Research Square

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Synthesis, Structure, and Properties of a Polymer Complex of Copper(II) With Maleic Acid

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Research Article

Keywords: copper(II) complex, maleic acid, copper acetate, coordination chemistry, IR spectroscopy, X-ray crystallography

Posted Date: July 25th, 2025

DOI: https://doi.org/10.21203/rs.3.rs-7140677/v1

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Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Transition Metal Chemistry on December 4th, 2025. See the published version at https://doi.org/10.1007/s11243-025-00705-y.

Abstract

A new polymeric copper(II) complex with maleic acid, used as a dicarboxylate ligand, were synthesized $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$. The resulting complex was characterized by elemental analysis, infrared and UV–visible spectroscopy, and X-ray crystallography. Spectroscopic data indicate that the maleinate ion coordinates in a chelating bidentate mode, creating a distorted octahedral coordination environment around Cu(II). X-ray crystallography confirmed the formulation $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$ and revealed that the central Cu^{2+} ion is in a distorted octahedral geometry. The maleinate ion acts as a bidentate chelator, coordinating through two carboxylate oxygens to form a stable five-membered ring. Two water molecules complete the coordination sphere of the Cu center, yielding a $[Cu(C_4H_2O_4)(H_2O)_2]^-$ unit This study extends our understanding of the coordination behavior of π-conjugated dicarboxylic acids with transition-metal ions. Molecular docking studies demonstrated that the polymeric copper(II)–maleic acid complex exhibited strong binding affinity toward B-DNA (1BNA), with a binding energy of − 10.2 kcal/mol and multiple stable hydrogen bond interactions.

1. Introduction

Coordination compounds of copper(II) are of significant interest due to their structural diversity, catalytic activity, photochemical properties, and biological relevance [1–3]. Cu(II) complexes play important roles in fields such as the development of functional materials, catalyst synthesis, and the creation of antibacterial and anticancer agents. Special attention is given to complexes featuring organic acids with multiple coordination sites, particularly dicarboxylic acids.

Maleic acid (cisbutenedioic acid) is a promising dicarboxylate ligand containing two closely spaced carboxyl groups capable of forming stable chelate complexes with transition metals. Due to its *cis* configuration, maleic acid exhibits distinct coordination behavior compared to its *trans* isomer, fumaric acid [4, 5]. These structural characteristics make maleic acid particularly interesting for the design of novel coordination polymers.

The biological activity of the copper(II)-maleinate complex arises from both the known antibacterial and antifungal properties of Cu^{2+} ions and the potential metabolic activity of the maleinate anion, a derivative of maleic acid. Copper(II) acts as an essential cofactor in numerous biological processes, including redox catalysis, electron transport, and the detoxification of reactive oxygen species. Cu(II) complexes are capable of interacting with bacterial proteins, enzymes, and nucleic acids, thereby disrupting their biological functions. Coordination with maleinate helps stabilize the copper ion in a biologically active form and may enhance its permeability across cell membranes[6–7].

Although extensive studies have been conducted on Cu complexes with other dicarboxylates such as fumarate, tartrate, and oxalate [8–10], copper maleinate complexes remain underexplored. Available data are fragmentary and mainly concern monomeric complexes or poorly defined coordination environments [11, 12]. In our previous work [13], we obtained a polymeric, polynuclear heterometallic

maleinate complex of Mn(II) and Co(II), $[Co_xMn_{1-x}(OOCCH = CHCOO).(H_2O)_2]_n$ by reacting mononuclear bismaleinate tetratedrate cobalt with manganese acetate.

The present study aims to synthesize a novel polynuclear Cu(II) maleinate complex under alkaline conditions and to comprehensively characterize its structure $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$. Particular focus is placed on elucidating the coordination environment of the Cu ion and the spatial organization of the polymeric matrix. Characterization methods include IR and UV–visible spectroscopy, elemental analysis, thermogravimetric analysis, and X-ray single crystal diffraction, providing an integrated picture of the complex's structure. The results expand our understanding of πconjugated dicarboxylate coordination possibilities and their potential in the development of new transition-metal–based materials.

2. Experimental

2.1. General and spectroscopic measurements

All chemicals were used as received without further purification. Copper(II) chloride, maleic acid ($C_4H_4O_4$), and sodium hydroxide (NaOH) were of analytical grade (SigmaAldrich). FT-IR spectra of samples in vaseline oil were recorded in the range 4000–400 cm^{-1} using a Nicolet IS10 spectrophotometer. Electronic absorption spectra were obtained with a SPECORD 50 spectrophotometer in aqueous solution over the UV range (200–400 nm) and visible region (400–1100 nm). Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449 F3 derivateograph under an inert atmosphere. Elemental analysis was carried out at the Tubitak Analytical Laboratory (Ankara) using a LECO CHNS 932 analyzer.

2.2. Synthesis of $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$

Copper(II) chloride (0.199 g, 1 mmol) was dissolved in 20 mL of water. To this solution, maleic acid (0.232 g, 2 mmol) was added and stirred at ambient temperature. The pH was adjusted to 6.0 using a NaOH solution. The resulting mixture was left undisturbed for 4–5 days, during which blue crystals (melting point > 250°C) formed. The crystals were filtered and dried in vacuo at room temperature, yielding 0.75 g (80%).For $C_8H_8CuNa_2O_{10}$: calculated: C 25.66%, H 2.13%, Cu 17.11%, Na 12.30%; found: C 25.70%, H 2.10%, Cu 17.18%, Na 12.25%.IR (ν, cm^{-1}): $\nu_{as}(COO^-)$ 1500, 1590; $\nu_s(COO^-)$ 1400, 1420.

2.3. Crystal Structure Determination

Single-crystal X-ray diffraction was performed on a Bruker APEX-3 CCD diffractometer using monochromatized Mo Kα radiation (λ = 0.71073 Å) at 293 K [14]. The empirical formula is $C_8H_8CuNa_2O_{10}$; (FW = 373.63). Unit cell parameters: a = 9.119(2) Å, b = 3.6871(8) Å, c = 17.913(4) Å, β = 92.557(8)°, V = 601.7(2) $Å^3$. Structure solution was done using SHELXS [15], and refinement using SHELXL [16] via least-squares on F^2. The refinement converged with R = 0.037, wR = 0.073, S = 1.11 for 1241 reflections with I > 2σ(I). The maximum and minimum residual electron densities are + 0.38 and − 0.39 e·$Å^{-3}$, indicating a high-quality model. CIF preparation and structural visualization were completed with WinGX and

Mercury. All hydrogen atoms were placed using constraints. The complex exhibits good crystallographic symmetry and stability, making it suitable for diverse chemical investigations. Crystallographic data and refinement details for $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$ are summarized in Table 1.

Table 1
Crystallographic data and refinement details for $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$

Empirical formula	**$C_8H_8CuNa_2O_{10}$**
Formula weight	373.66
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.119 (2)
b/Å	3.6871 (8)
c/Å	17.913 (4)
β/°	92.557 (8)
Volume/$Å^3$	601.7 (2)
Z	2
$\rho_{calc}g/cm^3$	2.063
μ/mm^{-1}	1.94
F(000)	374
Crystal size/mm^3	0.05 × 0.03 × 0.02
Radiation	Mo Kα, λ = 0.71073
θ range (°)	2.3–28.3
Reflections collected	3835
Independent reflections	1510
R[F2 > 2σ(F2)]	0.037
wR(*F*2)	0.073
S	1.11

2.4. *In Silico* Studies

Molecular docking was employed to estimate the binding affinity between the ligand and the DNA target, as well as to identify possible binding sites. The simulations were conducted using AutoDock Vina. The crystal structure of B-DNA (PDB ID: 1BNA) was retrieved from the Protein Data Bank (https://www.rcsb.org/). Prior to docking, the DNA structure was prepared by eliminating water molecules and non-standard residues to obtain a clean receptor model. Polar hydrogen atoms and Kollman partial charges were subsequently added using AutoDock Tools 1.5.6 [17]. Both the receptor and ligand structures were converted into the PDBQT file format via AutoDock Tools, ensuring compatibility with AutoDockVina. A grid box encompassing the binding region was defined in such a way that it allowed free rotation and flexible placement of the ligand within the DNA groove. The coordinates and dimensions of the grid box were recorded and incorporated into the configuration file required for docking. AutoDock Vina utilizes a scoring function based on a Lamarckian genetic algorithm to predict the optimal binding poses and their associated free binding energies. Among the multiple docking conformations generated, those with the lowest binding energy were selected for further analysis. Discovery Studio Visualizer 2021 [18] was employed to analyze and visualize the molecular interactions between the ligand and DNA target.

3. Results and Discussion

Previously, we reported that the reaction between bis(hydrogen maleinate)tetrahydrate Co(II) and Mn(II) acetate yielded a three-dimensional coordination polymer, $[Co_xMn_{1-x}(OOCCH = CHCOO).(H_2O)_2]_n$ containing both Co(II) and Mn(II) ions[13]. In the present work, we demonstrate that under alkaline conditions, maleic acid reacts with copper(II) chloride to form a polymeric heterometallic complex, $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$.

Elemental analysis confirmed the composition $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$, indicating a 1:1 complex between Cu^{2+} and the maleinate anion, with two coordinated water molecules.

The IR spectrum shows asymmetric and symmetric carboxylate $v_{as}(COO^-)/v_s(COO^-)$ stretching bands at 1592 and 1410 cm^{-1}, respectively. The frequency difference ($\Delta v \approx 180$ cm^{-1}) is characteristic of bidentate chelation of carboxylate groups, typical for complexes of dicarboxylic acids[19–20] (see Fig. 1).

The IR spectrum thus confirms the chelating bidentate coordination mode of the dicarboxylate ligand.

In the UV region, bands corresponding to ligand-centered intramolecular transitions are observed, while in the visible region, a broad absorption band is associated with d–d transitions of Cu(II), supporting the formation of an octahedral coordination environment around the copper ion.

In the electronic spectrum of the polymeric heterometallic complex in a methanolic solution, a broad band appears around 740 nm, corresponding to the *d–d* transitions of the Cu^{2+} ion in a distorted octahedral environment (Fig. 2). This feature is attributed to the Jahn–Teller effect, which is characteristic of Cu(II) complexes[21, 22]. .In the ultraviolet region, a ligand-centered absorption band is

observed at approximately 238 nm, attributed to π→π* transitions within the conjugated system involving the carboxylate groups[23] .

The EPR spectrum of the Cu(II)–maleinate complex, recorded at room temperature in the solid state, exhibits an anisotropic signal characteristic of Cu^{2+} ions with a d^9 electronic configuration[24–25].The spectrum includes a pronounced absorption maximum at $g_{\parallel} \approx 2.22$ and a minimum at $g_{\perp} \approx 2.07$, indicating axial symmetry of the copper environment in the complex. These g-factor values are consistent with a square-pyramidal or distorted octahedral coordination, where the z-axis is the elongation direction(Fig. 3).

The presence of a single clear multiplet without resolved hyperfine splitting suggests weak hyperfine interaction between the unpaired electron of copper and the $^{63/65}Cu$ nucleus (I = 3/2), which can be attributed to partial signal averaging or broad line widths. This also implies a relatively symmetric electron density distribution around the copper atom and weak spin density on the ligands .

These EPR spectral parameters align well with literature data for Cu(II) complexes with O,Odonor ligands like maleinate anions coordinated in the equatorial plane .

3.1. Structural Features

Considering the spectral data and analogies with known structures, it is proposed that the maleinate ligand coordinates via both carboxyl groups, thus forming a five-membered chelate ring[12]. Two additional water molecules complete the coordination sphere of the copper(II) ion.

X-ray crystallography confirmed the formulation $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$ and revealed that the central Cu^{2+} ion is in a distorted octahedral geometry. The maleinate ion acts as a bidentate chelator, coordinating through two carboxylate oxygens to form a stable five-membered ring. Two water molecules complete the coordination sphere of the Cu center, yielding a $[Cu(C_4H_2O_4)(H_2O)_2]^-$ unit (see Fig. 4).

The formation of a five-membered chelate ring by carboxylate ligands is well-documented in copper(II) complexes, often resulting in distorted octahedral or square-pyramidal geometries depending on axial ligation .

Sodium cations (Na^+) do not participate in the first coordination sphere of copper but play a crucial role in stabilizing the crystalline packing. Each Na^+ ion is coordinated with several oxygen atoms: from the carboxyl groups of the maleinate and from water molecules. These interactions form a spatial hydrogen-bonded network that unites individual complexes into a three-dimensional structure.

A similar role of alkali metals in the crystalline structures of complex compounds of dicarboxylic acids is known from the literature [5], where they provide additional stability through ion-dipole interactions and hydrogen bonds.

According to X-ray crystallographic analysis, the compound $C_8H_8CuNa_2O_{10}$ crystallizes in the monoclinic system, space group $P2_1/n$, with two formula units per unit cell (Z = 2). The asymmetric part of the structure includes one copper(II) ion, two sodium ions, and an organic ligand coordinated through oxygen atoms.

The copper (Cu^{2+}) ion is located at the inversion center and has a planar square coordination geometry formed by two equivalent oxygen atoms from two carboxyl groups (O1 and O3, with centrosymmetric arrangement). The Cu1–O1 and Cu1–O3 bond lengths are 1.957(2) Å and 1.922(2) Å, respectively, with O–Cu–O angles close to 90° and 180°, which is characteristic of an ideal planar square environment(Table 2).

Table 2
Bond lengths [Å] and angles [°] for $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$

C1-O2	**1.234(3)**	**Na1-O5-H5**	**85.0**
C1-O1	1.281(3)	Na1^{i}-C4-O3-Cu1	-126.89(19)
C3-H3	0.9300	Na1^{i}-C4-O3-Na1^{ii}	87.44(10)
C4-O4	1.231(3)	O4-C4-O3-Na1^{i}	-22.4(2)
C4-O3	1.286(3)	C3-C4-O3-Na1^{i}	161.0(2)
C4-Na1	2.992(3)	O3-C4-O4-Na1	-116.8(3)
Na1-O4	2.336(2)	C3-C4-O4-Na1	59.9(5)
Na1—O5Φ	2.406(2)	Na1^{i}C4-O4-Na1	-141.5(4)
Na1-O1	2.800(2)	O3-C4-O4-Na1^{i}	-158.60(19)
Cu(1)-O3	1.9223(18)		
Cu(1)-O1	1.9573(18)		
O5-H5	0.8500		
O5-Na1-Na1	139.88(5)		
O3-Na1-Na1	131.09(5)		
O4-Na1-Na1	65.56(6)		
O4-Na1-O5	97.76(8)		
O4-Na1-O3	113.25(8)		
O4-Na1-O4	74.54(7)		
O5-Na1-O4	105.61(8)		
O5-Na1-Na1^{ii}	139.28(5)		

Symmetry codes: (i) − *x* + 1, −*y* + 1, −*z* + 1; (ii) *x*, *y* − 1, *z*; (iii) − *x* + 1, −*y*, −*z* + 1; (iv) *x* − 1, *y*, *z*; (v) *x*, *y* + 1, *z*; (vi) − *x* + 2, −*y*, −*z* + 1; (vii) *x* + 1, *y*, *z*.

Sodium ions exhibit a semi-coordinated environment involving oxygens from carboxyl groups and oxygen atoms of other neighboring molecules, forming an extended network of coordination interactions. The Na–O bond lengths range from 2.336(2) to 2.800(2) Å. Multiple interionic Na···Na distances around 3.69 Å are present, which is typical for polymeric sodium-containing complexes [26–27].

The organic ligand is nearly planar, facilitating effective coordination both to the copper ion and to sodium ions. Bond lengths in the carboxyl groups, such as C1–O1 = 1.281(3) Å and C1–O2 = 1.234(3) Å, indicate delocalization of electron density and resonance nature of the bonding.

Molecular packing is stabilized by a system of hydrogen bonds between carboxyl and hydroxyl groups, as well as involving coordinated water molecules, forming a three-dimensional supramolecular network.

Measurements were performed at room temperature (293 K) using Mo Kα radiation (λ = 0.71073 Å). The structure was refined by least-squares method on F^2, resulting in R = 0.037, wR = 0.073, and S = 1.11 for 1241 reflections with I > 2σ(I). Maximum and minimum residual electron densities are + 0.38 $eÅ^{-3}$ and − 0.39 $eÅ^{-3}$, respectively, indicating good model quality.

Molecular Docking Results

The molecular docking study between the polymeric copper(II) complex with maleic acid and the B-DNA dodecamer (PDB ID: 1BNA) revealed a favorable binding affinity, as evidenced by a docking score of −10.2 kcal/mol. The complex forms conventional hydrogen bonds with the DNA, indicating a strong and specific interaction profile (Table 3). Notably, hydrogen bonding occurs between the ligand and several guanine and cytosine bases, including interactions with the O2 atom of cytosine (DC21) and the O4' atom of guanine (DG24), as well as the hydrogen atoms of guanine bases DG2, DG4, and DG22. The hydrogen bond distances range from 2.10 to 2.89 Å, suggesting the formation of stable, directional interactions that are typically indicative of biologically meaningful binding. Several of these interactions occur within or near the minor groove of the DNA helix, implying a potential groove-binding mode of the complex. Additionally, the presence of an intramolecular hydrogen bond within the ligand suggests conformational stability, which may further enhance its DNA-binding capability. Altogether, these findings suggest that the polymeric copper(II) complex exhibits a strong affinity for B-DNA, likely contributing to biological activity through DNA recognition or modulation. The molecular docking between the polymeric copper(II) complex with maleic acid and DNA is given in Fig. 5a, the hydrogen bond interaction map is given in Fig. 5b, and the 2D view of the interactions is given in Fig. 5c.

Table 3
Summary of Molecular Docking Results: the polymeric copper(II) complex with maleic acid and DNA (PDB ID: 1BNA)

Distance	Category	Types	Interacting Residue on DNA	Hydrogen Donor/Acceptor Site
2,10122	Hydrogen Bond	Conventional Hydrogen Bond	DC21:O2	H-Acceptor
2,46584	Hydrogen Bond	Conventional Hydrogen Bond	DG24:O4'	H-Acceptor
2,60628	Hydrogen Bond	Conventional Hydrogen Bond	DG2:H21	H-Donor
2,78374	Hydrogen Bond	Conventional Hydrogen Bond	DG2:H22	H-Donor
2,88637	Hydrogen Bond	Conventional Hydrogen Bond	DG4:H21	H-Donor
2,71917	Hydrogen Bond	Conventional Hydrogen Bond	DG22:H21	H-Donor

4. Conclusion

A new copper(II) coordination polymer complex with a maleate ligand was synthesized and characterized based on copper chloride $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$. The study revealed that maleic acid coordinates to the copper ion in a bidentate manner, forming a stable chelate structure. X-ray crystallographic analysis confirmed that the structure is further stabilized by sodium ions, which participate in secondary coordination with carboxyl groups and water molecules. The resulting complex is of interest for further studies on coordination compounds with π-conjugated dicarboxylic acids and their potential applications in materials science, catalysis, and coordination polymerization. The docking analysis revealed that the complex formed conventional hydrogen bonds with nucleotide residues located primarily within the minor groove of the DNA duplex. Key interactions were observed between the ligand and guanine and cytosine bases, particularly involving residues DG2, DC21, and DG24. Hydrogen bond distances ranged from 2.10 Å to 2.89 Å, indicating strong and directional binding, likely contributing to the stability of the complex–DNA association. The overall binding energy of − 10.2 kcal/mol supports a high binding affinity, suggesting that the polymeric Cu(II) complex could potentially interfere with DNA function through groove binding or sequence-selective recognition.

Declarations

DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors

Acknowledgements

This work was carried out under the research program of the Ministry of Science and Education at the Institute of Catalysis and Inorganic Chemistry named after Academician M. Nagiev (State Registration No. 0115). The authors acknowledge to Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer. CCDC- 2465966 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Author contributions G.E. synthesized the ingredients. She participated in the discussion of the article. M.A. participated in the organization and discussion of the article. R.I. participated in the organization and discussion of the article. B.M. Participated in drawing infrared spectra. B.Y. He played a role in drawing electronic spectra. F.E.O . conducted molecular docking studies. O.Sh. Performed single-crystal X-ray diffraction analysis .M.B. played a role in drawing EPR spectra.

Competing interests The authors declare no competing interests.

Funding

No funding was received for conducting this study.

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Figures

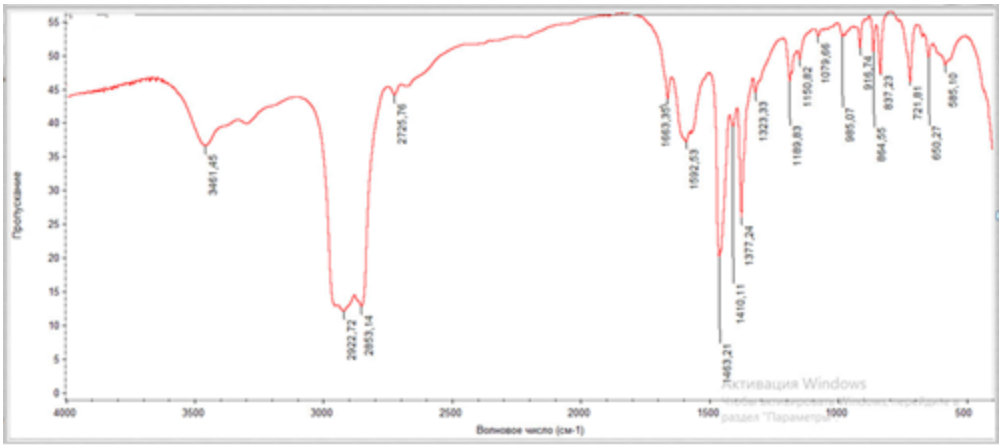


Figure 1

IR spectrum of heterometallic polymer complex $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$

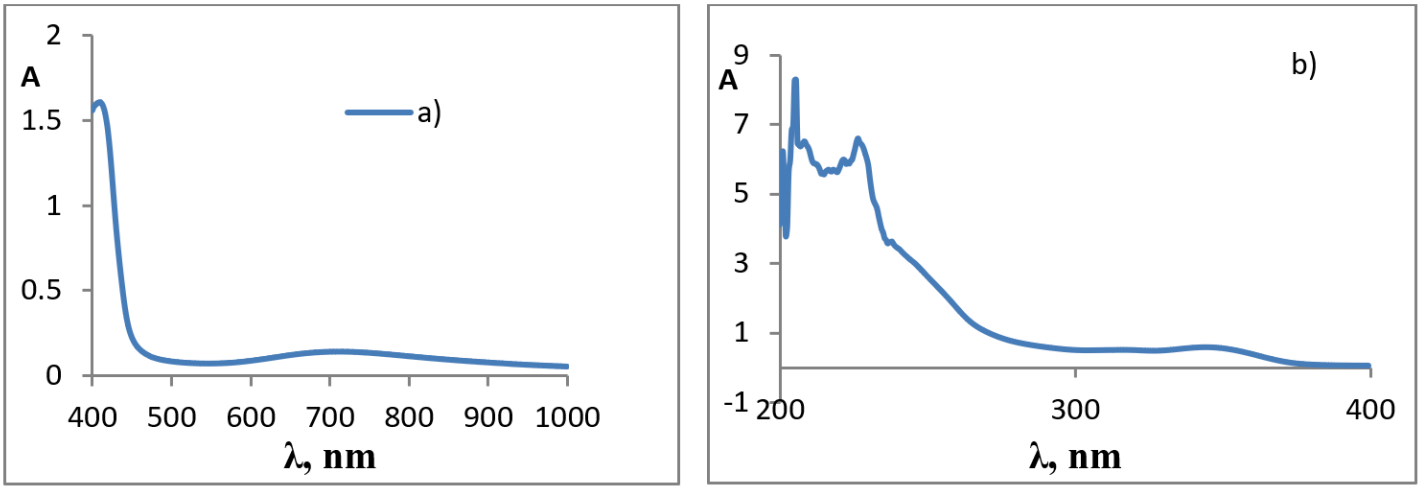


Figure 2

Electronic absorption spectra of the heterometallic polymeric complex $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$ in methanol: (a) visible region, (b) UV region.

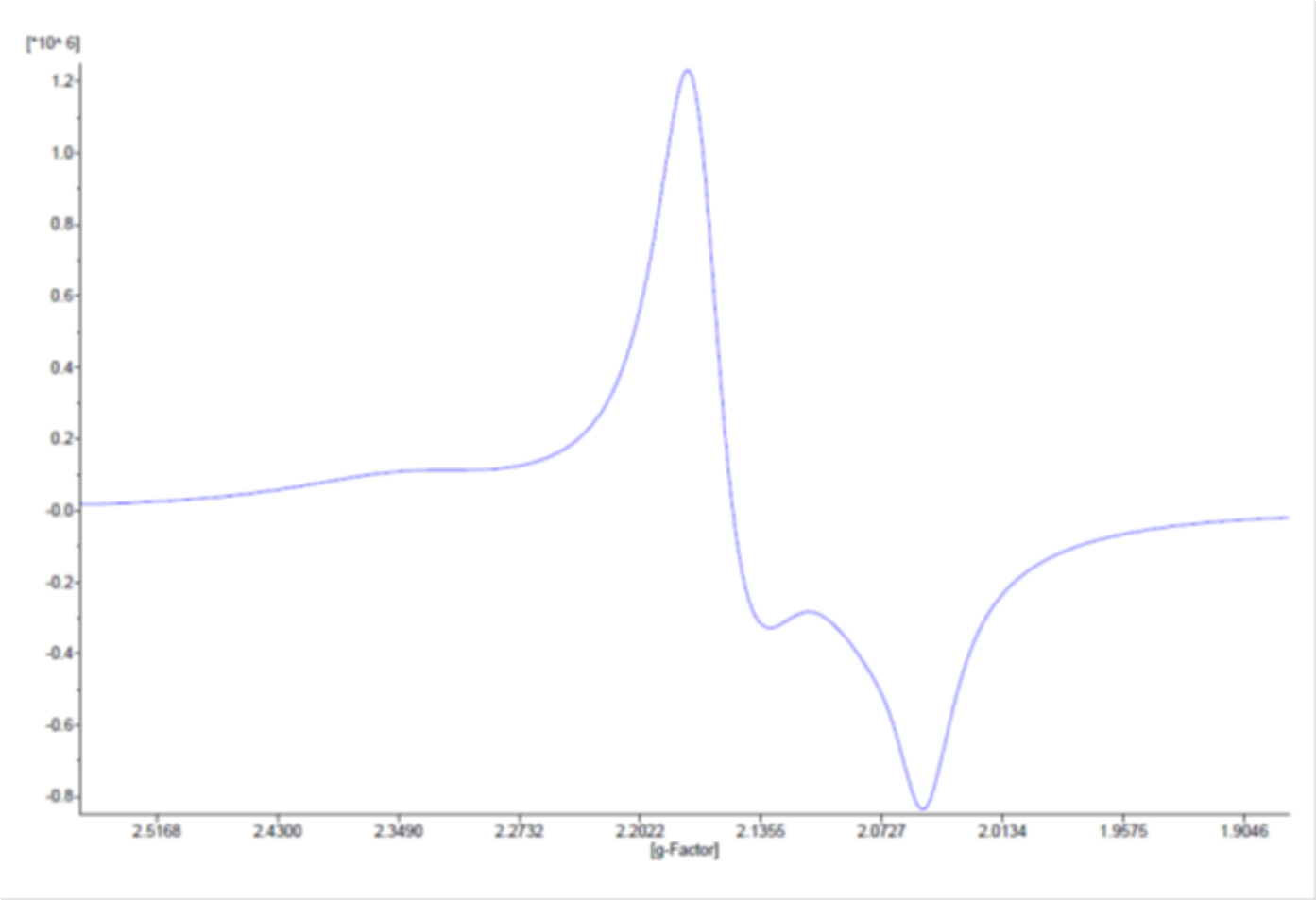


Figure 3

EPR Spectrum of the Heterometallic Polymer Complex $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$

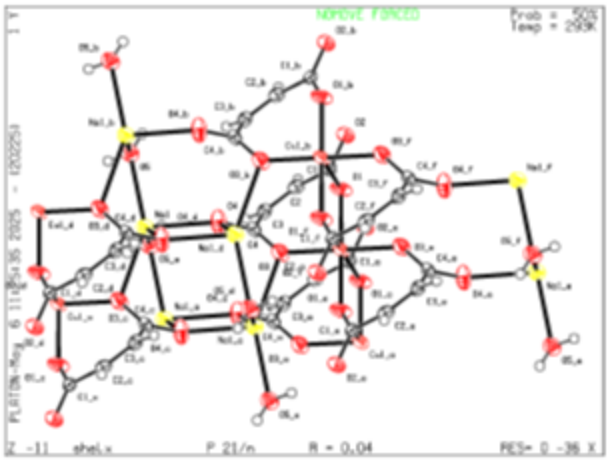


Figure 4

Molecular structure of the complex $Na_2[Cu(C_4H_2O_4)_2]\cdot xH_2O$

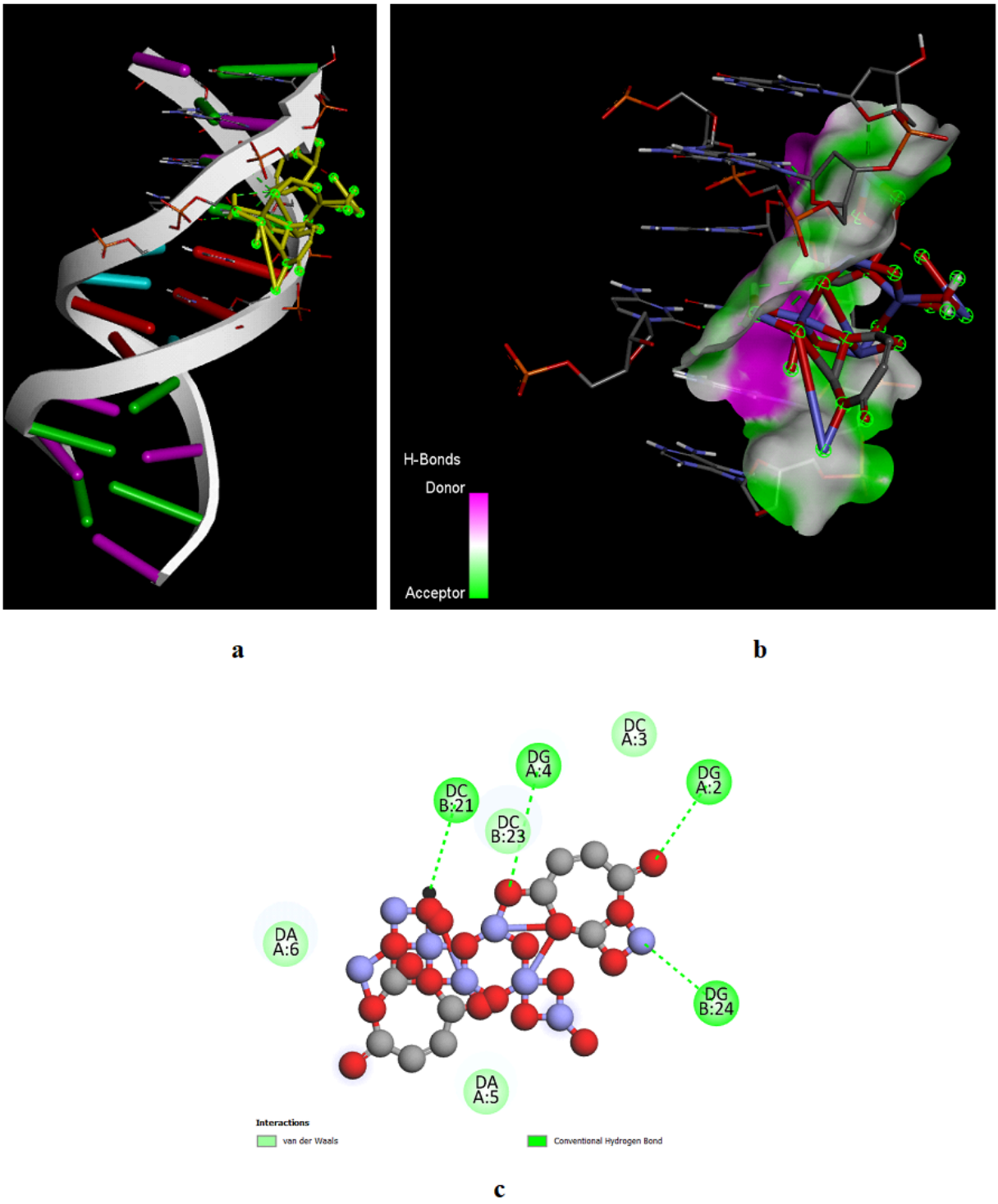


Figure 5

Molecular docking between the polymeric copper(II) complex with maleic acid and DNA (PDB ID: 1BNA) (a), Hydrogen bond interaction map between the polymeric copper(II) complex with maleic acid and DNA (PDB ID: 1BNA) (b), 2D view of the interactions between the polymeric copper(II) complex with maleic acid and DNA (PDB ID: 1BNA) (c)

Supplementary Files

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