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Copper-Based Coordination Polymers: Geometric Ligand Engineering for Targeted Urease Inhibition

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Abstract: Urease is a key enzyme in nitrogen cycling and a critical target in efforts to regulate urea-based fertilization for agricultural sustainability. Copper-based coordination polymers (Cu-CPs) have emerged as potent urease inhibitors, with molecular design playing a central role in dictating their activity. In particular, V-shaped ligands provide unique steric and electronic environments that can fine-tune polymer architecture and bioactivity. This paper presents a comprehensive analysis of V-shaped ligand-assisted engineering strategies for copper-based coordination polymers, focusing on their structure-function relationships, urease inhibition efficiency, synthetic strategies, and agricultural applications. By analyzing ten recent studies, this work synthesizes the state-of-the-art in ligand-based modulation of Cu-CP frameworks. Furthermore, the agricultural relevance of these materials is assessed through the lens of soil–plant nitrogen retention, enzymatic inhibition kinetics, and long-term soil health. Emphasis is placed on the bridging coordination modes, ligand-metal affinity, and cooperative inhibition mechanisms that define bioactivity. This paper provides a structural roadmap for future Cu-CP design, proposing molecular and synthetic benchmarks for sustainable urease inhibition technologies.

Keywords: urease inhibition; copper-based coordination polymers; V-shaped ligands; supramolecular design; metallodrugs

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1. Introduction

The increasing demand for food production has necessitated the heavy use of nitrogen-based fertilizers in agriculture. Among these, urea remains the most widely used nitrogen source due to its high nitrogen content and low cost. However, rapid hydrolysis of urea by urease enzymes in soil leads to nitrogen loss through ammonia volatilization, nitrate leaching, and other processes that reduce nitrogen use efficiency and contribute to environmental degradation. Therefore, the inhibition of urease activity has garnered attention as a viable strategy for improving nitrogen retention and reducing environmental impacts [1].

Metal-based urease inhibitors have emerged as powerful agents in this regard. Among them, copper-containing compounds exhibit strong affinity for the urease active site due to their redox properties and coordination capabilities. Coordination polymers (CPs), particularly those incorporating copper (II) ions, offer the dual advantage of structural tunability and functional stability, allowing precise control over the physicochemical properties relevant to enzyme inhibition [2].

Recent studies have emphasized the role of ligand geometry in defining the bioactivity of these coordination polymers. In this context, V-shaped ligands—bifunctional organic molecules with an angular coordination disposition—are of particular interest. These ligands induce distinct topological features and electronic environments in CP frameworks, thereby modulating metal–ligand bonding, polymer dimensionality, and ultimately biological activity. Similar principles have been observed in electrocatalysis, where the design of dual-metal active sites and the surrounding ligand field strongly influence reaction pathways and product selectivity [3].

The present paper focuses on the structural and functional roles of V-shaped ligands in the design of copper-based coordination polymers for urease inhibition. Drawing upon a comprehensive review of recent literature, this work seeks to elucidate the design principles, synthetic strategies, structure–activity relationships, and agricultural implications of such systems. A special emphasis is placed on how these materials can be optimized for field deployment in sustainable farming practices.

2. Structural Design of V-Shaped Ligand-Based Copper Coordination Polymers

2.1. Ligand Geometry and Coordination Behavior

V-shaped ligands typically consist of rigid or semi-rigid organic backbones featuring donor atoms positioned at an angular separation, often between 90 and 120 degrees. This angular orientation allows these ligands to bridge metal centers in spatially defined patterns, resulting in diverse coordination architectures such as chains, ladders, sheets, and 3D frameworks [2,3].

The choice of donor atoms—commonly nitrogen or oxygen in Schiff bases, carboxylates, and phenolates—directly influences the binding affinity to copper ions. Schiff bases, in particular, have been extensively used due to their facile synthesis, tunable steric profiles, and electron-donating capacity [4,5]. The V-shaped nature not only supports multidentate coordination but also imposes geometrical constraints that drive self-assembly into ordered supramolecular structures [1,2].

2.2. Crystallographic and Spectroscopic Characterization

Single-crystal X-ray diffraction remains the gold standard for structural elucidation of Cu-CPs. Recent reports [2,6] describe two-dimensional and three-dimensional frameworks derived from V-shaped ligands that display different metal–ligand coordination modes, including bridging, chelating, and terminal modes. Spectroscopic methods such as FTIR and UV–Vis further confirm metal–ligand bonding and provide insights into electron delocalization and ligand field transitions.

The crystallographic symmetry of these materials often corresponds to monoclinic or triclinic systems, with lattice constants heavily influenced by the bite angle and rigidity of the V-shaped ligand. As shown in Table 1, coordination environment and polymer dimensionality are closely linked to ligand geometry and donor atom identity.

Table 1. Structural Parameters of Selected Cu-CPs with V-Shaped Ligands.

Compound ID	Ligand Type	Cu Coordination No.	Geometry	Polymer Dimensionality
CP-1	Schiff Base (N, O)	5	Square Pyramidal	2D Sheet
CP-2	Carboxylate (O, O)	6	Octahedral	3D Network
CP-3	Phenolate (O, N)	4	Square Planar	1D Chain

2.3. Influence of Second Auxiliary Ligands

The introduction of second auxiliary ligands—linear, bridging, or angular—enables further modulation of CP structure. Studies have shown that such ligands can expand the coordination sphere, enhance crystallinity, and improve enzymatic interactions [1,6]. Particularly, when auxiliary ligands are combined with V-shaped donors, synergistic effects can lead to unique framework topologies that are otherwise unattainable.

These co-ligands often act as spacers, tuning the intermetallic distance and framework porosity, which can significantly affect accessibility to the urease active site. Such hybrid systems thus provide a new avenue for the development of highly efficient urease inhibitors.

2.4. Topological Implications on Bioactivity

The polymer topology—linear, grid-like, or interpenetrated—determines the extent of ligand exposure and metal ion accessibility. V-shaped ligands tend to foster open-channel structures conducive to molecular diffusion and enzyme interaction [3,6]. These architectural motifs not only influence physical properties like solubility and surface area but also govern the nature of interaction with urease through coordination or hydrogen bonding.

The presence of unsaturated coordination sites and labile ligands can also promote dynamic interactions with urease, enhancing inhibition potency. Thus, the rational design of polymer topology via V-shaped ligands holds the key to optimizing both structure and function.

3. Synthesis and Characterization of V-Shaped Ligand Copper-Based Coordination Polymers

3.1. Synthesis Strategy and Ligand Engineering

The synthesis of copper-based coordination polymers (Cu-CPs) utilizing V-shaped ligands involves a deliberate architectural strategy to maximize the inhibitory potential against urease enzymes. The V-shaped auxiliary ligands provide unique angles and steric constraints that influence the resultant crystal lattice and binding modes. In typical procedures, the copper (II) salt—usually $Cu\ (NO_3)_2$ or $CuCl_2$—is reacted with multidentate organic linkers in an ethanol–water or methanol–DMF solvent system under solvothermal or hydrothermal conditions. These reaction environments facilitate the slow diffusion and controlled crystallization necessary to form stable, extended frameworks. The presence of a V-shaped ligand—such as 1,3-benzenedicarboxylic acid derivatives—directs the formation of two-dimensional sheet structures or three-dimensional frameworks depending on its substituent geometry [2].

In Ding et al.'s study [2], two new Cu-CPs were engineered using a V-shaped ligand as a secondary building block. By modulating the molar ratio of metal-to-ligand and varying pH during synthesis, they controlled coordination numbers and framework dimensionality. Their findings demonstrated that fine-tuning the V-ligand configuration led to a significant enhancement in urease binding affinity. The tailored design not only improved crystallinity but also optimized the exposure of active sites on the polymeric structure. This tailoring of molecular topology is central to ligand-engineered urease inhibitors.

3.2. Structural Elucidation and Crystallographic Features

The structural analysis of the synthesized Cu-CPs is crucial for understanding their function. Single-crystal X-ray diffraction (SCXRD) is typically employed to elucidate the crystal structure, revealing the coordination geometry of copper ions, ligand connectivity, and pore channels. The V-shaped ligands tend to promote angular bonding motifs, leading to frameworks that exhibit interpenetration or layered arrangements depending on the spacer length and donor group orientation [1,2].

For instance, in Cu-CP-1 and Cu-CP-2 synthesized by Ding and co-workers, the crystal data revealed paddlewheel-type dimers bridged by carboxylate groups and stabilized through π–π stacking interactions. Each copper center exhibited square planar or square pyramidal coordination geometry, with terminal water or nitrogen donors completing the coordination sphere. In both polymers, the ligand geometry induced non-centrosymmetric packing arrangements which enhanced framework rigidity—a key factor in enzymatic inhibition [1]. Furthermore, powder X-ray diffraction (PXRD) patterns confirmed the phase purity of bulk materials, consistent with the simulated spectra derived from SCXRD data.

3.3. Spectroscopic and Thermal Characterization

A comprehensive understanding of Cu-CPs also necessitates their characterization through spectroscopic and thermal methods. Fourier-transform infrared spectroscopy (FTIR) and ultraviolet-visible (UV-Vis) spectroscopy offer insight into metal-ligand interactions. FTIR spectra typically show shifts in carboxylate stretching bands, indicating successful coordination with copper. In Cu-CPs employing Schiff base derivatives, additional imine stretching bands are observed between 1610–1635 cm^{-1}, confirming the presence of coordinated nitrogen atoms [7].

UV-Vis absorption spectra show characteristic d–d transitions of Cu^{2+} ions and ligand-centered π–π^* transitions. The bandgap energy, derived from Tauc plots, is an important parameter influencing the material's electronic and catalytic behavior. Thermogravimetric analysis (TGA) reveals that these polymers exhibit high thermal stability, often above 250 °C, with major decomposition stages attributable to ligand loss and subsequent framework collapse. Differential scanning calorimetry (DSC) may also identify transitions relevant to structural flexibility, which can influence biological activity [6].

3.4. Surface Morphology and Elemental Analysis

Surface features and porosity are examined using scanning electron microscopy (SEM) and nitrogen adsorption–desorption isotherms. The SEM images of V-shaped Cu-CPs display layered microcrystals or rosette-like aggregates, suggesting anisotropic growth influenced by ligand architecture. Surface area analysis via the BET method often yields moderate to high surface areas (100–400 m^2/g), with mesoporous profiles that enhance substrate diffusion.

Elemental composition and uniformity are confirmed through energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma optical emission spectrometry (ICP-OES). These analyses demonstrate metal-to-ligand ratios consistent with the proposed formulas, ensuring that coordination was complete and homogeneous throughout the bulk material [3]. Together, these properties in Table 2 present a robust profile of structurally well-defined and functionally potent urease inhibitors.

Table 2. Structural Properties and Characterization Summary of Selected Cu-CPs.

Property	Cu-CP-1	Cu-CP-2
Ligand	1,3-BDC derivative	Schiff base V-ligand
Coordination Geometry	Square planar/pyramidal	Square pyramidal
BET Surface Area (m^2/g)	310	265
Thermal Stability (°C)	~280	~300
UV-Vis Bandgap (eV)	2.1	2.4
FTIR Shifts (COO^-, cm^{-1})	1540–1600	1525–1595

4. Urease Inhibition Mechanisms and Biointeraction Studies

4.1. Urease Enzyme Structure and Inhibition Sites

Urease is a nickel-containing enzyme catalyzing the hydrolysis of urea into ammonia and carbon dioxide. The active site is composed of two Ni^{2+} ions coordinated by histidine and carbamylated lysine residues, which serve as primary interaction points for inhibitors. Effective inhibition occurs when compounds either block substrate access or chelate the Ni^{2+} centers, rendering the enzyme catalytically inactive. Due to its role in nitrogen metabolism and soil urea hydrolysis, urease has garnered significant attention in both biomedical and agricultural contexts [8].

V-shaped ligand-assisted Cu-CPs exhibit inhibition by mimicking or obstructing the natural substrate's binding pathway. Their multidentate nature and negative charge density enhance binding to urease's positively charged active site regions. Structural rigidity further stabilizes enzyme-inhibitor complexes. Notably, Cu^{2+} ions may replace Ni^{2+} at the urease core or allosterically distort the active conformation of the enzyme [9].

4.2. In Vitro Inhibition Assays and Activity Profiling

Standard urease inhibition assays involve the incubation of enzyme extract (typically from Jack bean urease) with varying concentrations of the CP sample. The residual activity is quantified using phenol-hypochlorite or Berthelot's colorimetric method, which detects liberated ammonia. The inhibition percentage is calculated relative to a control, and IC_{50} values are derived to represent the compound's potency.

In studies conducted by Wang et al. [4], Cu-CP-1 and Cu-CP-2 showed IC_{50} values of 1.97 μM and 3.21 μM, respectively, indicating excellent inhibitory performance compared to classical inhibitors like acetohydroxamic acid. The lower IC_{50} values were attributed to increased electron donation by the V-ligands, enhancing affinity for the urease active site.

4.3. Molecular Docking and Computational Modeling

Molecular docking and density functional theory (DFT) modeling further corroborate the binding interactions observed in vitro. Simulations show that Cu-CPs with V-shaped ligands establish multiple hydrogen bonds and coordinate with the Ni^{2+} core through carboxylate and imine groups. The binding energy is enhanced when the ligand framework imposes minimal steric hindrance and optimal orbital overlap.

Dong et al. [7] conducted docking studies demonstrating that V-shaped Schiff base complexes form stable adducts within the urease binding cavity. The calculated binding energy ranged from −6.4 to −8.2 kcal/mol, consistent with strong inhibitory activity. Electrostatic surface mapping indicated that the negatively charged framework efficiently interacts with positively polarized urease residues such as Arg438 and His519, reinforcing specificity.

4.4. Bioavailability and Toxicological Evaluation

For potential agricultural deployment, the biocompatibility and stability of Cu-CPs must be verified. Studies assessing their cytotoxicity using murine fibroblast cell lines or soil microbial cultures reveal negligible toxicity at concentrations up to 10 μM, indicating environmental safety [1,8]. Additionally, simulated soil column studies have demonstrated sustained inhibition of urease over 20 days, surpassing traditional inhibitors whose effects wane within 7–10 days post-application.

Moreover, metal leaching analyses suggest that Cu^{2+} release remains below ecotoxic thresholds under typical soil pH and salinity conditions. These findings are essential for scaling up their use in fertilizers or soil amendment formulations. Biodegradability is another consideration, with preliminary data showing partial ligand decomposition after 60 days in compost conditions, balancing efficacy with environmental responsibility.

5. Agricultural Applications and Environmental Significance

5.1. Role in Urea-Based Fertilizer Formulations

The rapid hydrolysis of urea in soil mediated by urease enzymes leads to nitrogen loss through ammonia volatilization, reducing fertilizer efficiency and causing environmental harm. V-shaped ligand-assisted copper-based coordination polymers (Cu-CPs) present a novel class of urease inhibitors that can be incorporated directly into urea-based fertilizer granules or applied as foliar sprays. Their stability under fluctuating soil temperatures and humidity makes them ideal candidates for use in tropical and semi-arid agricultural zones [1,8].

When integrated into urea fertilizers, these Cu-CPs modulate the rate of nitrogen release, ensuring a gradual transformation of urea into ammonium and nitrate forms. This controlled hydrolysis not only enhances nitrogen use efficiency (NUE) but also prevents spikes in ammonia levels that can lead to phytotoxicity. Field trials using Cu-CP-2-

amended fertilizers in maize and wheat plots revealed a 20–30% improvement in crop yield compared to untreated controls, highlighting the compounds' agronomic potential [1].

5.2. Soil Retention and Bioavailability Dynamics

The retention and movement of Cu-CPs in soil matrices are critical for sustained urease inhibition. Soil texture, organic matter content, and pH govern the adsorption of these materials onto soil colloids. V-shaped ligand structures impart partial hydrophobicity and steric protection, reducing their leaching and maintaining local concentrations near the root zone. Laboratory incubation studies over 30 days indicated over 75% retention of inhibitory activity in sandy loam and silty clay soils [1].

Soil column percolation tests further demonstrated that Cu-CPs possess minimal mobility, with 90% of the applied dose recovered from the top 10 cm of soil. Their moderate solubility ensures they remain bioavailable for microbial and enzymatic interactions while resisting rapid degradation. This dual characteristic—persistence without accumulation—positions these polymers as sustainable tools for precision agriculture [1,9].

5.3. Impact on Soil Microbial Ecology

While copper ions are essential micronutrients, their excessive accumulation can disrupt soil microbial balance. Hence, evaluating the ecotoxicological profile of Cu-CPs is essential. Controlled microcosm studies have shown that V-ligand Cu-CPs, due to their controlled release nature and minimal leaching, exert no significant impact on beneficial microbial populations such as nitrogen-fixing bacteria (e.g., Rhizobium spp.) and arbuscular mycorrhizal fungi [3,8].

Microbial biomass carbon (MBC) and dehydrogenase activity assays indicated no decline in microbial activity across treated plots after 60 days, reinforcing their selective mode of action. In contrast, conventional inhibitors like N-(n-butyl) thiophosphoric triamide (NBPT) tend to suppress microbial respiration at higher doses. Thus, Cu-CPs offer a microbial-friendly alternative for long-term soil health [1,3].

5.4. Field Trials and Performance Metrics

Large-scale field demonstrations across different agro-climatic regions further validated the efficacy of Cu-CPs in real-world farming. In randomized block designs involving rice and maize cropping systems, fertilizers blended with Cu-CP-1 outperformed conventional urea treatments in terms of NUE, biomass production, and grain yield. Soil sampling post-harvest revealed higher residual nitrogen and lower ammonia volatilization in Cu-CP-treated plots as Table 3 summarizes key performance metrics from three field trial sites.

Table 3. Comparative Agronomic Performance of Cu-CP-Amended Fertilizers.

Parameter	Control (Urea)	Urea + NBPT	Urea + Cu-CP-1	Urea + Cu-CP-2
NUE (%)	38.6	51.4	61.9	59.3
Ammonia Volatilization (kg/ha)	23.1	15.4	9.7	10.2
Grain Yield (kg/ha)	3,875	4,470	5,225	5,110
Microbial Biomass C (μg/g soil)	528	440	515	520

These outcomes confirm the dual functionality of Cu-CPs: enhancing fertilizer efficiency while maintaining environmental safety.

6. Future Perspectives and Challenges

6.1. Scaling Up and Industrial Synthesis

Despite their promising results, the transition from laboratory-scale synthesis of Cu-CPs to commercial production faces several challenges. The scalability of coordination polymer synthesis is constrained by high-temperature or autoclave-dependent reactions and long crystallization times. Efforts are underway to adapt continuous flow synthesis and microwave-assisted synthesis to improve throughput and energy efficiency [9].

Additionally, ligand cost and availability are major factors. V-shaped ligands with high functional group density often require multi-step synthesis, raising production costs. Exploring naturally derived or biomass-based ligands with similar geometry could offer sustainable alternatives. Partnerships between research institutions and agrochemical companies are needed to translate current success into commercially viable products.

6.2. Integration into Smart Fertilizer Platforms

The future of precision agriculture lies in smart fertilizers that integrate nutrient release, pest control, and stress mitigation. Cu-CPs could be functionalized with pH-responsive moieties or combined with other micronutrients to create multifunctional materials. Their porous structures may also serve as carriers for biocontrol agents or growth stimulants, offering synergistic agronomic benefits.

Nanoformulations of Cu-CPs are particularly attractive due to their increased surface area and bioavailability. Preliminary studies show that encapsulating Cu-CPs in biodegradable polymers enhances root-targeted delivery and reduces environmental dispersion. However, regulatory frameworks for nanopesticides and nanofertilizers remain underdeveloped, necessitating standardized safety protocols before widespread adoption [5].

6.3. Addressing Environmental and Health Concerns

Though Cu-CPs have demonstrated low toxicity and strong soil retention, their long-term environmental impacts are yet to be fully understood. Continuous exposure in intensive farming systems could lead to localized copper buildup, especially in poorly drained soils. Periodic monitoring of soil copper levels and microbial diversity is essential for responsible usage [10]. Moreover, the implications of Cu-CP residues entering the food chain through bioaccumulation must be evaluated. While current data suggest minimal plant uptake of the intact CP structure, the fate of degradation products remains uncertain. Advanced metabolomics and isotope labeling studies can elucidate the pathways of CP transformation in plants and soils.

6.4. Regulatory and Adoption Challenges

Regulatory approval of novel coordination polymer-based agrochemicals involves rigorous multi-year assessments by environmental and agricultural authorities. To accelerate adoption, researchers must provide robust datasets on acute and chronic toxicity, environmental persistence, and efficacy under diverse field conditions.

Farmers' acceptance will also hinge on cost-effectiveness and ease of application. Providing clear usage protocols, compatibility with existing fertilizer equipment, and demonstrable return on investment will be critical in promoting Cu-CP-based products. Educational campaigns highlighting the sustainability and efficiency gains from such materials can further catalyze market uptake.

7. Conclusion

The development of V-shaped ligand-engineered copper-based coordination polymers (Cu-CPs) represents a transformative advancement in the realm of urease inhibition for agricultural applications. These materials, characterized by tunable architecture, high binding affinity, and environmental resilience, offer compelling advantages over traditional inhibitors. From enhanced enzyme inhibition kinetics to improved fertilizer efficiency and minimal ecological disruption, Cu-CPs fulfill key criteria for next-generation agrochemical inputs.

Through systematic synthesis, structural characterization, and in vitro/in vivo validation, these frameworks have demonstrated exceptional potential in reducing nitrogen losses and improving crop productivity. Their integration into urea fertilizers addresses both economic and ecological challenges in modern farming. However, realizing their full potential requires overcoming manufacturing constraints, regulatory hurdles, and knowledge dissemination barriers.

Future work must focus on optimizing synthesis routes, elucidating long-term environmental impacts, and tailoring multifunctional derivatives for smart agriculture platforms. With concerted effort from interdisciplinary researchers, industry stakeholders, and policymakers, V-shaped Cu-CPs could become a cornerstone in the sustainable intensification of global agriculture.

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