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Synthesis and Structural Insights of Transition Metal Complexes Assembled by 1,4-Cyclohexanedicarboxylic Acid and 1,10-Phenanthroline

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Abstract: In this study, a series of transition metal complexes involving Zn(II), Cd(II) and Ni(II) were synthesized using 1,4 - Cyclohexane dicarboxylic acid (CHDA) and 1,10 - Phenanthroline (Phen) as co-ligands. These bidentate and flexible ligands were selected for their ability to form stable and multifunctional coordination frameworks. Comprehensive characterization was performed using FT-IR, PXRD, TGA, SEM, and EDAX techniques to evaluate the structural, thermal, and morphological attributes of the complexes. FT-IR confirmed coordination via carboxylate oxygen and nitrogen atoms, while PXRD revealed varying degrees of crystallinity influenced by metal-ligand interactions. TGA demonstrated distinct thermal decomposition profiles, indicating the formation of thermally stable metal oxides. SEM analysis showed metal-specific morphologies, ranging from amorphous to crystalline textures. The results underscore the potential of these complexes in applications such as catalysis, sensing, and materials engineering, where thermal stability and structural tunability are critical.

Keywords: 1,4-Cyclohexanedicarboxylic acid, 1,10-Phenanthroline, Metal complexes, Thermal stability, Transition metal

1. Introduction

Transition metal complexes have been extensively studied due to their intriguing structural diversity and wide range of applications in catalysis, sensing, and optoelectronic materials. The choice of ligands plays a crucial role in dictating the physicochemical properties and stability of such complexes. Among the various ligands, 1,4-Cyclohexane dicarboxylic acid (CHDA) and 1,10-Phenanthroline (Phen) have emerged as versatile chelating agents capable of forming robust metal-organic frameworks and coordination complexes with interesting electronic and thermal properties [1, 2]. Carboxylate ligands such as CHDA have been widely explored for their ability to form coordination networks with transition metals, offering structural rigidity and enhanced thermal stability [3-5]. Studies have demonstrated that CHDA, due to its flexible aliphatic backbone, allows for diverse coordination modes, leading to the formation of supramolecular architectures with tunable porosity and stability [6-8]. In particular, zinc and cadmium complexes with dicarboxylate ligands have exhibited promising applications in gas adsorption and catalysis. On the other hand, Phen is a well-known bidentate ligand that imparts additional electronic and photophysical properties to metal complexes. Its conjugated planar structure enhances metal-ligand interactions, making Phen-based complexes valuable in redox catalysis, luminescent materials, and molecular sensing [9, 10]. Ni(II), Ru(III), and other transition metals coordinated with Phen have been studied for their potential in electrochemical and photocatalytic applications, owing to their stability and ability to mediate electron transfer reactions [4, 11-14]. Despite these advancements, there is still limited research on the combined influence of CHDA and Phen ligands in metal complexes and their structural characterization. In this study, we report the synthesis and comprehensive characterization of Zn(II), Cd(II) and Ni(II) complexes incorporating CHDA and Phen ligands. The complexes were synthesised systematically and by correlating the structural characteristics with thermal and morphological properties, we aim to establish their potential applications in catalysis, gas sensing, and electronic materials. The findings from this study contribute to the growing body of knowledge on multifunctional metal-organic complexes, providing

insights into their structure-property relationships and practical usability in advanced material applications.

2. Experimental Methods

2.1 Materials and Methods

All the reagents and solvents utilized for the synthesized were purchased from Sigma Aldrich, India.

2.2 Characterisation Techniques

FT-IR spectrum of the complex were recorded using Shimadzu (IR Affinity 1) and UV-250 spectrometer between the range of 400 and 4500 cm^{-1}. The phase characterisation of the prepared metal complex samples were carried out using powder X-ray diffraction unit (M/s Explorer GNR, Italy) with Cu K_α radiation (λ =1.5418 Å) and Ni filter. The diffraction patterns were recorded from 20° - 60° in steps of 0.02° with an integration time of 1 s at each step. The thermal stability and different stages of decomposition of the complex was studied from 25 to 600 °C using SHIMADZU DTG-60. Further, the morphology elemental composition of the complex were confirmed using the results from FEI Quanta FEG 200 model - Scanning Electron Microscope, accompanied with EDAX.

2.3 Synthesis of NCP

A mixture of $NiCl_2.6H_2O$, 1,10-Phenanthroline, 1,4-Cyclohexane dicarboxylic acid in the molar ratio of 2:1:2 in ethanol was refluxed at 80°C for 2h. The resulting green coloured precipitate was filtered and washed with ethanol. The reaction scheme is shown in figure 1.

2.4. Synthesis of ZCP

A mixture of $ZnCl_2.6H_2O$, 1,10–Phenanthroline, 1,4-Cyclohexane dicarboxylic acid in the molar ratio of 2:1:2 in ethanol was refluxed at 80°C for 5h. The white precipitate was filtered and washed with ethanol. The synthesis of ZCP is depicted in figure 2.

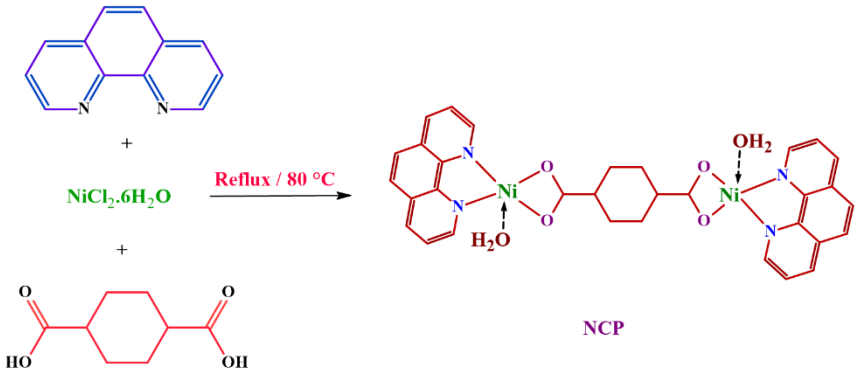

Figure 1. Reaction scheme for the synthesis of NCP

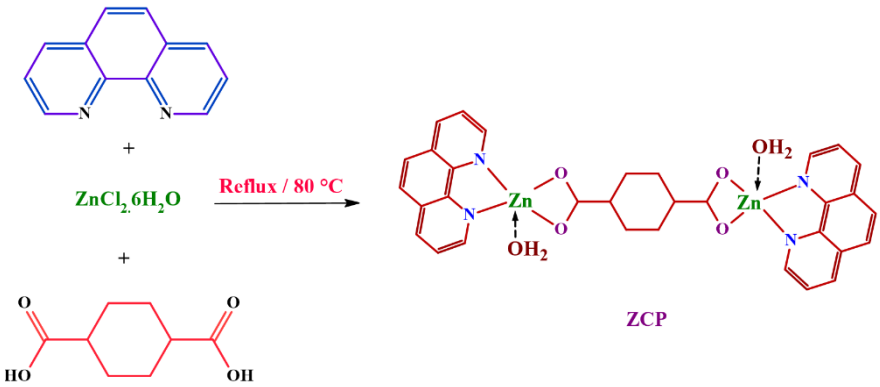

Figure 2. Reaction scheme for the synthesis of ZCP

2.5. Synthesis of DCP

A mixture of $Cd(CH_3COO)_2.2H_2O$, 1,10–Phenanthroline, 1,4–Cyclohexane dicarboxylic acid in the molar ratio of 2:1:2 in ethanol was refluxed at 80 °C for 4h. The resulting white precipitate was filtered and washed with ethanol. The scheme involved in synthesis of DCP is shown in figure 3.

3. Results and Discussion

3.1. FT-IR Spectroscopy

The stacked FT-IR spectrum of the complexes are shown in figure 4. The free CHDA exhibits a strong and broad stretching band in the range of 1700–1720 cm^{-1}, which is attributed to the C=O stretching of the carboxyl group. In the metal complexes, this band shifts to a lower frequency (1550–1650 cm^{-1}) due to the chelation of the carboxylate group with the metal center, confirming coordination. The asymmetric (v_as COO^-) and symmetric (v_s COO^-) stretching frequencies of coordinated carboxylates appear between 1550–1600 cm^{-1} and 1350–1450 cm^{-1} respectively. The $\Delta v < 200$ cm^{-1}, suggests bidentate coordination of ligand with the metal center [15, 16]. The sp^3 C-H stretching vibrations of the cyclohexane ring are observed in the range of 2800–3000 cm^{-1}, indicating the presence of the aliphatic backbone. The C-H bending appears in the region of 1300–1450 cm^{-1}. The characteristic C=N stretching of the heterocyclic ring in Phen appears in the region of 1580–1620 cm^{-1}. A noticeable shift in this band upon complexation confirms the coordination of nitrogen atoms with the metal center. The M-O stretching vibrations appear in the 400–600 cm^{-1} region, confirming the binding of carboxylate groups to the metal ions. The M-N stretching frequencies, indicative of coordination through nitrogen donor atoms, appear in the 450–550 cm^{-1} region [17, 18].

3.2 Powder X-Ray Diffraction

PXRD analysis is a crucial technique for determining the crystallinity, phase purity, and structural characteristics of metal complexes. The PXRD pattern (figure 5) of DCP shows weak peaks, indicating a non-crystalline nature. The presence of multiple high-intensity reflections between 5° and 40° (2θ) suggests a partially ordered arrangement of the molecules in a structured lattice. The sharp peaks at low 2θ values could be due to strong intermolecular interactions and periodic ordering within the unit cell.

The PXRD pattern of NCP shows multiple peaks, though with slightly broader reflections compared to DCP. The moderate sharpness of the peaks suggests a semi-crystalline nature, meaning it has both amorphous and crystalline regions. The broader peaks may be attributed to microstructural effects such as small crystallite size or lattice strain. The PXRD pattern of ZCP shows weak and broad peaks, indicating a low degree of crystallinity or possible amorphous nature. The lack of sharp reflections suggests disorder in the packing of the complex, which may be due to coordination flexibility or weak intermolecular interactions. The broad hump around 10°–30° (2θ) is characteristic of materials with significant amorphous character, possibly due to solvent effects or polymeric interactions in the solid state [17, 19-21].

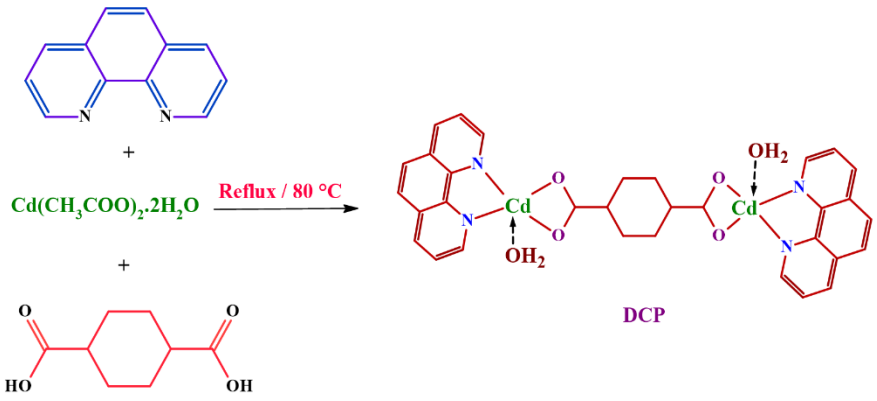

Figure 3. Reaction scheme for the synthesis of DCP

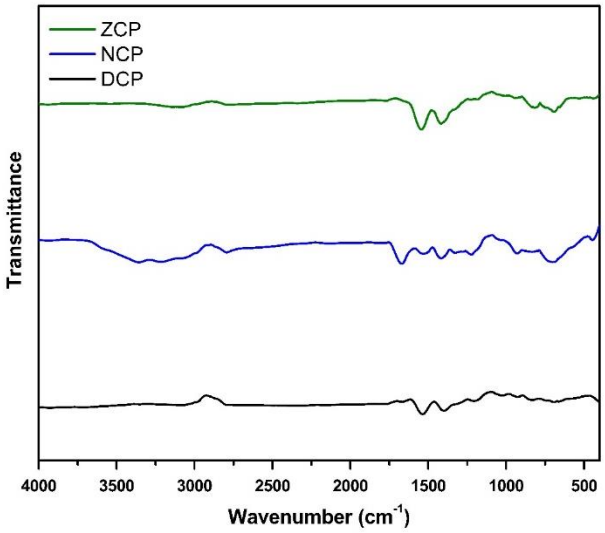

Figure 4. FT-IR spectrum of the synthesized complexes

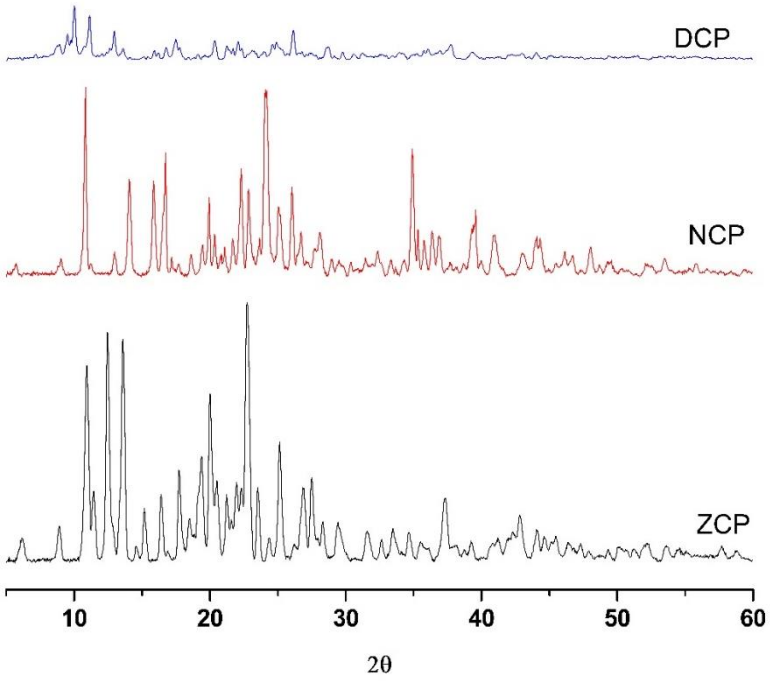

Figure 5. PXRD pattern of the synthesized complexes

3.3 Thermogravimetric Analysis

The TGA curve provides insight into the thermal stability and decomposition pathway of the coordination complex. The Ni-based coordination complex exhibits thermal stability up to ~250°C. The major decomposition occurs in two steps where the first stage of decomposition (~28.2%, below 300°C) corresponds to the removal of solvent molecules (fig 6). The temperature range suggests the loss of physically adsorbed or weakly coordinated water molecules. The second stage of decomposition (~34.4%, 300–600°C) is likely due to the decomposition of the organic ligands (CHDA and Phen). The complete thermal decomposition thus corresponds to the complete degradation of the organic framework, leaving behind the residual metal oxide (NiO). The TGA curve of the zinc complex (fig 7) containing 1,4-cyclohexane dicarboxylic acid and 1,10-phenanthroline shows first weight loss (~18.1%) at lower temperatures (~200-300°C) corresponding to the removal of lattice or coordinated water molecules. The second weight loss (~35.0%) in the range of

~300-600°C suggests the decomposition of organic ligands (1, 4-cyclohexane dicarboxylic acid and 1, 10-phenanthroline). The presence of phenanthroline may contribute to a significant mass loss due to its aromatic structure. The total decomposition results in the formation of likely zinc oxide (ZnO). The TGA curve of DSP (figure 8) reveals two different stages of decomposition where the first stage (~21.9%, Below 300°C) corresponds to the loss of solvent molecules (such as coordinated water or lattice solvents).The temperature range indicates the removal of physically adsorbed or weakly coordinated molecules. The second weight Loss (~41.9%, 300–600°C) is associated with the decomposition of the organic ligands (cyclohexane dicarboxylic acid and phenanthroline). The breakdown of the carboxylate groups and aromatic rings occurs in this region, contributing to significant weight reduction. The total weight loss (~75.9%) represents the complete degradation of the organic framework, leaving behind a stable inorganic residue. The remaining weight suggests the formation of Cadmium-based metal oxide [19, 22, 23].

3.4. Scanning Electron Microscopy (SEM)

The surface morphology of the synthesized metal complexes was investigated using scanning electron microscopy (SEM) and are depicted in figure 9-11. The Ni, Cd, and Zn complexes exhibited distinct morphological characteristics, highlighting the influence of metal coordination on the crystal growth and surface structure. The SEM images of the nickel complex revealed indefinite morphology with a rough surface.

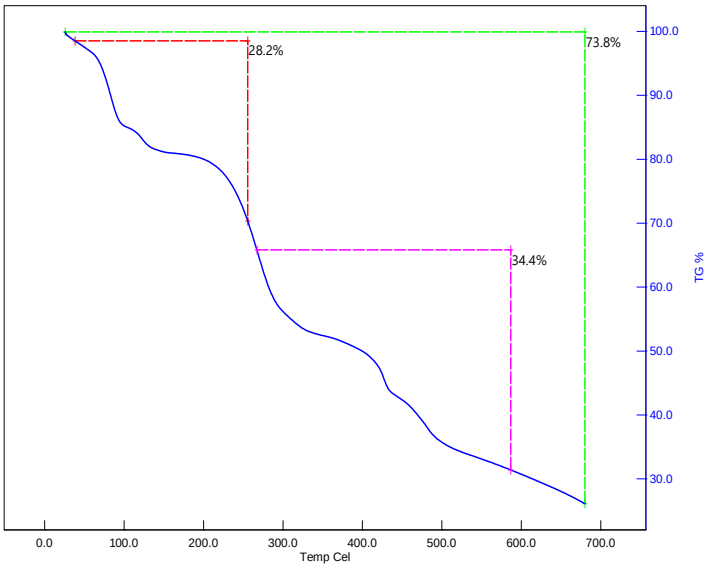

Figure 6. TGA graph of NCP

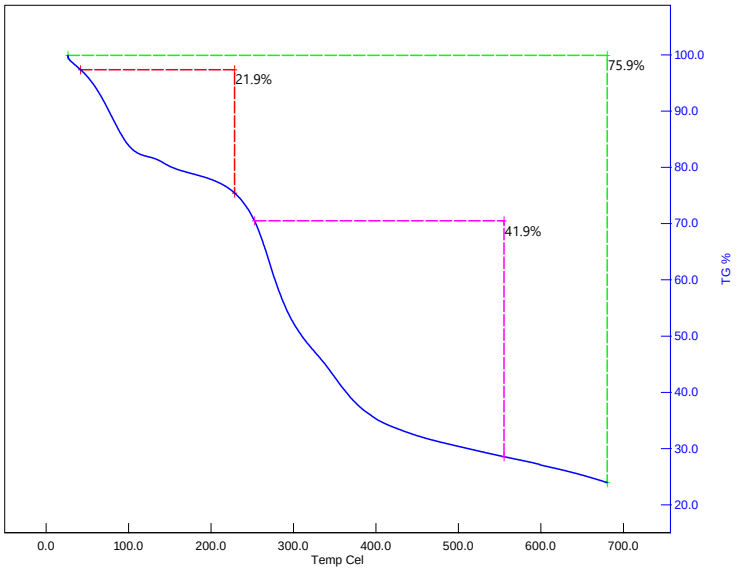

Figure 7. TGA graph of ZCP

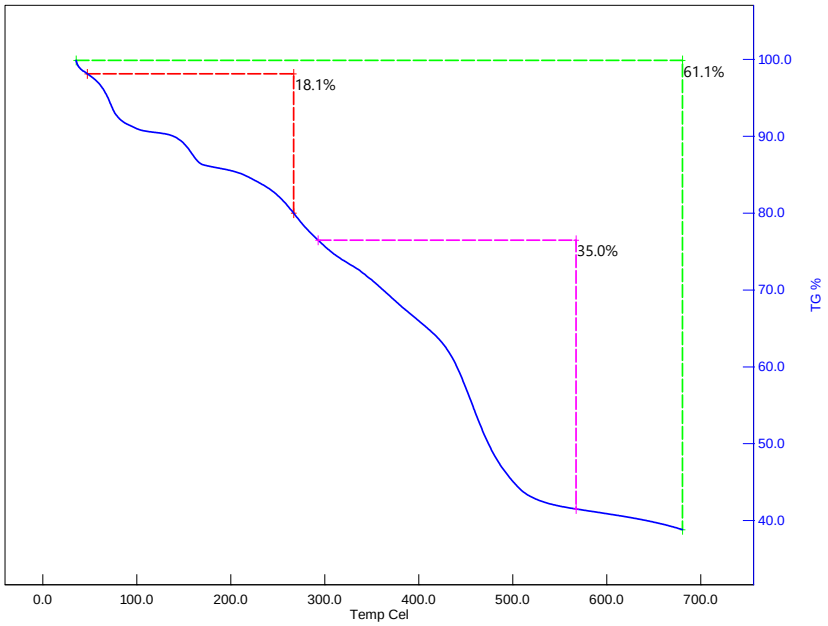

Figure 8. TGA graph of DCP

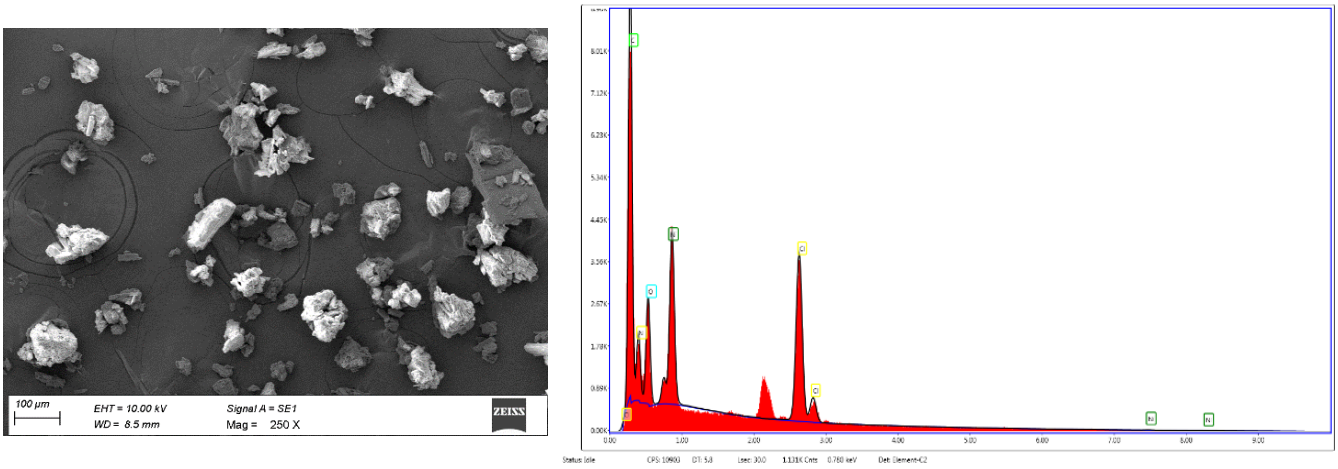

Figure 9. SEM and EDX images of NCP

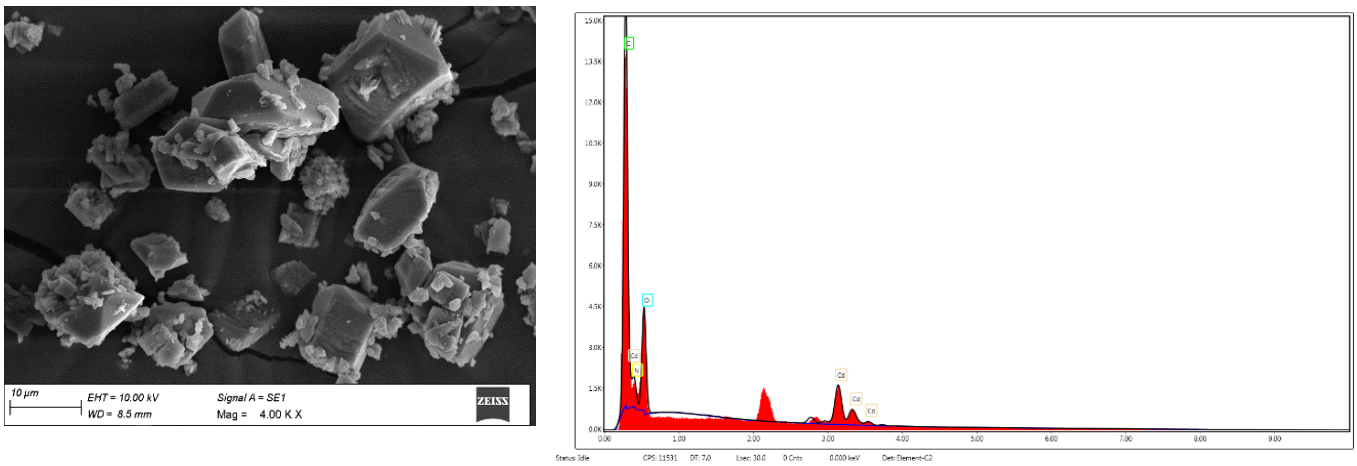

Figure 10. SEM and EDX images of DCP

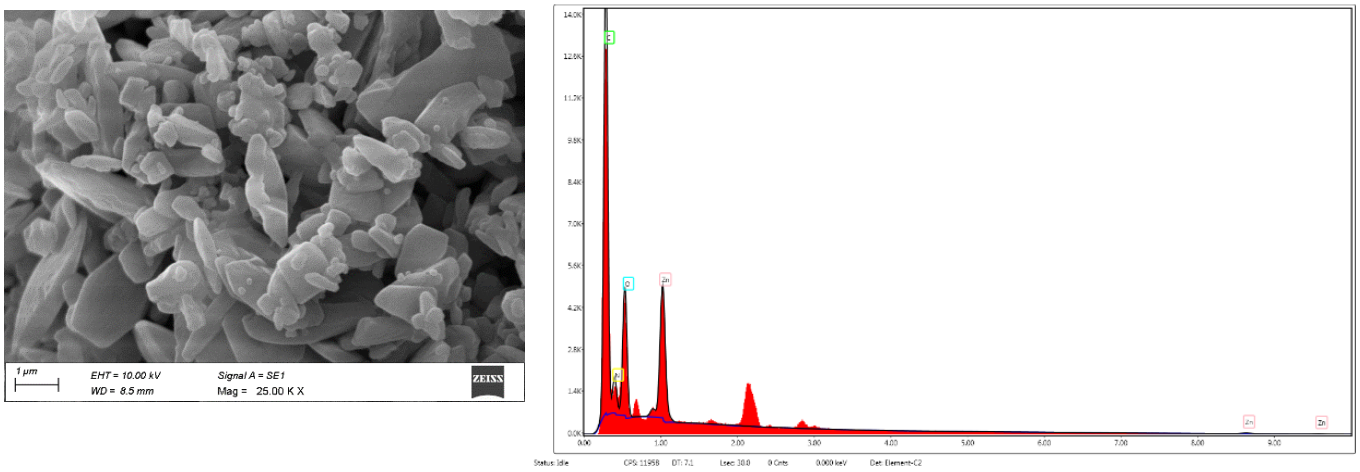

Figure 11. SEM and EDX images of ZCP

The cadmium complex displayed agglomerated, irregularly shaped particles, indicating strong interparticle interactions. The zinc complex exhibited a crystalline morphology with well-faceted particles, suggesting ordered molecular packing within the solid-state structure. The observed variations in surface morphology correlate well with the coordination environment of the metal centres and their interaction with the organic ligands [24-26]. The EDAX data depicted are also in accordance with the predicted structure.

4. Conclusion

The successful synthesis and detailed analysis of transition metal complexes with CHDA and Phen ligands revealed significant insights into their structural coordination, thermal behavior, and morphology. The distinct coordination patterns confirmed through FT-IR and PXRD analyses, along with the thermal stability profiles from TGA, highlight the robustness of these complexes. SEM imaging further supported the influence of metal centers on surface architecture. These findings not only validate the role of CHDA and Phen as effective ligands for constructing stable metal-organic frameworks but also pave the way for their application in areas requiring thermally resilient and structurally diverse materials. Future studies can expand upon this work by exploring their functional performance in catalytic or sensing environments.

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