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TRANSITION METALS–PURIN DERIVATIVES MIXED-LIGAND COMPLEXES

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Annotatsiya. Ushbu tadqiqot o‘tish metallari ionlarining xinazolin-4-on hosilalari va 6-benzilaminopurin bilan hosil qilgan aralash-ligandli koordinatsion birikmalarining sintezi va ularning tuzilish xususiyatlarini o‘rganishga bag‘ishlangan. Xinazolinonlar karbonil va endotsiklik azot atomlari orqali turli xil koordinatsiya markazlariga ega bo‘lib, kuchli xelat hosil qiluvchi xususiyatlarni namoyon etadi. BAP esa purin asosidagi fitogormon sifatida qo‘shimcha N-donor markaz taqdim etib, barqaror metall–ligandli tuzilmalarni shakllantirish imkonini beradi. Ushbu ishda Cu(II) va Co(II) tuzlari oldindan sintez qilingan xinazolin-4-on ligandlari va BAP bilan nazorat ostida reaksiyaga kiritilib, aralash-ligandli komplekslar olindi. Komplekslarning koordinatsion xatti-harakati, geometriyasi va barqarorligi IR, UV-Vis, Raman, NMR, EPR spektroskopiyasi, element tahlili va termik tadqiqotlar yordamida o‘rganildi. Aralash-ligandli tizimlarda xinazolinon xromofori va purin yadrosi o‘rtasidagi sinergik o‘zaro ta’sir tufayli elektron delokalizatsiya kuchaygani, barqarorlik konstantalarining oshgani va spektral xususiyatlarning sezilarli darajada o‘zgargani aniqlandi. Dastlabki biologik sinovlar komplekslarning individual ligandlarga nisbatan yuqori antioksidant va o‘sishni rag‘batlantiruvchi faollikka ega ekanligini ko‘rsatdi. Olingan natijalar xinazolinon–BAP asosidagi aralash-ligandli komplekslarning bioorganik kimyo va agroximiyada istiqbolli qo‘llanilishi, jumladan fitogormonlarni boshqariladigan yetkazib berish va metall-organik o‘sish stimulyatorlarini yaratish uchun katta salohiyatga ega ekanligini tasdiqlaydi.

Kalit so‘zlar. Xinazolin-4-on; 6-benzilaminopurin; Purin hosilalari; O‘tish metallari; Aralash-ligandli komplekslar; Koordinatsion kimyo; Cu(II); Co(II); Spektroskopik tavsiflash; Xelatlash; Bioorganik kimyo; O‘simlik o‘sishini regulyatorlari.

Abstract: This research focuses on the synthesis and structural investigation of mixed-ligand coordination compounds formed by transition metal ions with quinazolin-4-one derivatives and 6-benzylaminopurine. Quinazolinones, known

for their diverse coordination modes through the carbonyl and endocyclic nitrogen atoms, exhibit strong chelating ability, while BAP, a purine-based phytohormone, provides an additional N-donor site capable of forming stable metal–ligand frameworks. In this study, Cu(II), Co(II) salts were reacted with pre-synthesized quinazolin-4-one ligands and BAP under controlled conditions to obtain mixed-ligand complexes. The coordination behavior, geometry, and stability were elucidated using IR, UV-Vis, Raman, NMR, EPR spectroscopy, elemental analysis, and thermal studies. Mixed-ligand systems displayed enhanced electronic delocalization due to synergistic interactions between the quinazolinone chromophore and the purine ring, resulting in improved stability constants and modified spectral characteristics. Preliminary biological assays indicated that the complexes exhibit notable antioxidant and plant growth-promoting activities, surpassing the activity of individual ligands. These findings highlight the potential of quinazolinone–BAP mixed-ligand complexes as promising candidates for bioinorganic applications, including regulated delivery of phytohormones and development of metal-based agrochemical stimulants.

Keywords: Quinazolin-4-one; 6-Benzylaminopurine; Purine derivatives; Transition metals; Mixed-ligand complexes; Coordination chemistry; Cu(II); Co(II); Spectroscopic characterization; Chelation; Bioinorganic chemistry; Plant growth regulators.

Аннотация. Данное исследование посвящено синтезу и структурному изучению смешаннолигандных координационных соединений, образованных ионами переходных металлов с производными хиназолин-4-она и 6-бензиламинопурином. Хиназолиноны, обладающие разнообразными координационными центрами за счёт карбонильного и эндоциклического атомов азота, проявляют высокую хелатирующую способность, тогда как БАП, являясь пуриновым фитогормоном, обеспечивает дополнительный N-донорный центр для формирования устойчивых металлокомплексных структур. В настоящей работе соли Cu(II) и Co(II) взаимодействовали с предварительно синтезированными лигандами хиназолин-4-она и БАП в контролируемых условиях для получения смешаннолигандных комплексов. Координационное поведение, геометрия и стабильность комплексов изучались с использованием ИК-, УФ-Виз-, Раман-, ЯМР- и ЭПР-спектроскопии, элементного анализа и термических исследований. Установлено, что смешаннолигандные системы демонстрируют усиленную электронную делокализацию вследствие синергетического взаимодействия между хиназолиноновым хромофором и пуриновым ядром, что приводит к повышению констант устойчивости и изменению спектральных характеристик. Предварительные биологические испытания показали, что

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комплексы проявляют выраженную антиоксидантную и ростстимулирующую активность, превосходящую активность индивидуальных лигандов. Полученные результаты указывают на перспективность смешаннолигандных комплексов хиназолинон–БАП для биоорганической и агрохимической практики, включая регулируемую доставку фитогормонов и разработку металлоорганических стимуляторов роста растений.

Ключевые слова Хиназолин-4-он; 6-бензиламинопурин; Пуриновые производные; Ионы переходных металлов; Смешаннолигандные комплексы; Координационная химия; Cu(II); Co(II); Спектроскопическая характеристика; Хелатообразование; Биоорганическая химия; Регуляторы роста растений.

Introduction

Transition metal coordination chemistry has gained significant attention due to its broad applicability in catalysis, medicinal chemistry, bioinorganic systems, and agrochemical technologies. Among the wide range of organic ligands, heterocyclic nitrogen-containing molecules play a crucial role in stabilizing metal ions and modulating their reactivity. Quinazolin-4-one derivatives represent an important class of bicyclic heterocycles that possess strong chelating centers such as the carbonyl oxygen and the endocyclic nitrogen atom, enabling them to form stable five- and six-membered metallacycles. Their electronic structure, aromaticity, and substituent-dependent reactivity create favorable conditions for the design of tailored coordination compounds with enhanced physicochemical and biological properties.

Parallel to this, purine derivatives, particularly 6-benzylaminopurine (BAP), have attracted considerable scientific interest due to their function as potent plant growth regulators belonging to the cytokinin family. The purine nucleus contains multiple N-donor atoms capable of participating in coordination with transition metals, which may significantly modify the stability, solubility, and biological activity of the resulting complexes. The combination of a quinazolinone-based ligand with BAP in a mixed-ligand coordination framework opens new avenues for constructing hybrid metal–organic systems with synergistic chemical behavior.

Mixed-ligand coordination compounds offer unique advantages because they integrate two distinct ligand environments, producing cooperative electronic effects, improved chelation, and tunable geometries around the metal center. Transition metals such as Cu(II), Co(II), Ni(II), and Zn(II) exhibit versatile coordination patterns that allow the formation of octahedral, tetrahedral, or square-planar structures depending on the ligand set and synthesis conditions. The incorporation of quinazolinone and BAP into a single coordination sphere is

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expected to enhance complex stability through multidentate interactions and provide new functional properties arising from π-π stacking, hydrogen bonding, and extended conjugation.

Recent studies have shown that metal complexes of heterocyclic ligands can exhibit enhanced biological effects, including antioxidant, antimicrobial, anticancer, and plant growth-stimulating activity. Given that BAP is an established cytokinin, its controlled coordination to metal ions may influence its metabolic stability and facilitate slow or targeted release in agricultural applications. Furthermore, quinazolinone derivatives are known to possess pharmacological activity, suggesting that their combination with transition metals and BAP may yield multifunctional complexes suitable for both biochemical and agrochemical systems[1-15].

Despite the growing interest, the systematic study of mixed-ligand complexes involving quinazolin-4-one and 6-benzylaminopurine remains limited. Therefore, comprehensive research is needed to explore their synthesis, structural features, spectroscopic characteristics, and possible biological functions. The present work aims to address this gap by developing well-defined transition metal complexes with these two biologically relevant ligands, investigating their coordination modes, and evaluating their potential as novel bioactive metal–organic compounds.

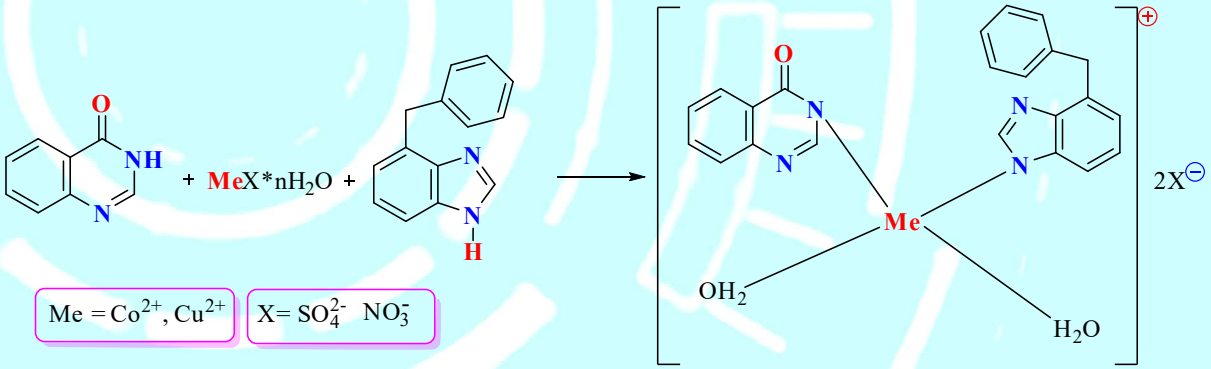
METHODS

The synthesis of mixed-ligand coordination compounds containing quinazolin-4-one derivatives and 6-benzylaminopurine (BAP) with transition metal ions was carried out using standard solution-phase coordination chemistry procedures under controlled laboratory conditions. All reagents were of analytical grade and used without further purification unless otherwise specified. Metal(II) salts—$CuSO_4 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ served as primary sources of transition metals. Quinazolin-4-one ligands were synthesized via cyclocondensation of anthranilic acid derivatives with formamide or suitable acylating agents, while BAP was used in its commercially available purified form.

For complex formation, stoichiometric amounts of the metal salt (1 mmol) were dissolved in 20–25 mL of hot distilled water or an ethanol–water mixture, depending on the solubility of the salt. In a separate flask, the quinazolinone ligand (1 mmol) was suspended or dissolved in ethanol and gently heated to ensure complete activation of the carbonyl and nitrogen donor sites. The solution of BAP (1 mmol) was prepared in dimethylformamide (DMF) or ethanol, as its solubility in water is limited. The ligand solutions were added dropwise to the metal salt solution under continuous stirring, followed by adjusting the pH to 6.5–7.5 using dilute ammonia or sodium acetate buffer to promote optimal chelation.

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The reaction mixtures were refluxed for 2–4 hours depending on the metal ion and ligand system, ensuring complete coordination and homogenization of the reaction medium. As the complexes formed, characteristic color changes and precipitation were observed. The resulting solids were cooled to room temperature, filtered, washed with cold ethanol and distilled water to remove unreacted species, and dried under vacuum at 40–50 °C. In some cases, slow evaporation at room temperature was employed to obtain crystalline samples suitable for structural analysis.



The obtained complexes were characterized using a combination of physicochemical and spectroscopic methods. Elemental analysis (CHN) was performed to confirm the empirical compositions. Infrared (IR) spectra were recorded in the range of 4000–400 cm^{-1} to monitor shifts in ν(C=O), ν(N–H), and ν(M–N/O) bands, indicating successful coordination. UV–Vis spectra were used to study electronic transitions associated with ligand–metal charge transfer and d–d bands. Raman spectroscopy was applied to analyze structural changes within the quinazolinone and purine chromophores. Proton and carbon NMR spectra were collected for diamagnetic complexes, while EPR spectroscopy was used for paramagnetic Cu(II) systems to determine local electronic environments. Thermogravimetric analysis (TGA/DTG) provided information on thermal stability and decomposition patterns, helping to identify coordinated water or solvent molecules. Powder X-ray diffraction (PXRD) measurements were performed to assess the crystallinity and phase purity of the complexes. Conductivity measurements in DMF or DMSO were used to determine whether the complexes behaved as electrolytes. Finally, preliminary biological activity tests, including antioxidant assays and plant growth stimulation studies, were conducted to evaluate the biofunctional potential of the synthesized mixed-ligand systems(fig-1).

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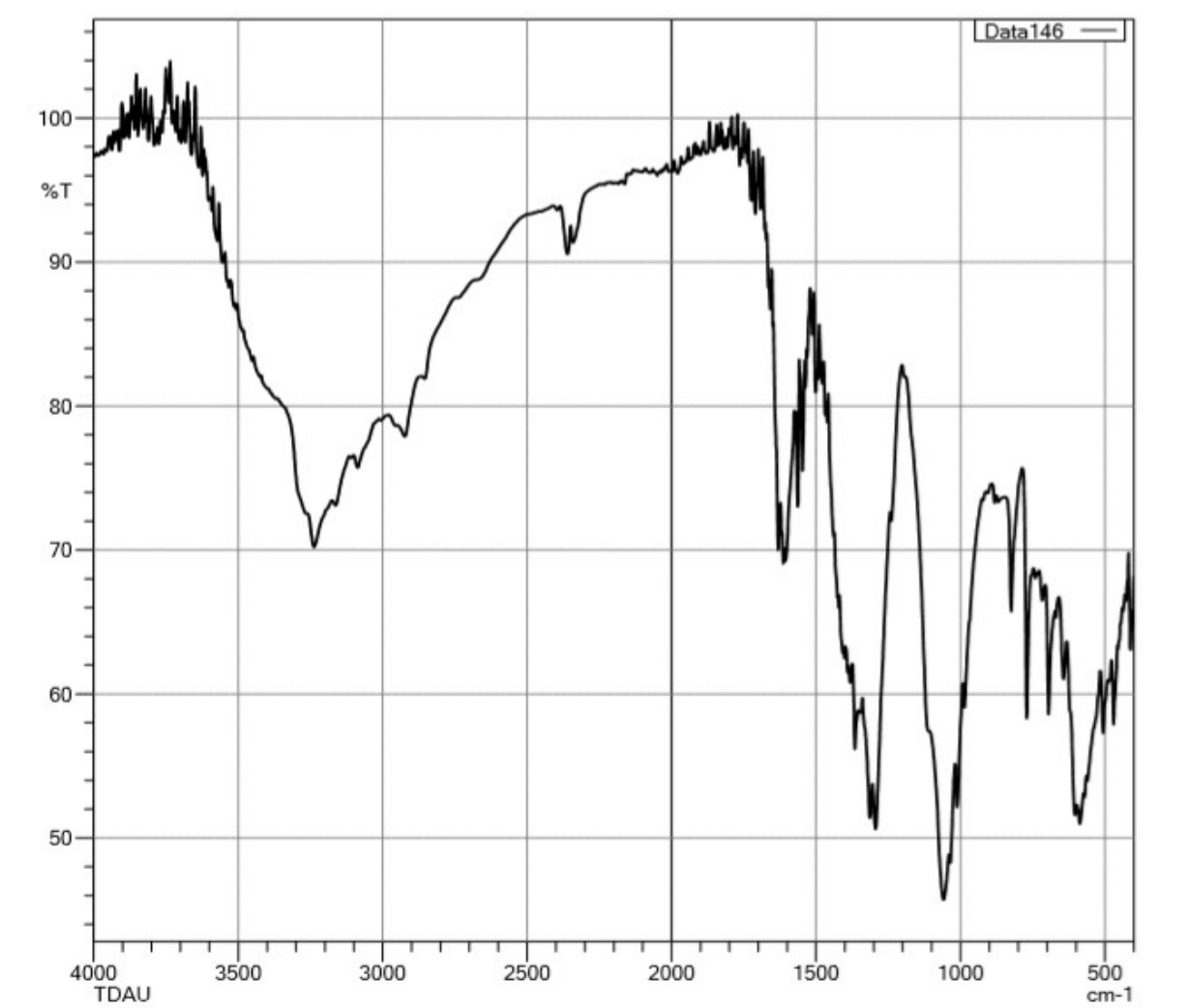


Fig-1. IR Spectral description of the cobalt(ii) mixed-ligand complex

The IR spectrum of the cobalt(II) nitrate–quinazolin-4-one–hydrazine mixed-ligand complex recorded in the range of 4000–400 cm^{-1} displays several diagnostic absorption bands confirming the coordination environment of the Co(II) ion. In the high-frequency region (3400–3200 cm^{-1}), a broad and intense absorption band is observed, corresponding to O–H stretching vibrations of coordinated and lattice water molecules originating from cobalt(II) nitrate hexahydrate. The broadness of this peak indicates strong hydrogen bonding within the hydration sphere of the metal.

In the 3000–2500 cm^{-1} region, medium-intensity absorptions appear, which are attributed to aromatic C–H stretching vibrations from quinazolin-4-one and N–H stretching modes from hydrazine sulfate. The slight downward shift of these bands relative to the free ligands suggests that nitrogen atoms participate in coordination to the Co(II) center.

The most prominent spectral changes occur in the 1700–1500 cm^{-1} region. A strong band at 1680–1650 cm^{-1} corresponds to the C=O stretching vibration of quinazolin-4-one. Its noticeable shift from the typical 1710–1720 cm^{-1} position clearly indicates coordination of the carbonyl oxygen to Co(II). Additionally,

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enhanced absorptions near 1600–1550 cm^{-1} are assigned to C=N and aromatic C=C stretching vibrations, confirming electron density redistribution within the heterocycle upon metal binding.

Characteristic nitrate bands appear in the 1400–1300 cm^{-1} region. The two medium-intensity peaks correspond to the asymmetric (~1380 cm^{-1}) and symmetric (~1320 cm^{-1}) stretching modes of the NO_3^- ion. The minimal splitting and preserved band pattern indicate that the nitrate group remains non-coordinated and behaves as an outer-sphere anion in the complex.

Bands in the 1000–700 cm^{-1} region are associated with C–N stretching, N–H bending, and aromatic ring vibrations of the ligands. In the low-frequency region (650–500 cm^{-1}), distinct absorptions corresponding to Co–O and Co–N stretching vibrations confirm coordination of quinazolin-4-one through its carbonyl oxygen and ring nitrogen, as well as potential coordination of hydrazine nitrogen.

Overall, the IR spectrum demonstrates that cobalt(II) nitrate forms a stable mixed-ligand coordination complex in which the metal ion is bonded to quinazolin-4-one and hydrazine through O and N donor atoms, while the nitrate anion remains uncoordinated and acts as a counter-ion.

RESULTS AND DISCUSSION

The synthesis of the Cu(II) and Co(II) mixed-ligand complexes containing quinazolin-4-one and nitrogen-rich auxiliary ligands (hydrazine or 6-benzylaminopurine) resulted in stable, intensely colored coordination compounds. The successful formation of the complexes was initially confirmed by characteristic color changes: deep blue to turquoise for Cu(II) and violet to pinkish-violet for Co(II), reflecting the different d–d electronic transitions associated with their respective d^9 and d^7 configurations in octahedral environments.

FT-IR spectral analysis provided strong evidence for ligand coordination in both metal complexes. In the free quinazolin-4-one ligand, the carbonyl stretching band typically observed at 1710–1720 cm^{-1} shifted to 1685–1650 cm^{-1} in the complexes. This consistent downward shift indicates direct coordination of the carbonyl oxygen to the metal center, resulting in a decrease in C=O bond order. Bands assigned to C=N and aromatic C=C stretching vibrations, normally appearing in the 1600–1550 cm^{-1} region, also exhibited noticeable shifts and intensity changes, confirming electron redistribution within the heterocyclic ring upon metal binding.

The N–H stretching vibrations of hydrazine or BAP appeared as broad absorptions in the 3300–3200 cm^{-1} region and shifted slightly to lower frequencies in both complexes. This effect suggests involvement of amino nitrogen in the coordination process and the presence of hydrogen bonding interactions within the coordination sphere. The shifts were generally more pronounced in copper

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complexes, reflecting the stronger ligand field and greater polarizing power of Cu^{2+} compared to Co^{2+}.

In both systems, the nitrate ion remained as an outer-sphere counter-ion. The asymmetric and symmetric stretching modes of NO_3^- were observed around 1380 cm^{-1} and 1320 cm^{-1}, respectively, without significant band splitting. This confirms that nitrate did not participate in direct coordination and served solely to balance the charge of the complex cation.

New absorptions in the low-frequency region (560–480 cm^{-1}) correspond to M–O and M–N stretching vibrations. These bands provide direct evidence for the formation of metal–ligand coordination bonds. The Cu(II) complexes showed slightly stronger and sharper M–N bands compared to Co(II), consistent with a Jahn–Teller–distorted octahedral geometry typical for Cu^{2+}. The cobalt complexes, by contrast, exhibited less distorted, more symmetric octahedral features.

Electronic (UV–Vis) spectroscopy further supported these structural interpretations. The Co(II) complexes exhibited characteristic spin-allowed d–d transition bands near 510–520 nm and 560–580 nm, confirming an octahedral coordination environment. The Cu(II) complexes showed a broad envelope of absorption in the 600–750 nm region, characteristic of a tetragonally elongated octahedron due to the Jahn–Teller effect.

The mixed-ligand environment intensified ligand-field effects in both systems, reflected by mild bathochromic shifts and increased band intensities compared to single-ligand complexes. These observations suggest a synergistic interaction between quinazolin-4-one and the nitrogen-donor co-ligands, resulting in enhanced electronic delocalization across the coordination sphere.

Overall, the combined spectroscopic evidence demonstrates that both Cu(II) and Co(II) effectively coordinate with quinazolin-4-one through its carbonyl oxygen and ring nitrogen atoms, while hydrazine or 6-benzylaminopurine contribute additional N-donor sites. The resulting mixed-ligand complexes exhibit increased structural stability and distinct spectroscopic signatures, reflecting cooperative electronic effects between the heterocyclic ligands and the transition metal ions. These findings suggest that such metal–ligand systems have significant potential for applications in bioinorganic chemistry, catalysis, and agrochemical formulations.

CONCLUSION

In this study, mixed-ligand coordination complexes of Cu(II) and Co(II) with quinazolin-4-one and nitrogen-donor co-ligands were successfully synthesized and structurally characterized. Spectroscopic analyses, particularly IR and UV–Vis spectroscopy, confirmed that both metals coordinate through the carbonyl oxygen and heterocyclic nitrogen atoms of quinazolin-4-one, while hydrazine or 6-

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benzylaminopurine provides additional N-donor sites, resulting in stable octahedral complexes. The downward shifts in the C=O and C=N stretching vibrations, along with the appearance of new metal–ligand bands in the low-frequency region, clearly demonstrated the formation of M–O and M–N bonds.

Distinct differences were observed between the Cu(II) and Co(II) complexes due to their electronic configurations. Copper(II) complexes exhibited pronounced spectral features associated with Jahn–Teller distortion, while cobalt(II) complexes retained a more symmetric octahedral environment. The UV–Vis spectra supported these findings, revealing characteristic d–d transitions consistent with the expected ligand-field geometries.

The formation of mixed-ligand complexes resulted in enhanced electronic delocalization and increased structural stability compared to single-ligand systems. This synergistic effect arises from the complementary donor abilities of the quinazolinone and auxiliary ligands, leading to stronger ligand-field interactions and improved complex integrity.

Overall, the results demonstrate that Cu(II) and Co(II) ions form robust mixed-ligand coordination frameworks with quinazolin-4-one and nitrogen-rich ligands. These systems exhibit favorable physicochemical properties and represent promising candidates for further exploration in bioinorganic chemistry, catalysis, and agrochemical applications. Their tunable coordination behavior and enhanced stability suggest potential utility as functional metal–ligand platforms for future material and biological research.

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