J. Chem. Sci. (2020) 132:64
https://doi.org/10.1007/s12039-020-01763-8

REGULAR ARTICLE

Synthesis, characterization, X-ray structure and DNA binding study of palladium(II) complex with new thioether containing ONS donor ligand

SUBRATA JANA, RAHUL NASKAR, CHANDAN KUMAR MANNA and TAPAN KUMAR MONDAL*

Department of Chemistry, Jadavpur University, Kolkata, West Bengal 700 032, India
E-mail: tapank.mondal@jadavpuruniversity.in

MS received 6 November 2019; revised 14 December 2019; accepted 17 December 2019

Abstract. A palladium(II) complex, [Pd(L)Cl] (**1**) with a new ONS donor azo–thioether ligand (L) (where L = 2,4-dihydroxy-5-((2-(methylthio)phenyl)diazenyl)(phenyl)(phenyl)methanone) is successfully synthesized. The ligand and complex are thoroughly characterized by several spectroscopic techniques. The geometry of the complex is confirmed by single-crystal X-ray analysis. Electronic structure and spectral properties are interpreted by DFT and TDDFT calculations. The interaction of the complex with CT DNA was investigated by UV-vis method and binding constant is found to be 5.42×10^4 M^{-1}. Competitive binding titration with ethidium bromide (EB) by fluorescence titration method was carried out to understand the efficiency of the complex to displace EB from EB-DNA complex. From fluorescence titration Stern-Volmer dynamic quenching constants, K_{sv} was calculated and is found to be 4.15×10^4 M^{-1}. Cyclic voltammogram of the complex exhibits significant shifting of the reduction couple to the negative potential region and decrease in current height in the presence of CT DNA.

Keywords. Palladium(II) complex; ONS donor azo–thioether ligand; X-ray structure; DNA binding study; DFT computation.

1. Introduction

In the past few decades, the chemistry of transition metal complexes with ONS donor ligand are extensively studied because of their plausible applications in fundamental, applied sciences and coordination chemistry beneficial in industrial and synthetic processes such as catalysis, photochemistry, and biological systems.[1–5] Due to the presence of both hard and soft donors, the chemistry of transition metals with ONS donor ligands is drawing unabated interest to gain the information about their mode of coordination, structural and spectral features.[6–9] Moreover, because of redox non-innocent nature of azo-thioether ligands, the transition metal complexes have gained augmented research interest in recent years owing to the participation in a variety of interesting redox reactions.[5,10,11] The complexes encompassing azo functional ligands have acknowledged escalated consideration owing to their interesting physical, chemical, photophysical and photochemical properties.[12–14] Besides, the study of compounds containing S and N atoms has engendered copious research interest in recent years due to their significant antifungal, antibacterial and anticancer activities.[15,16] Moreover, thioether ligands are of fascinating and more important to the coordination chemists to develop effective model complexes to mimic the active sites of several metallo proteins.[17–19]

Since the discovery of *cis*-platin as an antitumor drug, various closely related platinum and palladium complexes have designed and synthesized to improve the therapeutic activity of the antitumour drugs.[20] Because of the similarity in structure and coordination chemistry of these two metals, palladium-based complexes are also investigated significantly in the field of pharmaceutical chemistry.[21,22] Palladium(II) complexes

*For correspondence

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s12039-020-01763-8) contains supplementary material, which is available to authorized users.

Published online: 16 April 2020

with ligands containing pyridine derivatives, quinoline, pyrazole and 1,10-phenanthroline, have shown very promising antitumor activities.[23,24] The anticancer activity of these compounds is relying mostly on specific interactions with DNA, leading to damage and ultimately to cell death. The study of the interaction of transition metal complexes with DNA gives an idea to design the pharmaceutical molecules to elucidate the mechanism and principles involved in the site-specific recognition of DNA.[25]

As part of our continuing research on transition metal complexes with azo-thioether ligands,[26–31] herein we have designed and synthesized a new thioether containing ONS donor ligand (L) (L = 2,4-dihydroxy-5-((2-(methylthio)phenyl)diazenyl)(phenyl)(phenyl)methanone) and its palladium(II) complex, [Pd(L)Cl] (**1**). The compounds are characterized by several spectroscopic techniques. The geometry of palladium(II) complex is confirmed by a single-crystal X-ray study. The ability of the complex to bind with CT DNA is investigated by UV-Vis method, while the competitive binding with ethidium bromide (EB) is carried out by fluorescence method to assess the ability of the complex to displace EB from EB-DNA system. Theoretical calculations by DFT/B3LYP method are carried to interpret the electronic structure, redox and spectral properties of the complex.

2. Experimental

2.1 *Materials and methods*

All the reagents and solvents were purchased from commercial sources and used as received. 2-(Methylthio)aniline, 2,4-dihydroxy benzophenone, [n-Bu_4N][ClO_4] (TBAP) and $PdCl_2$ were purchased from Sigma Aldrich. The solutions spectral studies were carried out using spectroscopic grade solvents. CT DNA was purchased from Sisco Research Laboratory Pvt. Ltd. (SRL), India. The stock solution of CT-DNA was prepared by dissolving sodium CT-DNA salt in Tris-buffer solution (NaCl 50 mM, Tris-HCl 5 mM, pH was adjusted to 7.5 with 0.5 M NaOH) and stored at 4 °C in the refrigerator. The DNA concentration per nucleotide was determined UV-vis method using $\varepsilon = 6600\ M^{-1}\ cm^{-1}$ at 260 nm.[32]

Microanalyses (C, H, N) data were obtained using a PerkinElmer Series-II CHN-2400 CHNS/O elemental analyzer. Electronic spectra were measured on a Lambda 750 PerkinElmer spectrophotometer. Fluorescence spectra were taken on a Shimadzu RF-6000 spectro fluorophotometer. IR spectra were recorded on a RX-1 PerkinElmer spectrometer in the range of 4000–400 cm^{-1} with the samples in the form of KBr pellets. NMR spectrum was recorded in $CDCl_3$ on a Bruker (AC) 300 MHz FT-NMR spectrometer in the presence of TMS as an internal standard. HRMS mass spectra were obtained on a Waters (Xevo G2 Q-TOF) mass spectrometer. Cyclic voltammetric measurements were carried out using a CHI Electrochemical workstation. A platinum wire working electrode, a platinum wire auxiliary electrode and Ag/AgCl reference electrode were used in a standard three-electrode configuration. [n-Bu_4N][ClO_4] was used as the supporting electrolyte in acetonitrile and the scan rate used was 50 mV s^{-1} under nitrogen atmosphere.

2.2 *Synthesis of ligand (L)*

2-(Methylthio)aniline (1.529 g, 11 mmol) was dissolved in 20 mL of 6 M hydrochloric acid and cooled. To it, 10 mL sodium nitrite (0.759 g, 11 mmol) solution was added dropwise under constant stirring condition at 0 °C. The diazotized solution was then added to 30 mL 2,4-dihydroxy benzophenone (2.354 g, 11 mmol) solution in 5 M sodium hydroxide. A deep red precipitate was appeared and collected by filtration. The precipitate was washed with cold distilled water. The crude product was purified by column chromatography using silica gel (60–120 mesh). The desired red band of the ligand (L) was eluted with 30% (v/v) ethylacetate–petroleum ether mixture. The yield was 2.81 g, 70 %.

Anal. Calc. for $C_{20}H_{16}N_2O_3S$ (L): C, 65.92; H, 4.43; N, 7.69; Found: C, 65.7; H, 4.3; N, 7.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.69 (1H, s), 12.92 (1H, s), 8.28 (1H, s), 7.77 (1H, d, J = 6.2 Hz), 7.68 (1H, d, J = 7.2 Hz), 7.29–7.64 (7H, m), 6.72 (1H, s), 2.61 (3H, s). FT–IR υ (KBr, cm^{-1}): 3300–3400 υ(OH), 1677 υ(C=O), 1440 υ(N=N). λ_{max} (ε, $M^{-1}\ cm^{-1}$) in acetonitrile: 435 (2153), 328 (8511), 285 (12828). ESI-MS *m/z*: 364.2, $[M + H]^+$.

2.3 *Synthesis of palladium(II) complex, [Pd(L)Cl] (**1**)*

0.089 g (0.5 mmol) of $PdCl_2$ was dissolved in 25 mL acetonitrile under refluxing condition. To it 10 mL acetonitrile solution of L (0.182 g 0.5 mmol) was added and refluxed for 10 h. The initial orange colour was changed to deep red. The reaction mixture was cooled and solvent was removed under reduced pressure. The yield was 0.192 g, 76%.

Anal. Calc. for $C_{20}H_{15}ClN_2O_3PdS$, [Pd(L)Cl]: C, 47.54; H, 2.99; N, 5.54; Found: C, 47.4; H, 2.8; N, 5.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.45 (1H, s), 8.27 (1H, s), 7.76 (1H, d, J = 6.8 Hz), 7.64 (1H, t, J = 8.0 Hz), 7.28–7.57 (7H, m), 6.83 (1H, s), 3.02 (3H, s). FT–IR υ (KBr, cm^{-1}): 3337 υ(OH), 1657 υ(C=O), 1413 υ(N=N). λ_{max} (ε, M^{-1} cm^{-1}) in acetonitrile: 490 (2940), 405 (2977), 322 (14475), 286 (17228). ESI-MS *m/z*: 528.3, $[M + Na]^+$.

2.4 *DNA binding study*

The binding efficiency of the palladium(II) complex with CT DNA was carried out by UV-vis and fluorescence methods. All experiments involving CT DNA were performed in Tris-HCl/NaCl buffer solution, pH 7.5. UV-vis titration was performed for the complex by keeping the invariable concentration (5.0×10^{-5} M) of the complex in 1:10 acetonitrile/buffer solution while varying the concentration of CT DNA *via* steady addition of CT-DNA (1.0×10^{-3} M). The absorption spectra were recorded in the range of 250–700 nm. CT DNA solutions were added stepwise until a saturation state was achieved. After each addition, the solutions were allowed to equilibrate and the solutions were found to be in equilibrium by 5 min. The equilibrium binding constant (K_b) of the complex with CT DNA was determined from the UV-vis titration using the Benesi-Hildebrand relation given in eqn. (1).[33]

$$\frac{[DNA]}{(\varepsilon_a - \varepsilon_f)} = \frac{[DNA]}{(\varepsilon_b - \varepsilon_f)} + \frac{1}{K_b(\varepsilon_b - \varepsilon_f)} \quad (1)$$

where [DNA] is the concentration of CT DNA in base pairs. The ε_a, ε_f and ε_b are the apparent absorption coefficients correspond to A_{obsd}/[complex], to the absorbance for the free palladium(II) complex, and to the absorbance of the palladium(II) complex in the fully bound form, respectively. K_b is the equilibrium binding constant in M^{-1}.

The competitive binding study of palladium(II) complex with EB was carried out by fluorescence method to understand the efficiency of displacement of EB from CT DNA-EB system by the palladium(II) complex. The CT DNA-EB complex was prepared by adding 10 μM EB and 12 μM CT DNA in Tris-HCl/NaCl buffer solution, pH 7.5. The fluorescence spectra of EB bound to CT DNA at 602 nm were obtained at an excited wavelength of 540 nm. The intercalating effect of the palladium(II) complex with the DNA-EB was studied by the gradual addition of complex solution into the solution of the DNA-EB. The Stern-Volmer dynamic quenching constant (K_{sv}) was calculated from the linear Stern-Volmer equation (Eq. (2)).[34]

$$I_0/I = 1 + K_{sv}[Q] \quad (2)$$

Where, I_0 and I are the fluorescence intensities of the CT DNA solutions in the absence and in the presence of the complex, respectively. K_{sv} is the Stern-Volmer dynamic quenching constant and [Q] is the total molar concentration of the quencher. K_{sv} was calculated from the slope of the plot.

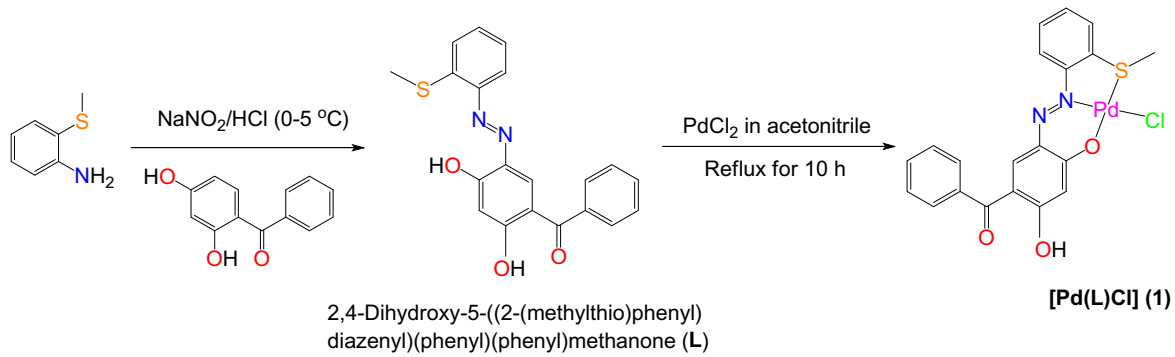
3. Results and Discussion

3.1 *Synthesis and spectral characterization*

The ONS donor azo–thioether ligand (L) (where L = 2,4-dihydroxy-5-((2-(methylthio)phenyl)diazenyl)(phenyl)(phenyl)methanone) was synthesized by diazo–coupling reaction between 2-(methylthio)aniline with 2,4-dihydroxy benzophenone in 1:1 mole ratio in sodium hydroxide solution. New palladium(II) complex, [Pd(L)Cl] (**1**) was synthesized under refluxing condition by the reaction of $PdCl_2$ and L (Scheme 1). Both the compounds were thoroughly characterized by several spectroscopic techniques. ^{1}H NMR data in $CDCl_3$ is well-supported the proposed structure of the ligand (L). Two sharp singlets for phenolic-OH protons appeared at 13.69 and 12.92 ppm. The singlet peak at 2.61 ppm corresponds to S-CH_3 protons. The aromatic proton signals appeared in the range of 6.72–8.28 ppm. IR spectrum of free ligand (L) shows characteristic υ(OH), υ(C=O) and υ(N=N) stretching at 3300–3400, 1677 and 1440 cm^{-1} respectively. The υ(N=N) stretching in the complex significantly reduced compare to free ligand value and observed at 1413 cm^{-1} suggesting the coordination of azo-N to palladium center. Electronic spectra of L and complex **1** were taken in acetonitrile and are shown in Figure 1. Free ligand exhibits moderately intense band at 435 nm along with intense bands at 328 nm and 285 nm. For palladium(II) complex moderately intense low energy bands appeared at 490 nm and 405 nm. In addition, two high energy intense sharp bands appeared at 322 and 286 nm.

3.2 *Crystal structure*

Suitable X-ray quality crystals of [Pd(L)Cl] (**1**) were grown by slow diffusion of dichloromethane solution of the complex into *n*-hexane. ORTEP plot of the



Scheme 1. Synthesis of ONS donor ligand (L) and its palladium(II) complex, [Pd(L)Cl] (**1**).

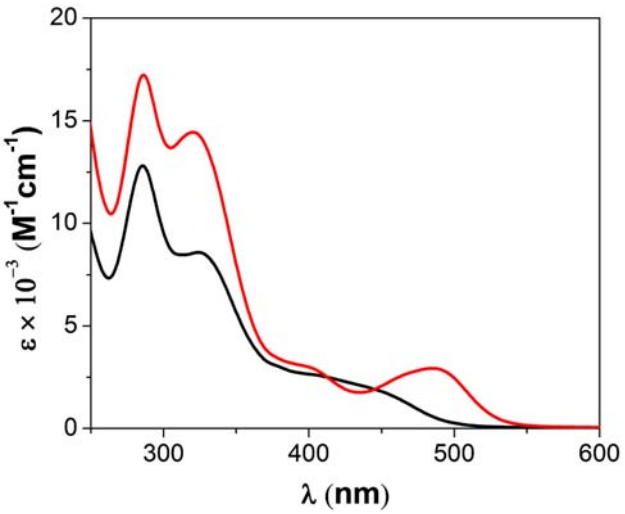


Figure 1. UV-vis spectra of L (—) and [Pd(L)Cl] (**1**) (—) in acetonitrile.

complex along with atom numbering scheme is shown in Figure 2 and selected bond distances and angles are summarized in Table S2 (Supplementary Information). The complex was crystallized in the monoclinic crystal system with $P2_1/c$ space group. The tridentate ONS donor ligand L binds to the palladium center through phenolic-O, azo-N and thioether-S atoms. The geometry of the coordination sphere of the complex can be described as square planar with a slight deviation of chelate bite angles from 90° (<N1-Pd1-O1, 92.19(10)° and <N1-Pd1-S1, 87.32(8)°). The azo bond distance, N1-N2 is found to be 1.271(4) Å in the complex. The Pd-N bond (Pd1-N1) distance 1.975(3) Å is comparable to the other reported Pd-N(azo) bond distances.[35–39] The Pd-O bond distance (Pd1-O1) 1.996(3) Å in the complex is also in good agreement with the reported palladium complexes.[39–43] Similarly, the Pd-S(thioether) bond (Pd1-S1, 2.2365(11) Å) distance is found to be well corroborated with the literature value.[38,44–46]

3.3 *DFT and TDDFT calculations*

The full geometry optimization of free ligand (L) and [Pd(L)Cl] (**1**) were carried out by DFT/B3LYP method. Calculated bond distances and bond angles are summarized in Table S2 (Supplementary Information) for **1**. The calculated structural parameter is in good agreement with the X-ray data. The maximum deviations in bond distances are observed for Pd-S and Pd-Cl bonds by ∼0.08 Å and ∼0.06 Å respectively.

For free ligand, HOMO and HOMO-1 have π-bonding in character, while HOMO-2 has non-bonding in nature and concentrated on azo(N=N) moiety (Figure S2, SI). The LUMOs of L have π anti-bonding in character and the HOMO-LUMO energy gap is found to be 3.31 eV. The HOMO of the complex **1** has 62% ligand contribution and concentrated on phenolate moiety along with 24% contribution of $p\pi$(Cl) orbitals and reduced contribution of $d\pi$(Pd) (14%). HOMO-1 is purely ligand character (83%), while HOMO-2 has 82% $p\pi$(Cl) and 11% $d\pi$(Pd) contributions (Table S3, Figure S3, SI). HOMO-4 and HOMO-6 have a significant contribution of $d\pi$(Pd) orbitals along with the contribution of $p\pi$(Cl) and π(L) orbitals. The LUMO of the complex has 97% π^*(L) character with significant contribution of π^*(N=N). The LUMO+1 has mixed $d\pi$(Pd) and π^*(L) character. LUMO+2 to LUMO+5 have 98–100% π^*(L) character. The HOMO-LUMO energy gap is significantly reduced in the complex compare to free ligand and found to be 3.12 eV.

To get deep inside into the electronic transitions in the compounds, TDDFT calculations were carried out by B3LYP/CPCM method in acetonitrile. The low energy moderately intense band for L at 435 nm corresponds to the HOMO → LUMO transition ($\lambda_{cal.}$ = 448 nm, f = 0.398) $\pi \rightarrow \pi^*$ transition (Table S4, SI). The intense band at 328 nm corresponds to mixed HOMO-1 → LUMO and HOMO → LUMO+1

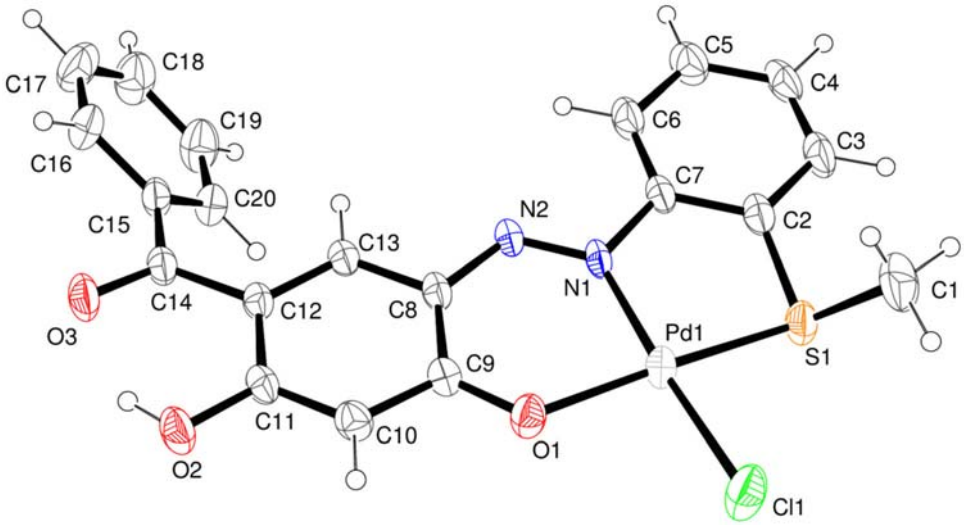


Figure 2. ORTEP plot of complex **1** with 35% ellipsoidal probability.

transitions. The sharp band at 285 nm corresponds to HOMO-3 → LUMO+1 ($\pi \rightarrow \pi^*$) transition. For complex, [Pd(L)Cl] the low energy moderately intense band at 490 nm has mixed ILCT and MLCT character and corresponds to HOMO → LUMO transition. The experimentally observed band at 322 nm corresponds the HOMO-5→LUMO transition having ILCT character. Similarly, the high energy band at 286 nm has ILCT character (Table S4).

3.4 *DNA binding studies*

3.4a *UV-vis method* The binding mode and efficiency of the palladium(II) complex, [Pd(L)Cl] (**1**) to CT DNA was studied by using UV-vis method. UV-vis titration is a well known method that is used to monitor the interaction of a compound with DNA. The binding ability of the complexes to CT DNA, in Tris buffer solution, was studied by measuring its effects on the UV-vis spectrum. Absorption titration experiment of the palladium(II) complex in buffer solution was performed using a fixed complex concentration (50 μM) to which DNA stock solution was gradually added. The binding of the complex to DNA led to a decrease in the absorption intensity at 322 nm (Figure 3). To compare quantitatively the affinity of the palladium(II) complex toward DNA, the intrinsic binding constant K_b of the compound bind to CT-DNA is calculated by monitoring the changes of absorbance with increasing concentration of DNA. The intrinsic binding constant K_b of the complex is found to be $5.42 \times 10^4\ M^{-1}$. This value is comparable to the reported values of binding constants for other palladium(II) complexes towards CT DNA.[41,47–51]

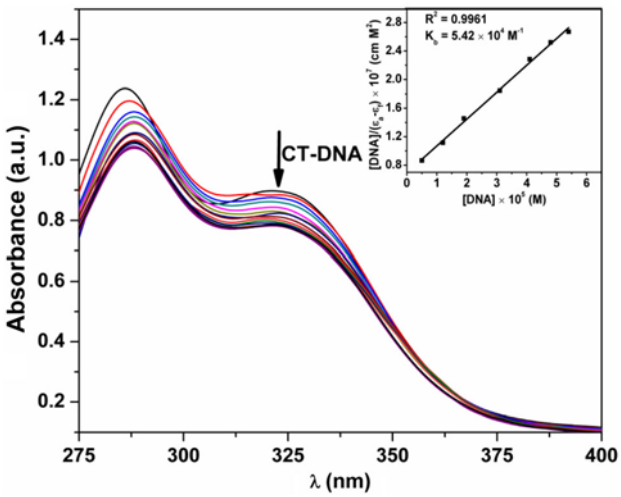


Figure 3. Change in absorption spectra of **1** (50 μM) in Tris-HCl/NaCl buffer with the gradual addition of CT DNA (0–140 μM). Inset: Plot of $[DNA]/(\varepsilon_b - \varepsilon_f)$ *versus* [DNA].

3.4b *Fluorescence method* Fluorescence method is an effective way to study the interaction of metal complexes with CT DNA. Ethidium bromide (EB) is one of the most sensitive fluorescence probes that can bind to DNA. Enhancement of fluorescence intensity is observed due to the intercalation of EB into CT DNA.[52] When metal complex intercalates into DNA it leads to a decrease in fluorescence intensity due to the replacement of EB from EB-CT DNA system.[53] Herein, palladium(II) complex was gradually added to CT DNA, pre-treated with EB and the fluorescence intensity gradually decreased with the increasing concentration of the complex (Figure 4). The titration curves indicate that the complex competes with EB to the binding sites of CT DNA. The Stern-Volmer

dynamic quenching constant is calculated from the slope of the linear plot of I_0/I vs. [Q]. For the complex, the K_{sv} is found to be 4.15×10^4 M^{-1}, which is corroborative to reported K_{sv} values of palladium(II) complexes.[38,54–56]

3.4c *Electrochemistry* Cyclic voltammetric study was carried out in acetonitrile using $[nBu_4N][ClO_4]$ as supporting electrolyte and Ag/AgCl reference electrode. When scanned in the potential range 1.5 to −1.5 V free ligand (L) exhibits an irreversible peak at −1.08 V, whereas complex **1** exhibits quasi-reversible reduction couple with $E_{1/2}$ = −0.55 V (ΔE = 110 mV). The reduction couple of the complex corresponds to the reduction of L as LUMO of the complex has 97% π^*(L) character with a significant contribution of π^*(N=N). Moreover, the cyclic voltammetric method was employed to study the interaction of complex **1** with CT-DNA. The cyclic voltammogram was taken upon the increasing concentration of CT-DNA (0–100 μM) to 1.0×10^{-3} M solution of the complex. It was observed that the peak current significantly decreased along with the negative shift of reduction peak potential (Figure 5). The noticeable decrease in peak current may be due to the decrease in free complex concentration and/or due to the slow diffusion of the complex bound to CT-DNA.[57] Further, to understand the specific changes in electrochemical potentials Differential Pulse Voltammetry (DPV) was performed using $[nBu_4N][ClO_4]$ as supporting electrolyte. The reduction potential of complex **1** is significantly shifted to lower potential region from −0.54 V to −0.61 V in the presence of CT DNA (Figure 6). These observations strongly suggest the interaction of palladium complex with CT-DNA.

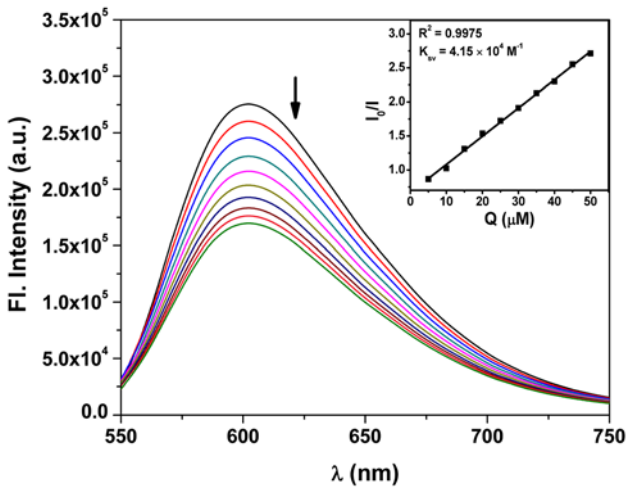


Figure 4. Emission spectra (λ_{ex} = 540 nm) of EB-CT DNA ([EB] = 1.0×10^{-5} M and [DNA] = 1.2×10^{-5}M) in presence of increasing concentration of complex **1** (0–100 μM). Inset: Plots of emission intensity I_0/I *versus* Q (Q is the total molar concentration of the **1**).

4. Conclusions

Herein, a new ONS donor azo-phenol ligand, L was synthesized and characterized. The palladium(II) complex (**1**) of the ligand was successfully synthesized and characterized by several spectroscopic techniques. The distorted square planar geometry of the complex is confirmed by single-crystal X-ray diffraction method. Electronic structure and spectral properties are interpreted by DFT and TDDFT calculations. The interaction of the complex with CT DNA was investigated by UV-vis method and binding constant revels that the complex strongly binds with CT DNA. Competitive binding titration with ethidium bromide (EB) by fluorescence titration method reveals that the

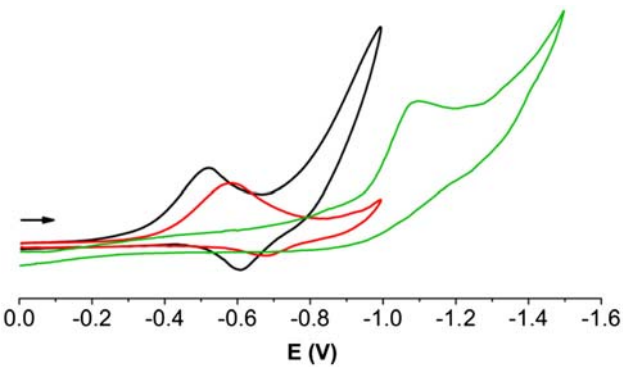


Figure 5. Cyclic voltammogram of free ligand (L) (—) and palladium(II) complex **1** (1 mM) in absent (—) and presence (—) of CT DNA (100 μM).

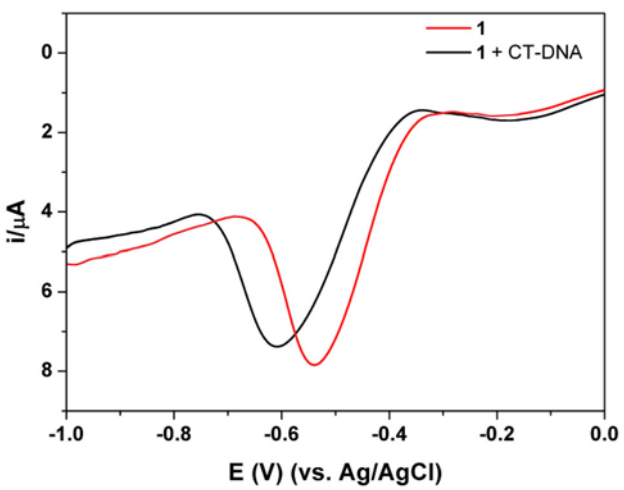


Figure 6. Differential Pulse Voltammograms of 1 mM of complex 1 (—) and in presence of 100 μM CT DNA (—).

complex efficiently displaces EB from EB-DNA system. The significant shifting of the reduction potential to the negative potential region and decrease in current height in cyclic voltammograms are also confirmed the binding of the complex with CT DNA.

Supplementary Information (SI)

Crystallographic data for the structure of [Pd(L)Cl] (**1**) was deposited with the Cambridge Crystallographic Data center with the CCDC No. 1845798. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www:htpp://www.ccdc.cam.ac.uk). Tables S1-S4 and Figures S1-S3 are available at www.ias.ac.in/chemsci.

Acknowledgement

Financial support received from the Science and Engineering Research Board (SERB) (No. EEQ/2018/000266), New Delhi, India is gratefully acknowledged. R. Naskar is thankful to UGC, New Delhi, India for fellowships.

Reference

1. Fayed F, Elsayed S A, El-Hendawy A M and Mostafa M R 2014 Complexes of cis-dioxomolybdenum(VI) and oxovanadium(IV) with a tridentate ONS donor ligand: Synthesis, spectroscopic properties, X-ray crystal structure and catalytic activity *Spectrochim. Acta A* **129** 293
2. Kongot M, Reddy D S, Singh V, Patel R, Singhal N K and Kumar A 2019 ONS donor entwined iron(III) and cobalt(III) complexes with exemplary safety profile as potent anticancer and glucose uptake agents *New J. Chem.* **43** 10932
3. Rahman F, Ali A, Duong H-Q, Ullah Khan I, Bhatti M Z, Li Z-T, Wang H and Zhang D-W 2019 ONS-donor ligand based Pt(II) complexes display extremely high anticancer potency through autophagic cell death pathway *Eur. J. Med. Chem.* **164** 546
4. Halder S, Peng S M, Lee G H, Chatterjee T, Mukherjee A, Dutta S, Sanyal U and Bhattacharya S 2008 Synthesis, structure, spectroscopic properties and cytotoxic effect of some thiosemicarbazone complexes of palladium *New J. Chem.* **32** 105
5. Biswas S, Sarkar D, Roy P and Mondal T K 2017 Synthesis and characterization of a ruthenium complex with bis(diphenylphosphino)propane and thioether containing ONS donor ligand: Application in transfer hydrogenation of ketones *Polyhedron* **131** 1
6. Sinha S, Chakraborty M, Pramanik N R, Raychaudhuri T K, Mondal T K, Sarkar D, Drew M G B, Ghosh S and Mandal S S 2013 Dimer formation by symbiotic donor–acceptor interaction between two molecules of a specially designed dioxomolybdenum(VI) complex containing both donor and acceptor centers—A structural, spectroscopic and DFT study *Polyhedron* **55** 192
7. Muthu T M, Mereiter K, Kirchner K and Karvembu R 2012 Ruthenium(II) carbonyl complexes containing "pincer like" ONS donor Schiff base and triphenylphosphine as catalyst for selective oxidation of alcohols at room temperature *J. Organomet. Chem.* **700** 194
8. Prabhakaran R, Huang R, Karvembu R, Jayabalakrishnan C and Natarajan K 2007 Formation of unusual ruthenium(III) carbonyl complex through ONS tricoordination of salicylaldehyde-*N*-phenylthiosemicarbazone *Inorg. Chim. Acta* **360** 691
9. Kumar S, Saleem F, Mishra M K and Singh A K 2017 Oxine based unsymmetrical (O-, N, S/Se) pincer ligands and their palladium(II) complexes: Synthesis, structural aspects and applications as a catalyst in amine and copper-free Sonogashira coupling *New J. Chem.* **41** 2745
10. Koley A P, Purohit S, Ghosh S, Prasad L S and Manoharan P T 1992 Studies on gold(II) complexes with hard and soft donor ligands. 2. Complexes with o-(methylthio)aniline and 1,2-bis((o-aminophenyl)thio)ethane *Inorg. Chem.* **31** 30
11. Jana M S, Pramanik A K, Kundu S, Sarkar D, Jana S and Mondal T K 2013 Synthesis, X-ray structure, spectroscopic and DFT study of *cis*-$[Ru(PPh_3)(L)X_2]$ complexes ($X = Cl^-$, Br^-, I^- and NCS^-) (L = 1-methyl-2-{(*o*-thiomethyl)phenylazo}imidazole) *Inorg. Chim. Acta* **394** 583
12. Ghosh B K and Chakravorty A 1989 Electrochemical studies of ruthenium compounds part I. Ligand oxidation levels *Coord. Chem. Rev.* **95** 239
13. Akasaka T, Mutai T, Otsuki J and Araki K 2003 Photoinduced energy transfer and its switching in dyad and triad chromophore systems composed of coumarin, Ru(II) and Os(II) terpyridine-type complexes *J. Chem. Soc. Dalton Trans.* 1537
14. Gatri R, Fillaut J-L, Mysliwiec J, Szukalski A, Bartkiewicz S, El-Ouazzani H, Guezguez I, Khammar F and Sahraoui B 2012 Synthesis and characterization of azo-containing organometallic thin films for all optical switching applications *Chem. Phys. Lett.* **535** 106
15. Valarmathy G, Subbalakshmi R, Renganathan R and Kokila R 2018 Synthesis of Schiff Base (E)-2-(((3-Hydroxyphenyl)imino)methyl)-6-methoxyphenol containing N and O donors and its metal complexes: Spectral, thermal, redox behaviour, fluorescence quenching, antimicrobial and anticancer studies *Asian J. Chem.* **30** 645
16. Al-Adilee K J and Jaber S A 2018 Synthesis, characterization and biological activities of some metal complexes derived from Azo Dye Ligand 2-[2′-(5-Methyl thiazolyl)azo]-5-dimethylamino benzoic acid *Asian J. Chem.* **30** 1537
17. Thomas F 2007 Ten years of a biomimetic approach to the copper(II) radical site of galactose oxidase *Eur. J. Inorg. Chem.* 2379
18. Zhou L, Powell D and Nicholas K M 2006 Tripodal Bis(imidazole) thioether copper(I) complexes: mimics of the Cu(B) site of hydroxylase enzymes *Inorg. Chem.* **45** 3840
19. Zhou L, Powell D and Nicholas K M 2007 Tripodal bis(imidazole) thioether copper(I) complexes: mimics

of the Cu_M site of copper hydroxylase enzymes *Inorg. Chem.* **46** 7789
20. Tsiveriotis P and Hadjiliadis N 1999 Studies on the interaction of histidyl containing peptides with palladium(II) and platinum(II) complex ions *Coord. Chem. Rev.* **190-192** 171
21. Maurya M R, Uprety B, Avecilla F, Tariq S and Azam A 2015 Palladium(II) complexes of OS donor N-(di(butyl/phenyl)carbamothioyl)benzamide and their antiamoebic activity *Eur. J. Med. Chem.* **98** 54
22. Bandyopadhyay N, Zhu M, Lu L, Mitra D, Das M, Das P, Samanta A and Naskar J P 2015 Synthesis, structure, spectral characterization, electrochemistry and evaluation of antibacterial potentiality of a novel oxime-based palladium(II) compound *Eur. J. Med. Chem.* **89** 59
23. Tan J H, Lu Y J, Huang Z S, Gu L Q and Wu J Y 2007 Spectroscopic studies of DNA binding modes of cation-substituted anthrapyrazoles derived from emodin *Eur. J. Med. Chem.* **42** 1169
24. Wei X, Yang Y, Ge J, Lin X, Liu D, Wang S, Zhang J, Zhou G and Li S 2020 Synthesis, characterization, DNA/BSA interactions and in vitro cytotoxicity study of palladium(II) complexes of hispolon derivatives *J. Inorg. Biochem.* **202** 110857
25. Fuentes L, Quiroga A G, Organero J A and Matesanz A I 2020 Exploring DNA binding ability of two novel α-N-heterocyclic thiosemicarbazone palladium(II) complexes *J. Inorg. Biochem.* **203** 110875
26. Paira M K, Mondal T K, López-Torres E, Ribas J and Sinha C 2010 Copper(II) complexes of thioarylazopentanedione: Structures, magnetism, redox properties and correlation with DFT calculations *Polyhedron* **29** 3147
27. Paira M K, Mondal T K, Ojha D, Slawin A M Z, Tiekink E R T, Samanta A and Sinha C 2011 Structures, redox behavior, antibacterial activity and correlation with electronic structure of the complexes of nickel triad with 3-(2-(alkylthio)phenylazo)-2,4-pentanedione *Inorg. Chim. Acta* **370** 175
28. Jana S, Jana M S, Sarkar D, Paira M K and Mondal T K 2013 Ruthenium carbonyl complexes of 3-(2-(methylthio)phenylazo)-4-hydroxy-3-penten-2-one: Synthesis, spectral characterization, electronic structure and catalytic activity *J. Mol. Struc.* **1054-1055** 83
29. Pramanik A K and Mondal T K 2014 Ruthenium(III) complexes with tetradentate NSNO donor ligand: Synthesis, electronic structure, catalytic activity and DFT calculation *Inorg. Chim. Acta* **411** 106
30. Pramanik A K, Sarkar D and Mondal T K 2015 A copper(II) complex with a thioether and ether containing azophenol ligand: Synthesis, spectra, X-ray structure and DFT computations *Polyhedron* **102** 32
31. Roy P, Sau Mondal A, Pramanik A K and Mondal T K 2017 Ruthenium carbonyl complex of a redox non-innocent ONS donor azophenol ligand: Electrochemistry, photophysical property, electronic structure and catalytic activity towards oxidation of alcohols *J. Organomet. Chem.* **828** 1
32. Sathyadevi P, Krishnamoorthy P, Bhuvanesh N S, Kalaiselvi P, Padma V V and Dharmaraj N 2012 Organometallic ruthenium(II) complexes: Synthesis, structure and influence of substitution at azomethine carbon towards DNA/BSA binding, radical scavenging and cytotoxicity *Eur. J. Med. Chem.* **55** 420
33. Anjomshoa M, Hadadzadeh H, Torkzadeh-Mahani M, Fatemi S J, Adeli-Sardou M, Rudbari H A and Nardo V M 2015 A mononuclear Cu(II) complex with 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine: Synthesis, crystal structure, DNA- and BSA-binding, molecular modeling, and anticancer activity against MCF-7, A-549, and HT-29 cell lines *Eur. J. Med. Chem.* **96** 66
34. Zhao Y, Zhu J, He W, Yang Z, Zhu Y, Li Y, Zhang J, Guo Z 2006 Oxidative DNA cleavage promoted by multinuclear copper complexes: Activity dependence on the complex structure *Chem. Eur. J.* **12** 6621
35. Pattanayak P, Parua S P, Patra D, Lai C -K, Brandao P, Felix V and Chattopadhyay S 2015 Ruthenium and palladium complexes incorporating amino-azo-phenol ligands: Synthesis, characterization, structure and reactivity *Inorg. Chim. Acta* **429** 122
36. Biswas S, Pramanik A K and Mondal T K 2015 Palladium(II) complex with thiazole containing tridentate ONN donor ligand: Synthesis, X-ray structure and DFT computation *J. Mol. Struct.* **1088** 28
37. Acharya S, Kejriwal A, Biswas A N, Neogi D N and Bandyopadhyay 2012 Design, synthesis, structure and biological evaluation of new palladium(II) hydrazone complexes *Polyhedron* **38** 50
38. Jana S, Pramanik A K, Manna C K and Mondal T K 2018 Palladium(II) complexes with thioether containing azophenol ligands: Synthesis, characterization, X-ray structure and DNA binding study *Polyhedron* **150** 118
39. Pattanayak P, Parua S P, Patra D and Chattopadhyay S 2019 Design and synthesis of immobilized orthopalladated catalyst for C-C coupling *Polyhedron* **157** 410
40. Tshabalala T A and Ojwach S O 2018 Hydrogenation of alkenes and alkynes catalysed by N̂O (imino)phenol palladium(II) complexes: Structural, kinetics and chemoselectivity studies *J. Organomet. Chem.* **873** 35
41. Ayyannan G. Mohanraj M. Raja G, Bhuvanesh N, Nandhakumar R and C. Jayabalkrishnan 2016 Design, synthesis, structure and biological evaluation of new palladium(II) hydrazone complexes *Inorg. Chim. Acta* **453** 562
42. Sedighipoor M, Kianfar A H, Mohammadnezhad G, Gorls G and Plass W 2018 Unsymmetrical palladium(II) N,N,O,O-Schiff base complexes: Efficient catalysts for Suzuki coupling reactions *Inorg. Chim. Acta* 476 20
43. Agahari B, Layek S, Anuradha, Ganguly R, Pathak D D 2018 Synthesis, crystal structures, and application of two new pincer type palladium(II)-Schiff base complexes in C-C cross-coupling reactions *Inorg. Chim. Acta* **471** 345
44. Biswas S, Roy P and Mondal T K 2017 Synthesis of palladium(II) complex with NNS donor Schiff base ligand via C-S bond cleavage: X-ray structure, electrochemistry and DFT computation *J. Mol. Struct.* **1142** 110
45. Canovese L, Visentin F, Scattolin T, Santo C and Bertolasi V 2016 Addition of halogens and interhalogens on palladacyclopentadienyl complexes stabilized by pyridyl−thioether N−S spectator ligands *J. Organomet. Chem.* **808** 48

46. Paul P and Bhattacharya 2014 Palladium complexes of pyrrole-2-aldehyde thiosemicarbazone:Synthesis, structure and spectral properties *J. Chem Sci.* **126** 1547
47. Bandyopadhyay N, Basu P, Kumar G S, Guhathakurta B, Singh and Naskar J P 2017 Biophysical studies on the interaction of a novel oxime based palladium(II) complex with DNA and RNA *J. Photochem. Photobiol. B* **173** 560
48. Barra C V, Rocha F V, Morel L, Gautier A, Garrido S S, Mauro A E, Frem R C G and Netto A V G 2017 DNA binding, topoisomerase inhibition and cytotoxicity of palladium(II) complexes with 1,10-phenanthroline and thioureas *Inorg. Chim. Acta* **446** 54
49. Shabbir M, Akhter Z, Ahmad I, Ahmed S, Shafiq M, Mirza B, McKee V, Munawar K S and Ashraf A R 2016 *J. Mol. Struct.* **1118** 250
50. Bandyopadhyay N, Pradhan A B, Das S, Lu L, Zhu M, Chowdhury S and Naskar J P 2016 Synthesis, structure, DFT calculations, electrochemistry, fluorescence, DNA binding and molecular docking aspects of a novel oxime based ligand and its palladium(II) complex *J. Photochem. Photobiol. B* **160** 336
51. Thakor K P, Lunagariya M V, Bhatt B S and Patel M N 2019 Fluorescence and absorption studies of DNA–Pd(II) complex interaction: Synthesis, spectroanalytical investigations and biological activities *Lumin.* **34** 113
52. Nyarko E, Hanada N, Habib A and Tabata M 2004 Fluorescence and phosphorescence spectra of Au(III), Pt(II) and Pd(II) porphyrins with DNA at room temperature *Inorg. Chim. Acta* **357** 739
53. Patra S C, Roy A K, Banerjee S, Banerjee A, Das Saha K, Bhadra R, Pramanik K and Ghosh P 2019 Palladium(II) and platinum(II) complexes of glyoxalbis(*N*-aryl)osazone: Molecular and electronic structures, antimicrobial activities and DNA-binding study *New J. Chem.* **43** 9891
54. Zianna A, Geromichalos G D, Hatzidimitriou A G, Coutouli-Argyropoulou E, Lalia-Kantouri M and Psomas G 2019 Palladium(II) complexes with salicylaldehyde ligands: Synthesis, characterization, structure, *in vitro* and *in silico* study of the interaction with calf-thymus DNA and albumins *J. Inorg. Biochem.* **194** 85
55. Saeidifar M, Mirzaei H, Nasab N A and Mansouri-Torshizi H 2017 Mononuclear Pd(II) complex as a new therapeutic agent: Synthesis, characterization, biological activity, spectral and DNA binding approaches *J. Mol. Struct.* **1148** 339
56. Eswaran R, Bertani R, Sgarbossa P, Karuppannan N, Nattamai S P 2016 Synthesis, crystal structure, DNA and protein binding studies of novel binuclear Pd(II) complex of 6-methoxy-2-oxo-1,2-dihydroquinoline-3-carbaldehyde-4(*N*,*N*)-dimethylthiosemicarbazone *J. Inorg. Biochem.* **155** 1
57. Zheng K, Liu F, Xu X-M, Li Y-T, Wu Z-Y and Yan C-W 2014 Synthesis, structure and molecular docking studies of dicopper(II) complexes bridged by N-phenolato-N′-[2-(dimethylamino)ethyl]oxamide: The influence of terminal ligands on cytotoxicity and reactivity towards DNA and protein BSA *New J. Chem.* **38** 2964