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STRUCTURE OF THE Zn(II) COMPLEX WITH 1,10-PHENANTHROLINE AND β-(N-BENZOXAZOLIN-2-THIONE)PROPIONIC ACID

***Abstract**: The work describes the synthesis and crystal structure of a new mixed-ligand Zn(II) complex containing 1,10-phenanthroline and β-(N-benzoxazolin-2-thione)propionic acid. The obtained compound, formulated as $[Zn(phen)(BOP)_2(H_2O)]\cdot H_2O$, was isolated in a stable individual form and characterized using single-crystal X-ray diffraction. Zn(II) exhibits an N_2O_3 coordination environment, including two N-donor atoms of phenanthroline, two carboxylate O-atoms and a coordinated water molecule. The supramolecular network is stabilized by O–H···O hydrogen bonds involving an external water molecule. The structural features demonstrate the potential of benzoxazolin-based ligands in designing coordination systems of d-metals.*

***Key words**: zinc complex, 1,10-phenanthroline, benzoxazolin-2-thione, crystal structure, coordination compounds.*
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Introduction

Benzoxazoline and its derivatives represent an important class of biologically active heterocyclic compounds [1, 2]. Owing to the combination of an aromatic core and two heteroatoms (N and O), these systems are capable of forming stable donor–acceptor contacts, participating in π–π interactions, and exhibiting a pronounced ability to coordinate metal ions. In the literature, benzoxazoline fragments are regarded as promising structural modules for targeted molecular design because of their polarizability, rigid aromatic platform, and the possibility of fine-tuning their electronic properties through functionalization. These features make the benzoxazoline scaffold highly attractive for the development of new biologically active compounds, including coordination complexes with d-metals [1, 2]. Notably, the introduction of a thione (C=S) group, as in benzoxazolin-2-thione derivatives, significantly enhances the coordinative versatility of these ligands by providing a soft sulfur donor atom, which can form stable bonds with borderline or soft metal ions, such as Zn(II), in its thioketo or thiolate forms [3].

Zinc is an essential bioelement for both humans and plants. In humans, Zn(II) is a component of a large number of enzymes and zinc-finger proteins and is involved in the regulation of immune response, metabolism, and antioxidant defense [4]. In higher plants, zinc is required for chlorophyll synthesis, nitrogen metabolism, photosynthetic efficiency, and resistance to stress factors. Zinc deficiency leads to growth retardation, weakened immunity, and the development of chlorosis [5]. In this regard, the investigation of the coordination features of Zn(II) and its interactions with ligands is an important task of bioinorganic chemistry. The coordination geometry of Zn(II) is highly adaptable (typically tetrahedral, square-pyramidal, or octahedral), which allows it to form diverse complexes with varied ligand environments, directly influencing the biological activity and physicochemical properties of the resulting compounds [6].

1,10-Phenanthroline (phen) is a classic rigid, planar diimine N,N′-chelating ligand capable of forming stable complexes with d-metals. Its planar π-structure promotes π–π interactions and intercalation, making phenanthroline a widely used ligand in bio- and supramolecular coordination chemistry [7]. Complexes containing the $[M(phen)]^{2+}$ core often exhibit enhanced DNA-binding properties, antimicrobial activity, and interesting photophysical behavior [8]. Therefore, the combination of phenanthroline with other biologically relevant ligands in mixed-ligand complexes is a fruitful strategy for creating compounds with synergistic properties and novel functions [9].

Mixed-ligand complexes, which incorporate two or more different types of organic ligands, often demonstrate superior biological activity, enhanced stability, and unique structural features compared to their homoleptic counterparts [9, 10]. The rational design of such complexes aims to harness the complementary properties of each ligand. In this context, the synthesis of complexes containing both a rigid aromatic diimine (like phen) and a flexible anionic ligand with O,S-donor atoms (like derivatives of benzoxazolin-2-thione propionic acid) is of particular interest. Such combinations can lead to the formation of intricate supramolecular architectures via hydrogen bonding and π-stacking, which can influence the compound's solubility, stability, and intermolecular interactions [11].

In the present work, we report the synthesis and structural investigation of a new mixed-ligand complex, $[Zn(phen)(BOP)_2(H_2O)]\cdot H_2O$, where phen = 1,10-phenanthroline and BOP = deprotonated anion of β-(N-benzoxazolin-2-thione)propionic acid. The choice of this ligand system is motivated by the potential synergy between the DNA-intercalating ability of the phenanthroline moiety and the bioactive benzoxazolin-thione core. A detailed structural analysis using single-crystal X-ray diffraction was performed to elucidate the coordination mode of the BOP ligand, the geometry around the Zn(II) center, and the role of non-covalent interactions in stabilizing the crystal lattice.

Materials and Methods

Reagents and starting materials

Analytical-grade reagents and solvents were used in all synthetic experiments without further purification. 1,10-Phenanthroline (phen, ≥99%) and zinc(II) nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$, ≥98%) were purchased from Sigma-Aldrich. The ligand β-(N-benzoxazolin-2-thione)propionic acid (HBOP) was synthesized according to a modified literature procedure [12] via the cyclocondensation of 2-aminophenol with 3,3'-thiodipropionic acid, followed by purification by recrystallization from ethanol. The identity and purity of HBOP were confirmed by elemental analysis (CHNS analyzer EuroVector EA3000), melting point determination (Stuart SMP30 apparatus), and IR spectroscopy (Shimadzu IRTracer-100). Absolute ethanol (EtOH, 99.8%) and distilled water were used as solvents. All manipulations were carried out at ambient temperature (~25 °C) unless stated otherwise.

Synthesis of the complex $[Zn(phen)(BOP)_2(H_2O)]\cdot H_2O$

The mixed-ligand complex was synthesized by a slow diffusion method to facilitate the growth of single crystals suitable for X-ray analysis [13].

To a stirred aqueous solution (5 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (0.10 mmol, 29.7 mg), an ethanolic solution (10 mL) containing a 2:1 molar ratio of the organic ligands was added dropwise over 15 minutes. The ligand solution was prepared by first dissolving HBOP (0.20 mmol, 47.6 mg) in warm ethanol (6 mL), followed by the addition of a clear solution of 1,10-phenanthroline (0.10 mmol, 18.0 mg) in ethanol (4 mL). The resulting mixture was stirred magnetically for 30 minutes at room temperature, yielding a clear, colorless solution. The final reaction mixture was filtered through a fine-porosity glass frit to remove any particulate matter and then transferred to a narrow glass vial. The vial was tightly capped, and small pinholes were made in the cap to allow for very slow evaporation of the solvents. Colorless, prismatic single crystals formed at the bottom of the vial after 7–12 days. The crystals were separated by filtration, washed with a small portion of a cold 1:1 ethanol/water mixture, and air-dried. Yield: ~70% (based on Zn). Anal. Calc. for $C_{34}H_{30}N_4O_7S_2Zn$: C, 54.58; H, 4.04; N, 7.49; S, 8.57. Found: C, 54.42; H, 4.11; N, 7.38; S, 8.46%.

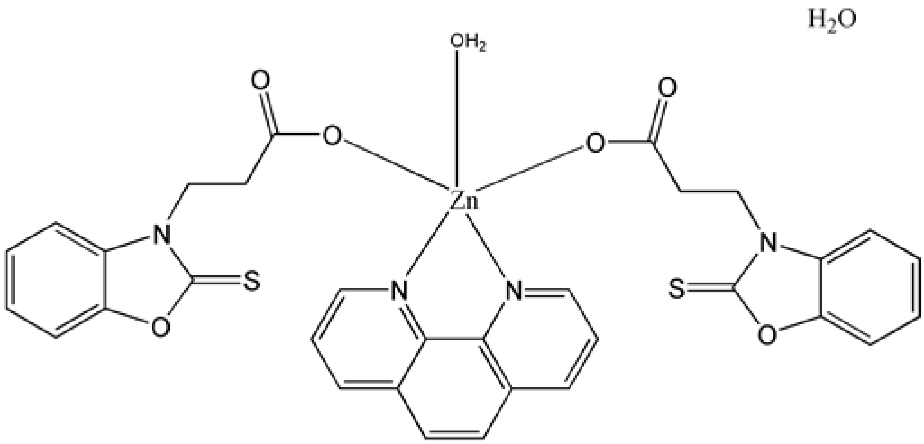
Single-Crystal X-ray Diffraction Study

A well-formed colorless prismatic crystal with approximate dimensions of 0.25 x 0.20 x 0.15 mm³ was selected and mounted on a MicroMount™ loop using Paratone-N oil. X-ray diffraction data were collected at 293(2) K on a Rigaku XtaLAB Synergy diffractometer, equipped with a HyPix3000 hybrid photon-counting detector and using microfocus Cu Kα radiation (λ = 1.54184 Å) from a PhotonJet (Cu) X-ray source. Data collection and unit cell refinement were performed using the CrysAlis PRO 1.171.42.67a software package (Rigaku Oxford Diffraction, 2022) [14]. Absorption corrections were applied empirically using the multi-scan method implemented in CrysAlis PRO.

The crystal structure was solved by intrinsic phasing using the SHELXT-2018/2 program [15] and refined by full-matrix least-squares minimization on F^2 using the SHELXL-2018/3 program [16] within the OLEX2 graphical interface [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using a riding model with Uiso(H) = 1.2 Ueq(C) (or 1.5 Ueq for methyl groups). Hydrogen atoms of the coordinated and lattice water molecules were located from difference Fourier maps and their positions and isotropic displacement parameters were refined with distance restraints (O–H = 0.84(2) Å, H···H = 1.36(3) Å). The final refinement converged satisfactorily.

Results and discussion

The complex was isolated in an individual form as homogeneous, transparent crystals and was characterized by single-crystal X-ray diffraction analysis, which enabled the unambiguous determination of its composition, the coordination environment of Zn(II), its geometry, and the stability of the supramolecular packing. A schematic representation of the structural formula of the complex is shown in Scheme 1. The obtained data demonstrate the influence of the nature of the mixed ligands on the conformational preference of the metal center and reveal the role of weak intermolecular interactions in the formation of stable structural motifs. The geometric parameters of the coordination sphere, the contribution of donor–acceptor contacts, interligand asymmetry, as well as the stabilizing effects of hydrogen bonding and π–π interactions were analyzed.



Scheme 1. Structural formula of the complex [Zn(phen)(BOP)$_2$(H$_2$O)]·H$_2$O (phen = 1,10-phenanthroline; BOP = β-(N-benzoxazolin-2-thione)propionate).

The Zn(II) center exhibits a distorted N_2O_3 coordination environment: the metal ion is coordinated by two nitrogen atoms of the planar chelating ligand 1,10-phenanthroline, two oxygen atoms from the carboxylate groups of the BOP^- ligands, and one oxygen atom of the coordinated water molecule. The nonequivalence of the donor atoms is reflected in the bond lengths: the Zn–O(carboxylate-1) distance of 1.9682(15) Å is the shortest and thus the strongest, whereas Zn–O(carboxylate-2) at 2.0455(17) Å is slightly elongated due to torsional displacement and participation in outer-sphere O–H···O hydrogen bonding. A similar asymmetry is observed in the phenanthroline chelate fragment: Zn–N(proximal) = 2.0983(18) Å and Zn–N(distal) = 2.1728(19) Å, arising from the rigid geometry of the diimine ring and the relatively small chelate angle (≈78.10°). The Zn–O bond to the coordinated water molecule (2.1332(18) Å) has an intermediate donor strength and stabilizes the equatorial positions.

The “trans” angles (161.45(7)° and 143.68(7)°), along with the valence angles (90–103°), are consistent with a distorted trigonal–bipyramidal geometry. The first carboxylate group lies nearly coplanar with the phenanthroline fragment, enhancing its donor contribution, whereas the second adopts a “forced” torsional orientation imposed by cooperative hydrogen bonding with the outer-sphere water molecule (H···O ≈ 1.9–2.4 Å, angle 157–171°), which stabilizes the packing and fixes the trans arrangement of the O-donors. Additional stabilization is provided by intermolecular π–π interactions between phenanthroline fragments, forming a dense supramolecular network.

Conclusion

The observed geometric asymmetries and distribution of donor functions reveal a delicate balance between the rigid N,N′-chelation of phenanthroline, the flexibility of the O,O′-donor BOP^- ligands, and the modifying role of water. The outer-sphere water molecule acts not only as a hydrogen-bonding stabilizer but also as a key factor influencing the torsional orientation of the carboxylate groups and, consequently, the entire supramolecular architecture. The obtained complex demonstrates the potential of benzoxazoline-based ligands for the targeted design of robust Zn(II) coordination structures with tunable electronic and conformational characteristics.

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