# Crystal Structure, Vibrational Spectroscopic Characterization

## and Bond Valence Sum (BVS) Analysis of a Copper(II)-$H_2$EDTA-Based Coordination Polymer $[Cu(H_2EDTA)]_n \cdot H_2O$

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## Abstract

***A new copper (II) coordination compound, [Cu (H2EDTA)]·H2O, was synthesized via slow evaporation from a mixed aqueous-DMF medium under controlled pH conditions. Single-crystal X-ray diffraction analysis revealed a six-coordinate copper (II) center surrounded by four oxygen and two nitrogen donor atoms from a partially deprotonated H2EDTA ligand, forming a distorted octahedral geometry. The crystallographic results confirmed the chelation of both carboxylate oxygen and amine nitrogen atoms to the Cu (II) ion.***

***Fourier-transform infrared (FT-IR) and Raman spectroscopic studies supported the coordination mode by identifying characteristic asymmetric and symmetric stretching vibrations of coordinated carboxylate groups. The observed Δv (v_asym-v_sym) values indicate predominantly bidentate coordination of the carboxylate moieties. Metal-ligand vibrations in the low-frequency region further confirmed Cu-O and Cu-N bond formation.***

***Bond Valence Sum (BVS) analysis yielded a value of 2.07, consistent with the +2 oxidation state of copper and supporting the structural data obtained from single-crystal analysis. Minor deviation from the ideal value reflects slight geometric distortion within the coordination sphere. Thermal behavior examined by TG-DTA demonstrated the presence of lattice water molecules and indicated stepwise decomposition of the coordinated framework.***

***The combined crystallographic and spectroscopic investigations provide a comprehensive understanding of the coordination environment and bonding characteristics of the Cu(II)- H2EDTA system, contributing to the structural chemistry of EDTA-based copper complexes.***



## Key words:

***Copper(II) complex; H2EDTA ligand; Single-crystal X-ray diffraction; FT-IR spectroscopy; Raman spectroscopy; Bond valence sum analysis; Coordination geometry; Chelation***


## Аннотация.

***Новое координационное соединение меди (II) [Cu (H2EDTA) ]·H2O было синтезировано путем медленного испарения из смешанной водно-ДМФ среды в контролируемых условиях pH. Монокристаллический рентгеноструктурный анализ выявил шестикоординатный центр меди (II), окруженный четырьмя атомами кислорода и двумя атомами-донорами азота из частично депротонированного лиганда H2EDTA, образующий искаженную октаэдрическую геометрию. Кристаллографические результаты подтвердили хелацию как карбоксилатного кислорода, так и аминного азота к иону Cu (II).***

***Фурье-трансформные инфракрасные (ФТ-ИК) и комбинационные спектроскопические исследования подтвердили координационный режим, выявив характерные асимметричные и симметричные удлиненные колебания координированных карбоксилатных групп. Наблюдаемые значения Δν (ν_asym-ν_sym) указывают на преимущественно бидентатную координацию карбоксилатных частей. Вибрации металл-лиганда в низкочастотной области дополнительно подтвердили образование связей Cu-O и Cu-N.***

***Анализ суммы валентностей связей (BVS) дал значение 2,07, соответствующее +2 степени окисления меди и подтверждающее структурные данные, полученные в результате монокристаллического анализа. Незначительное отклонение от идеального значения отражает незначительное геометрическое искажение в координационной сфере. Термическое поведение, исследованное TG-DTA, продемонстрировало наличие решетчатых молекул воды и показало поэтапное расщепление координированной структуры.***

***Комбинированные кристаллографические и спектроскопические исследования дают полное представление о координационной среде и характеристиках связи системы Cu (II)-H2EDTA, что способствует структурной химии комплексов меди на основе EDTA.***



## Ключевые слова:

***Комплекс меди (II); H2EDTA лиганд; Монокристаллическая рентгенодифракция; ИК-спектроскопия; Рамановская спектроскопия; Анализ суммы валентности облигаций; Геометрия координат; Хелация***


## Introduction

In recent years, there has been a significant increase in the synthesis of new coordination polymers[1]. Coordination polymers (CPs) are molecular structures formed through the regular bonding of metal centres and organic ligands, and their diverse properties and applications are being extensively studied. These compounds are distinguished by their high thermal and chemical stability, structural adaptability, and the ability to selectively incorporate functional groups[23]. As a result, they show great potential for wide-ranging applications in various fields such as gas storage and separation, catalysis, optoelectronics, magnetic materials, drug delivery systems,

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and sensor technologies[4,5,6]. At present, luminescent coordination polymers are attracting considerable scientific interest. The main reason is their high sensitivity in detecting heavy metal ions, particularly $Fe^{3+}$ ions[7]. Unlike conventional luminescent sensors, such coordination polymers offer advantages due to their structural flexibility, high porosity, and the possibility of fine-tuning their architecture through the careful selection of building blocks, which enables selective detection of various hazardous compounds[8]. Recent studies have also given special attention to the biological activity of coordination polymers and their prospects as environmentally friendly materials[9]. Porous coordination polymers (CP) and metal-organic frameworks (MOF) are of particular scientific importance as architectures formed at the molecular level[10,11].

1D coordination polymers possess a linear metal-ligand chain structure and serve as an important platform formolecular pathways (molecular wires), selective ionic conductivity, and host-guest dynamics[12]. 2D coordination polymers have a layered structure and are preferred for catalysis, membrane technology, and sensing applications due to their high surface area, electron conjugation, and compatible flexural arrangement[13]. 3D systems are widely used in areas such as gas storage, separation, and drug delivery owing to the high porosity, stability, and extensive functional capabilities of porous MOF[14]. Unlike ordinary crystals, 1D-3D coordination polymers have the ability to pre-design their structure based on reticular chemistry principles and tailor their properties by adding functional groups[15,16].

## Synthesis

HEDTA (0.556 g, 2 mM) was completely dissolved in a mixture of distilled water (20 mL) and dimethylformamide (DMF, 10 mL). Separately, $Cu(NO_3)_2.3H_2O$ (0.375 g, 2 mM) was dissolved in distilled water (30 mL), and the resulting solution was added dropwise to the ligand solution under continuous stirring. The reaction mixture was stirred magnetically for 1 h. A 0.05 M sodium hydroxide solution was then added dropwise until the pH of the solution reached 7. The mixture was subsequently sonicated in an ultrasonic cleaner (100 W, 40 kHz) for 30 min and sterilized. The resulting solution was filtered through standard filter paper to obtain a clear blue filtrate. For crystal growth, the filtrate was maintained in a thermostat at 55-60°C to allow slow evaporation over 43-45 days. After this period, well-defined blue crystals were obtained, with a yield of 78%. Anal. calcd. for $[Cu(H_2EDTA)].H_2O$: $C_{10}H_{18}CuN_2O_8$: C, 33.6%; H, 5.1%; O, 35.8%; N, 7.8%; Found: C, 33.2 %; H, 4.9%; O, 36.1%; N, 7.7 %.

## Characterization techniques

Elemental composition was determined by the Dumas combustion method using an ELEMENTARY UNICUBE® IZI analyzer. Vibrational features were examined through FT-IR spectroscopy (Bruker FT-IR) and Raman spectroscopy in the 100–3500 $cm^{-1}$ region with a Renishaw inVia instrument operating in FT-Raman mode. Morphological characteristics and elemental mapping were studied by SEM (JSM IT-200 LV) equipped with EDS. Thermal stability was assessed by TG-DTA on a Shimadzu DTG-60 under argon. Single-crystal X-ray diffraction data were collected on an Oxford Diffraction Xcalibur-R CCD diffractometer, and structural refinement was carried out using SHELXS-97 and SHELXL-97. [18].

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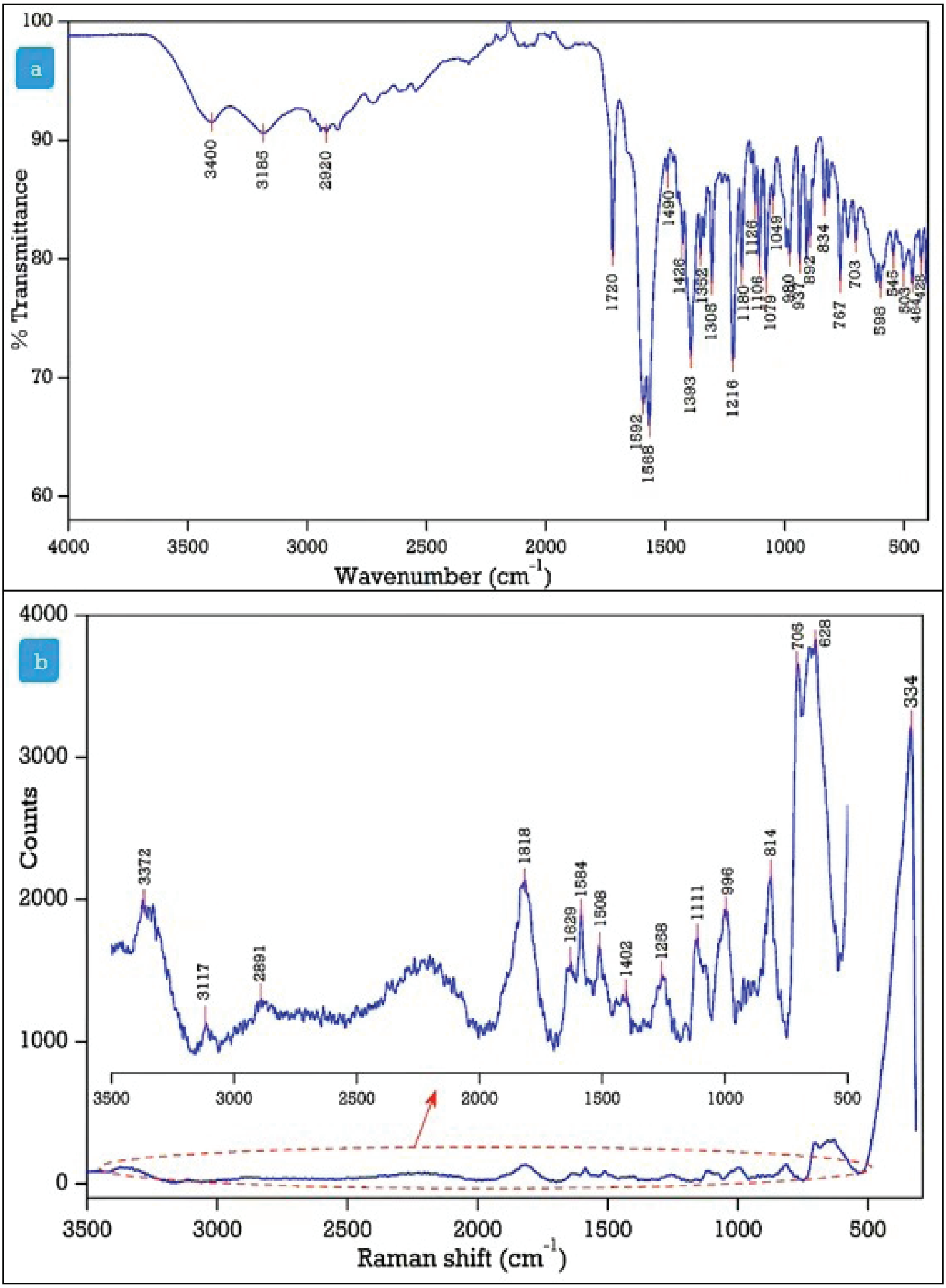


Fig. 1 (a) FT-IR spectrum and (b) Raman spectrum of [Cu(H2EDTA)].H2O.

## Results and discussion

## Fourier transform infrared and Raman spectral analysis

The FT-IR spectrum of $[Cu(H_2EDTA)].H_2O$ (Fig. 1(a)) displays characteristic vibrational bands that confirm coordination of the partially deprotonated EDTA ligand to the Cu(II) center. A broad band around 3400 $cm^{-1}$ is assigned to O-H stretching vibrations of lattice water molecules. The absorption at 3185 $cm^{-1}$ cans be attributed to hydrogen-bonded O-H stretching of residual carboxylic groups, while the band at 2920 $cm^{-1}$ corresponds to aliphatic C-H stretching vibrations. A sharp band at 1720 $cm^{-1}$ indicates the presence of non-coordinated protonated carboxylic groups (C=O). The strong bands at 1592 and 1393 $cm^{-1}$ are attributed to the asymmetric and symmetric stretching modes of coordinated carboxylate groups ($-COO^-$). The frequency difference between these two absorptions suggests bidentate coordination of the carboxylate groups to the copper center. Additional features at 1426, 1352, 1216, and 1106 $cm^{-1}$ are assigned to C-N stretching and C-C skeletal vibrations within the ethylenediamine backbone. Strong absorptions in the region 1049-980 $cm^{-1}$ arise from C-N stretching coupled with C-H deformation modes. In the lower wavenumber region, peaks at 767, 703, 545, and 464 $cm^{-1}$ correspond to metal-ligand vibrations, particularly Cu-O and Cu-N stretching, confirming the chelation of EDTA donor atoms to the Cu(II) center.

The Raman spectrum of $[Cu(H_2EDTA)].H_2O$ (Fig. 1(b)) further supports the vibrational assignments obtained from FT-IR. A broad band at 3372 $cm^{-1}$ is due to O-H stretching of lattice water molecules, while weak features at 3117 and 2891 $cm^{-1}$ are attributed to hydrogen-bonded carboxylic O-H and aliphatic C-H stretching modes, respectively. Intense Raman bands observed at 1818, 1629, and 1584 $cm^{-1}$ are assigned to C=O stretching and asymmetric $COO^-$ stretching vibrations, confirming carboxylate coordination. Additional peaks at 1508, 1402, and 1258 $cm^{-1}$ correspond to C-N stretching and C-H bending vibrations of the ligand framework[17].

Well-defined signals at 1111 and 996 $cm^{-1}$ are associated with skeletal vibrations of the ethylenediamine backbone coupled with carboxylate deformation modes. At lower wavenumbers, strong peaks at 814, 705, 628, and 334 $cm^{-1}$ are attributed to metal–ligand vibrations, specifically Cu–O and Cu–N stretching modes, validating the coordination of both oxygen and nitrogen donors from EDTA to the Cu(II) center.

## 3.2 Bond Valence Sum Analysis

Bond Valence Sum (BVS) analysis is a standard approach for evaluating the oxidation state of a metal center by correlating it with the lengths of its metal–ligand bonds[18,19]. In the present work, the copper atom is coordinated by four oxygen donors and two nitrogen donors, forming a heterogeneous coordination sphere with bonds of different strengths and lengths. These variations are reflected in the calculated BVS value, which provides insight into the overall bonding environment[20,21].

The BVS for copper was determined using the following relationship:

$$V = \sum v_{ij} = \sum exp\left(\frac{R_0 - R_{ij}}{b}\right)$$

here V is the total bond valence sum, $v_{ij}$ is the bond valence for each Cu–X interaction (X = O, N), $R_{ij}$ is the experimentally measured bond distance, and $R_0$ is the bond parameter characteristic of the Cu–X bond type. The parameter values employed were $R_0$=1.679 Å for Cu–O and $R_0$=1.7510 Å for Cu–N, with the empirical constant b taken as 0.36 for Cu–O and 0.37 for Cu–N. Summing the individual contributions from all Cu–O and Cu–N bonds yields a BVS value of 2.07 (Table 1), consistent with a +2 oxidation state for copper, which is the most common state for this metal in coordination compounds. The slight departure from the ideal integer value can be attributed to small distortions in the geometry, possibly caused by steric hindrance or electronic effects influencing bond distances. This outcome confirms that the copper center is predominantly in the divalent state, in agreement with the crystallographic results, and suggests a bonding framework with significant covalent character and minor ionic contributions[22].

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**Table 1.** Bond valance sum calculations of $[Cu(H_2EDTA)].H_2O$

| Co. No. | Bond distances (Å) | | | | | | $V = \Sigma v_{ij}$ |
|---|---|---|---|---|---|---|---|
| 6 | Cu(1)-N(1) | Cu(1)-N(2) | Cu(1)-O(1) | Cu(1)-O(2) | Cu(1)-O(3) | Cu(1)-O(4) | 2.07* |
| | 2.089(3) | 2.435(3) | 1.972(3) | 1.948(3) | 2.367(3) | 1.966(3) | |

## Conclusion

In summary, a copper(II)-$H_2EDTA$ coordination polymer, $[Cu(H_2EDTA)]_n{\cdot}H_2O$, was successfully synthesized under controlled pH conditions and structurally characterized by single-crystal X-ray diffraction. The crystallographic analysis revealed a hexacoordinated Cu(II) center involving both nitrogen and oxygen donor atoms from the partially deprotonated $H_2EDTA$ ligand, resulting in a distorted octahedral coordination environment. Vibrational spectroscopic investigations[23] (FT-IR and Raman) confirmed the coordination of carboxylate and amine functionalities to the metal center, with $\Delta\nu$ values consistent with the coordination mode observed crystallographically. Metal-ligand interactions were further supported by characteristic low-frequency Cu-O and Cu-N vibrational bands. Bond Valence Sum (BVS) analysis yielded a value of 2.07, verifying the +2 oxidation state of copper and supporting the reliability of the structural model. Thermal analysis demonstrated the presence of lattice water molecules and indicated a stepwise decomposition pattern, reflecting moderate thermal stability of the coordination framework.

Overall, the combined crystallographic, spectroscopic, and valence analyses provide a detailed understanding of the coordination behavior of the $H_2EDTA$ ligand toward Cu(II). The obtained results contribute to the structural chemistry of EDTA-based copper coordination polymers and may serve as a scientific basis for future development of functional materials, particularly in catalysis, sensing systems, and biologically active complexes.

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