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Copper(I/II) and Palladium(II) Complexes Containing Carbothioamide and Triphenylphosphine Ligands: Synthesis, Characterization, and Theoretical Studies

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Abstract

A carbothioamide ligand, 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carbothioamide, [$C_{17}H_{17}N_3OS$], has been synthesized from the condensation of 4-methoxychalcone with thiosemicarbazide. The carbothioamide (L) ligand and triphenylphosphine (Ph_3P) as co-ligand, was coordinated with Cu(I), Cu(II), and Pd(II) metal ions to synthesis the corresponding complexes: [$CuCl_2$(L)] **1**, [CuCl(L)(Ph_3P)] **2**, [$PdCl_2$(L)] **3**, and [PdCl(L)(Ph_3P)]Cl **4**. The ligand and all complexes were collected in solid form after the reactions and characterized by magnetic susceptibility, elemental analysis, molar conductivity, FT-IR, UV-Vis, and ^{1}H, ^{13}C, ^{31}P-NMR techniques. The molar conductance values in DMSO (5.8–16.3 Ω^{-1} cm^2 mol^{-1}) confirmed all the complexes to be non-electrolytic except for the Pd(II) complex **4** (32.6 Ω^{-1}cm^2 mol^{-1}) that behaves as a 1:1 electrolyte. According to spectroscopic evidence, the carbothioamide ligand behaves as an N, S donor and chelating agent. Magnetic susceptibility measurements combined with electronic spectral data suggest that the Cu(II) and Pd(II) complexes have square planar geometry, whereas the Cu(I) complex **2** has a tetrahedral geometry. Elemental analysis and ^{1}H-NMR spectroscopy confirmed the mononuclear structure of all complexes. DFT calculations showed that the synthesized complexes **1**, **3**, and **4** exhibit higher thermodynamic stability than the free ligand (L), with ΔE values of 1.4695, 2.1116 eV, 1.9076 eV, and 1.2980 eV, respectively. In contrast, complex **2** has ΔE = 0.5385 eV, indicating lower thermodynamic stability. Among the complexes, complex **2** (S = 3.7140 eV) exhibited the highest softness, and all complexes were observed to be softer than the triphenylphosphine ligand. According to the results, electron transitions are easier in certain complexes than in their ligands, which suggests that the prepared complexes could be used in the photocell in future studies.

Keywords: Carbothioamide, Cu(I/II) complexes, Pd(II) complexes, NBO analysis, DFT calculations, MEP surfaces

1. Introduction

Thioamides, such as thiosemicarbazone and carbothioamide, are an important class of compounds that have attracted considerable attention due to their remarkable pharmacological and biological properties.[1] The complexes of carbothioamide with transition metals have received significant attention because of their biological behaviors, including antitumor, antibacterial, antifungal, and anticarcinogenic activities.[2,3] In particular, when chalcone derivatives are combined with thiosemicarbazide, novel carbothioamides are often synthesized with better pharmacological activities.[4] In addition, carbothioamide ligands possess multiple donor atoms, enabling them to coordinate with metal ions through either N or S atoms.[5] Typically, these ligands act as chelating ligands for transition metal ions, ligated via sulfur (=S) and pyrazoline nitrogen (=N–). However, in certain cases, they exhibit monodentate behavior, binding entirely through the sulfur (=S) atom.[6,7] A previous study reported that the carbothioamide ligand coordinates with the Cu(II) center via its nitrogen and sulfur donor atoms, forming a five-membered chelated ring in the resulting copper complex.[8] In this study, Cu(I/II) and Pd(II) were selected as metal centers.

Copper(I/II) complexes exhibit a wide range of biological activity, including antiviral, antitumor, and anti-inflammatory properties.[9] Furthermore, Pd complexes, particularly with sulfur and nitrogen donor ligands, have demonstrated significant *in vitro* cytotoxicity against different cancer cell lines.[10] The addition of triphenylphosphine, an organophosphorus substance, as a co-ligand also plays a critical role in coordination chemistry.[11] Because it has strong sigma-donor and pi-acceptor abilities, it can form stable complexes with a variety of metal ions.[12] In palladium chemistry, mixed ligand complexes containing Ph_3P are commonly used as homogeneous catalysts in necessary organic transformations, such as Suzuki-Miyaura and Sonogashira coupling reactions, which play a crucial role in pharmaceutical and material science.[13] Similarly, mixed ligand copper complexes based on triphenylphosphine have demonstrated promising catalytic activity in azide-alkyne cycloadditions as well as in oxidation reactions.[14] There are a few studies that reported metal complexes that combine both carbothioamide and triphenylphosphine ligands; however, researchers have thoroughly studied carbothioamide metal complexes separately. An X-ray structure of a distorted tetrahedral copper(I) complex containing both 4-benzoylpyridinethiosemicarbazone and triphenylphosphine ligands has been reported.[15] Additionally, a square planar palladium complex containing a thioamide ligand was synthesized, and its cytotoxic activity was evaluated against colorectal (HT-29), human colon (Caco-2), and human cervical (HeLa) cancer cell lines using the MTT assay.[16] The current study describes the synthesis, characterization, and geometrical structure of new Cu(I) and Pd(II) complexes containing 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carbothioamide (L) and triphenylphosphine as co-ligands. These complexes were characterized by magnetic susceptibility, elemental analysis, molar conductivity, FT-IR, ^{31}P, ^{1}H, ^{13}C-NMR, and UV-Vis techniques. In addition, theoretical studies, including FMO (Frontier Molecular Orbital), NBO (Natural Bond Orbital), and MEP (Molecular Electrostatic Potential), were conducted on the synthesized complexes.

2. Experimental

2. 1. Materials, General Methods, and Instrumentation

$PdCl_2$ (59% Pd) was purchased from Sigma Aldrich and $CuCl_2{\cdot}2H_2O$ (99%) was purchased from BDH. Triphenylphosphine was purchased from Carl Roth. Methanol (99%), dimethyl sulfoxide (99%), and dimethylformamide (99.5%) were supplied by Chem-Lab Company and used directly without further purification. A Shimadzu FT-IR Affinity-1 spectrophotometer was used to record FT-IR spectra within the range 400-4000 cm^{-1} using KBr discs. The far–infrared spectra were obtained using a Shimadzu Affinity-ICE FTIR 800 cm^{-1} spectrophotometer using CsI discs in the 200-600 cm^{-1} frequency range. UV-Vis spectra were measured utilizing a Jenway 7205 UV-Visible spectrophotometer with DMSO as the solvent. ^{1}H, ^{13}C, and ^{31}P-NMR spectra were recorded on a Bruker 400 MHz Ultra-shield in DMSO-d_6 solvent at the University of Isfahan, Iran. In order to determine the carbon, hydrogen, and nitrogen content of the synthesized ligand and its complexes, ECS 4010 at the University of Isfahan, Iran was utilized. The conductivity measurement was taken in a 1×10^{-3} mol dm^{-3} solution at 25 °C by using the Jenway 4200 conductivity/TDS meter. Magnetic susceptibility measurements were performed with the auto magnetic susceptibility Sherwood Scientific device. In order to determine the melting point, a melting device, model DMP-800, manufactured by A&E Lab UK CO., LTD, was used.

2. 2. Synthesis Procedures

2. 2. 1. Synthesis of 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carbothioamide (L) ligand

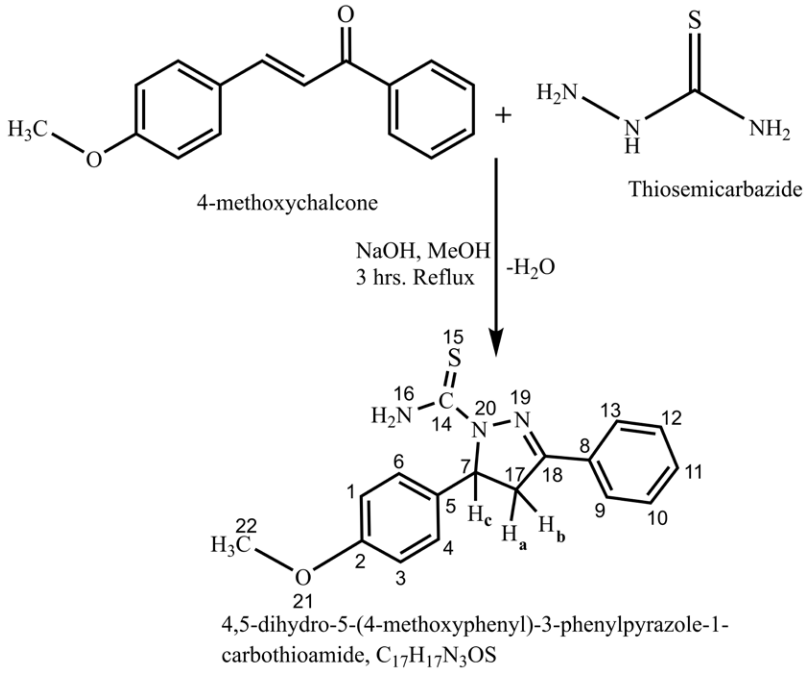
A mixture of thiosemicarbazide (0.006 mmol, 0.5468 g) and 4-methoxychalcone (0.006 mmol, 1.4296 g) was refluxed in 50 mL of methanol at 70 °C. Upon complete dissolution of the reactants, 10 mL of NaOH (1.2 mol/L) was added dropwise. The reaction mixture was further refluxed for 3 hours. Subsequently, the mixture was cooled in an ice bath, and the resulting precipitate was filtered, washed with cold ethanol/water (50:50%), and recrystallized in a mixture of chloroform-ethanol (4:1).

The synthesis route of Ligand (L) is displayed in Scheme 1.

Color: Light yellow powder, Melting point: 145-147 °C, Yield: 1.3304 g (71.21%); Elemental analysis for [$C_{17}H_{17}N_3OS$]: M.W. 311.40 g mol^{-1}; Calculated (%): C, 65.57; H, 5.50; N, 13.49. Found (%): C, 65.36; H, 5.19; N, 13.29; FT-IR spectral peak (v/cm^{-1}): 3406, 3255 (NH_2), 3147–3062 (ArC-H), 2960, 2837 (C-H of CH_3), 1654 (C=N), 1597-1481 (ArC=C), 1255 (C-O), 835 (C=S); ^{1}H NMR (DMSO-d_6) δ/ppm: 8.08 (s, 2H, NH_2), 7.89 (d. 2H, $H_{9,13}$), 7.47 (t, 1H, H_{11}), 7.44 (t, 2H, $H_{10,12}$), 7.07 (d, 2H, $H_{4,6}$), 6.86 (d, 2H, $H_{1,3}$), 5.88 (dd, 1H, H_c), 3.90 (dd, 1H, H_b), 3.70 (s, 3H, OCH_3), 3.14 (dd, 1H, Ha). ^{13}C NMR (DMSO) δ/ppm: 176.07 (C=S), 158.18 (C-2), 154.95 (C-18), 135.02 (C-8), 130.93 (C-5), 130.53 (C-11), 128.68 (C-10,12), 127.08 (C-9,13), 126.64 (C-4,6), 113.80 (C-1,3), 62.35 (C-7), 55.02 (C-22), 42.39 (C-17). UV-Vis. (λ_{max}/nm): 288, 358.

2. 2. 2. Synthesis of [$CuCl_2$(L)] 1

A solution of ligand (L) (2.40 mmol, 0.7473 g) in 20 mL of ethanol was added dropwise to a stirred solution of $CuCl_2{\cdot}2H_2O$ (2.40 mmol, 0.4091 g) in 20 mL of ethanol. The reaction mixture was then stirred at 50 °C for 3



Scheme 1. Synthetic route of carbothioamide ligand.

hours, resulting in the formation of a brown precipitate. The precipitate was filtered, washed with ethanol/diethyl ether mixture, and dried in air. Color: brown powder, Melting point: 160-161.5 °C, Yield: 0.7811 g (73%); Elemental analysis for $[C_{17}H_{17}Cl_2CuN_3OS]$: M.W. 445.85 g mol^{-1}; Calculated (%): C, 45.80; H, 3.84; N, 9.42. Found (%): C, 46.22; H, 3.50; N, 9.17; IR spectral peak (ν/cm^{-1}): 3446, 3244 (NH_2), 3147-3062 (ArC-H), 2956, 2835 (CH_3), 1608 (C=N), 1585–1444 (ArC=C), 1249 (C-O), 829 (C=S), 578 (Cu-N), 487 (Cu-S), 322 (Cu-Cl); ^{1}H NMR (DMSO-d_6) δ/ppm: 9.11 (s, 2H, NH_2), 8.13 (d. 2H, $H_{9,13}$), 7.78 (t, 1H, H_{11}), 7.45 (t, 2H, $H_{10,12}$), 6.80 (d, 2H, $H_{4,6}$), 6.65 (d, 2H, $H_{1,3}$), 5.74 (dd, 1H, H_c), 3.95 (dd, 1H, H_b), 3.70 (s, 3H, OCH_3), 2.87 (dd, 1H, H_a); Molar conductance (Λ_m/ $\Omega^{-1}cm^2$ mol^{-1}): 5.8; Magnetic moment (μ_{eff} / B.M.): 1.83; UV-Vis. (λ_{max} /nm): 292, 317, 363, 579.

2. 2. 3. Synthesis of [CuCl(L)(Ph_3P)] 2

To a solution of $CuCl_2{\cdot}2H_2O$ (1.440 mmol, 0.2455 g) in 10 ml of ethanol, a solution of ligand (L) (1.440 mmol, 0.4484 g) in 10 ml ethanol was added, followed by stirring for one hour at room temperature. To the brown precipitates formed, solid Ph_3P (0.3778 g, 1.440 mmol) was added and the contents were stirred for an additional 4 hours, the precipitate color was changed to white. The precipitate formed was isolated by filtration, washed with methanol, and dried in air. Color: white powder, Melting point: 197–199 °C, Yield: 0.4785 g (69%); Elemental analysis for $[C_{35}H_{32}ClCuN_3OPS]$: M.W. 672.69 g mol^{-1}; Calculated (%): C, 62.49; H, 4.80; N, 6.25. Found (%): C, 63.13; H, 4.45; N, 5.81; IR spectral peak (ν/cm^{-1}): 3441, 3244 (NH_2), 3142-3055 (ArC-H), 2953, 2833 (CH_3), 1602 (C=N), 1587, 1489 (ArC=C), 1435 (P-Ph), 1249 (C-O), 1097 (P-C), 831 (C=S), 565 (Cu-N), 476 (Cu-S), 384 (Cu-P), 338 (Cu-Cl); ^{1}H NMR (DMSO-d_6) δ/ppm: 8.91 (s, 2H, NH_2), 8.39 (d. 2H, $H_{9,13}$), 7.91 (t, 1H, H_{11}), 7.66 (t, 2H, $H_{10,12}$), 7.54-7.28 (m, 15H, Ph_3P), 7.08 (d, 2H, $H_{4,6}$), 6.89 (d, 2H, $H_{1,3}$), 5.55 (dd, 1H, H_c), 3.82 (dd, 1H, H_b), 3.72 (s, 3H, OCH_3), 2.77 (dd, 1H, H_a); ^{31}P-NMR (DMSO-d_6) δ/ppm: δ = –1.18; Molar conductance (Λ_m/ $\Omega^{-1}cm^2$ mol^{-1}): 8.6; Magnetic moment (μ_{eff} / B.M.): < 1.0; UV-Vis. (λ_{max}/nm): 301, 369.

2. 2. 4. Synthesis of [$PdCl_2$(L)] 3

$PdCl_2$ (1.1280 mmol, 0.200 g) was added to a stirred solution of ligand (L) (1.1280 mmol, 0.3513 g) in 20 mL of ethanol and stirred for 6 hours at 60 °C, during stirring a red-brown precipitate was formed. After completing the reaction, the product was filtered, washed with ethanol/diethyl ether mixture, and dried in air. Color: red-brown powder, Melting point: 183–185 °C, Yield: 0.3647 g (66%); Elemental analysis for $[C_{17}H_{17}Cl_2N_3OPdS]$: M.W. 488.72 g mol^{-1}; Calculated (%): C, 41.78; H, 3.51; N, 8.60. Found (%): C, 42.09; H, 3.29; N, 8.47; IR spectral peak (ν/cm^{-1}): 3414, 3250 (NH_2), 3145-3061 (ArC–H), 2956, 2833 (CH_3), 1608 (C=N), 1587-1446 (ArC=C), 1247 (C-O), 829 (C=S), 480 (Pd-N), 320 (Pd-S), 296 (Pd-Cl); ^{1}H NMR (DMSO-d_6) δ/ppm: 9.03 (s, 2H, NH_2), 8.08 (d. 2H, $H_{9,13}$), 7.74 (t, 1H, H_{11}), 7.46 (t, 2H, $H_{10,12}$), 7.03 (d, 2H, $H_{4,6}$), 6.89 (d, 2H, $H_{1,3}$), 5.89 (dd, 1H, H_c), 4.00 (dd, 1H, H_b), 3.73 (s, 3H, OCH_3), 3.33 (dd, 1H, H_a). Molar conductance (Λ_m/ $\Omega^{-1}cm^2$ mol^{-1}): 16.3; Magnetic moment (μ_{eff} / B.M.): < 1.0; UV-Vis. (λ_{max}/nm): 299, 346, 390, 476.

2. 2. 5. Synthesis of [PdCl(L)(Ph_3P)]Cl 4

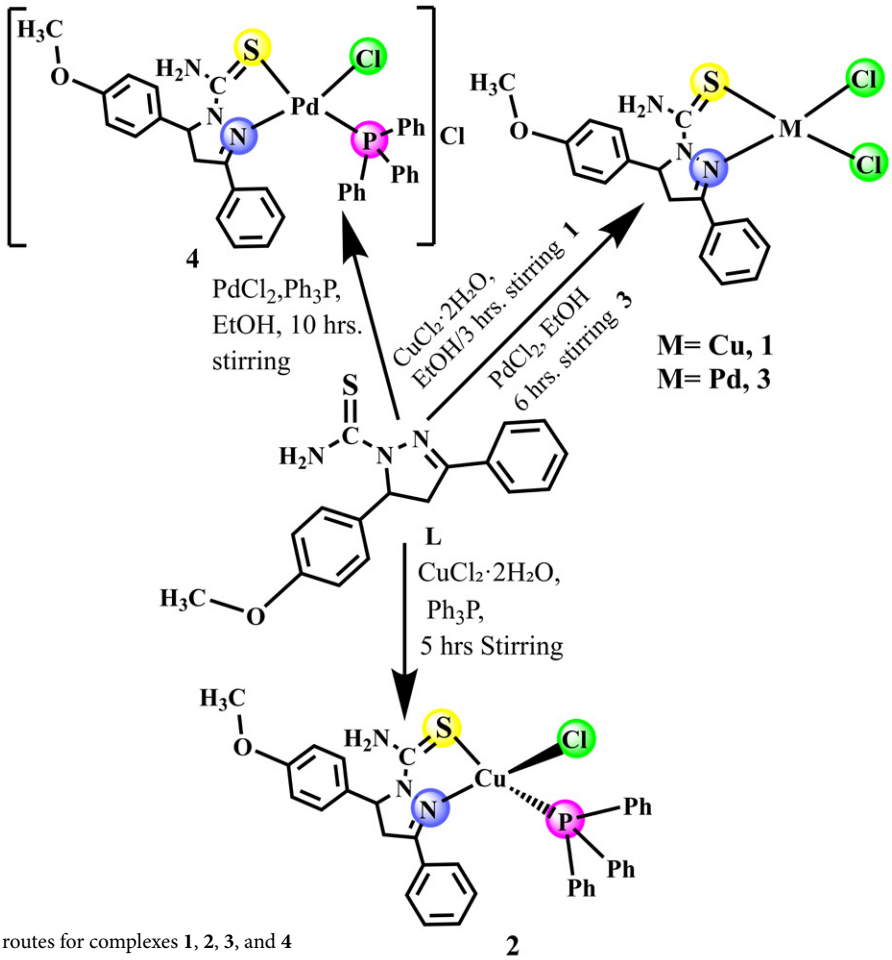
$PdCl_2$ (1.410 mmol, 0.2500 g) was added to a solution of Ph_3P (1.410 mmol, 0.3698 g) in ethanol (15 mL) and stirred for 2 hours at 60 °C. Subsequently, a solution of ligand (L) (1.410 mmol, 0.4390 g) in ethanol (10 mL) was added to the reaction mixture, and stirring was continued for an additional 8 hours. The resulting orange-yellow precipitate was collected by filtration, washed with methanol, and dried in air. Color: Orange-Yellow powder, Melting point: 216–218 °C, Yield: 0.8577 g (81%); Elemental analysis for [$C_{35}H_{32}Cl_2N_3OPPdS$]: M.W. 751.01 g mol^{-1}; Calculated (%): C, 55.98; H, 4.29; N, 5.60. Found (%): C, 56.40; H, 4.09; N, 5.11; IR spectral peak (ν/cm^{-1}): 3392, 3253 (NH_2), 3155-3055 (ArC-H), 2954, 2833 (CH_3), 1606 (C=N), 1583-1492 (ArC=C), 1435 (P-Ph), 1247 (C-O), 1095 (P-C), 827 (C=S), 457 (Pd-N), 364 (Pd-P), 321 (Pd-S), 297 (Pd-Cl); ^{1}H NMR (DMSO-d_6) δ/ppm: 8.84 (s, 2H, NH_2), 8.34 (d. 2H, $H_{9,13}$), 7.94 (t, 1H, H_{11}), 7.72 (t, 2H, $H_{10,12}$), 7.66-7.37 (m, 15H, Ph_3P), 7.27 (d, 2H, $H_{4,6}$), 7.06 (d, 2H, $H_{1,3}$), 5.84 (dd, 1H, H_c), 3.90 (dd, 1H, H_b), 3.69 (s, 3H, OCH_3), 3.32 (dd, 1H, H_a); ^{31}P-NMR (DMSO-d_6) δ/ppm: δ = 25.58; Molar conductance (Λ_m/Ω^{-1} cm^2 mol^{-1}): 32.6; Magnetic moment (μ_{eff} /B.M.): < 1.0; UV-Vis. (λ_{max}/nm): 294, 310, 360, 418.

2. 3. DFT Calculation

Density functional theory (DFT) calculations were carried out using the Gaussian 09 software package to gain better insights into the structural characteristics of the copper and palladium complexes. The Gauss View 6.0 software, with the B3LYP level of theory was utilized to analyze the frontier molecular orbitals of the 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carbothioamide (L) ligand, Cu(I), Cu(II) and Pd(II) complexes. The 6-311G basis set was employed for non-metal elements such as C, H, N, O, S, P, and Cl, while the LANL2DZ basis set was utilized for copper and palladium metal centers.[17] The molecular electrostatic potential (MEP) and natural bond orbital (NBO) calculations of the ligands and their complexes were carried out using the same Gaussian software.[18]

3. Results and Discussions

Triphenylphosphine (Ph_3P) and 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carboth ioamide (L) were employed as ligands for the coordination of copper and palladium ions as displayed in Scheme 2.



Scheme 2. Synthetic routes for complexes **1**, **2**, **3**, and **4**

One mole equivalent of $CuCl_2{\cdot}2H_2O$ reacts with one mole equivalent of carbothioamide (L) in ethanol to yield Cu(II) complex **1**, while the mixed ligand complex **2** results from the reaction of $CuCl_2{\cdot}2H_2O$ with equimolar amounts of Ph_3P and L ligands in ethanol. During the synthesis of complex **2**, the spontaneous reduction of Cu(II) to Cu(I) is caused by triphenylphosphine, which serves as a reducing agent. In addition, sterically demanding ligands containing sulfur also led to the reduction reaction, resulting in a color change from blue to white, indicative of the copper d^{10} electron configuration. Similarly, the reaction of anhydrous $PdCl_2$ salt with carbothioamide (L) under certain experimental conditions led to the synthesis of complex **3**, while the mixed ligand complex **4** was formed from the reaction of $PdCl_2$ with equimolar amounts of Ph_3P and L ligands in ethanol. The structural composition of the prepared complexes was confirmed by elemental analysis, magnetic susceptibility, molar conductivity, UV-Vis, FT-IR, and ^1H, ^{13}C, ^{31}P-NMR spectroscopy. In addition, the complexes were soluble in some organic solvents, such as dimethyl sulfoxide and dimethylformamide, at ambient temperatures; however, they were insoluble in ethanol, chloroform, acetone, diethyl ether, methanol, and water.

3. 1. IR Spectral Studies

The metal complexes were identified by studying their infrared spectra and comparing them with the FT–IR spectra of the free ligands used in their synthesis. The IR spectrum of free 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carbothioamide (L) (Figure S1) exhibits medium bands of the NH_2 group at 3406 and 3255 cm^{-1}, whereas the complex spectra of **1**, **2**, **3**, and **4** show medium bands of the -NH_2 group at (3446, 3244 cm^{-1}), (3441, 3244 cm^{-1}), (3414, 3250 cm^{-1}), and (3392, 3253 cm^{-1}), respectively.[19] In the solid state, NH_2 peaks are observed in complexes spectra, suggesting that the ligand remains in its thione tautomeric form.[20] The free ligand has a characteristic ν(C=N) band at 1654 cm^{-1}, but upon complexation, it was shifted to 1608, 1602, 1608, and 1606 cm^{-1} in **1**, **2**, **3**, and **4**, respectively, indicating the participation of pyrazoline nitrogen (C=N) in coordination with the corresponding metal ions. This is also supported by the appearance of new bands in the range of 578–565 cm^{-1} and 480–457 cm^{-1}, which have been assigned to ν(Cu-N) and ν(Pd-N), respectively.[21,22] The band observed at 835 cm^{-1} is related to ν(C=S) in the IR spectrum of the ligand (L) and is shifted towards a lower wave number in the IR spectra of the complexes (Figure S3–6). It suggests that thione sulfur is ligated to metal ions. Therefore, it can be concluded that the ligand acts as a bidentate chelating agent coordinated via pyrazoline nitrogen and thione sulfur.[23] The diagnostic of the ν(P-Ph) band at 1435 cm^{-1} supports the presence of coordinated triphenylphosphine.[24] Another definitive evidence is the appearance of weak new low-frequency absorption bands in the range of 384–364 cm^{-1} and 296–338 cm^{-1} that are assigned the ν(M-P) and ν(M-Cl) frequencies, respectively (Figure S7–10).[25]

3. 2. ^{13}C, ^1H, and ^{31}P–NMR Studies

The ^{13}C NMR spectrum of the ligand (L) showed a characteristic peak at δ = 176.07 ppm attributed to the thione carbon (C=S), whereas the carbon (C-2) appeared at δ = 158.18 ppm. The imine carbon (C-18) appeared at δ = 154.95 ppm. The aromatic carbons (C-8), (C-5), (C-11), (C-10,12), (C-9,13), (C-4,6), (C-1,3), (C-7), and (C-17) showed signals at δ = 135.02, 130.93, 130.53, 128.68, 127.08, 126.64, 113.80, 62.35, and 42.39 ppm, respectively. Additionally, the signal at δ = 55.02 ppm (C-22) was assigned to the methyl group (Figure S11).[26] The ^1H-NMR spectrum of the free ligand (L) showed a singlet at δ = 8.08 ppm, corresponding to the (NH_2) proton. The methoxy (OCH_3) protons appeared at δ = 3.70 ppm. In the ^1H-NMR spectrum of free ligand L, C-17 (Ha), C-17 (Hb), and C-7 (Hc) protons of the pyrazoline ring resonated as three doublets of doublets at δ 3.14–3.09, 3.90–3.82, and 5.88–5.84 ppm, respectively. These splittings arise from vicinal coupling with the two magnetically inequivalent C-17 methylene protons (Figure S12).[27] A signal was observed at δ = 3.34 ppm in the ^1H-NMR spectrum of the free ligand (L), attributed to trace amounts of water in the DMSO solvent.[28] The spectra of metal complexes (**1**-**4**) showed signals at δ 9.11, 8.91, 9.03, and 8.84 ppm, respectively, corresponding to the NH_2 group, although this signal is slightly downfield shifted from that of the free ligand; these observations are taken as evidence for coordination through the thione (C=S) group and chelate formation (Figures S13-16).[29] The ^{31}P-NMR spectra for complexes **2** and **4** (Figures S17 and S18) showed a single peak at δP = –1.18 and 25.58 ppm, respectively, which means there is only one type of isomer for each complex and confirms that they are pure.[30]

3. 3. Electronic Spectra, Magnetic Susceptibility and Molar Conductivity Studies

The UV-visible spectra of triphenylphosphine (Ph_3P), carbothioamide (L) ligands, and their corresponding complexes (**1**, **2**, **3,** and **4**) were recorded at room temperature in DMSO solution (10^{-3} mol. L^{-1}), as shown in (Figure 1). The Ph_3P and Carbothioamide (L) ligands exhibited electronic absorption bands at 34013 cm^{-1} (294 nm) and 34722 cm^{-1} (288 nm), attributed to $\pi\rightarrow\pi^*$ transitions, respectively. Also, the (L) ligand displayed an absorption band at 27932 cm^{-1} (358 nm), which is associated with $n\rightarrow\pi^*$ transition.[31] Complexes **1** and **2** exhibited absorption bands at 34246 cm^{-1} (292 nm), 33222 cm^{-1} (301 nm), 31545 cm^{-1} (317 nm), 27548 cm^{-1} (363 nm), and 27100 cm^{-1} (369 nm), attributed to intra–ligand transitions.[32] The observed bathochromic shifts in these bands are due to the coordination of the ligands with the metal centers. Additionally, a weak absorption band was observed at

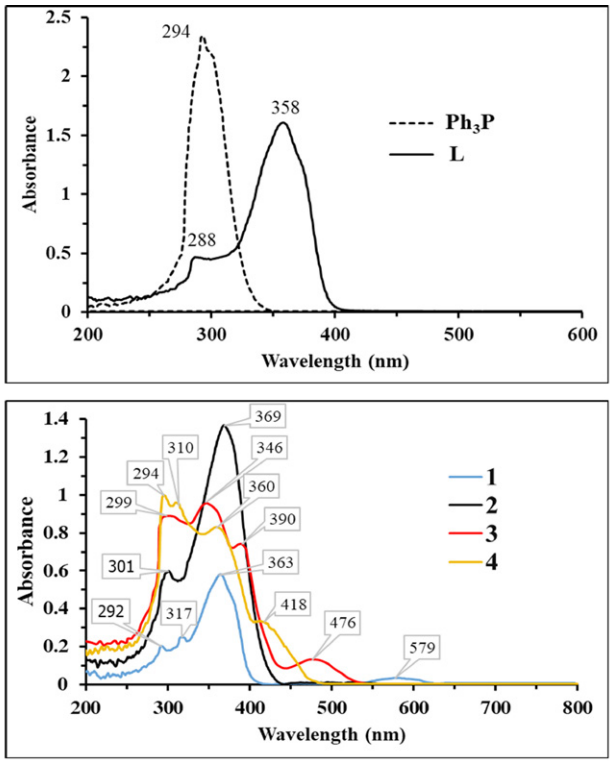


Figure 1. The UV-Vis spectra of Ph_3P, (L) ligands and their complexes

17271 cm^{-1} (579 nm) in complex **1**, which is assigned to the $^2B_{1g}\rightarrow{}^2A_{1g}$ transition, which is typical of a square planar Cu(II) complex.[33] The electronic spectra of complexes **3** and **4**, displayed two d–d transition bands in the ultraviolet and visible regions. The two d–d transition bands were observed in the ranges of 27777–25641 cm^{-1} (360-390 nm) and 23923–21008 cm^{-1} (418–476 nm) and have been attributed to the $^1A_{1g}\rightarrow{}^1E_g$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions, respectively. Furthermore, in the spectra of complexes **3** and **4**, the transitions situated within the spectral range of 34013–33444 cm^{-1} (294–299 nm) and 32258–28901 cm^{-1} (310–346 nm) are related to intra-ligand transitions.[34] The complexes **1**, **2**, and **3** exhibited molar conductivity values in DMSO at 5.8, 8.6, and 16.3 $\Omega^{-1}cm^2\ mol^{-1}$, respectively, indicating that they are non–ionic and have chlorine inside the coordination sphere.[35] In contrast, the complex **4** [Pd-Cl(L)(Ph_3P)]Cl showed a molar conductivity value of 32.6 $\Omega^{-1}cm^2\ mol^{-1}$, suggesting the presence of only one chloride ion outside the coordination sphere, and the complex is ionic at a ratio equal to 1:1.[36] Complex **1** has (μ_{eff} = 1.83 B.M.), which confirms that the Cu(II) complex is square planar and paramagnetic due to a $3d^9$ electron configuration. In contrast, complexes **2**, **3**, and **4** show (μ_{eff} < 1.0 B.M.), confirming that these complexes are diamagnetic.[37]

3. 4. Theoretical Studies

Frontier molecular orbitals (FMOs) and their energy gaps are crucial parameters in quantum chemistry computations. FMO analysis demonstrates chemical reactivity and stability. The negative values of E_{HOMO} and E_{LUMO} are indicators of a molecule's chemical stability. Higher E_{HOMO} values indicate that the molecule is an

Table 1. Quantum chemical parameters (eV) and NBO Charges (e).

Parameter	Ph_3P	L	1	2	3	4
$_{EHOM}O$	−5.7176	−1.4544	−2.4735, −3.2762	−1.5517	−2.6014	−2.5932
E_{LUMO}	−0.7055	−0.4655	−1.004, −1.1646	−1.0132	−0.6938	−1.2952
ΔE	5.0121	0.9889	1.4695, 2.1116	0.5385	1.9076	1.2980
I	5.7176	1.4544	2.4735, 3.2762	1.5517	2.6014	2.5932
A	0.7055	0.4655	1.004, 1.1646	1.0132	0.6938	1.2952
η	2.5061	0.4944	0.73475, 1.0558	0.2693	0.9538	0.6490
S	0.3990	2.0224	1.3610, 0.9471	3.7140	1.0484	1.5408
χ	3.2116	0.9600	1.73875, 2.2204	1.2825	1.6476	1.9442
μ	−3.2116	−0.9600	−1.73875, −2.2204	−1.2825	−1.6476	−1.9442
ω	2.0578	0.9318	2.0573, 2.3348	3.0542	1.4230	2.9121
The NBO charge of Ph_3P, L ligands and their complexes						
Atom	**Ph_3P**	**L**	**1**	**2**	**3**	**4**
Cu	–	–	−0.419, −0.393	−0.221	–	–
Pd	–	–	–	–	−0.214	−0.459
Cl	–	–	−0.304	–	−0.456	−0.515
Cl	–	–	−0.179	−0.514	−0.354	–
N	–	−0.098	0.254	−0.091	0.014	0.171
S	–	0.114	0.726	0.399	0.270	0.495
P	0.7610	–	–	1.040	–	1.126

Ionization potential ($I = -E_{HOMO}$); Electron affinity ($A = -E_{LUMO}$); Hardness ($\eta = (I - A)/2$); Softness ($S = 1/\eta$); Electronegativity ($\chi = (I + A)/2$); Chemical potential ($\mu = -(I + A)/2$); Electrophilicity ($\omega = \mu^2/2\eta$).

electron donor crucial for forming a charge-transfer complex between it and the biological target. Low E_{HOMO} values, in contrast, suggest that a molecule's ability to donate electrons is weak, whereas E_{LUMO} values indicate a molecule's capacity to accept an electron.[38] The chemical hardness of compounds can be used to determine their chemical stability. In general, soft molecules tend to be more polarizable since they require less energy to excite electrons from the HOMO to the LUMO. Hard molecules have a large energy gap, whereas soft molecules have a small energy gap.[39] In this study, we computed the electronic properties of the Ph_3P, 4,5-dihydro-5-(4-methoxyphenyl)-3-phenylpyrazole-1-carbothioamide (L) ligands, and complexes **1**, **2**, **3**, and **4** using the B3LYP method and the 6-311G and LANL2DZ basis sets, respectively. The Ph_3P, L ligands, and complexes **1**, **2**, **3**, and **4** E_{HOMO}, E_{LUMO}, and $\boldsymbol{\Delta E}$ energy gaps are presented in (Figures 2, 3) along with their positive and negative areas. Positive and negative phases are indicated by green and red, respectively. The quantum chemical parameters of the ligands and complexes are listed in Table 1. Each of the ligands and complexes has a singlet spin, except complex **1**, which has a doublet spin. The free Ph_3P and (L) ligands have an energy gap ($\boldsymbol{\Delta E}$) of 5.0121 and 0.9889 eV, while complexes **1**, **2**, **3**, and **4** have a $\boldsymbol{\Delta E}$ of (1.4695, 2.1116), (0.5385), (1.9076), and (1.2980) eV, respectively. The results show that complex **2** is softer (S= 3.7140 eV) than the other complexes because it has the smallest energy gap ($\boldsymbol{\Delta E}$= (0.5385 eV). Therefore, the synthesized Cu(I) complex **2** is more reactive and less stable than the other complexes. Based on ΔE, the stability trend was in the following order: Ph_3P > Cu(II) complex **1** > Pd(II) complex **3** > Pd(II) complex **4** > ligand (L) > Cu(I) complex **2**. The chemical potential values for the synthesized complexes are negative, revealing that they are stable and do not decompose into their components.[40]

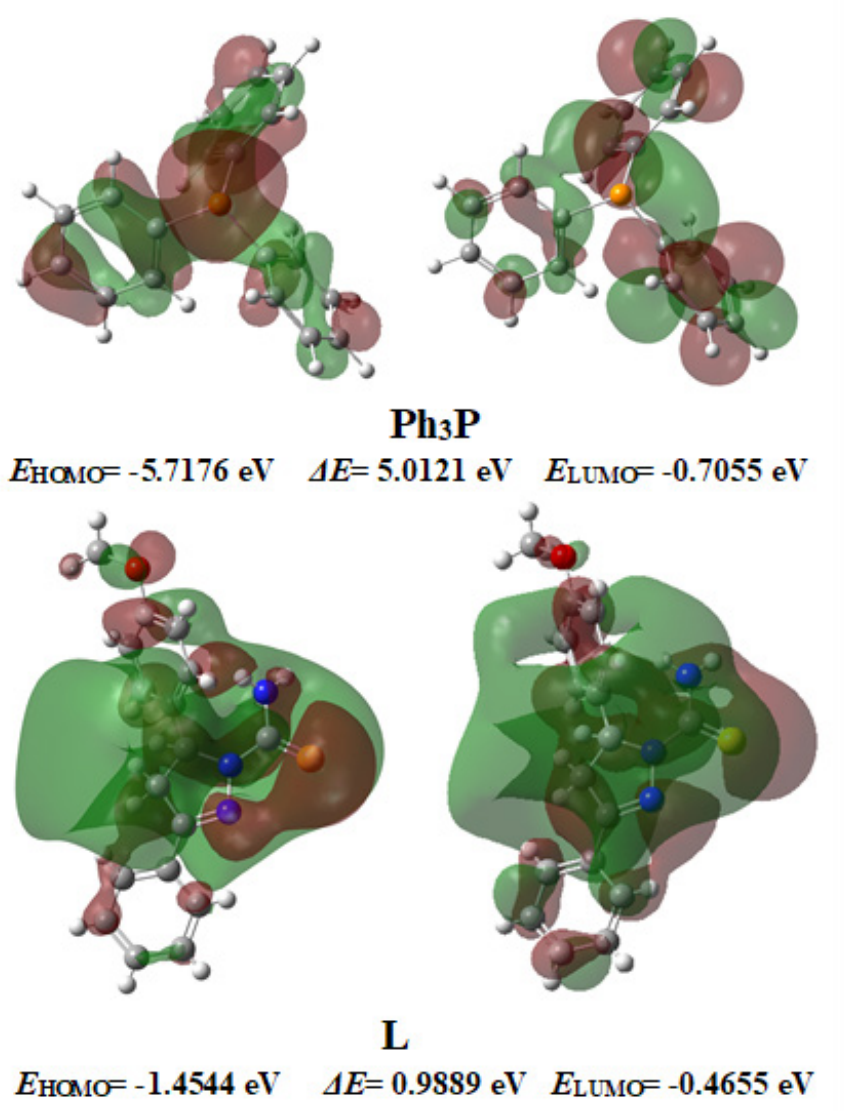


Figure 2. Surface plots of HOMO-LUMO orbitals of Ph_3P and L ligands

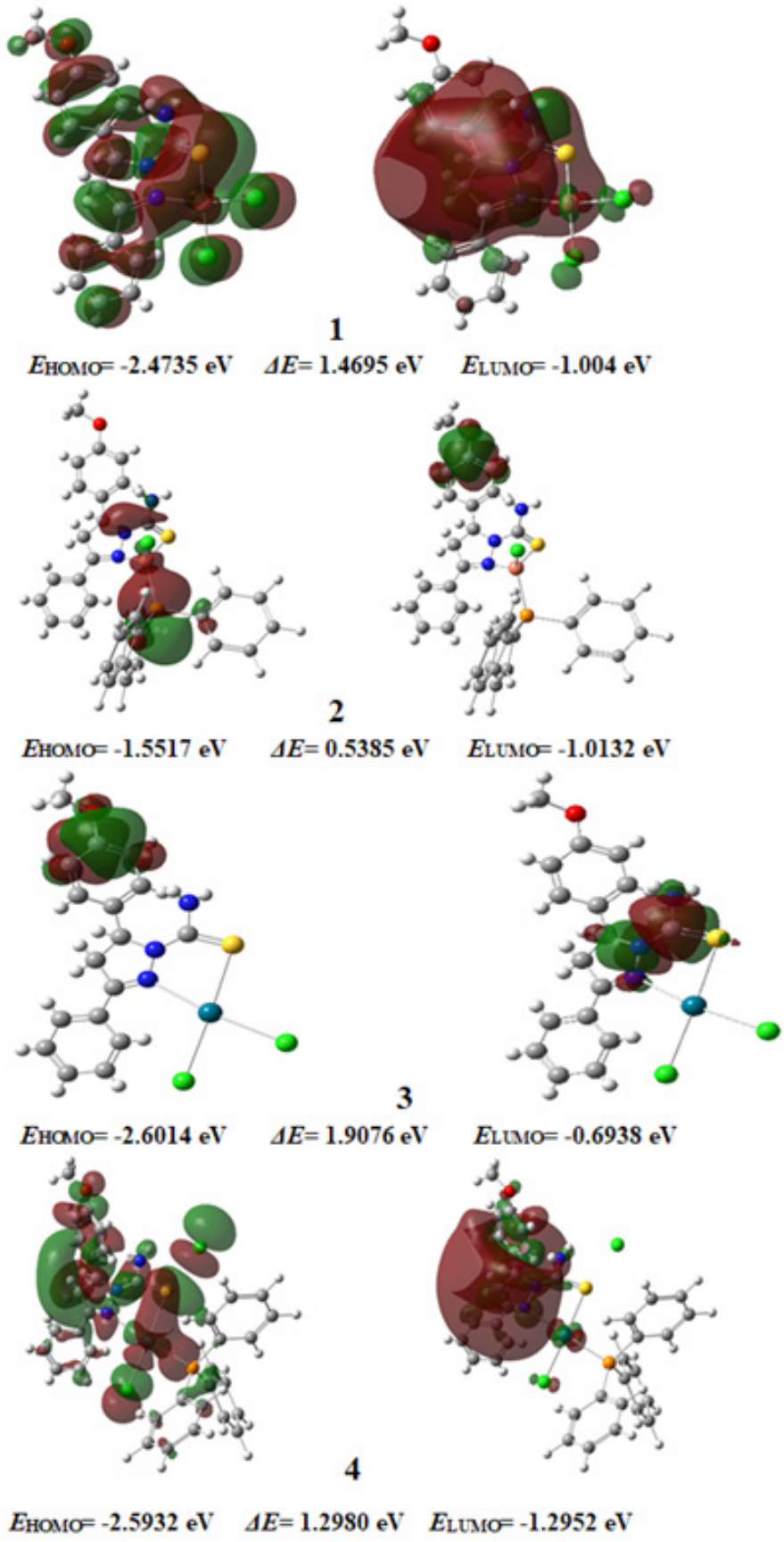


Figure 3. Surface plots of HOMO-LUMO orbitals of complexes **1**, **2**, **3**, and **4**

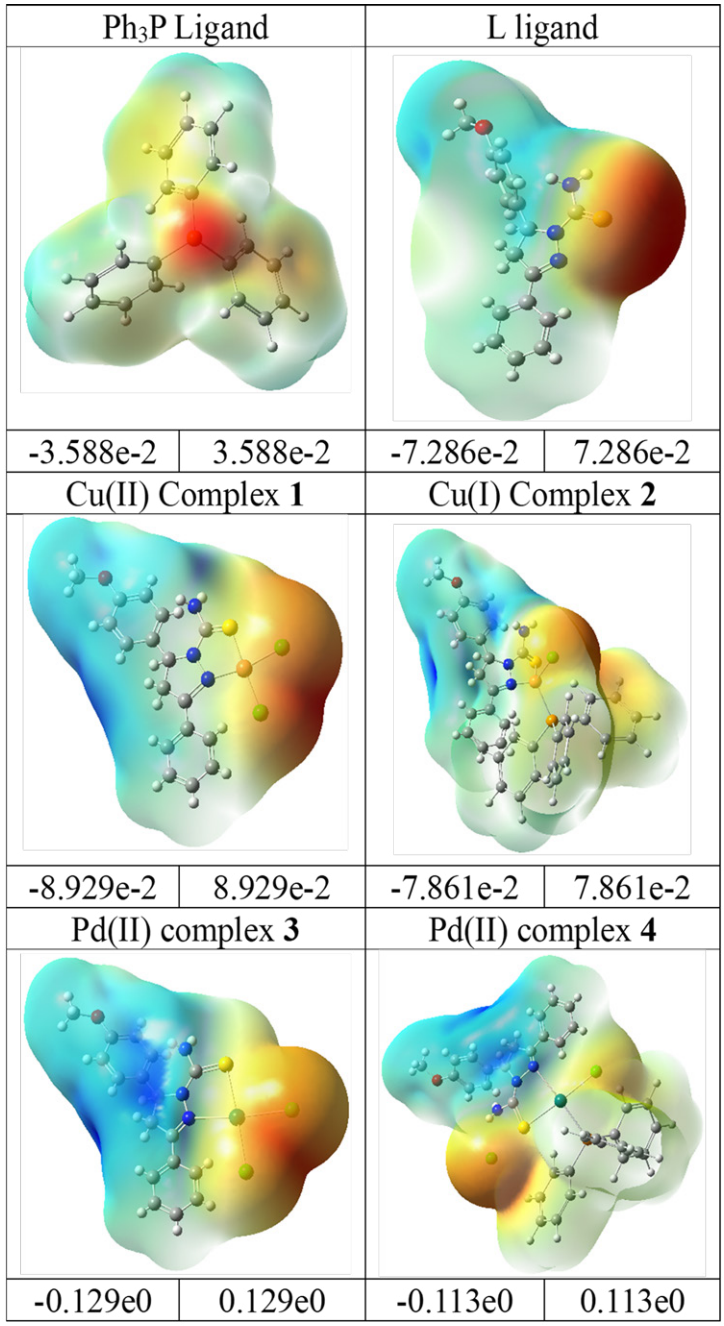


Figure 4. MEP surfaces of the target compounds

Analysis of natural bond orbitals (NBOs) can be used to investigate intermolecular and intramolecular bonding, interactions between donors (ligands) and acceptors (metal centers), as well as charge transfer in molecular structures.[41] According to NBO analysis, the natural electron configuration (NEC) of Cu metal in mononuclear complex **1** is $[Ar]4S^{0.46}\ 3d^{9.59}\ 4P^{1.00}\ 5S^{0.18}\ 4d^{0.03}\ 5P^{0.16}$ and $[Ar]4S^{0.49}\ 3d^{9.55}\ 4P^{0.97}\ 5S^{0.21}\ 4d^{0.05}\ 5P^{0.20}$, containing 11.04974, 11.13174 valence electrons and 0.37680, 0.33826 Rydberg electrons. The natural charge of Cu atom in complex **1** is -0.419 and -0.393e supporting ligand–to–metal charge transfer. The occupancies of the Cu 3d orbitals are $d_{xy}^{1.7362}\ d_{xz}^{1.9904}\ d_{yz}^{1.9819}\ d_{X^2-Y^2}^{1.900}\ d_{z^2}^{1.9790}$ and $d_{xy}^{1.7505}\ d_{xz}^{1.9802}\ d_{yz}^{1.9801}\ d_{X^2-Y^2}^{1.8600}\ d_{z^2}^{1.9792}$. Natural electron configuration (NEC) of Cu atom in complex **2** is $[Ar]4S^{0.01}\ 3d^{9.63}\ 4P^{0.02}\ 5S^{0.45}\ 4d^{0.01}\ 5P^{1.13}$ containing 11.20146 valence electrons and 0.04595 Rydberg electrons. The Cu atom's natural charge is -0.221e, which validates electron transfer to copper metal. The occupancy of the Cu 3d orbitals are $d_{xy}^{1.90008}\ d_{xz}^{1.9693}\ d_{yz}^{1.9243}\ d_{X^2-Y^2}^{1.8774}\ d_{z^2}^{1.9546}$. The NEC of

the Pd atom in complex **3** is [Ar]$5S^{0.48}$ $4d^{9.13}$ $5P^{0.18}$ $5d^{0.01}$ $6P^{0.42}$, containing 10.18715 valence electrons and 0.03024 Rydberg electrons.[42] The natural charge of the Pd atom is –0.214e, confirming electron transport to palladium metal. The occupancy of the Pd 4d orbitals is $d_{xy}^{1.30797}$ $d_{xz}^{1.95286}$ $d_{yz}^{1.93445}$ $d_{X^2-Y^2}^{1.98573}$ $d_{z^2}^{1.94596}$. Also, the NEC of the Pd atom in complex **4** is [Ar]$5S^{0.51}$ $4d^{9.39}$ $5P^{0.34}$ $5d^{0.01}$ $6P^{0.23}$, containing 10.4485 valence electrons and 0.0214 Rydberg electrons. The Pd atom's natural charge is -0.459e, indicating electron transfer to palladium metal. The occupancy of the Pd 4d orbitals is $d_{xy}^{1.70578}$ $d_{xz}^{1.96137}$ $d_{yz}^{1.97689}$ $d_{X^2-Y^2}^{1.81095}$ $d_{z^2}^{1.93072}$. The NBO data indicates that the positive charge on the P (0.7610) atom in the free ligand increases in complexes **2** and **4** due to the transfer of electron density from the filled p orbital of the phosphorus atom to the vacant metal d orbitals (p-d sigma-bonding).[43]

The molecular electrostatic potential (MEP) surfaces for the ligands and their corresponding complexes were calculated and are shown in (Figure 4). In MEP surfaces, red areas signify electrophilic reactivity, whereas blue areas indicate nucleophilic reactivity.[44] The phosphorus atom in Ph_3P and the sulfur atom in the (L) ligand, with their red regions, are identified as reactive sites for electrophilic attack due to the high electronegativity of these atoms. In all complexes, the chlorine atoms located at the negative electrostatic region represented by the red color is a good target for an electrophilic attack.[45]

4. Conclusions

In this research paper, we describe the synthesis and spectral characterization of the complexes $[CuCl_2(L)]$ **1**; $[CuCl(L)(Ph_3P)]$ **2**; $[PdCl_2(L)]$ **3**; and $[PdCl(L)(Ph_3P)]Cl$ **4,** which contain carbothioamide (L) and triphenylphosphine ligands. Spectroscopic studies have shown that carbothioamide (L) acts as an SN-donor bidentate ligand. Magnetic moment, elemental analysis, and electronic spectral data indicate that all synthesized complexes are mononuclear. Moreover, structural analysis suggests that complexes **1**, **3**, and **4** display a square planar geometry, while complex **2** shows a tetrahedral geometry. The magnetic susceptibility measurements indicated that the Pd(II) and Cu(I) complexes are diamagnetic, related to their d^8 and d^{10} electron configurations, respectively. In contrast, the Cu(II) complex demonstrates paramagnetic behaviour, in agreement with the d^9 configuration. UV-Vis spectral analysis detected the $^2B_{1g}\rightarrow{}^2A_{1g}$ transition at 579 nm in complex **1**. Also, d-d transitions were observed at (390–360 nm) and (476–418 nm), which were attributed to the $^1A_{1g}\rightarrow{}^1E_g$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions in complexes **3** and **4**, respectively. NBO analysis showed that the charges on the copper and palladium metal centres, coordinated to the sulfur, nitrogen, and phosphorus atoms of the ligands, were computed as Cu= –0.419, –0.393 e **1**, Cu = –0.221 e **2**, Pd= –0.214 e **3**, and Pd= –0.459 e **4**. These values are less than the formal charge of the $Cu^{+1/+2}$ and Pd^{+2}, supporting electron density transfer from the ligands to the metal ions. MEP surface analysis indicated that electrophilic sites are mainly localized on chlorine atoms in all complexes.

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Povzetek

S kondenzacijo 4-metoksihalkona s tiosemikarbazidom smo sintetizirali karbotioamidni ligand, 4,5-dihidro-5-(4-metoksifenil)-3-fenilpirazol-1-karbotioamid [$C_{17}H_{17}N_3OS$]. Karbotioamidni ligand (L) in trifenilfosfin (Ph_3P) kot koligand sta se vezala na ione kovin Cu(I), Cu(II) in Pd(II) za sintezo ustreznih kompleksov: [$CuCl_2$(L)] (**1**), [CuCl(L)(Ph_3P)] (**2**), [$PdCl_2$(L)] (**3**) in [PdCl(L)(Ph_3P)]Cl (**4**). Ligand in vse komplekse smo izolirali v trdni obliki ter karakterizirali z magnetno susceptibilnostjo, elementno analizo, molsko prevodnostjo, FT-IR, UV-Vis in NMR spektroskopijami (^{1}H, ^{13}C, ^{31}P). Vrednosti molske prevodnosti v DMSO (5,8–16,3 Ω^{-1} cm^2 mol^{-1}) potrjujejo, da so vsi kompleksi neelektrolitski, razen Pd(II) kompleksa **4**, ki se obnaša kot 1:1 elektrolit (32,6 Ω^{-1} cm^2 mol^{-1}). Spektroskopski podatki kažejo, da se karbotioamidni ligand koordinira kot N,S-donor in kelatni ligand. Meritve magnetne susceptibilnosti skupaj z elektronsko spektroskopijo nakazujejo, da imajo kompleksi Cu(II) in Pd(II) kvadratno planarno geometrijo, medtem ko ima Cu(I) kompleks **2** tetraedrično strukturo. Elementna analiza in ^{1}H NMR spektroskopija potrjujeta enojedrno strukturo vseh kompleksov. DFT-računi kažejo, da imajo sintetizirani kompleksi **1**, **3** in **4** večjo termodinamsko stabilnost kot prosti ligand (L), s pripadajočimi vrednostmi ΔE (1,4695; 2,1116 eV), (1,9076 eV) in (1,2980 eV). V nasprotju s tem ima kompleks **2** nižjo termodinamsko stabilnost (ΔE = 0,5385 eV). Med sintetiziranimi kompleksi je največjo mehkobo pokazal kompleks **2** (S = 3,7140 eV), sicer pa so bili vsi kompleksi mehkejši od trifenilfosfinskega liganda. Rezultati kažejo, da v določenih kompleksih elektronski prehodi potekajo lažje kot v njihovih ligandih, kar nakazuje možnost njihove uporabe v fotocelicah v prihodnjih raziskavah.