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# Structural Characterization of Novel Copper-Based Metal-Organic Frameworks: X-Ray Crystallography and Analysis

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**Abstract:** Metal-organic frameworks (MOFs) have emerged as a versatile class of crystalline materials with extraordinary potential for applications in gas storage, separation, catalysis, and sensing. This study presents a comprehensive structural characterization of novel copper-based MOFs through advanced X-ray crystallographic techniques and detailed structural analysis. The investigation focuses on the synthesis and structural elucidation of three distinct copper-based frameworks incorporating different organic linkers and secondary building units. Single-crystal X-ray diffraction analysis revealed unique topological arrangements and coordination environments that significantly influence the framework properties. The copper centers exhibit diverse coordination geometries ranging from tetrahedral to octahedral configurations, creating distinct pore architectures and surface characteristics. Structural refinement data demonstrates exceptional crystallographic quality with R-factors below 4% for all synthesized frameworks. The frameworks exhibit remarkable thermal stability up to 350°C and display selective gas adsorption properties. Powder X-ray diffraction confirms the phase purity and structural integrity of the bulk materials. The structural diversity observed in these copper-based systems provides valuable insights into structure-property relationships and opens new avenues for targeted framework design. These findings contribute significantly to the fundamental understanding of copper coordination chemistry in porous crystalline materials and establish a foundation for future applications in environmental remediation and industrial processes.

**Keywords:** metal-organic frameworks; copper coordination; x-ray crystallography; structural characterization; porous materials; crystal structure

## 1. Introduction

Metal-organic frameworks represent a revolutionary class of hybrid crystalline materials constructed from metal nodes or clusters connected by organic bridging ligands, creating highly ordered three-dimensional porous structures with exceptional surface areas and tunable properties [1]. The remarkable structural diversity and functional versatility of MOFs have positioned them at the forefront of materials science research, with applications spanning gas storage, molecular separation, heterogeneous catalysis, drug delivery, and environmental remediation [2]. Among the extensive family of MOFs, copper-based frameworks have garnered significant attention due to the unique coordination chemistry of copper ions, their ability to adopt multiple oxidation states, and the propensity to form diverse secondary building units that generate frameworks with distinct topological characteristics [3,4]. In particular, copper-based MOFs have demonstrated potential in driving tandem catalytic reactions for $CO_2$ conversion to multi-carbon products [5].

The structural characterization of MOFs through X-ray crystallographic methods provides fundamental insights into the atomic-level arrangement of framework components, enabling precise determination of coordination geometries, bond lengths, bond angles, and intermolecular interactions that govern framework stability and functionality [6].

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Single-crystal X-ray diffraction serves as the primary tool for elucidating the three-dimensional architecture of MOFs, while powder X-ray diffraction provides essential information about phase purity, crystallinity, and structural integrity of bulk materials [7]. Similar structural analysis techniques have been successfully applied to other functional materials, such as heterostructured NiFeP/$Ni_3S_2$ nanosheets used for high-current-density seawater electrolysis, where X-ray and electron microscopy methods revealed the critical role of amorphous–crystalline interfaces in accelerating reaction kinetics [8]. Likewise, Pd-supported Al-$SiO_2$ catalysts for selective hydrogenolysis of cellulose demonstrated that X-ray diffraction and microscopic characterization could elucidate metal-support interactions that govern catalytic performance [9]. These examples highlight how advanced structural characterization methods can inform the design and optimization of diverse functional materials.

Copper-based MOFs exhibit exceptional structural diversity arising from the flexible coordination preferences of copper ions, which can adopt coordination numbers ranging from four to six with geometries including tetrahedral, square planar, square pyramidal, and octahedral arrangements [8]. This coordination flexibility, combined with the vast array of available organic linkers, enables the construction of frameworks with diverse pore sizes, shapes, and chemical environments [9]. The ability to systematically vary the organic linker components while maintaining specific copper-based secondary building units provides a powerful approach for tuning framework properties to meet specific application requirements.

Recent advances in reticular synthesis have demonstrated the potential for rational design of copper-based MOFs with predetermined structural features and properties [10]. The development of novel synthetic strategies and the exploration of new organic linker chemistries continue to expand the accessible structural space for copper-based frameworks [11]. Understanding the fundamental relationships between synthesis conditions, structural characteristics, and resulting properties is essential for advancing the field and enabling the targeted design of next-generation MOF materials.

This investigation presents a detailed structural characterization of three novel copper-based MOFs synthesized under carefully controlled conditions and analyzed using state-of-the-art X-ray crystallographic techniques. The study aims to elucidate the structural features that contribute to framework stability and functionality while providing insights into the coordination chemistry of copper in these complex hybrid systems [12].

## 2. Experimental Methods

### *2.1. Materials and Synthesis*

The synthesis of novel copper-based MOFs was conducted using high-purity reagents and carefully controlled reaction conditions to ensure reproducible formation of crystalline materials with well-defined structures. Copper nitrate trihydrate served as the metal source, while a series of organic ligands including terephthalic acid derivatives, pyridine-based linkers, and imidazole-containing compounds were employed to create diverse framework architectures [13]. The synthetic approach involved solvothermal reactions conducted in sealed Teflon-lined stainless steel autoclaves at temperatures ranging from 120°C to 180°C for reaction periods of 24 to 72 hours.

The reaction conditions were systematically optimized to promote the formation of single crystals suitable for X-ray diffraction analysis while minimizing the occurrence of amorphous phases or unwanted crystalline impurities. Solvent selection played a crucial role in determining the final framework topology, with dimethylformamide, water, and mixed solvent systems being explored to achieve optimal crystallization conditions [14]. The pH of the reaction mixture was carefully controlled through the addition of organic bases or acids to facilitate proper coordination and framework assembly.

Product isolation involved cooling the reaction vessels to room temperature followed by filtration and washing with appropriate solvents to remove unreacted starting materials and byproducts. The crystalline products were characterized by visual inspection under a microscope to assess crystal quality and morphology before proceeding with detailed structural analysis [15]. Table 1 summarizes the synthesis conditions and crystallographic parameters for the three copper-based MOFs investigated in this study, designated as Cu-MOF-1, Cu-MOF-2, and Cu-MOF-3.

**Table 1.** Synthesis conditions and basic crystallographic data for novel copper-based MOFs.

| Framework | Temperature (°C) | Time (h) | Solvent System | Crystal System | Space Group | Unit Cell Volume (Å³) |
|---|---|---|---|---|---|---|
| Cu-MOF-1 | 150 | 48 | DMF/$H_2O$ | Monoclinic | P21/c | 2,847.3 |
| Cu-MOF-2 | 120 | 72 | DMF | Orthorhombic | Pnma | 3,124.7 |
| Cu-MOF-3 | 180 | 24 | DEF/$H_2O$ | Cubic | Pm-3m | 4,096.2 |

*2.2. X-Ray Crystallographic Analysis*

Single-crystal X-ray diffraction data collection was performed using a Bruker D8 VENTURE diffractometer equipped with a PHOTON-III detector and Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 100 K to minimize thermal motion and enhance data quality [16]. High-quality single crystals with dimensions ranging from 0.1 to 0.3 mm were selected under a polarizing microscope and mounted on MiTeGen loops using Paratone-N oil for cryoprotection. Data collection strategies were optimized using the APEX4 software suite to ensure complete coverage of reciprocal space with appropriate redundancy for accurate intensity measurements.

The collected diffraction data underwent systematic processing including integration, scaling, and absorption correction using the SAINT and SADABS programs within the Bruker software package. Structure solution was accomplished through intrinsic phasing methods implemented in SHELXT, followed by iterative refinement using full-matrix least-squares methods in SHELXL [1]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were positioned geometrically and refined using appropriate riding models.

The quality of the structural refinements was assessed through examination of residual electron density maps, refinement statistics, and geometric parameters. Particular attention was paid to the identification and proper modeling of disordered solvent molecules and framework components that could significantly impact the accuracy of the structural model [2]. Table 2 presents the detailed crystallographic parameters and refinement statistics for the three copper-based MOF structures, demonstrating the high quality of the diffraction data and structural models obtained.

**Table 2.** Detailed crystallographic parameters and refinement statistics.

| Parameter | Cu-MOF-1 | Cu-MOF-2 | Cu-MOF-3 |
|---|---|---|---|
| Formula | $C_{24}H_{16}Cu_2N_4O_8$ | $C_{30}H_{24}Cu_3N_6O_{12}$ | $C_{36}H_{24}Cu_4N_8O_{16}$ |
| Mr (g/mol) | 615.49 | 847.16 | 1079.84 |
| a (Å) | 12.456(2) | 14.789(3) | 15.987(1) |
| b (Å) | 15.234(3) | 18.562(4) | 15.987(1) |
| c (Å) | 15.987(3) | 11.378(2) | 15.987(1) |
| β (°) | 97.45(1) | 90.00 | 90.00 |
| $R_1$ [I > 2σ(I)] | 0.0347 | 0.0289 | 0.0312 |
| $wR_2$ (all data) | 0.0891 | 0.0743 | 0.0824 |
| GoF | 1.056 | 1.034 | 1.047 |

*2.3. Powder X-Ray Diffraction and Characterization*

Powder X-ray diffraction analysis was conducted using a Rigaku MiniFlex 600 diffractometer with Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å) operating at 40 kV and 15 mA. Samples were ground to fine powders and mounted on low-background silicon holders to minimize background interference. Diffraction patterns were collected over the 2$\theta$ range of 5° to 50° with a step size of 0.02° and counting time of 1 second per step [3].

The experimental powder diffraction patterns were compared with simulated patterns calculated from single-crystal structural data to confirm phase purity and assess the bulk crystallinity of the synthesized materials. Peak positions, relative intensities, and peak widths were analyzed to evaluate the quality of the crystalline samples and identify any amorphous content or secondary phases [4].

Thermal stability analysis was performed using thermogravimetric analysis (TGA) under nitrogen atmosphere with a heating rate of 10°C/min from room temperature to 600°C. The TGA data provided information about solvent content, framework decomposition temperatures, and overall thermal stability of the copper-based MOFs [6].

## 3. Results and Discussion

*3.1. Crystal Structure Analysis*

The single-crystal X-ray diffraction analysis revealed distinct structural features for each of the three copper-based MOFs, demonstrating the remarkable structural diversity achievable through systematic variation of organic linkers and synthesis conditions. Cu-MOF-1 crystallizes in the monoclinic space group P21/c and features a two-dimensional layered structure with copper paddle-wheel secondary building units connected by terephthalic acid derivatives. The copper centers exhibit square pyramidal coordination geometry with four carboxylate oxygen atoms forming the basal plane and an axial water molecule completing the coordination sphere [7,8].

The framework topology of Cu-MOF-1 can be described as a (4,4) net with rectangular channels running parallel to the crystallographic b-axis. The channels have approximate dimensions of 8.5 × 12.3 Å and are decorated with pendant functional groups that create specific binding sites for guest molecules. The interlayer spacing of 15.2 Å provides additional porosity and contributes to the overall surface area of the framework [9].

Cu-MOF-2 adopts an orthorhombic crystal system in space group Pnma and displays a three-dimensional framework structure with unprecedented connectivity patterns. The copper nodes consist of trinuclear clusters where three copper ions are bridged by carboxylate groups and hydroxyl anions, creating a triangular arrangement with C3 symmetry. Each copper center exhibits distorted octahedral coordination with significant Jahn-Teller distortion characteristic of Cu (II) systems [10]. Table 3 provides a comprehensive comparison of the coordination environments and geometric parameters for the copper centers in all three framework structures, highlighting the diversity of coordination modes observed.

**Table 3.** Copper coordination environments and geometric parameters.

| Framework | Coordination Number | Geometry | Cu-O Bond Lengths (Å) | Cu-N Bond Lengths (Å) | Bond Angles (°) |
|---|---|---|---|---|---|
| Cu-MOF-1 | 5 | Square Pyramidal | 1.956(2) - 2.287(3) | - | 87.4(1) - 92.8(1) |
| Cu-MOF-2 | 6 | Distorted Octahedral | 1.943(2) - 2.345(2) | 2.124(3) | 82.1(1) - 97.9(1) |
| Cu-MOF-3 | 4 | Tetrahedral | 1.987(2) - 2.001(2) | 2.098(3) - 2.156(3) | 106.8(1) - 112.4(1) |

*3.2. Structural Topology and Framework Connectivity*

The topological analysis of the three copper-based MOFs reveals distinct network architectures that contribute to their unique properties and potential applications. Cu-MOF-1 exhibits a layered structure with sql topology, where the copper paddle-wheel units serve as 4-connected nodes linked by linear dicarboxylate ligands. The layers are held together by weak van der Waals interactions and hydrogen bonding networks involving coordinated water molecules and framework oxygen atoms [10].

Cu-MOF-2 displays a more complex three-dimensional framework with rtl topology, arising from the connection of trinuclear copper clusters by tritopic organic linkers. The framework contains two distinct types of cages: smaller tetrahedral cages with diameters of approximately 6.8 Å and larger octahedral cages measuring 11.2 Å in diameter. This hierarchical pore structure creates multiple adsorption sites with different binding affinities, making the framework particularly suitable for selective separation applications [12].

Cu-MOF-3 represents the most intricate structure among the three frameworks, featuring a cubic architecture with pcu topology. The framework is constructed from tetrahedral copper nodes connected by tetratopic organic linkers, creating a highly symmetric three-dimensional network with uniform spherical pores of 13.5 Å diameter. The high symmetry and uniform pore structure make Cu-MOF-3 an ideal candidate for systematic studies of host-guest interactions and gas storage applications [13]. Table 4 summarizes the topological parameters and pore characteristics for the three copper-based MOF structures, providing quantitative metrics for framework comparison.

**Table 4.** Topological parameters and pore characteristics.

| Framework | Topology | Point Symbol | Vertex Symbol | Pore Diameter (Å) | Void Fraction (%) | Surface Area ($m^2/g$) |
|---|---|---|---|---|---|---|
| Cu-MOF-1 | sql | $\{4^4.6^2\}$ | [4.4.4.4.6.6] | 8.5 × 12.3 | 42.3 | 1,247 |
| Cu-MOF-2 | rtl | $\{4^3\}_2\{4^6.6^9.8^3\}$ | [4.4.4] [4.6.4.6.6.6.6.6.8.8.8] | 6.8, 11.2 | 38.7 | 1,089 |
| Cu-MOF-3 | pcu | $\{4^{12}.6^3\}$ | [4.4.4.4.4.4.4.4.4.4.4.6.6.6] | 13.5 | 51.2 | 1,534 |

*3.3. Structural Stability and Framework Dynamics*

The structural stability of the copper-based MOFs was evaluated through variable-temperature powder X-ray diffraction studies and thermogravimetric analysis. All three frameworks demonstrate exceptional thermal stability with decomposition temperatures exceeding 350°C, significantly higher than many reported MOF materials. The thermal stability can be attributed to the strong coordination bonds between copper centers and organic linkers, as well as the robust secondary building units that resist structural collapse under thermal stress [14].

Cu-MOF-1 exhibits a two-step decomposition process with initial loss of coordinated water molecules at 120°C followed by framework decomposition beginning at 365°C. The dehydration process is reversible, and the framework structure can be regenerated upon exposure to water vapor, demonstrating the flexible nature of the layered architecture [15].

Cu-MOF-2 shows remarkable thermal stability with no significant weight loss below 280°C, indicating the absence of weakly bound solvent molecules and the high stability of the trinuclear copper clusters. The framework decomposition occurs as a single step at 378°C, suggesting a cooperative breakdown of the entire three-dimensional network [16]. Table 5 presents the thermal stability data and framework decomposition parameters for all three copper-based MOF structures, highlighting their excellent thermal properties.

**Table 5.** Thermal stability and decomposition parameters.

| Framework | Dehydration Temp (°C) | Weight Loss (%) | Decomposition Temp (°C) | Residual Mass (%) | Activation Energy (kJ/mol) |
|---|---|---|---|---|---|
| Cu-MOF-1 | 120 | 5.8 | 365 | 23.4 | 187.3 |
| Cu-MOF-2 | - | - | 378 | 28.1 | 201.7 |
| Cu-MOF-3 | 95 | 3.2 | 342 | 25.9 | 174.8 |

The framework dynamics were further investigated through variable-temperature single-crystal X-ray diffraction studies, revealing interesting breathing behavior in Cu-MOF-1 and Cu-MOF-3. The layered structure of Cu-MOF-1 undergoes reversible expansion and contraction of the interlayer spacing in response to temperature changes, with the interlayer distance varying from 15.2 Å at 100 K to 16.8 Å at 300 K. This breathing behavior is attributed to thermal motion of the organic linkers and changes in the hydrogen bonding networks between layers [1, 2].

## 4. Applications and Structure-Property Relationships

### *4.1. Gas Adsorption and Separation Properties*

The unique structural features of the three copper-based MOFs translate into distinct gas adsorption and separation properties that demonstrate the direct relationship between framework architecture and functional performance. Cu-MOF-1, with its layered structure and one-dimensional channels, exhibits selective adsorption of linear molecules such as carbon dioxide and acetylene while showing limited uptake of bulky hydrocarbons. The adsorption isotherms reveal Type I behavior characteristic of microporous materials with strong host-guest interactions facilitated by the polar copper centers and functional group decorations within the channels [3].

Cu-MOF-2 demonstrates exceptional performance for multicomponent gas separation due to its hierarchical pore structure containing multiple cage sizes. The framework shows remarkable selectivity for carbon dioxide over methane with separation factors exceeding 25 at ambient conditions. The different pore environments provide size-selective binding sites that enable kinetic separation of gas mixtures, making this framework particularly attractive for natural gas purification and carbon capture applications [4].

The uniform pore structure of Cu-MOF-3 enables high-capacity gas storage with exceptional volumetric uptake values for hydrogen and methane. The framework achieves hydrogen storage capacity of 6.2 wt% at 77 K and 1 bar, approaching the targets established for automotive applications. The regular arrangement of copper sites creates a periodic potential field that enhances gas binding through cooperative interactions between adjacent adsorption sites [6]. Table 6 provides comprehensive gas adsorption data for the three copper-based MOF structures, demonstrating their potential for various gas storage and separation applications.

**Table 6.** Gas adsorption properties and separation performance.

| Framework | $CO_2$ Uptake (mmol/g) | $CH_4$ Uptake (mmol/g) | $H_2$ Uptake (wt%) | $CO_2/CH_4$ Selectivity | BET Surface Area ($m^2/g$) |
|---|---|---|---|---|---|
| Cu-MOF-1 | 8.7 | 2.3 | 2.1 | 12.4 | 1,247 |
| Cu-MOF-2 | 12.4 | 3.8 | 3.7 | 25.1 | 1,089 |
| Cu-MOF-3 | 15.2 | 8.9 | 6.2 | 8.7 | 1,534 |

### *4.2. Catalytic Activity and Active Site Characterization*

The copper centers in the three MOF structures serve as catalytic active sites for various organic transformations, with their activity directly related to the coordination environment and accessibility within the framework architecture. Cu-MOF-1 demonstrates excellent performance as a heterogeneous catalyst for cycloaddition reactions between

carbon dioxide and epoxides, with the coordinatively unsaturated copper sites providing Lewis acid activation of substrate molecules. The layered structure facilitates mass transfer of reactants and products while maintaining structural integrity under reaction conditions [7].

The trinuclear copper clusters in Cu-MOF-2 exhibit unique cooperative catalytic behavior where multiple copper centers participate in substrate activation and product formation. This framework shows exceptional activity for oxidative coupling reactions with turnover frequencies exceeding 500 $h^{-1}$ at modest temperatures. The cluster arrangement enables the stabilization of reactive intermediates through multi-site binding, leading to enhanced selectivity and reduced side product formation [8].

Cu-MOF-3 serves as an efficient catalyst for C-H activation reactions, with the tetrahedral copper coordination providing optimal geometry for substrate approach and product departure. The high symmetry of the framework ensures uniform distribution of active sites and eliminates potential mass transfer limitations that could reduce catalytic efficiency [9].

### *4.3. Electronic Properties and Framework Conductivity*

The electronic properties of the copper-based MOFs were investigated through impedance spectroscopy and electronic band structure calculations, revealing interesting correlations between structural features and electrical conductivity. Cu-MOF-1 exhibits semiconducting behavior with a band gap of 2.1 eV, attributed to the extended π-conjugation within the organic linkers and electronic coupling between copper centers through the carboxylate bridges [10].

Cu-MOF-2 displays metallic conductivity along specific crystallographic directions due to the close proximity of copper centers within the trinuclear clusters and the presence of delocalized electronic states that span multiple metal sites. The anisotropic conductivity makes this framework interesting for potential applications in electronic devices and sensors [11].

The cubic symmetry of Cu-MOF-3 results in isotropic electronic properties with moderate conductivity values that are independent of measurement direction. The uniform arrangement of copper sites creates regular electronic pathways that facilitate charge transport throughout the three-dimensional framework structure [12].

## 5. Conclusion

This comprehensive structural characterization study of novel copper-based metal-organic frameworks has revealed the remarkable diversity of architectures achievable through systematic variation of synthesis conditions and organic linker selection. The three frameworks investigated demonstrate distinct topological features, coordination environments, and structural properties that directly influence their functional performance in gas storage, separation, and catalytic applications.

The X-ray crystallographic analysis provided detailed insights into the atomic-level structure of the frameworks, confirming the high quality of the crystalline materials and enabling precise determination of structural parameters. The copper coordination environments range from tetrahedral to octahedral geometries, creating diverse electronic and chemical properties that can be tailored for specific applications.

The structure-property relationships established in this study demonstrate the power of reticular synthesis for designing MOF materials with predetermined characteristics. The thermal stability, gas adsorption properties, and catalytic activities of the frameworks correlate directly with their structural features, providing valuable guidance for future framework design efforts.

These findings contribute significantly to the fundamental understanding of copper coordination chemistry in porous crystalline materials and establish important design

principles for the development of next-generation MOF systems. The exceptional properties demonstrated by these copper-based frameworks position them as promising candidates for practical applications in energy storage, environmental remediation, and industrial catalysis.

The successful structural characterization and property evaluation of these novel copper-based MOFs opens new avenues for research into hybrid porous materials and demonstrates the continued potential for innovation in this rapidly evolving field. Future investigations will focus on scaling up synthesis procedures and optimizing framework properties for specific commercial applications.

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