

DNA Binding test, X-Ray Crystal Structure, Spectral, TG-DTA, and Electrochemistry of $[\text{CoX}_2(\text{dmdphphen})]$ (dmdphphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, X= Cl and NCS) Complexes

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Two new neutral mixed-ligand cobalt(II) complexes, $[\text{CoCl}_2(\text{dmdphphen})]$ **1** and $[\text{Co}(\text{NCS})_2(\text{dmdphphen})]$ **2** where dmdphphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, were synthesized and characterized by an elemental analysis, UV-Vis, IR, TG/DTA, cyclic voltametry CV and single X-ray diffraction. Complex **2** crystallized as monoclinic with a space group $P2_1/c$. Co(II) ions are located in a distorted tetrahedral environment. TG/DTA result shows that these complexes are very stable and decomposed through one step reaction. The two complexes exhibit a quasi-reversible one electron response at -550 and -580 mV vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$, which has been assigned to Co(I)/Co(II) and Co(II)/Co(III) couples. Absorption spectral studies reveal that the such complexes exhibit hypochromicity during their interaction with CT-DNA.

1. Introduction

1,10-phenanthroline and their derivatives are very attractive ligands for metal complexes [1-3]. In addition, their metal complexes are frequently used as catalyst for the enantioselective hydrolysis of *N*-protected amino acid esters, allylic substitutions, reduction of acetophenone [3-6] and Oxidation of olefins [7]. Also, Cobalt (II) complexes with a reversible Co(II)/Co(III) is a good oxygen carrier and can oxidize the double bond of the olefins [8-10].

The ability of the cobalt phenanthroline complexes to bind and to cleave DNA under physiological conditions are of current interests because of their potential applications in nucleic acids chemistry [11]. Also, these complexes are useful in footprinting studies [12-17]. The cleavage of DNA usually occur through the heterocyclic bases, deoxyribose sugar moiety or phosphodiester linkage [18-20]. For the mixed-ligand complexes to interact efficiently with DNA, the ligands need to be flat, large surface area and have a spatial geometry to interact with the base pairs in DNA [15-23]. By changing the ligands or the metal ions, it is possible to modify the interaction with nucleic acids [23-26].

Previously, a series of several mixed-ligand mononuclear [27-28] and dinuclear [29-30] metal complexes have a general formula $MX_2(dmphen)$ (2,9-dimethyl-1,10-phenanthroline, X= Cl, Br) were prepared in our lab. These complexes were found to be suitable precursors for spherical shape metal oxide nanoparticles [31]. Herein, two new neutral mixed-ligand cobalt(II) complexes, $[CoCl_2(dmdphphen)]$ **1** and $[Co(NCS)_2(dmdphphen)]$ **2** where dmdphphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), were synthesized and characterized by different spectroscopic methods. Also, the DNA binding and the catalytic oxidation of styrene in the presence of H_2O_2 for the complexes were investigated.

2. Experimental Section

2.1. Material and instrumentation

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand, $CoCl_2 \cdot 6H_2O$ and $Co(NCS)_2$ were purchased from Acros Organics. Elemental analyses were carried out on an Elementar Vario EL analyzer. The IR spectra for samples were recorded using (Perkin

Elmer Spectrum 1000 FT-IR Spectrometer). The UV-vis spectra were measured by using a TU-1901 double-beam UV-visible spectrophotometer. TG/DTA spectra were measured by using a TGA-7, Perkin-Elmer thermo-gravimetric analyzer. The cyclic voltammograms for the complexes were measured in CH₃CN and 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAHF) using BAS 100 B/W electrochemical workstation (Bioanalytical Systems, West Lafayette, IN, USA) and controlled by a standard 80486 personal computer (BAS control program version 2.0). All electrochemical experiments were carried out at room temperature under argon with a three-electrode cell. Voltalab 80 potentiostat PGZ402 with Pt-disk electrode (Metrohm, A = 0.0064 cm²) was used as working electrode. Platinum wire (ϕ 1 mm) spiral with diameter 7 mm was used as a counter electrode. Haber-Luggin double reference electrode was used as a reference one. All potentials in this paper are reported to an external Cp₂Fe^{0/+} standard [36].

2.2. General procedure for the preparation of the desired complexes

A mixture of CoX₂ salt (2 mmol) in distilled ethanol (15 mL) and free ligand (2.1 mmol) in methanol (10 mL) is stirred for around 0.5 h at room temperature until the precipitation appeared which was filtered, washed with ethanol and dried. Suitable crystals for X-ray diffraction analysis were growing up by slow diffusion of ethanol into a solution of the complex in CH₂Cl₂ after two days (yield, 88%).

2.2.1. Complex 1:

Yield: 0.76 g (90%). Anal. Calc. for C₂₆H₂₀Cl₂CoN₂: C, 63.69; H, 4.11; N, 5.71. Found. C, 63.43; H, 4.21; N, 5.48. UV-Vis (nm) bands in dichloromethane: 655, 572, 360, 240, 280 and 304. M.p 320°C. Conductivity in CH₃CN: 10.28 (μS/cm).

2.2.2. Complex 2:

Yield: 0.94 g (88%). C₂₈H₂₀CoN₄S₂: Cal. C, 62.80; H, 3.76; N, 10.46; S, 11.97 Found. C, 62.92; H, 3.85; N, 10.33; S, 11.86. UV-Vis (nm) bands in dichloromethane: 645, 566, 358, 242, 282 and 305. M.p 290°C. Conductivity in CH₃CN: 9.52 (μS/cm).

2.3. Crystallography

A suitable single crystal complex **2** with dimensions of $0.23 \times 0.22 \times 0.21$ mm was chosen for an X-ray diffraction measurement. X-ray intensity data were collected at 296 K on a Bruker CCD diffractometer equipped with Cu K_{α} radiation ($\lambda = 1.54178$ Å). Data were collected with the φ and ω scan method. The final unit cell parameters were based on all reflections. Data reduction of all the collected reflections and absorption correction were carried out using the APEX 2 [37] package. The structure was solved by direct methods using SHELXS [38]. The structure was then refined by a full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms using SHELXL [38]. All the non-hydrogen atoms were revealed in the first Fourier map, itself. After several cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residual saturated to 0.0671. Details of data collection and refinement are given in Table 1. The geometrical calculations were carried out using the program *PLATON* [39]. The molecular and packing diagrams were generated using the software *MERCURY*[40].

2.4. DNA binding and cleavage experiments

Absorbance measurement was performed to clarify the binding affinity of cobalt(II) complexes by emissive titration at room temperature. The complexes were dissolved in mixed solvent of Tris–HCl buffer (5 mM Tris–HCl/50 mM NaCl buffer for pH = 7.2) for all the experiments and stored at 4 °C for further use and used within 2 days. Tris–HCl buffer was subtracted through base line correction. The absorption experiments were performed by keeping the concentration of cobalt(II) complexes constant (1.5×10^{-4} mol/L) and increasing the concentration of DNA gradually (1.0×10^{-4} – 1×10^{-3} mol/L).

3. Results and Discussion

3.1. Synthesis of the desired complexes

The mononuclear $\text{CoCl}_2(\text{dmdphphen})$ complex **1** and $\text{Co}(\text{NCS})_2(\text{dmdphphen})$ complex **2** were isolated in a good yield without side product as seen in Scheme 1.

Scheme 1. Synthesis of the Co(II)-complexes**1** and**2**.

The structures of the desired complexes were confirmed by using elemental analysis, IR, UV-vis, TG/DTA and X-ray single crystal measurement for complex **2**. The analytical data of the complexes show the formation of [1:1:2] [M:dmdphphen: 2X] ratio in a good agreement with the suggested formula [CoX₂(dmdphphen)] of the isolated complexes. The isolated solid complexes are insoluble in water, ethanol, *n*-hexane and ethers, but soluble in chlorinated solvents as CHCl₃ and CH₂Cl₂. The solubility and molar conductance showed that the two complexes are non-electrolytic in their nature.

3.2.X-Ray Crystal structure

Crystal structure data and selected bonds length for Complex **2** are compiled in Table 1 and Table 2 respectively. ORTEP drawing of the complex is shown in Figure 1. The central cobalt metal ion is coordinated to the two nitrogen atoms (N2 & N13) of the dmdphphen ligand and to two nitrogen atoms (N30 & N33) of the isothiocyanate ligand in a tetrahedral symmetry. The **phenanthroline ring in the** dmdphphen moiety is

essentially planar with a rms deviation of 0.0752 Å. The phenyl rings (C8-C13 & C24-C29) are twisted out of the plane of the dmdphphen moiety as indicated by the dihedral angle values of 43.2(4) °and 47.2(4)° respectively. All coordination distances and bond angles are similar to those found in similar compounds [32]. No classic hydrogen bonds were observed. In the crystal structure there is a π - π stacking interaction between adjacent dmdphphen with distances 3.7109(17) Å and 3.8070(17) Å, which may account in stabilizing the crystal structure (Figure 2). The packing of the molecules when viewed down along the *a* axis indicates that the molecules are interlinked by weak hydrogen bonds to form one dimensional chain.

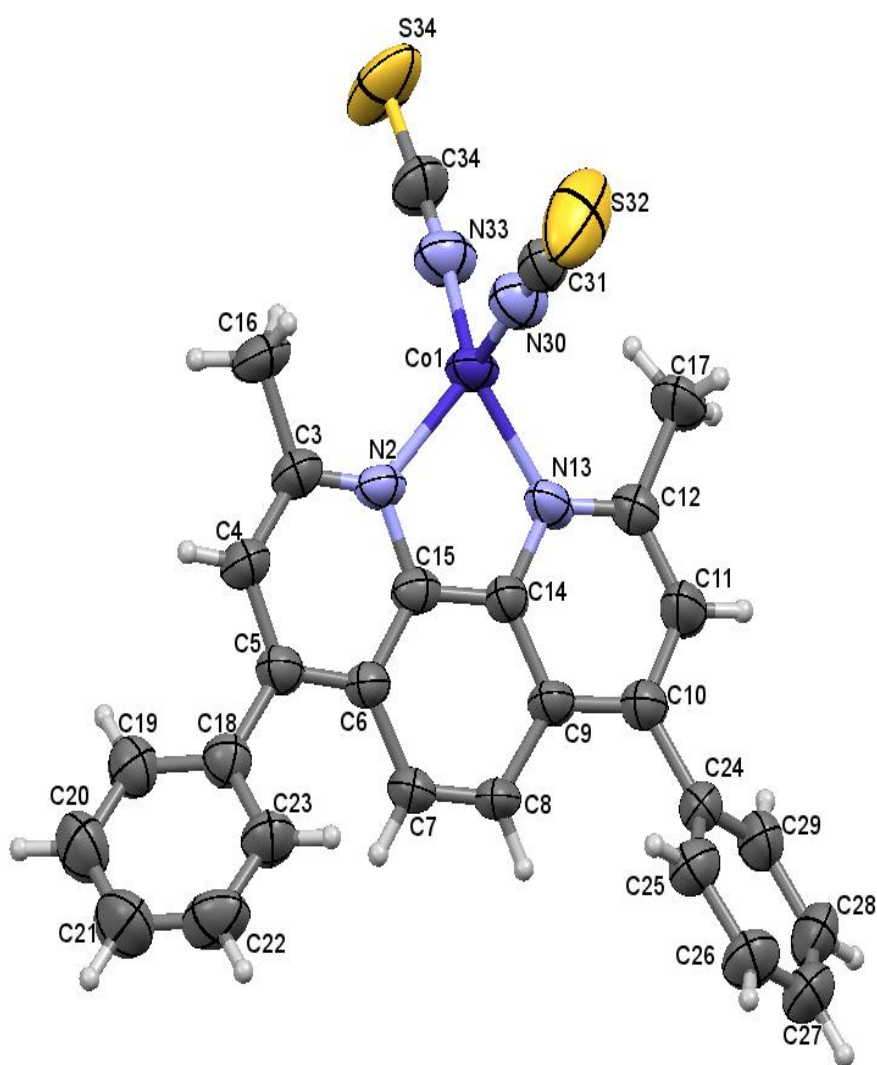


Figure1. ORTEP of the complex2 with atom labelling. Thermal ellipsoids are drawn at the 50% probability level

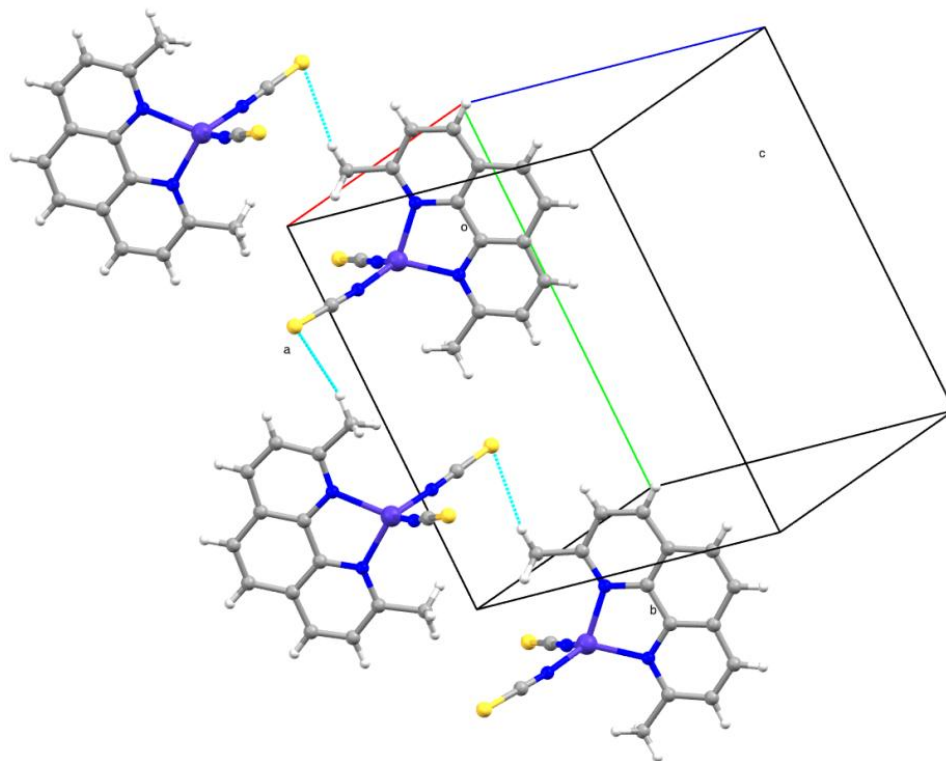


FIGURE 2. A crystal packing of complex **2** viewed (perspective) along crystallographic **a** direction.

TABLE 1. Crystal data and structure refinement for Ligand and complex **2**

	Complex 2
Empirical formula	C ₂₈ H ₂₀ N ₄ S ₂ Co
Formula weight	535.55
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	<i>P2₁/c</i>
Unit cell dimensions	<i>a</i> = 14.8373(12) Å α = 90 ° <i>b</i> = 21.0942(11) Å β = 100.191(4)°. <i>c</i> = 8.2470(6) Å γ = 90°.
Volume	2540.4(3) Å ³
Z	4
Density (calculated)	1.400 Mg/m ³
Absorption coefficient	7.017 mm ⁻¹
F(000)	1100
Crystal size	0.30 x 0.25 x 0.15 mm ³
Theta range for data collection	3.03° to 63.94°
Index ranges	-15 ≤ <i>h</i> ≤ 17, -21 ≤ <i>k</i> ≤ 24, -9 ≤ <i>l</i> ≤ 6
Reflections collected	8247
Independent reflections	3934 [R(int) = 0.0671]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3934 / 0 / 318
Goodness-of-fit on F ²	1.047
Final R indices [I > 2σ(I)]	<i>R</i> 1 = 0.0671, <i>wR</i> 2 = 0.1910
R indices (all data)	<i>R</i> 1 = 0.1715, <i>wR</i> 2 = 0.2661
Largest diff. peak and hole	0.641 and -0.870 e. Å ⁻³

TABLE 2. Selected bond distances (Å) and bond angles (°) of the complex **2**.

Bond angles (°)		Bond distances (Å)	
N2-Co1-N13	82.11(18)	Co1-N13	2.035(4)
N2-Co1-N30	108.7(2)	Co1-N2	2.032(4)
N2-Co1-N33	122.3(2)	Co1-N30	1.923(7)
N13-Co1-N30	109.3(2)	Co1-N33	1.905(5)
N13-Co1-N33	122.8(2)	N2-C15	1.374(6)
N30-Co1-N33	109.0(2)	N13-C14	1.360(6)

3.3. IR spectrum

The IR spectrum of complex **1** (Figure 3b) showed four characteristic absorptions peaks in the range 3060, 2950, 550 and 350 cm^{-1} [7-10] which was assigned to H-Ph, H-CH₃, Co-N and Co-Cl stretching vibrations, respectively. New band at 2150 cm^{-1} which was assigned to NCS vibrations was observed in IR-spectrum of Complex **2** (Figure. 3c). The H-Ph, H-CH₃, dmdphphen bands were appeared in their expected areas (Figure 3a).

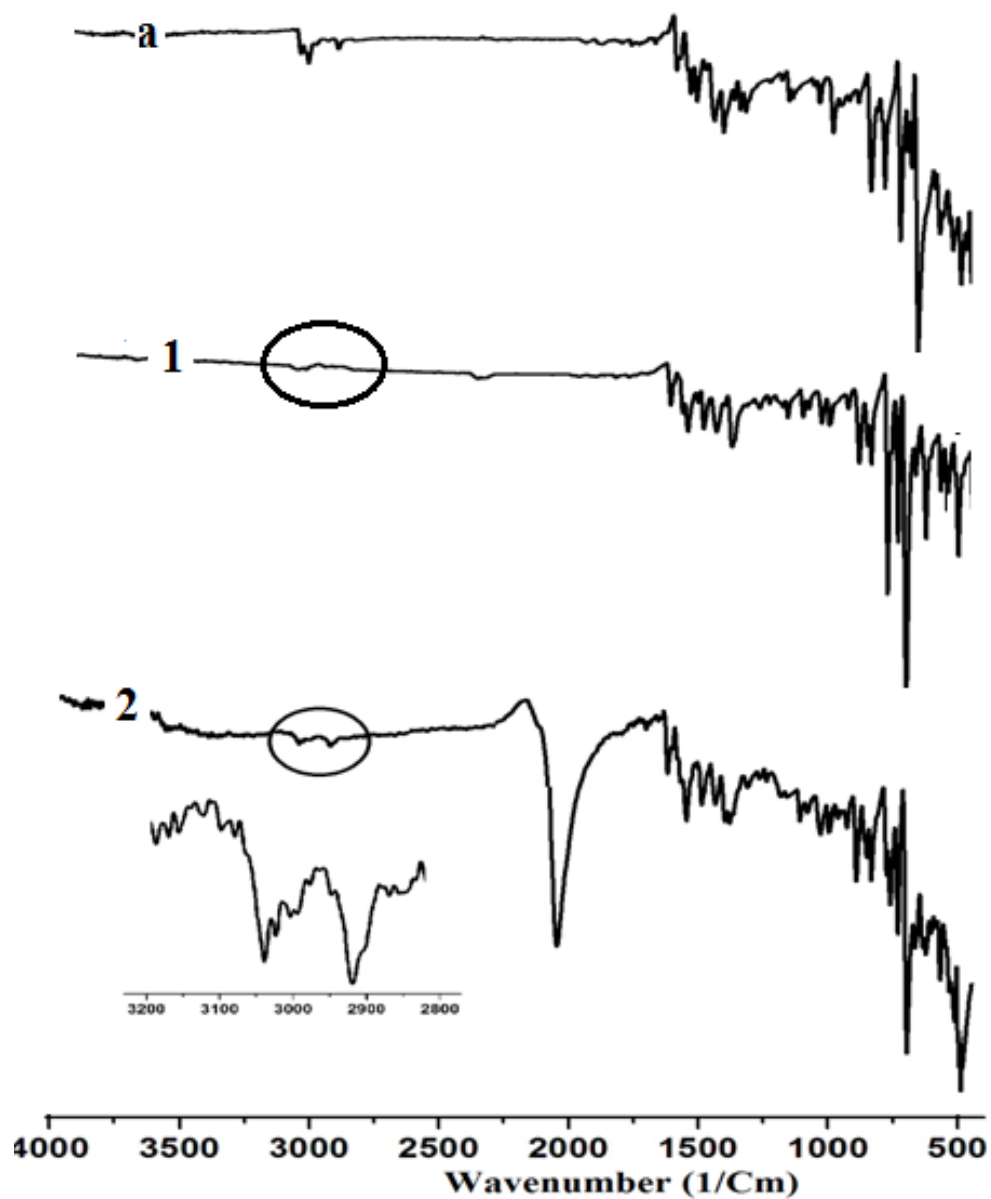


FIGURE 3. IR-KBr disk spectra of free ligand (a) and their desired complexes **1**, **2**.

3.4. Electronic absorption spectral study

The experimental absorption spectra (UV–Vis) of the $[\text{CoX}_2(\text{dmphen})]$ complexes **1,2** in dichloromethane solution presented three dominant bands in the region 200–800 nm (Figure 4). The bands in the UV region centered at around 240, 280 and 300 nm were assigned ligand-centered $\pi-\pi^*$ transitions (in both complexes). The bands at 360, 572 and 655 nm for complex **1** (above) and at 365, 560 and 645 nm for complex **2** (down) can be assigned to the $d \rightarrow d$ transition and MLCT, respectively [14-20].

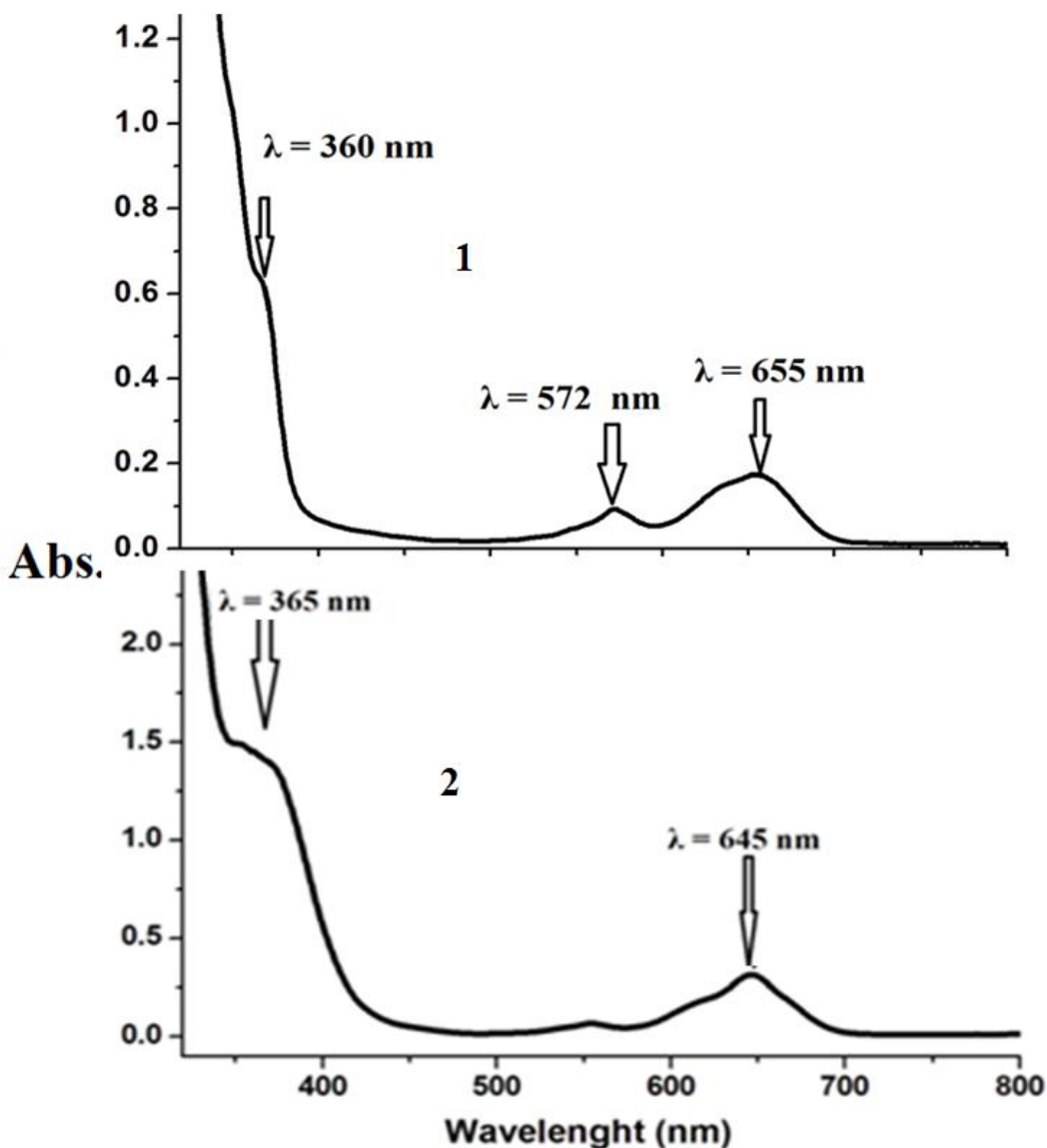


FIGURE 4. UV–Vis spectrum of the desired complexes (**1** and **2**) in dichloromethane at RT.

3.5. Thermal decomposition analysis of complexes 1

The thermal analysis of complex 1 (Figure 5) was investigated in the range of 0–600 °C and heating rate of 10 °C/min. Figure 5 shows there is no uncoordinated or coordinated water in the range 0-150 °C and 150- 180 °C respectively. Also, it shows that there are no decomposition intermediate steps of the coordinated chloride and dmdphenligands, both inorganic and organic ligands de-structured away from the Co metal with one step broad decomposition in 200-330 °C with weight loss ~ 81 % and an exothermic DTA signal at ~ 315 °C, the final residue was confirmed by IR to be CoO.

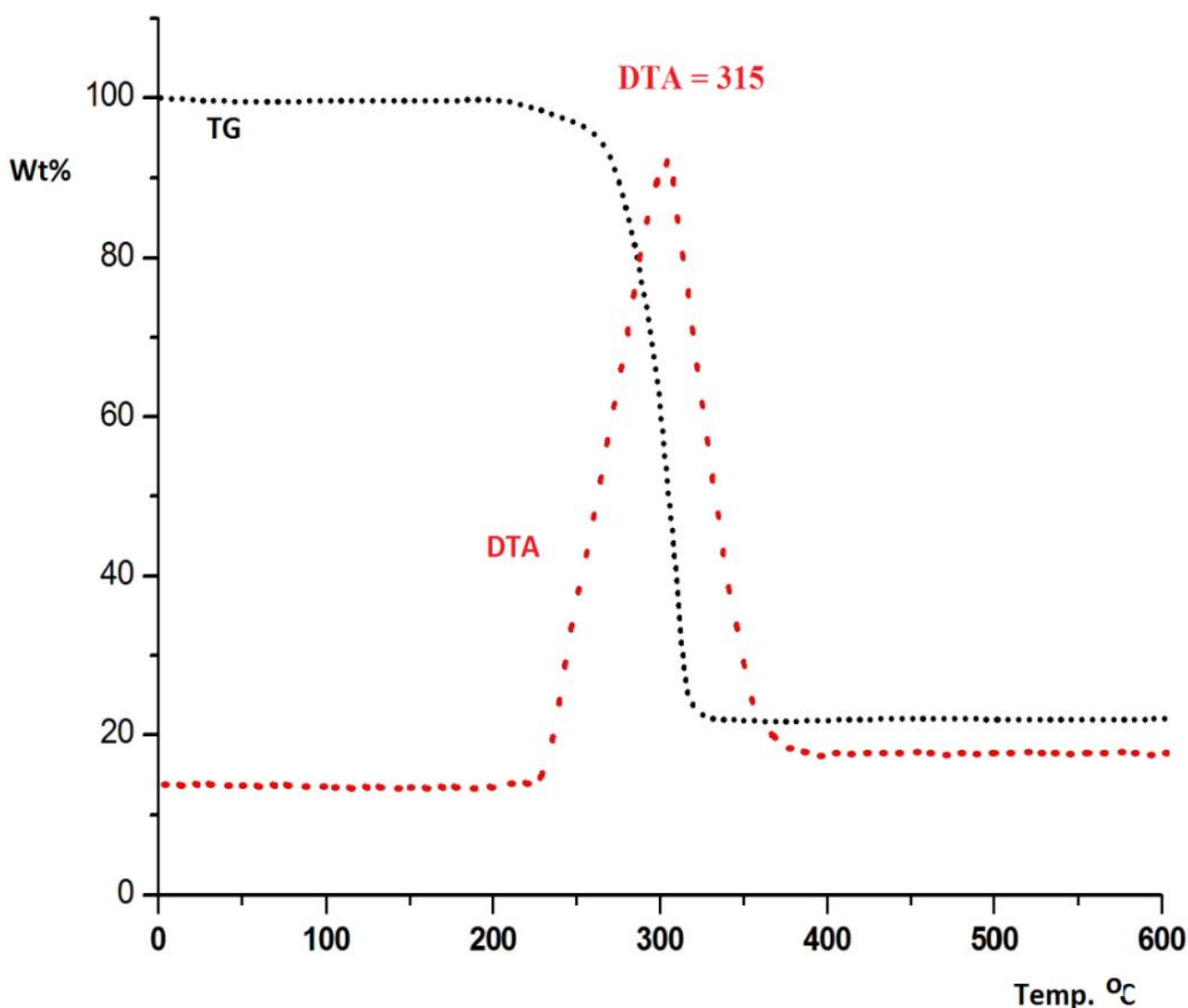


FIGURE 5. TG/DTA thermal curves of the desired complex1.

3.6. Electrochemistry

The electron-transfer behavior of the complexes in acetonitrile solution was examined by cyclic voltammetry. As a representative example, the cyclic voltammogram for complex **2** is shown in Figure 6. Complex **2** exhibited two single electron reversible oxidative response at -550 and 580 mV vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$, which has been assigned to Co(I)/Co(II) and Co(II)/Co(III) couples, respectively. The dmdphphen ligand is electro-inactive over the studied range of +1.5 to -1.5 V. Both complexes exhibit the similar behavior during the cyclic voltammetry experiments.

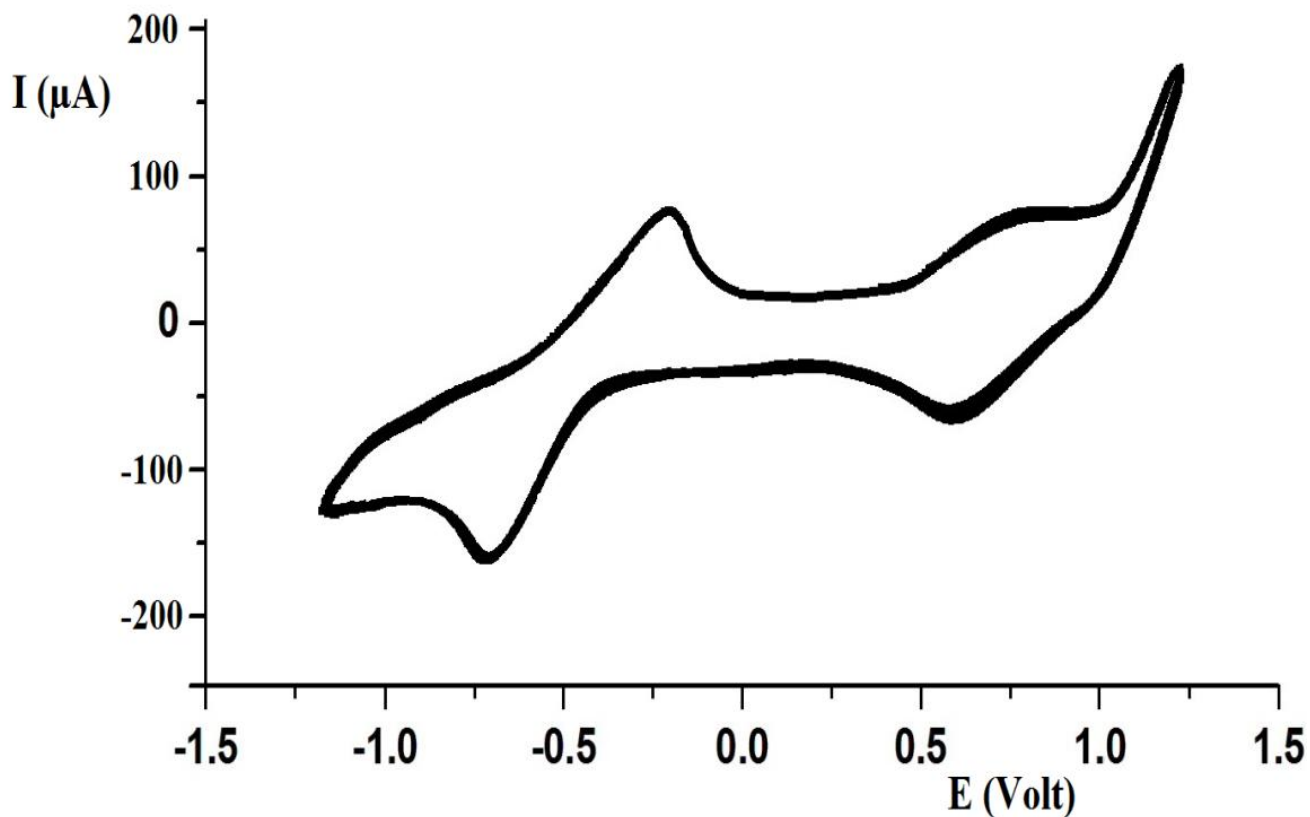


FIGURE 6. Voltammogram diagram of complex **2** ($c = 1 \times 10^{-3}$ M, in acetonitrile solution, 0.1 M TBAHF, Scan rate: 100 mV/s at RT).

3.7. DNA-complex **1** binding test

The affinity of Co(II) complexes for double-stranded CT-DNA was explored using UV-visible titrations in deionised water. The results of representative titrations are shown in Figure 7. Complex **1** showed good DNA binding affinity. Complex **1** has three

characteristic absorption peaks at 360 nm, 572 nm and 655 nm, respectively. There is a decrease in an intensity for all peaks for complex **1** by adding several concentration of DNA. This suggests that the cobalt complex might be bind to DNA by an intercalative mode [33]. However, by comparing the small shift for complex **1** with 7 nm red-shift values for $\text{Os}(\text{phen})_2(\text{dppz})^{2+}$ [34] and 9 nm for $[\text{Co}(\text{phen})_2(\text{pdtp})]^{3+}$ [35], this demonstrating that the intercalative strength of such complexes into DNA are not very strong.

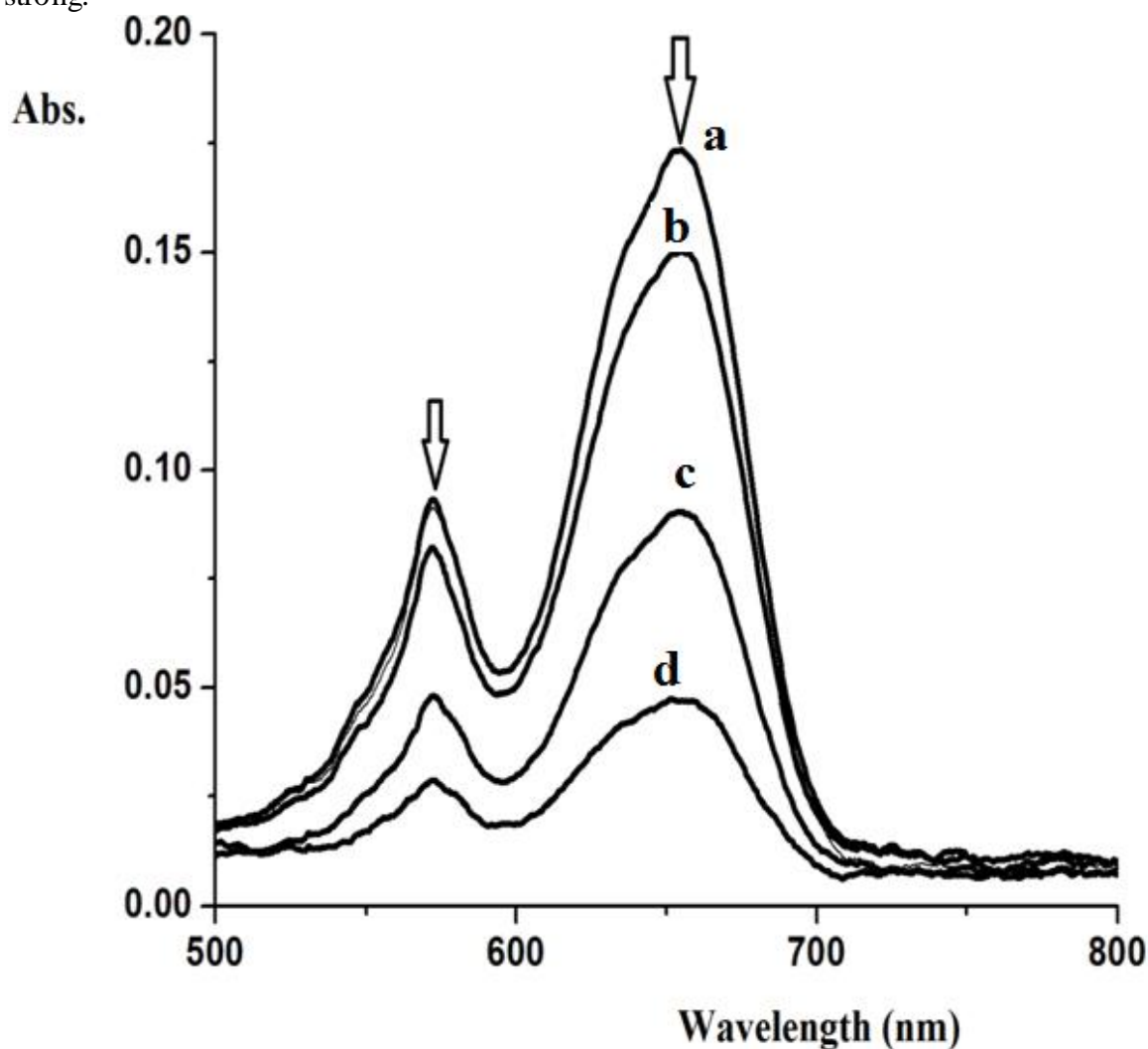


FIGURE. 7. Visible spectra of 1.5×10^{-4} mol/L of complex **1** interacting with a - 0, b -1.0×10^{-4} , c -5×10^{-4} , d -1×10^{-3} mol/L CT-DNA at RT.

4. Conclusions

Tetrahedral cobalt(II) complexes [CoCl₂(dmdphphen)] **1** and [Co(NCS)₂(dmdphphen)] **2** were made available in good yield. Complex **2** was solved by XRD as monoclinic with a space group P2₁/c. Co(II) ions are located in a distorted tetrahedral environment. TG/DTA result shows that these complexes are very stable and decomposed through one step reaction, the complexes exhibit a quasi-reversible one electron response at ~ -550 mV assigned to Co(I)/Co(II) and ~ 580 mV assigned to Co(II)/Co(III) vs. Cp₂Fe/Cp₂Fe⁺. Absorption spectral studies reveal that such complexes exhibit good DNA binding.

Supplementary material

Crystallographic data for complex **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1014019. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

1. C. Allen, Chemistry of Heterocyclic Compounds: Six Membered Heterocyclic Nitrogen Compounds with Three Condensed Rings. Inter science publisher, Inc. New York, vol. 12, 1958.
2. A. Bencini, V. Lippolis, 1, 10-Phenanthroline: A versatile building block for the construction of ligands for various purposes. Coord. Chem. Rev. no. 254, pp. 2096–2180, 2010.

3. F. Barigelletti, B. Ventura, J.-P. Collin, R. Kayhanian, P. Gavina, J.-P. Sauvage, Electrochemical and Spectroscopic Properties of Cyclometallated and Non-Cyclometallated Ruthenium(II) Complexes Containing Sterically Hinderig Ligands of the Phenanthroline and Terpyridine Families. *Eur. J. Inorg. Chem.*, pp. 113–119, 2000.
4. J. Weijnen, A. Koudijs, J. Engbersen, Synthesis of chiral 1,10-phenanthroline ligands and the activity of metal-ion complexes in the enantioselective hydrolysis of N-protected amino acid esters. *J. Org. Chem.*, vol. 57, no. 26, pp. 7258–7265, 1992.
5. E. Peña-Cabrera, P. Norrby, M. Sjögren, A. Vitagliano, V. De Felice, J. Oslob, S. Ishii, D. Neill, B. Åkermark, P. Helquist, Molecular Mechanics Predictions and Experimental Testing of Asymmetric Palladium-Catalyzed Allylation Reactions Using New Chiral Phenanthroline Ligands. *J. Am. Chem. Soc.*, vol. 118, pp. 4299–4313, 1996.
6. S. Gladiali, G. Chelucci, F.J. Socolini, Optically active phenanthrolines in asymmetric catalysis. *J. Organomet. Chem.*, vol. 370, no. (1-3), pp. 285–294, 1989.
7. R.A. Sheldon, J.K. Kochi *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, pp. 340–349, 1981.
8. Y. Li, Z. Zhang, W. Sun, C. A. Xia magnetically recyclable heterogeneous catalyst: Cobalt nano-oxide supported on hydroxyapatite-encapsulated γ -Fe₂O₃ nanocrystallites for highly efficient olefin oxidation with H₂O₂. *Catal. Commun.*, vol. 10, no. 2, pp. 237–242, 2008.
9. Y. He, C. Cai, Polymer-supported macrocyclic Schiff base palladium complex: An efficient and reusable catalyst for Suzuki cross-coupling reaction under ambient condition. *Catal. Commun.*, vol. 12, no. 7, pp. 678–680, 2011.
10. M. Ma, Q. Zhang, D. Yin, J. Dou, H. Zhang, H. Xu, Preparation of high-magnetization Fe₃O₄-NH₂-Pd(0) catalyst for Heck reaction. *Catalysis Communications*, vol. 17, pp. 168–172, 2012.
11. G. Pratviel, B. Bernadou, Meunier, DNA And RNA Cleavage by Metal Complexes *Adv. Inorg. Chem.*, pp. 251–312, 1998.
12. R. Burger, Cleavage of Nucleic Acids by Bleomycin. *Chem. Rev.*, vol. 98, no. 3, pp. 1153–1170, 1998.
13. K. Erkkila, D. Odom, J. Barton, Recognition and Reaction of Metallointercalators with DNA *Chem. Rev.*, vol. 99, no. 9, pp. 2777–2796, 1999.
14. H. Chifotides, K. Dunbar. Interactions of Metal–Metal-Bonded Antitumor Active Complexes with DNA Fragments and DNA. *Accounts Chem. Res.*, vol. 98, no. 2, pp. 146–156, 2005.
15. C. Burrows, J. Muller, Oxidative Nucleobase Modifications Leading to Strand Scission. *Chem. Rev.*, vol. 98, no. 3, pp. 1109–1152, 1998.

16. C. Metcalfe, J. Thomas. Kinetically inert transition metal complexes that reversibly bind to DNA. *Chem. Soc. Rev*, vol.32, no.4, pp.215-224, 2003.
17. K. Szaciłowski, W. Macyk, A. Drzewiecka-Matuszek, M. Brindell, G. Stochel. Bioinorganic Photochemistry: Frontiers and Mechanisms, *Chem. Rev*, vol.105, no. 6, pp. 2647-2694, 2005.
18. S. Wolkenberg, D. Boger. Mechanisms of in Situ Activation for DNA-Targeting Antitumor Agents. *Chem. Rev*, vol.102, no.7, pp.2477-2496, 2002.
19. A. Sreedhara, J. Cowan. Catalytic hydrolysis of DNA by metal ions and complexes. *J. Biol. Inorg. Chem*, vol.6, no.4, pp.337-347, 2001.
20. B. Macías, M. Villa, F. Sanz, J. Borrás, M. González-Álvarez, G. Alzuet. Cu(II) complexes with a sulfonamide derived from benzoguanamine. Oxidative cleavage of DNA in the presence of H₂O₂ and ascorbate. *J. Inorg. Biochem*. vol.99, no.7, pp.1447-1448, 2005.
21. Y. Li, Y. Wu, J. Zhao, P. Yang. DNA-binding and cleavage studies of novel binuclear copper(II) complex with 1,1'-dimethyl-2,2'-biimidazole ligand. *J. Inorg. Biochem*, vol.101, no.2, pp.283-290, 2007.
22. S. Dhar, D. Senapati, P. Das, P. Chattopadhyay, M. Nethaji, A. Chakravarty. Ternary Copper Complexes for Photocleavage of DNA by Red Light: Direct Evidence for Sulfur-to-Copper Charge Transfer and d-d Band Involvement. *J. Amer. Chem. Soc*, vol. 125, no. 40, pp. 12118-12124, 2003.
23. A. Friedman, J. Chambron, J. Sauvage, N. Turro, J. Barton. A molecular light switch for DNA: Ru(bpy)₂(dppz)²⁺. *J. Amer. Chem. Soc*. vol.112, no.12, pp. 4960-4962, 1990.
24. T. Shields, J. Barton. Sequence-Selective DNA Recognition and Photocleavage: A Comparison of Enantiomers of Rh(en)₂phi³⁺. *Biochemistry*, vol. 34, no.46, pp. 15037-15048, 1995.
25. A. Sitlani, E. Long, A. Pyle, J. K. Barton. DNA photocleavage by phenanthrenequinonediimine complexes of rhodium(III): shape-selective recognition and reaction. *J. Amer. Chem. Soc*, vol. 114, no.7, pp.2203-2312, 1992.
26. S. Ramakrishnan, M. Palaniandavar. Mixed-ligand copper(II) complexes of dipicolylamine and 1, 10-phenanthrolines: The role of diimines in the interaction of the complexes with DNA. *J. Chem. Sci*, vol. 117, pp.179-186, 2005.
27. I. Warad, A. Boshala, S. Al-Resayes, S. Al-Deyab, M. Rzaigui. (2,9-Dimethyl-1,10-phenanthroline-κ² N,N') diiodidocadmium, *Acta Cryst*. vol.67, no.12, pp. m1650 - m1650, 2011.
28. I. Warad, M. Al-Noaimi, S. Haddad, R. Othman, Dichlorido(2,9-dimethyl-1,10-phenanthroline-κ² N,N') mercury(II), *Acta Cryst*, vol.69, no.2, pp. m109- m109, 2013.
29. I. Warad, B. Hammouti, T. BenHadda, A. Boshala, S. Haddad. X-ray single-crystal structure of a novel di-μ-chloro-bis[chloro(2,9-dimethyl-1,10-

- phenanthroline)nickel(II)] complex: synthesis, and spectral and thermal studies. Res. Chem. Intermed, vol.39, no. 9, pp. 4011-4020, 2012.
30. I. Warad, M. Al-Ali, B. Hammouti, T. Ben Hadda, R. Shareiah, M. Rzaigui. Novel di- μ -chloro-bis[chloro(4,7-dimethyl-1,10-phenanthroline)cadmium(II)] dimer complex: synthesis, spectral, thermal, and crystal structure studies, Res. Chem. Intermed, vol.39, no.6, pp.2451-2461, 2012.
 31. A. Barakat, M. Al-Noaimi, M. Suleiman, A. Aldwayyan, B. Hammouti, T. Ben Hadda, S. Haddad, A. Boshala, I. Warad. One Step Synthesis of NiO Nanoparticles via Solid-State Thermal Decomposition at Low-Temperature of Novel Aqua(2,9-dimethyl-1,10-phenanthroline)NiCl₂ Complex, Inter.J. Mol. Sci, vol.14, no.12, pp. 23941-23957, 2013.
 32. M. Lalia-Kantouri, C. Papadopoulos, A. Hatzidimitriou, M. Sigalas. Quirós M.; Skoulika S. Different geometries of novel cobalt(II) compounds with 2-hydroxybenzophenones and neocuproine: Crystal and molecular structures of [Co(2-hydroxybenzophenone)₂(neoc)], [Co(2-hydroxy-4-methoxybenzophenone)(neoc)Br] and [Co(neoc)Br₂] \cdot CH₃OH \cdot H₂O. Polyhedron, vol.51, pp.1306-1316, 2013.
 33. A. Pyle, J. Rehmann, R. Meshoyrer, C. Kumar, N. Turro, J. Barton. Mixed-ligand complexes of ruthenium(II): factors governing binding to DNA. J. Amer. Chem. Soc, vol.111, no.8, pp.3051-3058, 1989.
 34. R. Holmlin, J. Barton. Os(phen)₂(dppz)²⁺: A Red-Emitting DNA Probe Inorg.Chem, vol.34, no.1, pp.7-8, 1995.
 35. Wang, X.; Chao, H.; Li, H.; Hong, X.; Liu, Y.; Tan, L.; Ji, L. DNA interactions of cobalt(III) mixed-polypyridyl complexes containing asymmetric ligands J. Inorg.Biochem, vol.98, no.6, pp.1143-1150, 2004.
 36. G. Gritzner, J. Kůta. Recommendations on reporting electrode potentials in nonaqueous solvents Electrochimica Acta, vol.29, no.6, pp.869-873, 1984.
 37. Bruker APEX2, SADABS, SAINT-Plus and XPREP. Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
 38. G. Sheldrick. A short history of SHELX, Acta Crystallographica Section A Foundations of Crystallography, vol.64, no.1, pp.112-122, 2007.
 39. A. L. Spek, Acta. Cryst. C34, vol.46, 1990.
 40. C. Macrae, I. Bruno, J. Chisholm, P. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. de Streek, P. Wood. Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures, Journal of Applied Crystallography, vol.41, no.2, pp.466-470, 2008.