

Computational Investigation of Transition Metal Aspartic Acid Complexes as Corrosion Inhibitors for Iron

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Abstract

The growing demand for sustainable corrosion control has shifted focus toward green inhibitors that are biodegradable and non-toxic. This study presents a comprehensive computational investigation of aspartic acid transition metal complexes as corrosion inhibitors of iron. Integrating quantum chemical calculations via Spartan '14 and Monte Carlo (MC) adsorption simulations via BIOVIA Materials Studio 2023, the research elucidates adsorption mechanisms and electronic properties. Molecular structures were optimized using the semi-empirical PM3 method to calculate parameters including E-HOMO, E-LUMO, and energy band gap (ΔE). The Ni(II) complex exhibited superior reactivity with the highest E-HOMO (-3.96 eV), the lowest E LUMO (2.70 eV), and the smallest ΔE (6.66 eV). MC simulations on the Fe(110) surface confirmed that the Ni(II) complex achieved the most stable configuration, yielding a highly negative adsorption energy of -854.097 kcal/mol. This can be attributed to the planar orientation of the compound, which ensures maximum surface coverage. The sequence of inhibition efficiency was determined as Ni(II) > Co(II) > Cu(II) > Fe(II). Strong correlation between theoretical descriptors and simulation outcomes validates this computational approach, establishing the Ni(II) aspartic acid complex as a highly effective, eco-friendly corrosion inhibitor.

Introduction

Corrosion is the deterioration of materials, particularly metals, due to chemical or electrochemical reactions with their environment. It is a natural process where a refined metal reverts to a more stable, oxidized state, such as rust forming on iron. The global economic toll of metallic corrosion is staggering, with estimates placing its annual cost at approximately 3.4% of worldwide GDP, amounting to more than US\$2.5 trillion^[1]. Infrastructure failures in pipelines, aircraft, automobiles, marine vessels, and industrial plants underscore the urgency of effective corrosion mitigation strategies^[2].

The mechanism of corrosion generally involves anodic and cathodic processes. The anodic reaction involves metal dissolution ($M \rightarrow M^{n+} + ne^-$), while cathodic reactions may include oxygen reduction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) or hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2$). Corrosion can be classified into several types: uniform, pitting, crevice, galvanic, stress corrosion cracking, and intergranular corrosion^[1].

Conventional corrosion inhibitors, many of which are based on toxic chromates, phosphates, and synthetic organic compounds, pose significant environmental and health hazards. This creates a pressing need for eco-friendly alternatives that are both efficient and sustainable^[3]. Amino acids and their metal complexes have emerged as promising green corrosion inhibitors because of their non-toxic nature, biodegradability, and the presence of multiple functional groups ($-NH_2$, $-COOH$, and $-CH$) that can coordinate with metal surfaces^[4].

Computational chemistry provides a faster and more economical alternative to experimental approaches, allowing prediction of adsorption energies, electronic properties, and molecular reactivity before laboratory validation^[8]. The present study aims to computationally investigate the potential of Cu(II), Co(II), Ni(II) and Fe(II) aspartic acid complexes as corrosion inhibitors of iron, using quantum chemical calculations and Monte Carlo adsorption simulations.

Experimental

Computational equipment A Toshiba Portege R30-A computer system with Intel Core i5-4210M CPU @ 2.60 GHz, 8.00 GB RAM, 64-bit operating system running Spartan '14 and BIOVIA Materials Studio 2023 software was used.

Structure generation and geometry optimization

The 2D structure of aspartic acid was obtained from the literature^[13] and its 3D structure and those of its Cu(II), Co(II), Ni(II), and Fe(II) complexes were drawn using Spartan '14 software as shown in Fig. 1. Energy minimization was carried out to find the most stable geometry on the potential energy surface using the same software.

Quantum chemical calculations.

Quantum chemical calculations were performed using the semi-empirical PM3 method. The energy of the highest occupied molecular orbital (E-HOMO), the energy of the lowest unoccupied molecular orbital (E-LUMO), and dipole moment of the optimized

structures were obtained. The energy band gap (ΔE), absolute hardness (η), absolute softness (S), ionization energy (IE), absolute electronegativity (EN), and electron affinity (EA) were calculated using the following equations [7, 9]:

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{Eq. 1}$$

$$\eta = (\Delta E) / 2 \tag{Eq. 2}$$

$$S = 1 / 2\eta \tag{Eq. 3}$$

$$IE = - E_{HOMO} \tag{Eq. 4}$$

$$EN = (E_{HOMO} + E_{LUMO}) / 2 \tag{Eq. 5}$$

$$EA = - E_{LUMO} \tag{Eq. 6}$$

Monte Carlo simulations. The Fe(110) surface was selected to model the adsorption behaviour of the complexes. An 8×8 Fe(110) surface consisting of eleven atomic layers was created based on a pre-optimized bulk structure as shown in Fig. 2. A vacuum layer of 30 Å was applied. The adsorption behaviour was investigated using the Adsorption Locator module of Materials Studio [11]. The search for the global minimum was based on the simulated annealing metaheuristic algorithm with 10 temperature cycles and 100,000 steps each. The COMPASS force field was employed to optimize the structures on the Fe(110) surface [6]. Adsorption energy was calculated as:

$$E_{ads} = E_{total} - (E_{metal+solution} + E_{inhibitor}) \tag{Eq. 7}$$

Results and Discussion

Quantum chemical study. Quantum chemical parameters were calculated using the semi-empirical PM3 method. The results are presented in Table 1. According to molecular orbital theory, the reactivity of a molecular species is related to the energies of HOMO and LUMO [7]. Inhibition efficiency is expected to increase with increasing E-HOMO and decreasing E-LUMO values; lower energy gaps correspond to softer, more reactive molecules and better corrosion inhibition efficiency [9].

According to Table 1, Ni(II) aspartic acid complex shows the highest inhibition efficiency due to the highest E-HOMO value (−3.96 eV) and lowest E-LUMO value (2.70 eV). The trend of inhibition efficiency with increasing E-HOMO follows the order Ni(II) > Co(II) > Cu(II) > Fe(II). The energy gap (ΔE) provides a measure of molecular reactivity: smaller ΔE corresponds to higher softness and better adsorption tendency [5, 9]. Ni(II) complex had the smallest gap (6.66 eV), followed by Co(II) (6.71 eV), Cu(II) (7.37 eV), and Fe(II) (8.13 eV).

Table 1
Calculated quantum chemical parameters (eV) of the inhibitors.

Complex	E(HOMO) (eV)	E(LUMO) (eV)	ΔE (eV)	IE (eV)	EA (eV)	Hardness (eV)	Softness (eV)	EN (eV)
Cu(II)	−4.56	2.81	7.37	4.56	−2.81	−3.685	−0.136	−0.875
Co(II)	−4.00	2.71	6.71	4.00	−2.71	−3.355	−0.149	−0.645
Ni(II)	−3.96	2.70	6.66	3.96	−2.70	−3.330	−0.150	−0.630
Fe(II)	−5.18	2.95	8.13	5.18	−2.95	−4.065	−0.123	−1.115

HOMO and LUMO distributions. Ni(II) and Co(II) complexes displayed HOMO densities strongly localized on the donor atoms (−NH₂ and −COOH groups of aspartic acid), suggesting a high tendency for electron donation toward vacant d-orbitals of Fe atoms as shown in Fig. 3 (a) and (b). Such strong donor interactions account for their superior inhibition efficiency [5, 10]. Cu(II) complex exhibited moderate HOMO delocalization, indicating good but less pronounced donor ability compared to Ni(II) and Co(II). Fe(II) complex showed weaker HOMO electron density, indicating poor donor character, correlating with its lower inhibition efficiency.

Ni(II) and Co(II) complexes presented LUMO densities spread over π -systems and functional groups, suggesting they can accept back-donated electrons from Fe surface orbitals, thereby reinforcing chemisorption. Effective corrosion inhibition requires overlap

between the HOMO of the inhibitor and the vacant d-orbitals of Fe (electron donation) as well as overlap between the LUMO of the inhibitor and filled Fe orbitals (back-donation) [8]. Ni(II) and Co(II) fulfil both requirements, explaining their superior inhibition performance.

The calculated electron affinity (EA), ionization energy (IE), electronegativity (EN), hardness (η), and softness (S) values further support the adsorption behaviour of the complexes [9]. Lower hardness and higher softness values observed for Co(II) and Ni(II) indicate greater molecular reactivity and stronger tendency for electron transfer during adsorption on the Fe surface [7]. The higher ionization energy and lower softness of Fe(II) indicate lower electron-donating ability and weaker adsorption interaction with the metal surface. The electronegativity values show that Co(II) and Ni(II) have better ability to interact with the Fe surface through electron sharing and back-donation mechanisms, consistent with their higher adsorption tendency and inhibition performance.

Monte Carlo simulation study. Monte Carlo simulations were carried out using the Adsorption Locator module in Materials Studio [11] to investigate the adsorption of the complexes on the Fe(110) surface. Adsorption energies and configurations were obtained as shown in Table 2.

Adsorption energy provides a direct measure of the interaction strength between the inhibitor and the metal surface. A more negative value indicates stronger adsorption and higher inhibition efficiency [12]. Ni(II) complex exhibited the most negative adsorption energy (−854.097 kcal/mol), followed by Co(II) (−851.941 kcal/mol), Cu(II) (−851.578 kcal/mol), and Fe(II) (−539.125 kcal/mol). The adsorption energy trend correlates with the quantum chemical descriptors: Ni(II) > Co(II) > Cu(II) > Fe(II).

Table 2
Adsorption energy values (kcal/mol) for the studied complexes on the Fe(110) surface.

S/N	System	Total Energy (kcal/mol)	Adsorption Energy (kcal/mol)
1	Fe(110)/Ni(II)	−56.464	−854.097
2	Fe(110)/Co(II)	−48.728	−851.941
3	Fe(110)/Cu(II)	−48.364	−851.578
4	Fe(110)/Fe(II)	−48.362	−539.125

Adsorption configurations. Visual analysis of the optimized configurations showed that Ni(II) Fig. 5 (a) and Co(II) Fig. 5 (b) complexes preferentially adopted planar orientations, allowing maximum surface coverage and stronger binding interactions. Cu(II) Fig. 5 (c) exhibited mixed orientations, leading to moderate adsorption. Fe(II) Fig. 5 (d) displayed weaker and less stable adsorption, consistent with its poor quantum descriptors. The predominance of flat-lying orientations for Ni(II) and Co(II) complexes enhances surface coverage, reducing available sites for corrosive species, thereby improving inhibition efficiency [11, 12].

Both quantum chemical and Monte Carlo approaches consistently indicate that Ni(II) aspartic acid complex has the highest inhibition potential due to high E-HOMO and low E-LUMO values [7, 9], the smallest ΔE and highest softness, the strongest adsorption energy [11], and favorable planar configuration on the Fe(110) surface [12].

Conclusions

This study presented a computational investigation of the corrosion inhibition properties of Cu(II), Co(II), Ni(II) and Fe(II) aspartic acid complexes on the Fe(110) surface using quantum chemical calculations (PM3 semi-empirical method) and Monte Carlo adsorption simulations. The following conclusions are drawn:

1. Ni(II) complex exhibited the most favorable frontier orbital energies: highest E-HOMO (−3.96 eV), lowest E-LUMO (2.70 eV), and the smallest band gap ($\Delta E = 6.66$ eV), making it the most reactive and efficient inhibitor.
2. Ni(II) and Co(II) complexes showed HOMO density concentrated on donor groups (−NH₂, −COOH), promoting strong adsorption via electron donation to Fe d-orbitals, while LUMO distributions allowed effective back-donation.
3. Monte Carlo simulations confirmed adsorption energies following: Ni(II) (−854.097 kcal/mol) > Co(II) (−851.941 kcal/mol) > Cu(II) (−851.578 kcal/mol) > Fe(II) (−539.125 kcal/mol), with Ni(II) and Co(II) adopting planar orientations for maximum surface

coverage.

4. Computational chemistry is demonstrated as a reliable and cost-effective tool for predicting corrosion inhibition behaviour, supporting the design of green, eco-friendly inhibitors based on amino acid metal complexes.

Declarations

Ethics approval and consent to participate

Not applicable. This study did not involve human participants, animals, or human data.

Consent for publication

Not applicable.

Data Availability

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing Interests

The authors declare that they have no competing interests.

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Author Contributions

Hussaini Mustapha Shehu: Conceptualization, methodology, software, investigation, formal analysis, visualization, writing of the original draft.

Sa'adatu Auwal Hamza: Supervision, review and editing.

Safiya Abdulsalam: Validation, review and editing.

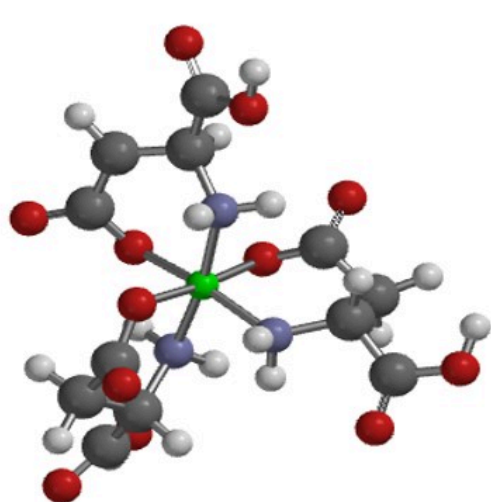
Muhammad Tukur Abubakar: Supervision, project administration, review and editing.

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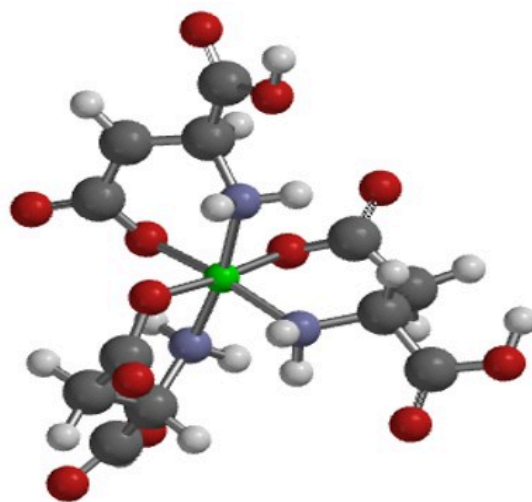
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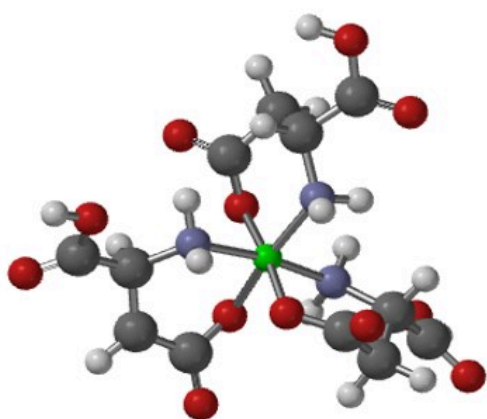
Figures



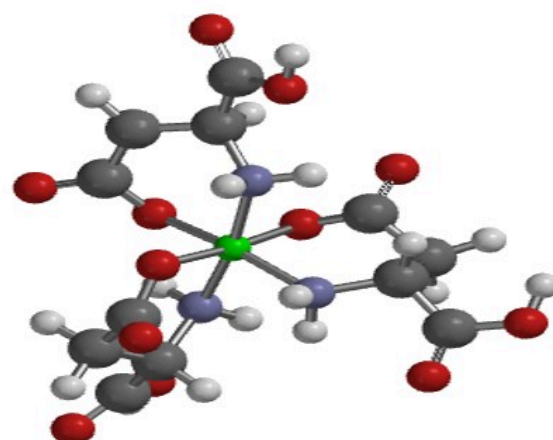
(a)



(b)



(c)



(d)

Figure 1

The left-hand side: structure of (a)Ni(ii), (c) Co(ii), right-hand side: structure of (b) Cu(ii), (d)Fe(ii)) aspartic acid complexes.

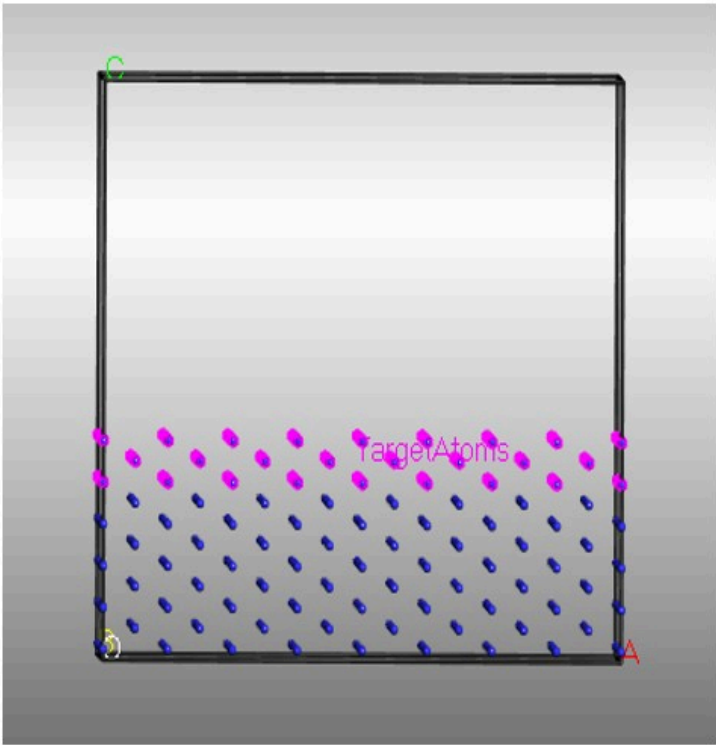
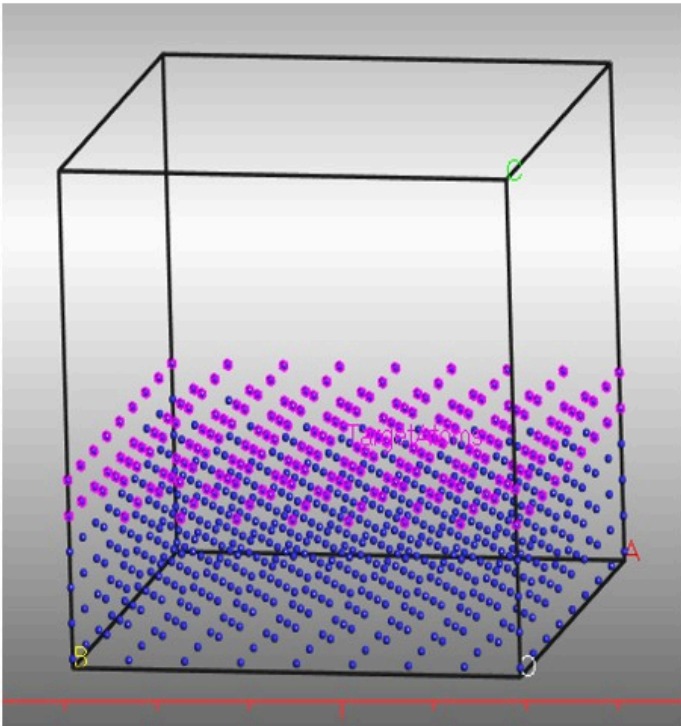
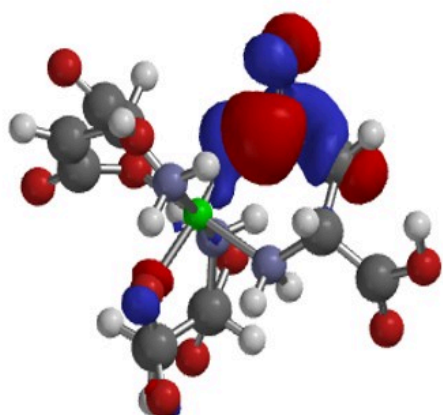


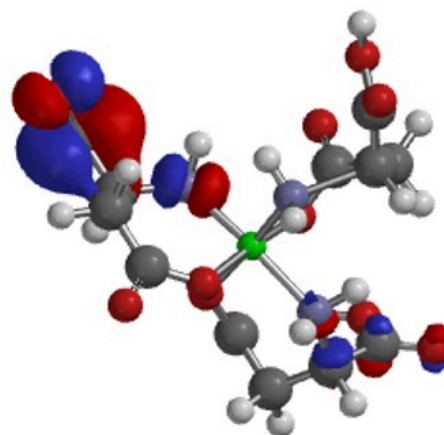
Figure 2

Side-view of the periodic slab for the Fe(110) metal surface used in Monte Carlo simulations.

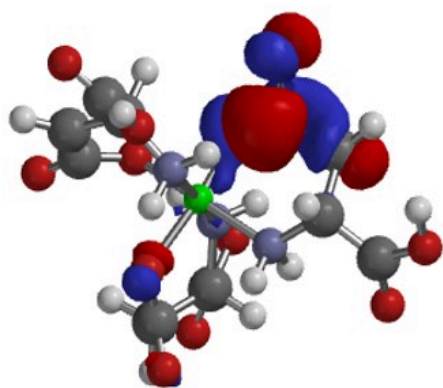
(a) HOMO



(a) LUMO



(b) HOMO



(b) LUMO

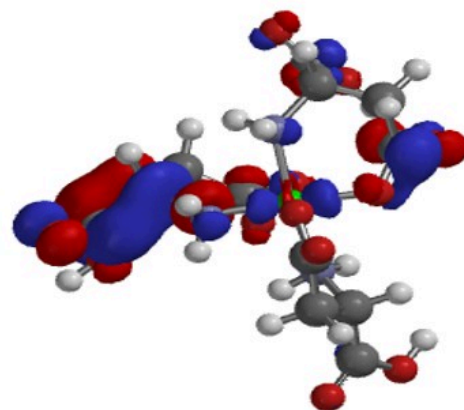
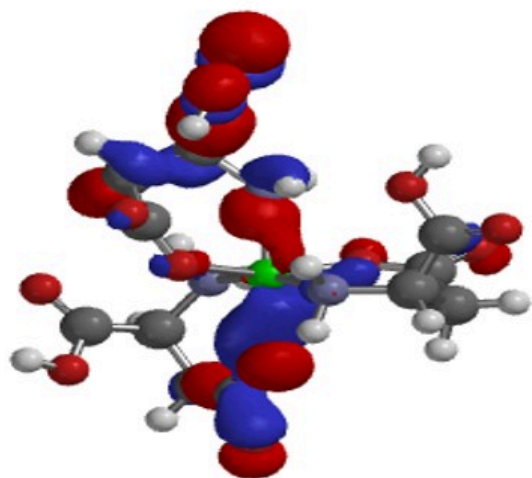


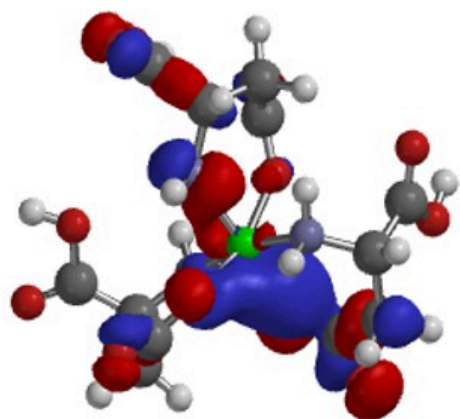
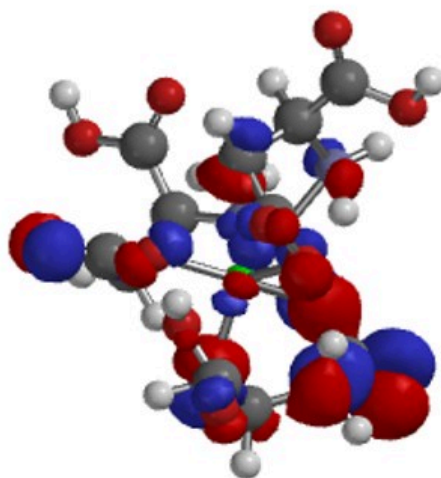
Figure 3

left-hand side: HOMO Frontier MO of (a) Co(ii) and (b) Ni(ii); and right-hand side: LUMO Frontier MO of (a)Co(ii), (b) Ni(ii) aspartic acid complexes.

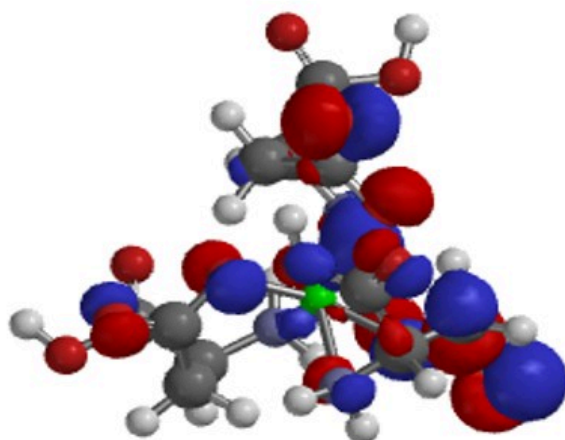
(c) HOMO



(c) LUMO



(d) HOMO



(d) LUMO

Figure 4

left-hand side: HOMO Frontier MO of (a) Cu(ii) and (c) Fe(ii); and right-hand side: LUMO Frontier MO of (b) Cu(ii), (d) Fe(ii) aspartic acid complexes

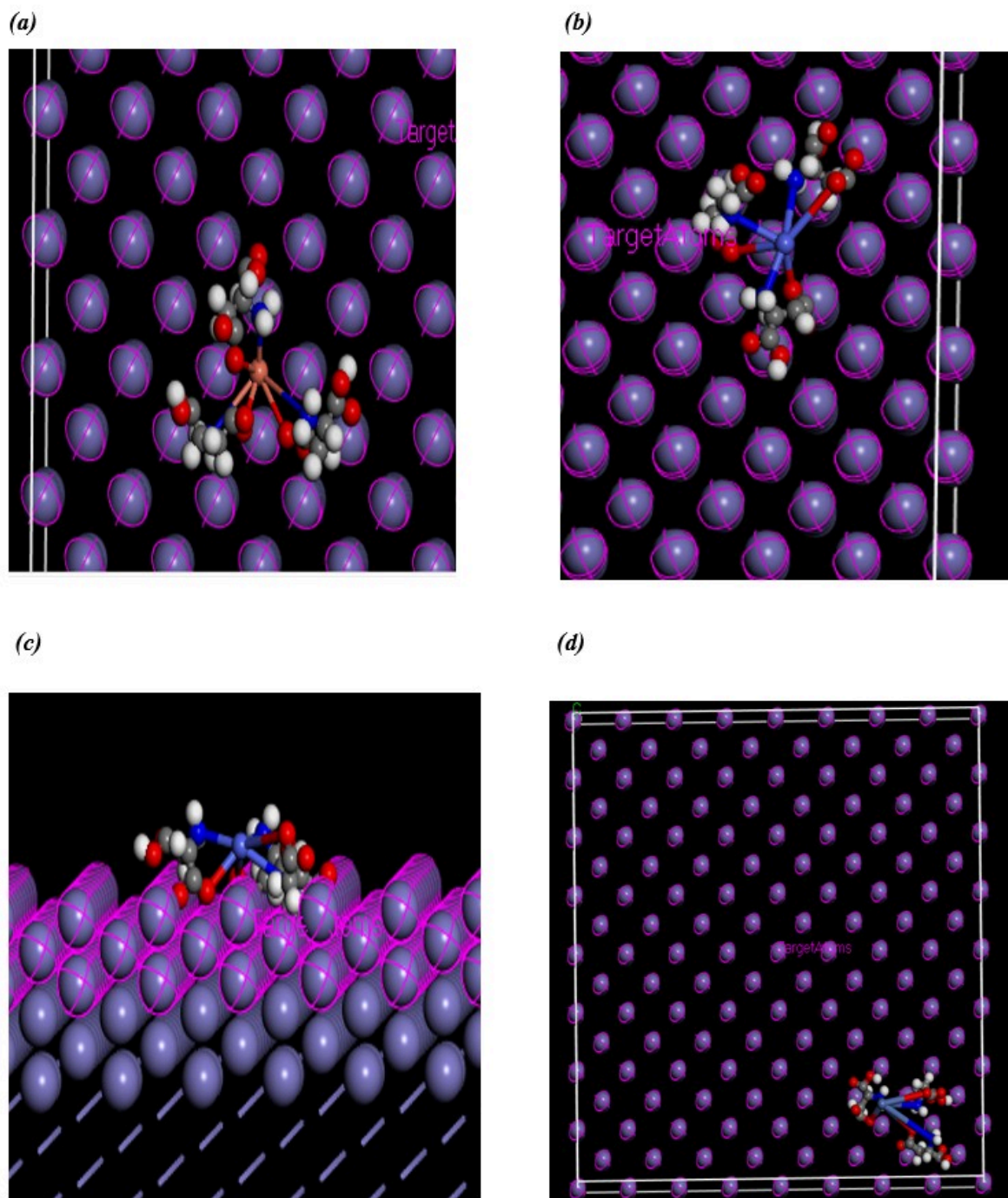


Figure 5

Visual analysis of the optimized configurations of (a) Ni(II), (b) Co(II), (c) Cu(II) and (d) Fe(II) complexes on the Fe(110) metal surface.