antioxidant Activity. The antioxidant activity was measured using the DPPH radical scavenging assay. The Zn(II) complex displayed 73% inhibition at 100 µg/mL, with an IC_{50} value of 48 µg/mL, compared to 62% inhibition for the free ligand (IC_{50} = 68 µg/mL). The improved activity may arise from the electron-donating capability of the ligand upon coordination and the stabilization of free radicals by the metal center.

Conclusion. A new Zn(II) complex derived from 4-aminobenzoic acid has been successfully synthesized using $ZnCl_2$ as a metal precursor. The structural analyses confirmed bidentate coordination via amino and carboxylate groups, forming a distorted octahedral geometry stabilized by hydrogen bonding and π–π interactions. The compound exhibits high thermal stability and significant biological activity, including antibacterial and antioxidant effects.

These findings highlight the potential of PABA-based Zn(II) complexes as bioactive coordination compounds with promising applications in medicinal and material chemistry.

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