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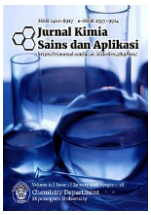

Computational Design and Evaluation of Formaldehyde-Free Modified Tannins for Enhanced Copper Ion Removal

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Abstract

Pollution from heavy metal ions, such as copper (Cu^{2+}), in textile wastewater poses a significant environmental challenge. Modified condensed tannins (TyD) show promise as coagulants for heavy metal removal, but current formaldehyde-based modification methods are concerning due to formaldehyde's carcinogenic nature. This in silico study aimed to optimize TyD design by replacing formaldehyde with safer alternatives: acetone (TyDA), ethyl methyl ketone (TyDE), and benzaldehyde (TyDB), and evaluating their interaction stability with Cu^{2+} ions. Using Density Functional Theory (DFT) with a B3LYP-D3/6-31G(d,p) basis set, this study performed calculations for interaction energy (Ei) and complex activity (HOMO-LUMO, affinity, electronegativity, energy gap). The results indicated that the TyDB-1 design exhibited the most optimal interaction energy with Cu^{2+} ions, showing an Ei value of -943.39 kJ.mol^{-1} for TyD...Cu^{2+} and -1,271.86 kJ.mol^{-1} for TyD...Cu^{2+}...TyD interactions. In the single TyD...The Cu^{2+} complex, TyDB-1, demonstrated superior stability, stronger binding, and better Cu^{2+} attraction compared to the formaldehyde-modified TyDF, despite a higher energy gap (1.354 eV vs. 1.090 eV). A higher HOMO-LUMO energy gap indicates reduced electronic reactivity and enhanced complex stability, signifying that TyDB-1 forms a more stable coordination with Cu^{2+} ions. However, in the presence of an additional TyD molecule (TyD...Cu^{2+}...TyD), TyDB-1, while showing strong bonds and good attraction, was found to be more reactive than TyDF. Overall, TyDB-1 represents a promising, safer alternative for Cu^{2+} coagulation, highlighting the utility of computational chemistry in designing high-performance coagulants.

1. Introduction

Modified condensed tannins (TyD) [1] are compounds with coagulation properties that have the ability to bind and remove heavy metals [2]. Extensive research has been conducted on the modification of condensed tannins for coagulation applications [2, 3, 4, 5, 6, 7, 8, 9, 10]. TyD is obtained by reacting condensed tannins with an iminium ion, which is formed from amines (primary or secondary) and aldehydes or ketones. The modification of TyD generally involves variation in amine groups and the use of formaldehyde. The use of formaldehyde is considered a harmful substance that is carcinogenic; therefore, it is essential to replace this compound with a safer alternative. This problem, which refers to the carcinogenic and environmentally hazardous nature of formaldehyde, was also noted by Ibrahim *et al.* [1] in their literature review.

One of the major sources of water pollution in Indonesia originates from untreated textile industry effluents, which are frequently discharged directly into rivers. These effluents contain various heavy metal ions, including copper (Cu). Copper contamination can be overcome using compounds with coagulation properties. A study conducted by Lugo *et al.* [2] demonstrated that a mixture of TyD from condensed tannins, ammonium chloride, and formaldehyde was capable of reducing Cu

ion levels by up to 60%. This result is smaller when compared to other heavy metals treated with TyD, such as Cr (87%) [2]. These findings indicate that the current TyD formulation is less effective for Cu ion removal, highlighting the need to optimize TyD design to enhance its coagulation performance toward Cu ions.

This study optimizes the design of TyD by replacing formaldehyde with a safer, more environmentally friendly, and economically viable carbonyl compound for iminium ion formation. Based on these criteria, acetone, ethyl methyl ketone, and benzaldehyde were selected as formaldehyde alternatives due to their lower toxicity, accessibility, and sufficient electrophilic reactivity to generate iminium intermediates under mild conditions. The modified TyD designs were evaluated against the TyD system reported by Lugo *et al.* [2] using in silico approaches to assess their stability in forming complexes with Cu^{2+} ions. In silico modeling enables explicit identification of molecular-level interactions within chemical systems [11, 12]. The method used to approach quantum mechanics is Density Functional Theory (DFT). DFT is capable of measuring the properties of atoms based on electron density [13], a technique commonly used in studying structures ranging from large to small [12]. To approximate the behavior of extended tannin chains, dimer models were used within the DFT framework to represent molecular interactions [14, 15]. The structure of the dimer represents an interaction with larger structures (such as trimers and oligomers) due to their symmetrically undifferentiated structure [16].

This study is significant in that it (1) advances understanding of tannin–Cu^{2+} interactions at the molecular level, (2) supports the rational design of efficient and environmentally friendly coagulants, and (3) demonstrates the utility of computational chemistry as a tool for green material development.

2. Experimental

The study was conducted remotely from Satya Wacana Christian University, Salatiga, utilizing a computer server located at Diponegoro University, Semarang. The calculations were performed using the B3LYP functional with Grimme's D3 dispersion correction. Although coagulation occurs in aqueous media, an implicit solvent model (such as CPM or CPCM) was not included in this stage to focus on the intrinsic electron behavior of the tannin Cu system without solvent perturbation. This gas-phase approach provides a reliable first approximation for evaluating intrinsic binding trends and relative stability among derivatives. Future work will incorporate implicit solvation (PCM water model) and explicit Cu–H_2O coordination to better represent realistic coagulation conditions in aqueous environments.

For the Cu^{2+} center, the LANL2DZ effective core potential (ECP) and its associated basis set were employed to account for relativistic core effects, while the 6-31G (d,p) basis set was applied to all nonmetal atoms (C, H, N, O). All structures were fully optimized without symmetry constraints, and frequency calculations confirmed that each geometry corresponds to a true minimum on the potential-energy surface. Interaction energies were corrected for basis-set superposition error (BSSE) using the counterpoise method.

The calculations were performed with the Linux Operating system. Calculations were carried out using ORCA 5.0 in the gas phase with Grimme's D3 dispersion correction. Solvent effects were not considered at this stage. Avogadro and Chemcraft were used to visualize the calculations, and Notepad++ was used for creating input files [17, 18, 19, 20, 21].

Data from the design and calculations show the magnitude of the interaction energy and complex activity of the compounds. An analysis of the stability and efficiency of the design compound is conducted to determine a more stable and easily formed design. The results of the analysis of properties related to the fullness of coagulation properties were also based on the ability to be inactive after interacting with Cu^{2+}, the strength of binding to Cu^{2+}, and the ability to attract Cu^{2+} compared to the old design of TyD [2].

2.1. Modified Tannin Optimization

Compound optimization in this study was based on the work of Lugo *et al.* [2], who reported the use of aldehydes or ketones, specifically formaldehyde, in the synthesis of TyD (TyDF). In the present work, formaldehyde was replaced with acetone (TyDA), ethyl methyl ketone (TyDE), and benzaldehyde (TyDB) to obtain modified TyD structures. The selection of these carbonyl compounds was primarily based on safety considerations, availability, and general physicochemical properties as reported in their respective material safety data sheets (MSDS), which indicate lower toxicity and safer handling profiles compared to formaldehyde.

Previous studies have shown that the introduction of amino-containing linkages and carbonyl-derived substituents into the tannin framework enhances coagulation efficiency and cation adsorption capacity [22]. The discussion of electronic characteristics, steric effects, and molecular reactivity of the modified tannin structures presented in this work is not derived from MSDS data, but is instead based on established principles of physical organic chemistry and coordination chemistry. Alkyl substituents are known to exert inductive electron-donating effects, while aromatic substituents provide resonance stabilization through π-electron delocalization, both of which influence iminium stability and metal–ligand interactions [23, 24, 25, 26].

Accordingly, the designed TyD derivatives were evaluated for their interactions with Cu^{2+} ions in several configurations: TyD–TyD (TyD...TyD), TyD–Cu^{2+} (TyD...Cu^{2+}), and a bridged complex involving two TyD molecules coordinated to a Cu^{2+} ion (TyD...Cu^{2+}...TyD). Interaction energy calculations were performed for all designed structures, and the results were compared with those of TyDF to assess the effect of formaldehyde replacement on Cu^{2+} binding performance.

2.2. Interaction Energy Calculation

The interaction energy (Ei) was calculated for each optimized TyD compound and its corresponding complexes. The optimized structures represent the minimum-energy configurations obtained from DFT calculations. The interaction energy reflects the electronic stabilization resulting from the association of two or more fragments and does not directly correspond to thermodynamic enthalpy, as enthalpy also includes vibrational, entropic, and temperature-dependent contributions [27]. Compounds with more negative Ei values exhibit stronger and more favorable interactions, indicating a higher tendency for complex formation [28]. The interaction energy of the TyD–Cu^{2+} complex, Ei (TyD...Cu^{2+}), was calculated using Equation (1), whereas the interaction energy of the TyD–Cu^{2+}–TyD complex, Ei (TyD...Cu^{2+}...TyD), was calculated using Equation (2).

$$E_i^{AB} = E_{AB} - (E_A + E_B) + E_{BSSE}^{AB} \text{ [29]} \quad (1)$$

$$E_i^{ABC} = E_{ABC} - E_{AB} - E_{BC} - E_{AC} + E_A + E_B + E_C + E_{BSSE}^{ABC} \text{ [30]} \quad (2)$$

2.3. Complex Activity Analysis and Interaction Identification

The complex activity was analyzed based on frontier molecular orbital (FMO) parameters obtained from DFT calculations, namely the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) energies. From this orbital, several descriptors, electron affinity (A), electronegativity (χ), and energy gap (E_{gap}), were estimated using the Koopmans' theorem approximation, which relates orbital energies to ionization potential and electron affinity [29, 30]. The parameters were calculated using Equations 3 to 5.

$$A = -E_{LUMO} \quad (3)$$

$$\chi = -\frac{(E_{HOMO}+E_{LUMO})}{2} \quad (4)$$

$$E_{gap} = E_{LUMO} - E_{HOMO} \quad (5)$$

Where, A represents the tendency of the molecule to accept electrons (electron affinity, in eV), χ denotes its overall electron-attracting ability (electronegativity, in eV), and E_{gap} (in eV) reflects the chemical reactivity or stability of the complex; smaller gaps indicate higher reactivity, whereas larger gaps correspond to more stable, less reactive systems [23].

3. Results and Discussion

3.1. Modified Tannin Optimization (TyD)

The optimization of TyD was performed by substituting alternative carbonyl sources, including acetone, ethyl methyl ketone, and benzaldehyde. While MSDS documents were used to confirm material identity, safety classification, and general physicochemical properties, the interpretation of electronic behavior, steric effects, and reactivity trends of the resulting modified tannin structures is based on theoretical considerations and literature-reported chemical principles.

These substituents differ in their electronic and steric characteristics, which significantly influence the stability and reactivity of the resulting modified tannin structures. Specifically, alkyl groups ($-CH_3$, $-C_2H_5$) introduce inductive electron-donating effects that can stabilize the adjacent iminium center, whereas the phenyl group ($-C_6H_5$) in benzaldehyde contributes extended π-electron delocalization and resonance stabilization. Furthermore, increasing steric bulk from methyl, ethyl, to phenyl substituents can influence molecular conformation and accessibility of coordination sites, thereby modulating the interaction strength between the modified tannin (TyD) and Cu^{2+} ions. These combined electronic and steric effects, rather than material safety data, are the primary determinants of molecular stability and interaction behavior [23, 24, 25, 26].

3.1.1. Formaldehyde TyDF

TyDF, as reported in the study by Lugo *et al.* [2], is a compound formed from tannins (condensed), formaldehyde, and ammonium chloride. The structure of the compound is shown in Figure 1. The optimized TyDF structure interacts with the Cu^{2+} ion through coordination at nitrogen and carbon sites, as illustrated in Figure 2. The calculated Cu-ligand bond distance for both single (TyD...Cu^{2+}) and bridged (TyD...Cu^{2+}...TyD) complexes is summarized in Table 1. These data indicate that coordination primarily occurs through the N and C atoms of the iminium-modified regions, with bond lengths ranging from 1.975 Å to 2.336 Å, suggesting moderately strong coordination interactions. The slightly shorter Cu-N bonds in the bridged complex suggest stronger coordination and possible chelation behavior, enhancing complex stability compared to the single TyD...Cu^{2+} configuration.

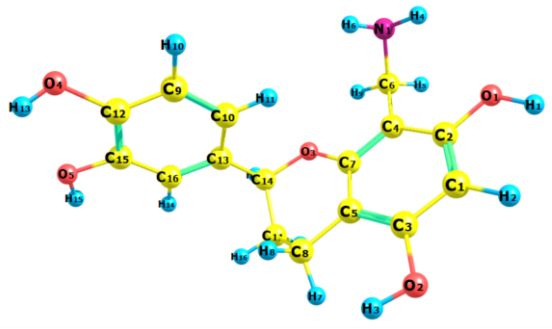

Figure 1. Molecular design of TyDF

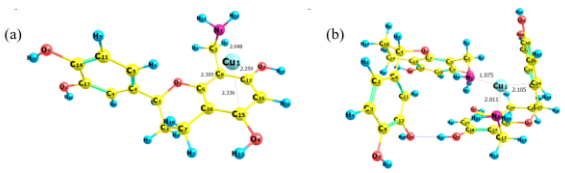

Figure 2. Optimized structures of TyDF interacting with Cu^{2+}: (a) TyD...Cu^{2+} complex and (b) TyD...Cu^{2+}...TyD complex

Table 1. Cu-ligand bond distance for TyDF complexes

Complex type	Cu-ligand interaction	Bond length (Å)
TyD...Cu^{2+}	Cu1-N1	2.048
TyD...Cu^{2+}	Cu1-C6	2.305
TyD...Cu^{2+}	Cu1-C12	2.259
TyD...Cu^{2+}	Cu1-C15	2.336
TyD...Cu^{2+}...TyD	Cu1-N1	1.975
TyD...Cu^{2+}...TyD	Cu1-N2	2.011
TyD...Cu^{2+}...TyD	Cu1-C24	2.105

3.1.2. Acetone TyD (TyDA)

The TyDA derivative was designed by replacing formaldehyde with acetone. In this system, acetone reacts with ammonium chloride to generate an iminium ion intermediate, which subsequently condenses with condensed tannins to form TyDA (Figure 3). Compared to TyDF, TyDA contains an additional methyl substituent introduced through the acetone-based iminium linkage. This $-CH_3$ group exerts a mild electron-donating inductive effect (+I), which slightly increases the electron density around the nitrogen center, thereby enhancing the local polarization of the C–N bond. The methyl group also introduces greater steric hindrance than hydrogen, influencing molecular conformation and possibly altering the accessibility of the coordination site for Cu^{2+} binding. These combined electronic and steric effects account for the difference in reactivity and stability observed between TyDA and TyDF. The resulting steric interactions arise primarily from van der Waals forces between methyl substituents and adjacent aromatic regions [23, 24, 25, 26].

The optimized TyDA structure forms stable coordination complexes with Cu^{2+} ions, as illustrated in Figure 4. The calculated Cu-ligand bond distance for both single (TyD...Cu^{2+}) and bridged (TyD...Cu^{2+}...TyD) configurations is summarized in Table 2. The data indicate that Cu–N and Cu–C bonds within the bridged TyD...Cu^{2+}...TyD complexes are slightly shorter than those in the single complex, suggesting stronger coordination and improved binding stability. The electron-donating methyl group likely enhances local polarization, promoting effective Cu^{2+} attraction despite mild steric constraints.

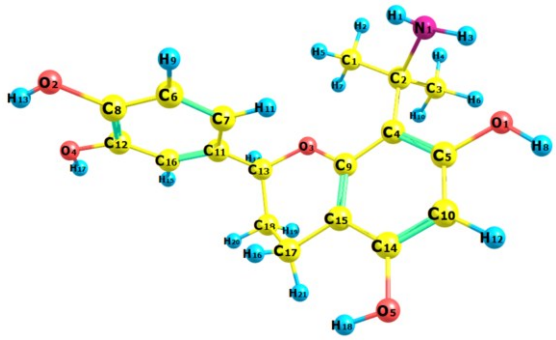

Figure 3. Molecular design of TyDA

Table 2. Cu-ligand bond distances for TyDA complexes

Complex type	Cu-ligand interaction	Bond length (Å)
TyD...Cu^{2+}	Cu1-C3	2.236
TyD...Cu^{2+}	Cu1-C6	1.999
TyD...Cu^{2+}	Cu1-C8	2.222
TyD...Cu^{2+}	Cu1-C9	2.456
TyD...Cu^{2+}...TyD	Cu1-N2	1.975
TyD...Cu^{2+}...TyD	Cu1-C3	2.033
TyD...Cu^{2+}...TyD	Cu1-C25	2.486

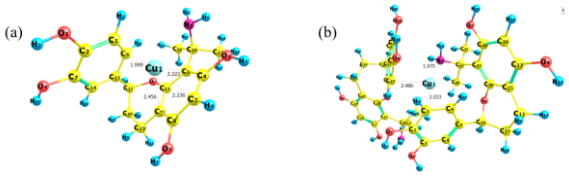

Figure 4. Optimized structures of TyDA interacting with Cu^{2+}: (a) TyD...Cu^{2+} complex and (b) TyD...Cu^{2+}...TyD complex

3.1.3. Ethyl Methyl Ketone TyD (TyDE)

The TyDE derivative was designed by replacing formaldehyde with ethyl methyl ketone, which reacts with ammonium chloride to form an iminium ion intermediate that subsequently bonds with condensed tannins to produce TyDE (Figure 5). The introduction of both methyl ($-CH_3$) and ethyl ($-C_2H_5$) substituents into the iminium linkage increases the overall steric bulk and introduces mixed electronic effects [23, 26]. The methyl and ethyl groups act as weak electron-donating substituents (+I effect), slightly increasing electron density at the nitrogen center and stabilizing the iminium cation. However, the greater steric demand of the ethyl group may cause slight distortion in local geometry, influencing Cu^{2+} accessibility at coordination sites.

The optimized TyDE structure exhibits chirality at the C4 atom, resulting in two distinct isomers, TyDE-1 and TyDE-2 (Figure 5). These differ in the spatial arrangement of ethyl and methyl substituents, leading to slight variations in their interaction geometries with Cu^{2+} ions. Both isomers form stable Cu^{2+} complexes in single (TyD...Cu^{2+}) and bridged (TyD...Cu^{2+}...TyD) configurations (Figures 6 and 7). The Cu-ligand bond distances are summarized in Table 3.

The average Cu-ligand distance in TyDE-1 is slightly shorter (≈1.88 Å) than in TyDE-2 (≈2.11 Å), indicating stronger coordination in TyDE-1, allowing more effective orbital overlap between Cu^{2+} and donor atoms. This suggests that TyDE-1 is the more reactive and stable isomer, consistent with its more favorable interaction energy observed in computational analysis.

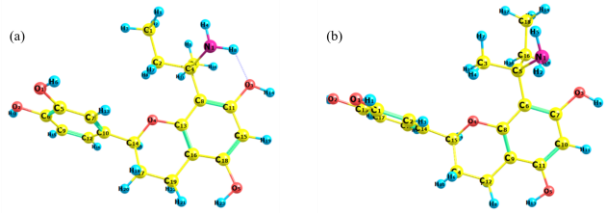

Figure 5. TyDE isomers: (a) TyDE-1 and (b) TyDE-2

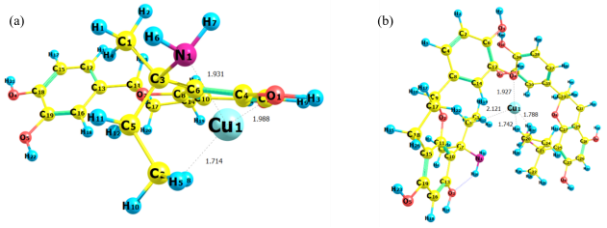

Figure 6. Optimized structure of TyDE-1 isomers interacting with Cu^{2+}: (a) TyD...Cu^{2+} complex and (b) TyD...Cu^{2+}...TyD complex

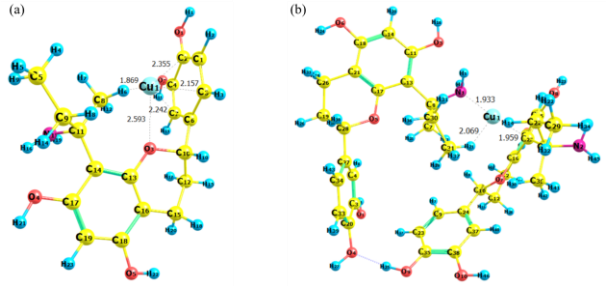

Figure 7. Optimized structure of TyDE-2 isomers interacting with Cu^{2+}: (a) TyD...Cu^{2+} Complex and (b) TyD...Cu^{2+}...TyD complex

Table 3. Cu-ligand bond distances for TyDE complexes

Compound	Complex type	Cu-ligand interaction	Bond length (Å)
TyDE-1	TyD...Cu^{2+}	Cu1-N1	1.931
	TyD...Cu^{2+}	Cu1-H5	1.714
	TyD...Cu^{2+}	Cu1-O1	1.988
	TyD...Cu^{2+}...TyD	Cu1-O4	1.927
	TyD...Cu^{2+}...TyD	Cu1-H13	2.121
	TyD...Cu^{2+}...TyD	Cu1-H25	1.724
	TyD...Cu^{2+}...TyD	Cu1-H21	1.788
TyDE-2	TyD...Cu^{2+}	Cu1-H1	1.869
	TyD...Cu^{2+}	Cu1-O3	2.593
	TyD...Cu^{2+}	Cu1-C7	2.242
	TyD...Cu^{2+}	Cu1-C2	2.355
	TyD...Cu^{2+}...TyD	Cu1-N1	1.933
	TyD...Cu^{2+}...TyD	Cu1-H21	2.069
	TyD...Cu^{2+}...TyD	Cu1-C25	1.959

3.1.4. Benzaldehyde TyD (TyDB)

The TyDB derivative was synthesized in silico by replacing formaldehyde with benzaldehyde, which reacts with ammonium chloride to form an aromatic iminium ion that subsequently condenses with condensed tannins (Figure 8). The presence of the phenyl ($-C_6H_5$) substituent introduces strong π-electron delocalization and extended conjugation, enhancing resonance stabilization of the iminium linkage. This delocalization enables better charge dispersion across the aromatic ring, increasing electronic stability while maintaining moderate steric bulk. Compared to TyDF and TyDE, TyDB exhibits higher polarizability and π-donor capacity, which facilitates stronger coordination with transition metal ions, such as Cu^{2+}.

The TyDB design also exhibits chirality at the C4 atom, resulting in two distinct isomers, TyDB-1 and TyDB-2 (Figure 8). The optimized geometries of both isomers interacting with Cu^{2+} ions are shown in Figures 9 and 10. The corresponding Cu-ligand bond distances are summarized in Table 4. The average Cu-ligand distance in TyDB-1 (≈2.18 Å) is slightly shorter than in TyDE-2 (≈2.20 Å), indicating stronger Cu^{2+} coordination. The enhanced interaction in TyDB-1 is attributed to π- electron delocalization across the benzene ring, which stabilizes charge transfer to the metal center and increases overall interaction energy.

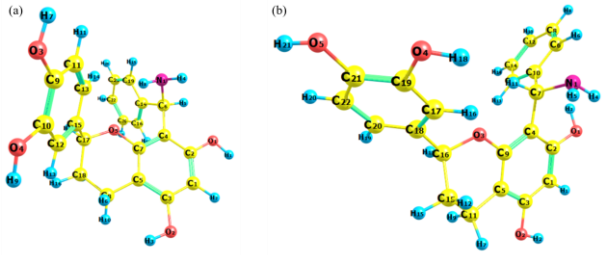

Figure 8. TyDB isomers: (a) TyDB-1 and (b) TyDB-2

Table 4. Cu-ligand bond distances for TyDB complexes

Compound	Complex type	Cu-ligand interaction	Bond length (Å)
TyDB-1	TyD...Cu^{2+}	Cu1-C7	2.130
	TyD...Cu^{2+}	Cu1-C11	2.222
	TyD...Cu^{2+}	Cu1-C17	2.125
	TyD...Cu^{2+}	Cu1-C6	2.555
	TyD...Cu^{2+}...TyD	Cu1-C4	2.180
	TyD...Cu^{2+}...TyD	Cu1-C8	2.086
	TyD...Cu^{2+}...TyD	Cu1-C19	2.051
TyDB-2	TyD...Cu^{2+}	Cu1-O2	1.992
	TyD...Cu^{2+}	Cu1-C2	2.074
	TyD...Cu^{2+}	Cu1-C4	2.044
	TyD...Cu^{2+}...TyD	Cu1-C19	2.279
	TyD...Cu^{2+}...TyD	Cu1-C12	2.239
	TyD...Cu^{2+}...TyD	Cu1-C17	2.087
	TyD...Cu^{2+}...TyD	Cu1-C28	2.300

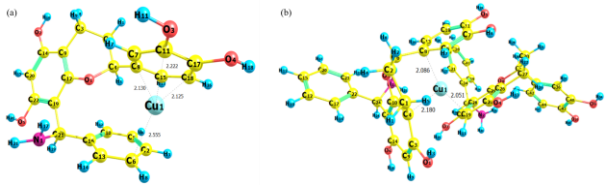

Figure 9. Optimized structure of TyDB-1 isomers interacting with Cu^{2+}: (a) TyD...Cu^{2+} complex and (b) TyD...Cu^{2+}...TyD complex

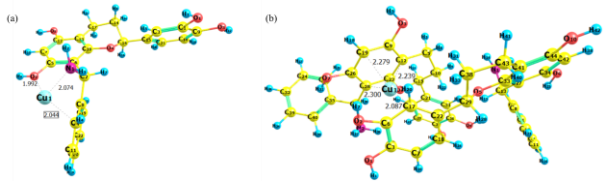

Figure 10. Optimized structure of TyDB-2 isomers interacting with Cu^{2+}: (a) TyD...Cu^{2+} complex and (b) TyD...Cu^{2+}...TyD complex

3.2. Structure–Energy Relationship and Coagulation Mechanism

The stability and coagulation of the modified tannin derivatives were analyzed based on their optimized geometries, DFT total energies, and calculated interaction energies. The Cu^{2+} ion was modeled using the LANL2DZ effective core potential (ECP), which provides an accurate and computationally efficient treatment of transition-metal centers by explicitly describing the valence electrons (3d and 4s) while replacing the inner-core electrons with an effective potential. This approach accounts for relativistic effects and electron-core shielding, which is important for second-row transition metals such as copper. The LANL2DZ basis has been widely validated for DFT studies of Cu-ligand complexes, producing reliable bond distances, charge distribution, and interaction energies compared to higher-level all-electron basis sets. In combination with the 6-31G(d,p) basis for non-metal atoms (C, H, N, and O), this mixed-basis scheme yields a balanced description of metal-ligand coordination with a reasonable computational cost, making it suitable for evaluating the formaldehyde-free modified tannins-Cu interaction in this work.

3.2.1. Total Energy Components

To calculate the interaction energies, total DFT electronic energies were first obtained for each individual component (TyD, Cu^{2+}, and TyD...Cu^{2+} complexes). These energies, expressed in $\times 10^6$ kJ.mol^{-1}, are summarized in Table 5. The values represent the optimized ground-state energies of isolated and complex species, which were subsequently used to calculate the interaction energies presented in Table 6. The high negative magnitudes reflect total system energies proportional to molecular size and electron number. These values serve as the basis for calculating relative Ei, which provides a more accurate representation of the stability of complexes.

3.2.2. Interaction Energies and Bond Length Correlation

Ei were derived using the equations defined in Section 2.3, with correction for BSSE. The resulting values are shown in Table 6. The order of average Cu-ligand bond length from shortest to longest is: TyDE-1 (1.8838 Å) < TyDB-2 (2.1139 Å) < TyDE-2 (2.1259 Å) < TyDF (2.1335 Å) < TyDB-1 (2.1819 Å) < TyDA (2.1965 Å). In general, shorter Cu-ligand bonds correspond to stronger local coordination. Yet, a comparison with interaction energies shows that TyDB-1, with slightly longer bonds, achieves the most negative Ei value (-1,271.86 kJ.mol^{-1}), indicating superior thermodynamic stability. This divergence arises from π-electron delocalization and polarizability introduced by the benzaldehyde ring, which enhances charge transfer to Cu^{2+} and reduces total electronic energy. Thus, while TyDE-1 exhibits strong local binding through short Cu-N/O bonds, TyDB-1 gains greater overall stability via resonance and extended conjugation. The results confirm that both geometric and electronic factors govern coordination strength, with delocalized aromatic substituents producing the most stable complexes.

In the optimized geometries, Cu^{2+} primarily coordinates through oxygen and nitrogen donor atoms, originating from hydroxyl, carbonyl, and amino groups in the tannin framework. Apparent Cu...C or Cu...H distance that appear in the raw coordinate output correspond to secondary noncovalent contacts or van der Waals proximity effects within the coordination sphere rather than direct chemical bonds. Therefore, only Cu–O and Cu–N distances are considered and discussed as primary coordination interactions. The labeling of donor atoms (O1, O2, N1, etc.) has been standardized across all figures and tables to ensure consistent interpretation of the coordination geometry.

Table 5. Total DFT energies of TyD derivatives and complexes ($\times 10^6$ kJ.mol^{-1})

Sample	TyD	Cu^{2+}	TyD...Cu^{2+}	TyD...TyD	TyD...Cu^{2+}...TyD
TyDA	-2.963500	-4.303467	-7.267910	-5.926985	-10.231598
TyDE-1	-3.066618	-4.303467	-7.371141	-6.133238	-10.437826
TyDE-2	-3.066616	-4.303467	-7.371079	-6.133223	-10.437812
TyDB-1	-3.363445	-4.303467	**-7.667856**	**-6.726899**	**-11.031630**
TyDB-2	-3.363466	-4.303467	**-7.667893**	**-6.726.937**	**-11.031567**
TyDF	-2.757228	-4.303467	-7.061660	-5.514461	-9.819064

Note: Value represents total DFT electronic energies (not interaction energies). These large magnitudes are typical for molecular systems and are reported here in 10^6 kJ.mol^{-1} units to improve readability. Interaction energies (Table 2) are given in kJ.mol^{-1}.

Table 6. Ei calculation of modified tannin derivatives (kJ.mol^{-1})

Sample	TyD...Cu^{2+} interaction	TyD...TyD interaction	E3	TyD...Cu^{2+}...TyD interaction
TyDA	-943.03	14.25	740.59	-1,131.22
TyDE-1	**-1,055.17**	-0.27	989.21	-1,121.39
TyDE-2	-996.16	8.60	870.63	-1,113.09
TyDB-1	-943.39	**-7.17**	**622.09**	**-1,271.86**
TyDB-2	-958.95	-3.25	754.94	-1,166.20
TyDF	-964.61	-3.79	793.91	-1,139.11

3.2.3. Coagulation Mechanistic Interpretation

The geometric and energetic characteristics of the complexes directly influence their coagulation behavior. Efficient coagulation requires two simultaneous effects: (1) strong charge neutralization of metal ions or suspended particles, and (2) sufficient molecular flexibility for polymeric bridging between particles.

Derivatives with very short, rigid Cu-ligand bonds (e.g., TyDE-1) provide strong charge attraction but limited flexibility for bridging. In contrast, TyDB-1 exhibits slightly longer yet more electronically delocalized coordination, which enables both effective charge neutralization and adaptable molecular conformation for multi-site binding. This balance yields enhanced particle destabilization and floc growth, corresponding to its most negative interaction energy (-1,271.86 kJ.mol^{-1}). Therefore, the π-conjugated aromatic substituent, in TyDB-1, provides optimal electronic and steric characteristics, making it the most promising formaldehyde-free tannin derivative for Cu^{2+} coagulation.

3.2.4. Summary of Structure-Function Trends

The combined analysis of bond length, interaction energy, and coagulation behavior reveals a clear structure-function relationship among the modified tannin derivatives. The sequence of average Cu-ligand bond lengths, from shortest to longest, is TyDE-1 < TyDB-2 < TyDE-2 < TyDF < TyDB-1 < TyDA, indicating that TyDE-1 exhibits the strongest local coordination with Cu^{2+} due to its short and compact bonding geometry. However, when Ei values are compared, a different trend emerges: TyDB-1 < TyDB-2 < TyDF < TyDA < TyDE-1 < TyDE-2 (from most to least negative). This suggests that overall stability is not solely governed by geometric proximity, but also by the degree of electronic delocalization and polarizability of substituents.

While shorter Cu-ligand bonds generally imply stronger local attraction, the presence of conjugated aromatic groups in TyDB derivatives allows for greater π-electron delocalization and enhanced charge transfer to Cu^{2+}, which significantly lowers the total electronic energy of the system. In contrast, aliphatic derivatives such as TyDE and TyDA provide localized binding but lack extended conjugation, limiting their capacity for long-range electronic stabilization. Consequently, TyDB-1, which combines moderate bond distances with a highly polarizable and delocalized electronic structure, achieves the most favorable balance between geometric strength and electronic flexibility. This balance leads to superior energetic stability and enhanced coagulation efficiency, identifying TyDB-1 as the most promising formaldehyde-free tannin derivative for Cu^{2+} ion removal applications.

3.3. Complex Activity Analysis and Interaction Identification

The FMO analysis was conducted to evaluate the complex activity and electronic behavior of the optimized structures. The HOMO-LUMO energies were obtained from geometry-optimized structures of each complex at the B3LYP-D3/6-31G(d,p) level of theory. For Cu, a +2 charge and doublet spin multiplicity ($^2S+1 = 2$) were used. The analysis focused on TyDB-1, the most stable derivative based on interaction energy results, and was compared with the unmodified reference compound, TyDF.

3.3.1. Activities of TyD...Cu^{2+} Complex

The FMO results for the single complexes are presented in Table 7 and illustrated in Figure 11. These parameters (E_{HOMO}, E_{LUMO}, E_{gap}, and χ) describe the electronic reactivity and stability of the complexes. The results show that the E_{gap} of TyDB-1 (1.351 eV) is higher than that of TyDF (1.090 eV), suggesting that TyDB-1 exhibits lower electronic reactivity but higher thermodynamic stability. A larger E_{gap} indicates greater resistance to electron excitation and, consequently, a more stable complex. The slightly higher E_{LUMO} (-10.502 eV) of TyDB-1 implies that the complex requires more energy to accept an incoming electron, which supports its lower reactivity.

Additionally, the χ value of TyDB-1 (11.178 eV) is slightly smaller than that of TyDF (11.456 eV), implying a stronger ability of TyDB-1 to donate electrons to the Cu^{2+} ion during coordination. This electron-donating character results in a more stable Cu-ligand bond. Collectively, the data confirm that TyDB-1 forms a stronger and more stable coordination complex with Cu^{2+} than TyDF due to its delocalized π-electron structure and favorable energy alignment.

3.3.2. Activities of TyD...Cu^{2+}...TyD Complex

The corresponding results for the bridged complexes (TyD...Cu^{2+}...TyD) are summarized in Table 8 and visualized in Figure 12.

Table 7. HOMO-LUMO energies, E_{gap}, and χ values for TyD...Cu^{2+} complexes

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	χ (eV)
TyDF	-12.001	-10.911	1.090	11.456
TyDB-1	-11.853	-10.502	1.354	11.178

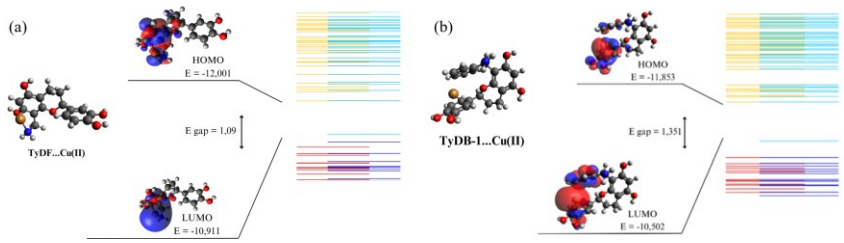

Figure 11. HOMO-LUMO distribution in TyD... Cu^{2+} complexes: (A) TyDF and (B) TyDB-1

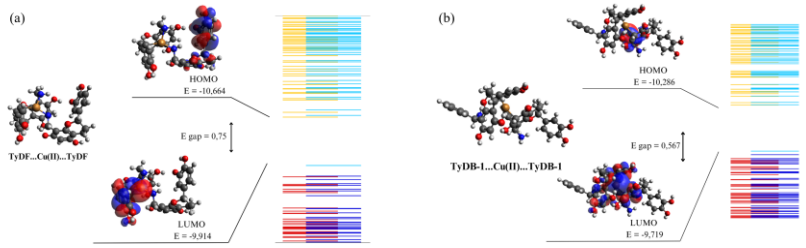

Figure 12. HOMO-LUMO distribution in TyD...Cu^{2+}...TyD interaction: (A) TyDB-1 and (B) TyDF

Table 8. HOMO-LUMO energies, E_{gap}, and χ values for TyD...Cu^{2+}...TyD complexes

Compound	E_{HOMO} (eV)	E_{LUMO} (A) (eV)	E_{gap} (eV)	χ (eV)
TyDF	-10.664	-9.914	0.750	10.289
TyDB-1	-10.286	-9.719	0.567	10.003

In the bridged complexes, the E_{gap} of TyDB-1 (0.567 eV) is smaller than that of TyDF (0.750 eV), indicating that the TyDB-1 system becomes more electronically responsive and reactive when forming a multi-ligand coordination with Cu^{2+}. This reduced energy gap suggests easier charge transfer within the complex, facilitating efficient electron delocalization through the benzaldehyde aromatic ring.

The E_{LUMO} value of TyDB-1 (-9.719 eV) is higher than that of TyDF (-9.914 eV), consistent with a stronger capacity for electron acceptance by the Cu^{2+} center. Meanwhile, the χ value of tyDB-1 (10.003 eV) is slightly lower than that of TyDF (10.289 eV), which again supports a stronger Cu-ligand interaction and higher charge-transfer efficiency. Thus, the TyDB-1 derivative demonstrates improved electron mobility and enhanced stability within the bridged configuration, confirming its superior coordination performance.

3.3.3. Interpretation and Correlation

Comparing both single and bridged complexes, TyDB-1 consistently shows a more favorable electronic configuration than TyDF. In the single complex, a wider E_{gap} ensures structural robustness, while in the bridged complex, a smaller E_{gap} facilitates electron delocalization across multiple coordination sites. This dual behavior highlights TyDB-1's adaptive electronic characteristics, enabling both stable bonding and efficient charge transfer when multiple ligands are present.

The combination of Higher E_{HOMO}, moderate E_{LUMO}, and balanced E_{gap} values implies that TyDB-1 can interact strongly with Cu^{2+} ions while maintaining energetic stability. These properties, derived from the optimized structures, confirm that the benzaldehyde-based modification provides the most effective electronic environment for Cu^{2+} binding and coagulation, outperforming the formaldehyde-derived TyDF in both reactivity and thermodynamic stability.

4. Conclusion

This DFT-based study was designed to evaluate formaldehyde-free modified tannin derivatives (TyDF, TyDA, TyDE, and TyDB) as potential coagulants, revealing that benzaldehyde substitution (TyDB-1) produced the most stable and reactive complex with Cu^{2+}. TyDB-1 exhibited the most negative interaction energy (-1,271.86 $kJ.mol^{-1}$), balanced Cu-ligand bond lengths (~2.18 Å), and favorable HOMO-LUMO characteristics, indicating strong yet adaptable coordination through π-electron delocalization. These results highlight the synergistic effects of electronic delocalization, polarizability, and steric modulation in enhancing coagulation performance. However, the calculations were performed in the gas phase, without considering solvent effects, and potential spin contamination in the open-shell Cu^{2+} system may slightly affect the accuracy. Experimental validation and solvent-phase modeling are recommended to confirm the practical coagulation efficiency and environmental applicability of TyDB-1. It is essential to note that all calculations were performed in the gas phase. Future studies will incorporate solvation models (PCM/CPCM) and explicit Cu–H_2O coordination to simulate the aqueous environment where coagulation occurs, thereby enabling more realistic predictions of coagulant performance.

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