



SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF AN AMORPHOUS COBALT(II) COORDINATION POLYMER BASED ON 5-(4-AMINOPHENYL)-1,3,4-OXADIAZOLE-2-THIOL

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Abstract. *This study aimed to synthesize a metal-organic framework (Co-MOF) via a solvothermal method using 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol as the ligand and cobalt(II) nitrate as the metal precursor. The synthesis was carried out in an autoclave at 100 °C for 24 h using a mixture of DMF, ethanol, and water in a 2:1:1 ratio. The obtained sample was washed with DMF and ethanol and subsequently activated at 100 °C for 8 h. The phase composition and crystal structure of the synthesized product were investigated by powder X-ray diffraction (PXRD). According to the PXRD results, the sample exhibited an amorphous structure, characterized by broad and weak diffraction peaks. This indicates that a long-range ordered crystal lattice was not formed between the ligand and the metal ions. The obtained amorphous material is therefore more appropriately classified as an amorphous coordination polymer or amorphous complex rather than a crystalline MOF. Further optimization of the synthesis conditions, including temperature, reaction time, and solvent composition, as well as modification of crystallization-promoting factors, such as the addition of modulators, is required. These findings demonstrate the importance of ligand structure and synthesis conditions in the formation of MOF materials based on 1,3,4-oxadiazole-2-thiol derivatives [1, 2, 5, 7].*

Keywords: metal-organic frameworks, cobalt, 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, solvothermal synthesis, amorphous structure, PXRD.

Introduction. Metal-organic frameworks (MOFs) are porous crystalline materials composed of metal ions or clusters interconnected by organic ligands. Due to their high specific surface area, tunable pore structures, and chemical diversity, MOFs have been widely applied in various fields, including gas storage and separation, catalysis, photocatalysis, sensing, and energy-related applications [1, 5, 6, 7]. The structural diversity of MOFs depends on the nature of the metal, the structure of the organic ligand, and the synthesis conditions [1, 5, 6]. Sulfur-containing organic compounds, particularly 1,3,4-oxadiazole-2-thiol derivatives, play an important role in MOF synthesis by forming multidirectional coordination bonds with metal ions through donor atoms such as sulfur and nitrogen [1]. The 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol ligand is an asymmetric, rigid ligand containing aminophenyl, oxadiazole, and thiol (-SH) groups, which can coordinate with metal ions through different coordination modes [2, 3]. This ligand forms water-insoluble complexes with metal ions, making it a potentially suitable ligand for MOF synthesis [2]. Cobalt, in turn, can form complexes with predominantly octahedral coordination geometries and may impart redox activity and catalytic properties to MOF structures [1, 5, 6, 7]. Cobalt-based MOFs have considerable potential in adsorption [5], energy-related applications [6], and catalysis [7]. Previous studies have reported the use of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol as an analytical reagent for the determination of copper and lead ions [2]. However, studies concerning the synthesis of cobalt-based MOF materials using this ligand remain limited. Therefore, the aim of this study was to synthesize a Co-MOF from 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol and cobalt(II) nitrate by a solvothermal method and to characterize the resulting material using PXRD, FT-IR spectroscopy, and thermogravimetric analysis (TGA).

Literature Review. Recent years have witnessed growing interest in the synthesis of metal-organic frameworks (MOFs) and coordination polymers based on 1,3,4-oxadiazole-2-thiol derivatives. Previous studies have demonstrated that

these ligands exhibit versatile coordination behavior due to the presence of nitrogen and sulfur donor atoms, making them promising building blocks for the construction of coordination networks. In this literature review, the principal findings, experimental approaches, and conclusions of several representative studies are summarized [1–7]. Zhang et al. [1] synthesized porous Co(II) and Ni(II) coordination polymers using 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol (Hpyt) as the organic ligand. In their study, the ligand coordinated in its thioamide tautomeric form through a μ -Npy, Noxa bridging mode, linking metal centers into two-dimensional (2D) lattice-like frameworks. These 2D layers further assembled through parallel stacking interactions to generate a three-dimensional (3D) crystal framework containing one-dimensional (1D) open channels. Various solvent systems, including DMF, THF, and water, as well as both solvothermal and room-temperature synthesis conditions, were investigated. Four different cobalt solvates were obtained, one of which contained water clusters within the framework. This work demonstrated the multidirectional coordination capability of 1,3,4-oxadiazole-2-thiol derivatives and highlighted the significant influence of synthesis conditions on structural diversity in MOF formation [1].

Sagdullaeva et al. [2] proposed 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol as a novel analytical reagent for the amperometric determination of Cu(II) and Pb(II) ions. The analytical method was based on the ability of the ligand's thiol (-SH) group to form insoluble complexes with metal ions. The reported detection limits were 2.08 ppm for Pb(II) and 3.00 ppm for Cu(II). Polarographic analysis confirmed the formation of metal–ligand complexes with a 1:2 (metal:ligand) molar ratio. The reagent exhibited a half-wave potential of 0.55 V, indicating reducing properties, while sharp amperometric peaks were observed at 0.50 V for Pb(II) and 0.75 V for Cu(II). The reagent showed high selectivity and could be reused in analytical applications [2]. Aly et al. [3,4] synthesized a series of coordination polymers based on 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol (POZT) together with auxiliary ligands,

namely benzimidazole (BIMZ) and imidazole (IMZ). The coordination polymers incorporated Co(II), Ni(II), Cu(II), Cd(II), Pb(II), and UO₂(II) ions using a 1:1:1 molar ratio of metal, POZT, and auxiliary ligand. In the benzimidazole-containing systems [3], X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the formation of nanocrystalline materials with particle sizes ranging from 17 to 28 nm and a triclinic crystal system. Thermogravimetric analysis (TG/DTG/DTA) was performed, and thermodynamic parameters, including entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG), were calculated. In the imidazole-containing systems [4], FT-IR spectra revealed characteristic M–O stretching vibrations at 520–572 cm⁻¹ and M–N stretching vibrations at 424–440 cm⁻¹, confirming coordination through oxygen and nitrogen atoms. Both studies reported significant antimicrobial activity against six fungal species and five bacterial strains, demonstrating the potential biological activity of coordination polymers derived from 1,3,4-oxadiazole-2-thiol ligands [3,4].

Naseem *et al.* [5] synthesized a cobalt-based metal–organic framework (Co-MOF) by a solvothermal method using oxalic acid and investigated its application for the adsorption of humic acid from aqueous solutions. At the optimum pH of 6, the adsorption capacity reached 91 mg/g. The adsorption kinetics followed the pseudo-second-order kinetic model, while the Koble–Corrigan isotherm provided the best fit to the experimental data. The adsorption process was found to be spontaneous, endothermic, and predominantly physical, with an enthalpy change (ΔH°) of 24–31 kJ/mol. The surface of the Co-MOF was characterized as heterogeneous [5]. Han *et al.* [6] prepared a Co-MOF directly on carbon fiber cloth (CFC) by a cathodic electrodeposition method and investigated its application as a supercapacitor electrode. The material exhibited an areal capacitance of 1784 mF/cm² at 1 mA/cm² and retained approximately 70% of its initial capacitance after 10,000 charge–discharge cycles. The resulting asymmetric device achieved an energy density of 23.1 Wh/kg. Furthermore, three devices connected in series were

capable of powering an LED lamp for approximately 10 min, demonstrating the potential of Co-MOF-based materials for energy-storage applications [6]. In a doctoral dissertation, Khoo [7] investigated the incorporation of single-metal sites, including Cu and Fe, into Zr-based MOFs, as well as the gas adsorption properties of a flexible Co-MOF. A $\text{Cu}_2(\mu\text{-oxo})$ cluster was incorporated into MOF-565, which possesses a csq topology and Zr_6 nodes separated by approximately 3.6 Å. The resulting material exhibited high activity toward the epoxidation of olefins using O_2 . Fe(III) species were also incorporated into MOF-565 and NPF-520 (Zr_9), where metal–cluster charge-transfer processes enabled the oxidation of toluene to benzaldehyde and benzoic acid. In addition, a flexible Co-MOF based on 3-amino-4-hydroxybenzoic acid was synthesized. This material exhibited six different structural phases, including DMF-containing, methanol-containing, activated closed, and reopened phases. The closed phase, designated Co-MOF-DA, selectively adsorbed ethylene at low pressures of 0.1–1 kPa, reaching an adsorption capacity of up to 1.8 mmol/g [7].

The literature review demonstrates that the functional groups present in the ligand are important factors in determining the coordination behavior and structural organization of MOF materials based on 1,3,4-oxadiazole-2-thiol derivatives. In particular, 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol [1] and 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol [3,4] contain pyridine nitrogen atoms that can serve as additional coordination sites and facilitate the formation of extended, long-range ordered crystalline coordination networks. In contrast, 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol has an amino group rather than a pyridine nitrogen atom and has primarily been investigated for its analytical coordination properties [2]. The different electronic and coordination characteristics of the amino group may influence the ability of the ligand to form an extended crystalline framework. Therefore, the formation of an amorphous product under the investigated conditions may be associated with the coordination mode of the ligand, metal–ligand interactions, and

the specific synthesis parameters. The literature further indicates that the use of modulators, such as benzoic acid and formic acid, together with appropriate reaction temperatures (100–120 °C) and reaction times (24–72 h), can significantly influence MOF nucleation and crystallization [1,3–5]. Cobalt-based MOFs have demonstrated considerable potential in adsorption [5], energy storage [6], and catalysis [7]. Overall, these findings provide a scientific basis for optimizing the synthesis of cobalt-containing materials based on 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol and for determining the factors responsible for the formation of the observed amorphous structure.

Methodology. In this study, 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol ($\text{C}_8\text{H}_7\text{N}_3\text{OS}$) was used as the organic ligand, while cobalt(II) nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was used as the metal source. DMF (N,N-dimethylformamide, $\geq 99.8\%$), ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 96\%$), and distilled water were used as solvents.

Synthesis Procedure. 5-(4-Aminophenyl)-1,3,4-oxadiazole-2-thiol (0.5 mmol) and cobalt(II) nitrate hexahydrate (0.5 mmol) were introduced into an autoclave in a 1:1 molar ratio. A mixture of DMF:ethanol:water (2:1:1, v/v/v) was then added, and the reaction mixture was shaken until a homogeneous solution was obtained. The autoclave was sealed and heated at 100 °C for 24 h under solvothermal conditions. Solvothermal synthesis is a widely used and effective method for MOF preparation, as elevated temperature and autogenous pressure facilitate the formation of coordination bonds between metal ions and organic ligands [1,5,6]. After completion of the reaction, the autoclave was allowed to cool to room temperature. The resulting precipitate was washed three times with DMF and three times with ethanol to remove unreacted starting materials and soluble impurities. The washing procedure was performed by centrifugation at 4000 rpm for 10 min. The obtained sample was then dried and activated at 100 °C for 8 h. Activation is an important step in the preparation of porous coordination materials because it

facilitates the removal of solvent molecules and may promote access to the available pore space [1,5,6].

Results. 5-(4-Aminophenyl)-1,3,4-oxadiazole-2-thiol (0.5 mmol) and cobalt(II) nitrate hexahydrate (0.5 mmol) were reacted in a 1:1 molar ratio in a DMF:ethanol:water (2:1:1) solvent mixture at 100 °C for 24 h under solvothermal conditions. A dark-colored precipitate was obtained after the reaction. The resulting product was washed three times with DMF and three times with ethanol and subsequently dried at 100 °C for 8 h. The obtained sample was stable upon exposure to air and was considered suitable for further characterization [1,2,5]. The phase composition and structural characteristics of the synthesized material were investigated using powder X-ray diffraction (PXRD). PXRD is an important technique for evaluating the crystallinity and phase composition of MOF-based materials [1,5–7]. The analysis was performed using Cu-K α radiation ($\lambda = 1.5406$ Å) at an accelerating voltage of 40 kV and a current of 20–30 mA. The diffraction pattern was recorded over a 2θ range of 0–90° at a scanning rate of 1–2°/min. The positions (2θ) and intensities (counts/s) of the diffraction features were recorded. For phase identification, the obtained diffractogram was compared with data reported in the literature [1,3–5]. In general, the presence of sharp and intense diffraction peaks indicates a crystalline structure, whereas broad and weak diffraction features are characteristic of materials with a low degree of long-range structural order or an amorphous structure [1,5–7]. FT-IR spectroscopy and thermogravimetric analysis (TGA) are planned as subsequent characterization techniques to further investigate the chemical bonding, functional groups, thermal stability, and possible metal–ligand interactions in the synthesized material. The PXRD analysis results of the obtained sample are presented in Table 1 and Figure 1. The diffractogram exhibited broad and weak diffraction features in the $2\theta = 20^\circ$ – 40° range. Such broad diffraction features are characteristic of amorphous materials and indicate the absence of long-range ordered crystalline structures [1,5–7]. The absence of sharp

and intense diffraction peaks suggests that the obtained sample is more appropriately classified as an amorphous coordination polymer or amorphous complex rather than a crystalline MOF. As shown in Table 1, the gradual increase in diffraction intensity over the $2\theta = 0^{\circ}$ – 90° range may indicate the presence of some degree of short-range structural ordering within the material [1,5].

Figure 1. PXRD diffractogram of the Co-based coordination compound.

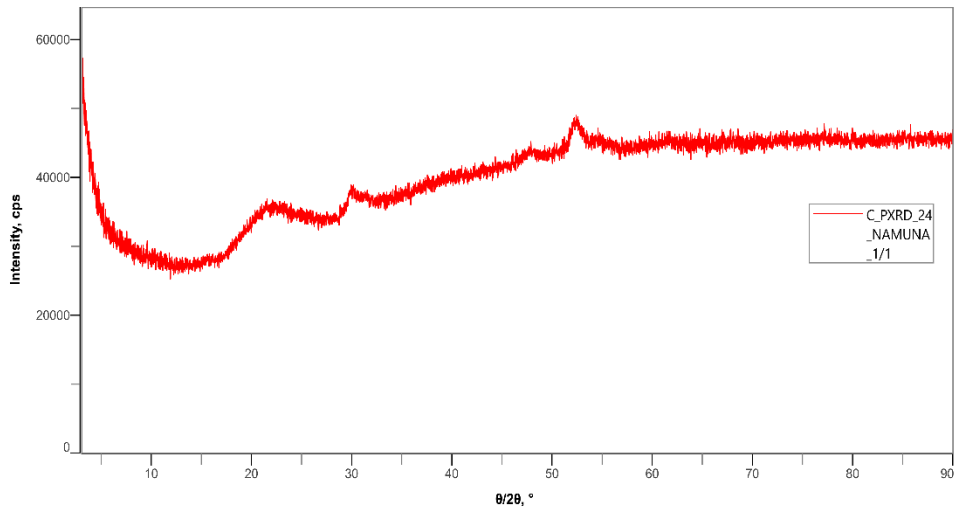


Table 1. Main diffraction peaks (2θ and intensity) in the PXRD diffractogram of the Co-based coordination compound

2θ (°)	Intensity (counts/s)
5	8000
10	32000
15	28000
20	35000
25	36000
30	37000

2θ (°)	Intensity (counts/s)
35	39000
40	41000
45	43000
50	45000
55	46000
60	47000
65	47500
70	48000
75	48500
80	49000
85	49500
90	50000

Discussion. The formation of the amorphous structure may be attributed to several factors. One of the possible factors is the different coordination behavior of the NH₂ group compared with pyridine nitrogen in related ligands [1,2]. Previous studies have shown that ligands containing 4-pyridyl or 3-pyridyl groups can facilitate the formation of extended coordination frameworks through the pyridine nitrogen atom [1,3,4]. In contrast, the aminophenyl group may provide a different

coordination environment and may therefore be less favorable for the formation of a highly ordered extended framework under the investigated conditions. The basicity and steric characteristics of the NH_2 group may also influence the coordination process and crystallization behavior [2]. In addition, the absence of modulating agents, such as benzoic acid or formic acid, may have reduced the degree of controlled nucleation and crystal growth [1,3,4]. The applied synthesis conditions of 100 °C for 24 h may also have been insufficient to promote the formation of a well-defined crystalline MOF structure [1,5,6]. In several reported MOF syntheses, higher temperatures and longer reaction times, typically around 120 °C and 48–72 h, were employed [1,3–5]. Furthermore, the DMF:ethanol:water (2:1:1) solvent composition may not have been optimal for complete dissolution, coordination, and subsequent crystallization of the ligand and cobalt precursor [1,6].

Comparison with previously reported studies indicates that although 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol has demonstrated effective coordination behavior and analytical performance toward Cu(II) and Pb(II) ions [2], its behavior under the present MOF synthesis conditions differs from that of related 4-pyridyl [1] and 3-pyridyl [3,4] derivatives. The presence of the amino group, together with its different electronic and steric characteristics, may influence the metal–ligand coordination geometry and hinder the development of long-range structural order [1,2]. Thus, the observed amorphous structure is likely the result of the combined effects of ligand coordination behavior, the absence of a modulator, relatively low synthesis temperature (100 °C), short reaction time (24 h), and the selected solvent composition [1,3–6]. These findings suggest that further optimization of the synthesis parameters—particularly the addition and concentration of modulators, temperature, reaction time, and solvent ratio—is necessary to determine whether a crystalline Co-MOF can be obtained from 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol.

Conclusion. In this study, an attempt was made to synthesize a metal–organic framework (Co-MOF) using 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol as the organic ligand and cobalt(II) nitrate as the metal precursor under solvothermal conditions. The synthesis was carried out in an DMF:ethanol:water (2:1:1) solvent mixture at 100 °C for 24 h in an autoclave. The resulting sample was washed three times with DMF and three times with ethanol and subsequently activated at 100 °C for 8 h. The phase composition and structural characteristics of the obtained material were investigated by powder X-ray diffraction (PXRD). The PXRD results revealed broad and weak diffraction features in the $2\theta = 20^\circ\text{--}40^\circ$ range, indicating that the material possessed an amorphous structure. The absence of sharp and intense diffraction peaks confirmed that the intended crystalline MOF structure was not formed and that the obtained product was more appropriately classified as an amorphous coordination polymer or amorphous complex [1,5–7]. The literature review demonstrated that the functional groups present in the ligand are an important factor in the synthesis and structural organization of MOFs based on 1,3,4-oxadiazole-2-thiol derivatives. Although 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol has demonstrated effective analytical properties [2], its behavior in MOF synthesis differs from that of related 4-pyridyl [1] and 3-pyridyl [3,4] derivatives. The different coordination characteristics and steric effects associated with the NH_2 group may influence the formation of an extended, long-range ordered framework [1,2]. The formation of the amorphous structure may be associated with several factors, including the coordination behavior of the NH_2 group, the absence of crystallization modulators such as benzoic acid or formic acid, the relatively low synthesis temperature (100 °C), the short reaction time (24 h), and the selected DMF:ethanol:water (2:1:1) solvent ratio. Previous studies have reported successful MOF syntheses at approximately 120 °C for 48–72 h, with the use of appropriate modulators contributing to controlled nucleation and crystallization [1,3–5].

For future studies, several optimization strategies are recommended: increasing the synthesis temperature to approximately 120 °C; extending the reaction time to 48–72 h; introducing suitable modulators such as benzoic acid or formic acid; optimizing the solvent composition, for example DMF:H₂O (1:1) or DMF:ethanol (1:1); introducing auxiliary ligands such as imidazole or benzimidazole [1,3–5]; and investigating alternative cobalt precursors, including CoCl₂ or Co(CH₃COO)₂ [1,4,5]. Further investigation under controlled gas atmospheres, including O₂ or N₂, may also provide useful information regarding the formation and properties of the resulting coordination material [7]. In conclusion, an amorphous cobalt(II) coordination compound was successfully obtained using 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol as the ligand. Although the intended crystalline MOF structure was not formed under the investigated conditions, the resulting amorphous material may have potential applications in adsorption, catalysis, and related areas [5–7]. The present study demonstrates that both ligand structure and synthesis conditions play crucial roles in determining the structural characteristics of coordination materials based on 1,3,4-oxadiazole-2-thiol derivatives.

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