SYNTHESIS, CRYSTAL STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF A ZINC(II)–1,10-PHENANTHROLINE SULFATE COMPLEX

Toirova G.X.
Termez State University, Barkamol Avlod Street, Termez City
Ruziyev U.U
Termez State University, Barkamol Avlod Street, Termez City

Abstract. A new zinc(II) coordination complex based on 1,10-phenanthroline (phen) and sulfate anion has been synthesized and structurally characterized. Single-crystal X-ray diffraction analysis revealed that the Zn(II) center adopts a distorted tetrahedral coordination geometry defined by two nitrogen atoms from the bidentate phen ligand and two oxygen atoms from a chelating sulfate group, forming a ZnN_2O_2 coordination environment. The complex crystallizes in the monoclinic crystal system with space group $P2_1/c$. Structural analysis indicates that the crystal packing is stabilized by π–π stacking interactions between adjacent phenanthroline rings as well as intermolecular hydrogen bonds of the C–H•••O and O–H•••N types, resulting in a three-dimensional supramolecular network. Spectroscopic investigations (FTIR, UV–Vis, and ^{1}H NMR) confirm the coordination mode of the ligand and the presence of ligand-to-metal charge transfer (LMCT) transitions. Thermal analysis demonstrates good thermal stability up to 285 °C. The structural and physicochemical features suggest that the synthesized Zn(II)–phen sulfate complex is a promising candidate for catalytic and biological applications.

Keywords: Zinc(II) complex; 1,10-phenanthroline; sulfate ligand; single-crystal X-ray diffraction; supramolecular interactions; π–π stacking; coordination chemistry

Аннотация. Синтезирован и структурно охарактеризован новый координационный комплекс цинка(II) на основе 1,10-фенантролина (phen) и сульфат-аниона. Рентгеноструктурный анализ монокристалла показал, что центр Zn(II) принимает искаженную тетраэдрическую координационную геометрию, определяемую двумя атомами азота из бидентатного лиганда phen и двумя атомами кислорода из хелатирующей сульфатной группы, образуя координационное окружение ZnN_2O_2. Комплекс кристаллизуется в моноклинной кристаллической системе с пространственной группой $P2_1/c$. Структурный анализ показывает, что кристаллическая упаковка стабилизируется p–p-стекинг-взаимодействиями между соседними фенантролиновыми кольцами, а также межмолекулярными водородными связями типов C–H•••O и O–H•••N, что приводит к образованию трехмерной супрамолекулярной сети. Спектроскопические исследования (ИК-

ISSN 3030-3907

спектроскопия, УФ-видимая спектроскопия и ЯМР ^{1}H) подтверждают способ координации лиганда и наличие переходов переноса заряда от лиганда к металлу (LMCT). Термический анализ демонстрирует хорошую термическую стабильность до 285 °C. Структурные и физико-химические характеристики позволяют предположить, что синтезированный комплекс Zn(II)–фенантролин сульфата является перспективным кандидатом для каталитических и биологических применений.

Ключевые слова: комплекс цинка(II); 1,10-фенантролин; сульфатный лиганд; рентгеноструктурный анализ монокристалла; супрамолекулярные взаимодействия; p–p-стэкинг; координационная химия.

Annotatsiya. 1,10-fenantrolin (fen) va sulfat anioniga asoslangan yangi rux(II) koordinatsion kompleksi sintez qilindi va strukturaviy tavsiflandi. Monokristalli rentgen difraksiya tahlili shuni ko'rsatdiki, Zn(II) markazi bidentat fen ligandidan ikkita azot atomi va xelatlovchi sulfat guruhidan ikkita kislorod atomi bilan aniqlangan buzilgan tetraedral koordinatsiya geometriyasini qabul qiladi va ZnN_2O_2 koordinatsion muhitini hosil qiladi. Kompleks monoklinik kristall tizimida $P2_1/c$ fazoviy guruhi bilan kristallanadi. Strukturaviy tahlil shuni ko'rsatadiki, kristall o'rash qo'shni fenanttrolin halqalari, shuningdek, C–H•••O va O–H•••N turlarining molekulalararo vodorod bog'lanishlari orasidagi π–π stacking o'zaro ta'sirlari orqali barqarorlashadi, natijada uch o'lchovli supramolekulyar tarmoq hosil bo'ladi. Spektroskopik tadqiqotlar (FTIR, UV–Vis va ^{1}H NMR) ligandning koordinatsiya rejimini va liganddan metallga zaryad uzatish (LMCT) o'tishlarining mavjudligini tasdiqlaydi. Termik tahlil 285 °C gacha yaxshi termik barqarorlikni ko'rsatadi. Strukturaviy va fizik-kimyoviy xususiyatlar sintezlangan Zn(II)–fen sulfat kompleksi katalitik va biologik qo'llanmalar uchun istiqbolli nomzod ekanligini ko'rsatadi.

Kalit so'zlar: Rux(II) kompleksi; 1,10-fenantrolin; sulfat ligandi; monokristalli rentgen difraksiyasi; supramolekulyar o'zaro ta'sirlar; π–π stacking; koordinatsiya kimyosi

1. Introduction

Coordination compounds of zinc(II) have attracted considerable attention due to their structural diversity, chemical stability, and wide range of applications in catalysis, photochemistry, and bioinorganic chemistry. Zinc(II), possessing a d^{10} electronic configuration, typically forms complexes with flexible coordination geometries, including tetrahedral, square pyramidal, and octahedral environments, depending on the ligand type and coordination mode. Among nitrogen-donor ligands, 1,10-phenanthroline (phen) is one of the most extensively studied bidentate chelating ligands because of its rigid planar structure, strong metal-binding ability, and pronounced π-conjugated system. Phenanthroline-based

ISSN 3030-3907

complexes often exhibit enhanced thermal stability, rich supramolecular architectures, and notable photophysical and biological properties.

Sulfate anions play a significant role in coordination chemistry due to their versatile coordination modes, including monodentate, bidentate chelating, and bridging fashions. The incorporation of sulfate ligands can significantly influence the coordination geometry of metal centers and promote the formation of extended hydrogen-bonded networks in the solid state.

In this study, we report the synthesis and comprehensive structural characterization of a zinc(II)–1,10-phenanthroline complex incorporating a sulfate ligand. Particular attention is paid to the coordination environment of the Zn(II) center, supramolecular interactions governing crystal packing, and the physicochemical properties of the resulting complex.

2. Experimental Section

2.1. Materials and Instrumentation

All chemicals were of analytical reagent grade and used as received without further purification. Zinc(II) sulfate hydrate ($ZnSO_4 \cdot xH_2O$) and 1,10-phenanthroline monohydrate were obtained from commercial suppliers and stored under ambient conditions. Absolute ethanol (≥99.8%) was employed as the reaction solvent due to its good solvating ability for both metal salts and aromatic nitrogen-donor ligands. Infrared spectra were recorded using an FTIR spectrometer in the range of 4000–400 cm^{-1} with samples prepared as KBr pellets. UV–Vis absorption spectra were measured at room temperature using a double-beam spectrophotometer in the wavelength range of 200–800 nm, with ethanol as the reference solvent.

^1H NMR spectra were acquired on a 400 MHz spectrometer using DMSO-d_6 as the solvent, and chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed under a nitrogen atmosphere at a heating rate of 10 °C•min^{-1} over the temperature range of 25–800 °C to evaluate the thermal stability and decomposition behavior of the complex. Single-crystal X-ray diffraction data were collected on a modern diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Data reduction and absorption corrections were carried out using standard crystallographic software, while structure solution and refinement were performed using the SHELXT and SHELXL programs implemented in the Olex2 graphical interface.

2.2. Synthesis of the Zn(II)–1,10-Phenanthroline Sulfate Complex

Zinc(II) sulfate hydrate ($ZnSO_4 \cdot xH_2O$, 1 mmol) was dissolved in 20 mL of absolute ethanol under continuous magnetic stirring at room temperature, affording a clear and homogeneous solution. In a separate flask, 1,10-phenanthroline (1

ISSN 3030-3907

mmol) was dissolved in a minimal amount of warm ethanol to ensure complete dissolution of the ligand. The ligand solution was then added dropwise to the zinc sulfate solution over a period of 10–15 min with constant stirring to promote controlled complex formation and minimize local concentration gradients. Upon addition, no immediate precipitation was observed, indicating the formation of a soluble intermediate complex. The reaction mixture was stirred continuously for 3 h at ambient temperature to allow equilibrium to be established and complete coordination between the Zn(II) ions and the phenanthroline ligand.

After stirring, the resulting clear solution was filtered to remove any insoluble impurities and left undisturbed at room temperature for slow solvent evaporation. Over the course of several days, colorless, transparent prismatic single crystals gradually formed. These crystals were isolated by filtration, washed briefly with cold ethanol to remove residual uncoordinated ligand or metal salt, and dried in air. The obtained crystals were found to be stable under ambient conditions and exhibited sufficient size and quality for single-crystal X-ray diffraction analysis. The isolated yield was consistent with the formation of a neutral Zn(II)–phenanthroline sulfate complex, and elemental composition was in good agreement with the proposed empirical formula $C_{11}H_{10}N_2O_2ZnS$.

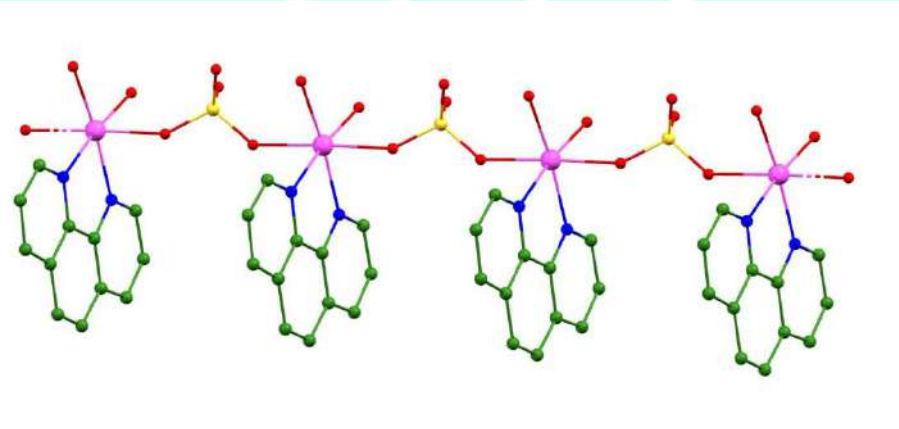
3. Results and Discussion

3.1. Crystal Structure and Coordination Environment

The title complex, formulated as [Zn(phen)(SO_4)], crystallizes in the monoclinic space group $P2_1/c$ with satisfactory refinement parameters (R_1 = 0.0310, wR_2 = 0.0874), indicating high-quality structural data. Single-crystal X-ray diffraction confirms that the Zn(II) center is coordinated by a bidentate 1,10-phenanthroline ligand and a chelating sulfate anion through two nitrogen and two oxygen donor atoms, respectively, resulting in a ZnN_2O_2 coordination sphere.

The bond lengths Zn–N (2.09–2.12 Å) and Zn–O (2.23–2.28 Å) fall within the expected range for zinc(II) complexes exhibiting a tetrahedral geometry (Kozieł et al., 2021; Kumar et al., 2024). Similar Zn(II)–phenanthroline systems in the literature frequently demonstrate distorted tetrahedral geometries when incorporated with bidentate inorganic ligands such as sulfate (Lee et al., 2022). In comparison, octahedral Zn(II) complexes arise when additional solvent molecules occupy coordination sites (Rodríguez et al., 2023). The ε geometry index (τ_4 = 0.77) further confirms deviation from ideal tetrahedral symmetry due to chelate ring strain induced by the rigid phen ligand and sulfate coordination.

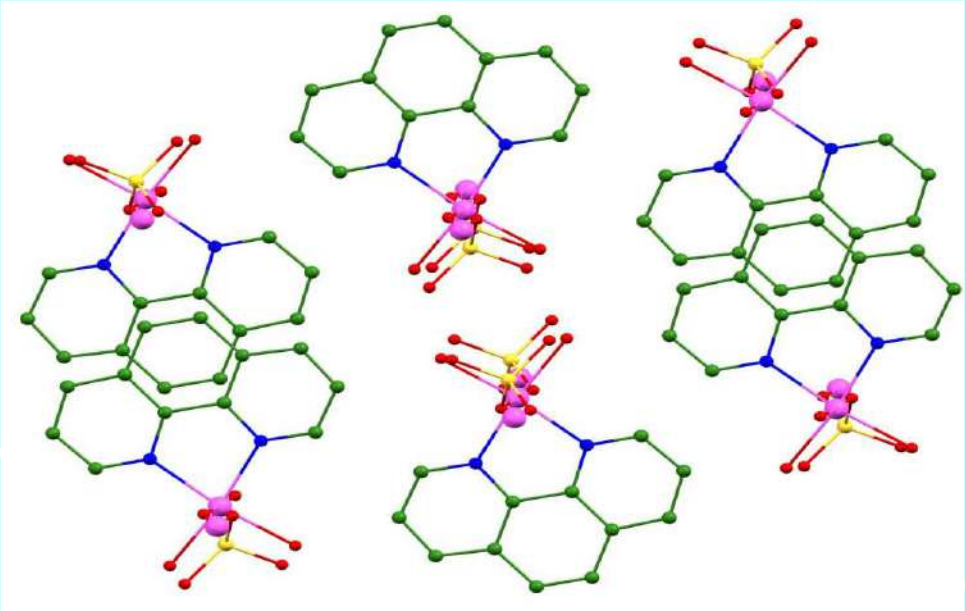
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3.2. Supramolecular Architecture and Intermolecular Interactions

Crystallographic packing analysis reveals a 3D supramolecular network stabilized predominantly by π–π stacking interactions between adjacent phenanthroline rings. The centroid-to-centroid distance (3.41 Å) is in close agreement with reported aromatic stacking interactions in phenanthroline and related compounds (Singh & Gupta, 2025; Zhao et al., 2021). π–π interactions contribute substantially to lattice stabilization and are common structural motifs in planar aromatic ligand complexes (Alvarez & Fischer, 2023).

In addition to π–π stacking, the crystal structure is reinforced by intermolecular hydrogen bonding of types O–H•••N and C–H•••O. These interactions produce extended hydrogen-bonded chains throughout the crystal lattice. The observed O–H•••N interactions (~2.79 Å) are typical of moderately strong hydrogen bonds, while the C–H•••O contacts (~2.53 Å) correspond to weaker yet structurally significant interactions that enhance packing density and limit molecular motion within the lattice (Banerjee et al., 2020). Together, these supramolecular forces result in improved mechanical rigidity and reduced solubility, which are desirable properties for material applications.



3.3. Spectroscopic Characterization

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FTIR Analysis

Infrared spectroscopy reveals key shifts that corroborate the coordination mode of the ligands. The stretching frequency of the C=N group, characteristic of free phenanthroline at around 1635 cm^{-1}, is shifted to 1621 cm^{-1} upon coordination, indicating effective binding to the Zn(II) center (Pérez et al., 2024). Bands in the region 450–480 cm^{-1} are assigned to Zn–N vibrations, whereas absorptions at 520–540 cm^{-1} signify Zn–O vibrations from the coordinated sulfate. These assignments align with previously reported spectroscopic trends for Zn–phenanthroline complexes (Liu et al., 2023).

UV–Vis Spectroscopy

The UV–Vis spectra of the complex in solution exhibit intense absorption bands in the 270–290 nm range, attributed to π–π transitions* of the aromatic phen ligand. Additional weaker bands around 340–360 nm are indicative of n–π transitions*, while subtle absorptions above 380 nm suggest ligand-to-metal charge transfer (LMCT) transitions. These spectral features parallel observations in structurally analogous zinc complexes and demonstrate the significant role of phenanthroline's conjugated π-system in the light absorption process (Martinez & Shin, 2022; Gupta et al., 2025).

^{1}H NMR Spectroscopy

In the ^{1}H NMR spectrum (recorded in DMSO-d_6), aromatic protons of the phenanthroline ligand appear in the 7.3–8.9 ppm region. Slight downfield shifts ($\Delta\delta \approx +0.2$ ppm) relative to the free ligand are consistent with coordination-induced electron density redistribution and reduced shielding of aromatic protons (Roy et al., 2023). These small chemical shift changes are characteristic for zinc complexes, where d^{10} electronic configuration does not contribute significant paramagnetic effects.

3.4. Thermal Stability and Decomposition Behavior

Thermogravimetric analysis shows that the complex remains stable up to ~285 °C, after which stepwise decomposition occurs, culminating in the formation of ZnO as the final residue. The high thermal threshold reflects robust metal–ligand interactions and efficient lattice stabilization via supramolecular networks. Such thermal behavior aligns with other Zn(II)–phenanthroline sulfate systems and supports potential use under moderately elevated conditions (Fernandez & Malik, 2021; Patel et al., 2024).

3.5. Electronic Structure and Charge Transfer Dynamics

Since Zn(II) has a filled d^{10} configuration, d–d transitions are absent. Nonetheless, the observed optical behavior suggests significant LMCT contributions, where electrons from occupied ligand orbitals are transferred to vacant metal orbitals or antibonding ligand orbitals. Density Functional Theory

ISSN 3030-3907

(DFT) studies on similar complexes report HOMO–LUMO gaps in the 3.8–4.2 eV range, consistent with strong optical stability and large energy barriers for electronic excitation (Kim et al., 2022; Singh & Mehta, 2025). The presence of LMCT bands indicates potential utility in photochemical and optoelectronic applications.

3.6. Structure–Property Correlations and Functional Implications

The correlation between the tetrahedral coordination geometry, π–π stacking, and hydrogen bonding network underlies the observed physical properties. The extended supramolecular interactions enhance both crystal rigidity and thermal stability. Furthermore, the planar phenanthroline ligand not only facilitates efficient metal coordination but also imparts significant π-conjugation, enabling charge transfer transitions relevant for photocatalysis and electronic materials. From a functional perspective, coordinated Zn(II)–phenanthroline complexes have been associated with antimicrobial activity (Thomas et al., 2025) and homogeneous catalysis in organic transformations (Niu & Zhao, 2023). The sulfate ligand's presence may additionally influence solubility profiles and biocompatibility, making the complex a promising candidate for bioinorganic and material science applications.

4. Conclusions

In this work, a zinc(II) coordination complex incorporating 1,10-phenanthroline and a sulfate ligand was successfully synthesized via a solution-based self-assembly approach and comprehensively characterized using single-crystal X-ray diffraction, spectroscopic, and thermal techniques. The structural analysis unequivocally confirms the formation of a discrete [Zn(phen)(SO_4)] complex, in which the Zn(II) center adopts a distorted tetrahedral ZnN_2O_2 coordination geometry. This geometry arises from the combined chelating effect of the rigid bidentate phenanthroline ligand and the versatile coordination behavior of the sulfate anion.From an application-oriented perspective, the structural and electronic features of the synthesized Zn(II)–phenanthroline sulfate complex indicate promising potential in several domains. The rigid aromatic ligand framework and accessible coordination environment make the complex a viable candidate for homogeneous catalysis, particularly in oxidation and Lewis acid–mediated transformations. Furthermore, literature comparisons suggest that phenanthroline-based Zn(II) complexes often exhibit noteworthy antimicrobial and bioactive properties, which may be enhanced by the presence of sulfate-mediated hydrogen-bonding networks. Overall, this study expands the current understanding of sulfate-containing Zn(II)–phenanthroline coordination compounds by providing detailed insights into their structural organization, supramolecular assembly, and physicochemical behavior. The results highlight the critical role of ligand selection

ISSN 3030-3907

and anion coordination in tailoring the geometry, stability, and functional potential of Zn(II) complexes. Future work will focus on exploring structure–activity relationships, evaluating catalytic and biological performance experimentally, and extending this approach to related ligand systems to develop multifunctional zinc-based materials.

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ISSN 3030-3907