Al-Qadisiyah Journal of Pure Science

Manuscript 1225

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Wesam Dheyab Kzar

Hasan Shamran Mohammed

Álvaro Fernández Álvarez

Vishwa Deepak Tripathi

Zizi Zahia

ARTICLE

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Wesam D. Kzar [a], Hasan S. Mohammed [a,*], Álvaro F. Álvarez [b], Vishwa D. Tripathi [c], Zizi Zahia [d]

[a] College of Science, Al-Qadissiyah University, Iraq
[b] Universidad Complutense de Madrid, Spain
[c] Department of Chemistry, M. K. College, Lalit Narayan Mithila University, Darbhanga, 846003, India
[d] Laboratory of Materials and Physico-chemical for Environment and Health, University of Sidi Bel Abbes, Algeria

Abstract

Azo dye ligand (DCPAC) namely (1E,6E)-4-((E)-(2,5-dichlorophenyl)diazenyl)-1,7-bis(4-hydroxy-3-methoxyphenyl) hepta-1,6-diene-3,5-dione was prepared by coupling diazonium salt of 2,5-dichloroaniline with curcumin in basic conditions. The ligand (DCPAC) and its Pd(II) complex were characterized by elemental analysis (C.H.N.), mass spectroscopy, ^{1}H NMR, FT-IR, UV−Visible spectra, and molar conductivity. The molar ratio method was applied to ascertain the stoichiometric composition of pd(II) complex in aqueous solution which was 1:2 (metal ion to ligand). Azo curcumin ligand binding with Pd (II) ion used the enolate form moiety of curcumin under alkaline conditions which was observed by infrared spectra. New azo curcumin (DCPAC) and its Pd(II) complex have been evaluated as latent fingerprints detection.

Keywords: Curcumin, Azo dye, Latent fingerprints, Coordination compound, Palladium

1. Introduction

Curcumin is one of the most famous yellow and red dyes respectively, and it is considered as an active and powerful component in Turmeric (*Curcuma longa*) [1] and its chemical formula was approved by (Roughley & Whiting in 1973) [2] and it is called (Di feruloylmethane). It has systematic name according to the (IUPAC) system as follows.

(E,E)-1,7-Bis (4 -Hydroxy)-3 Methoxyphenyl 1,6-Heptadiene-3,5- Dione). Several studies in recent years have shown that curcumin is a potent inhibitor of the initiation and promotion of tumor formation chemicals induced by carcinogens in animals [3] and contains potent antioxidant, anti-inflammatory and antitumor promoting activities. Curcumin showed induce apoptosis in HL-60 leukemia cells at low concentrations as 3.5 μg/mL and Curcumin's ability to induce apoptosis was somewhat dose- and time-dependent [4].

Curcumin can coordinate with many metals and form stable complexes [7], in recent decades, complexes of curcumin with different metals have been synthesized to overcome the problems associated with curcumin such as solubility and to make it more effective. From a biological point of view [5], the detection of latent fingerprints is an important topic in forensic sciences, as this is reflected in the benefit of society as a whole. The most common method for identifying fingerprints is powder dust. The powder dust method depends on the adhesion of the powder powders. Turmeric particles to the sediments of fingerprints such as oil, sweat, and other substances that can leave behind the

Received 30 June 2023; accepted 11 April 2024.
Available online 28 September 2024

* Corresponding author.
E-mail address: hasan.sh.mohemmed@qu.edu.iq (H.S. Mohammed).

https://doi.org/10.29350/2411-3514.1225

fingerprint, and these powders were classified into colored, fluorescent, and magnetic powder was used to photograph fingerprints on basic materials [6] and was also used with silicon nanoparticles (SiNPs) in imaging (LFPS), where the image of (LFPS) developed under ultraviolet light appeared with high and different quality and it could retain a clear contrast in the fingerprints [7,8]. In this study, we prepare novel azo dye of curcumin and its palladium complex and study their ability to detection the hidden fingerprints.

2. Materials and methods

2.1. Materials

The used materials in this study were bought from different companies as following, 2,5-Dichloroaniline (FERAK, 97%), Sodium nitrite, (Thomas baker,98%), Sodium hydroxide (LOBA, 98%), Palladium chloride (B.D.H, 98%), Curcumin crystalline (CDH, 96%), Hydrochloric acid (CGH, 38%) and Dimethyl sulfoxide (LOBA, 99%).

2.2. Instrumentations

We used the following devices to do the work, Shimadzu FT-IR 8400S Spectrophotometer, Uv-1650 PC UV–Visible Spectrophotometer, Sturat digital melting Point/SMP3, Bruker500 MHZ300, Agilent 5375 USA for mass spectra, Euro Ea 300 for elemental analysis.

2.2.1. Preparation of the (DCPAC) dye

This dye was prepared by dissolving (0.23 g, mole 0.002) 2,5-dichloroaniline in (15 mL ethanol), then adding (3 mL, 12 M of HCl) and cooling the solution to 0 °C. Sodium nitrite 0.2g, 0.002 mol was dissolved in 5 mL of distilled water under cooling to (0 °C), which was added to the acidic solution of 2,5-dichloroaniline to produce the diazonium salt. The solution of the diazonium salt was left 1 h under cooling and stirring then the solution was mixed with the cooling solution of curcumin 0.5 g, 0.002 mol in 10%, 5 mL of sodium hydroxide. The mixture solution was left overnight then it was filtered and it was washed with distilled water many times then the powder was put in desiccator to dry. Elemental analysis of the ligand Experimental%, C 59.79, H 4.24 N 5.19, Theoretical% C 59.90, H 4.10, N 5.17.

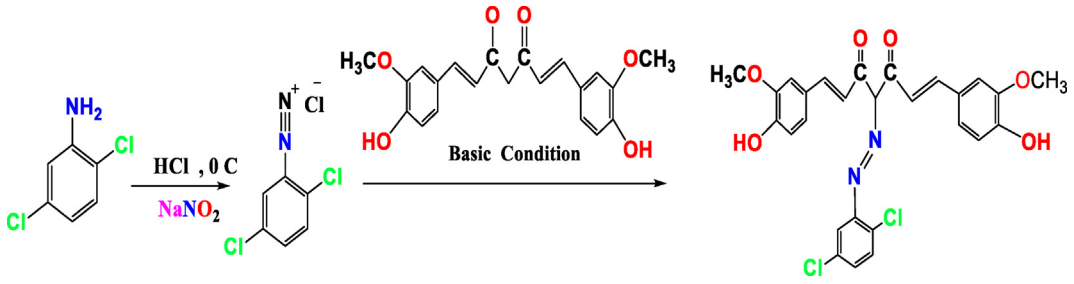
2.2.2. Pd(II) complex preparation

This complex was prepared by dissolving (0.04 g, 0.00023 mol) of palladium (II) chloride in 5 mL of distilled acidified water by adding drops of dilute hydrochloric acid and heating for (10 min) to complete the dissolving, the ligand (DCPAC) (0.25 g, 0.00046 mol) was dissolved in (20 mL) of ethyl alcohol. The ligand solution was added slowly to the palladium metal solution with a metal: ligand molar ratio (2:1) and checking the acidity to be 9. The reaction mixture was refluxed for 2 h with a temperature of (60–70) C. Then filtered and washed with distilled water more than once, dried. Elemental analysis of the Pd (II) complex, Experimental%, C 54.67, H 3.63, N 4.78, Theoretical%, C54.63, H 3.57, N 4.72

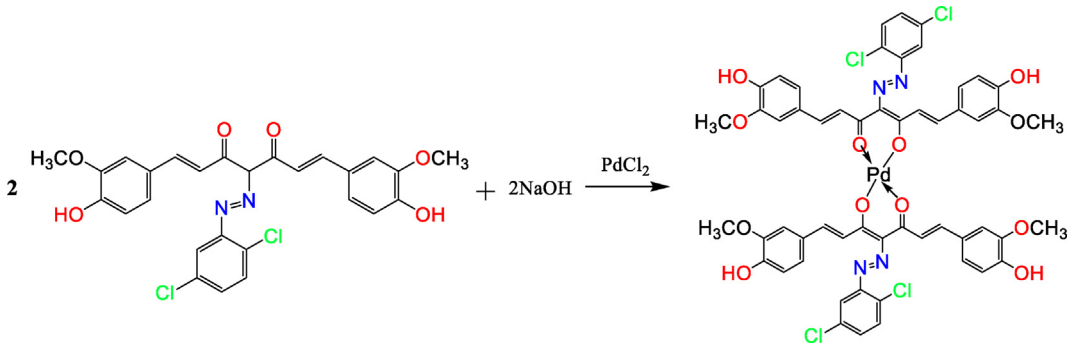
3. Results and discussion

The azo curcumin ligand was prepared by reacting diazonium salt of 2,5-dichloroanilin with curcumin as shown in Scheme 1. The resulting dye namely (1E,6E)-4-((E)-(2,5-dichlorophenyl)diazenyl)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione (DCPAC) was dark brown powder with a percentage of 85% and melting point is 102 °C. The solid DCPAC ligand was insoluble in water but completely soluble in some solvents such as dimethylsulfoxide, ethanol and acetone.

The Pd (II) complex was prepared by reacting the $PdCl_2$ with two equivalents of DCPAC ligand as shown in Scheme 2. Mass spectrum of DCPAC dye (Fig. 1) provided a molecular ion peak at 543, and the molecular ion peak of Pd(II) complex was at 1187 which are correspond to predict molecular weight of



Scheme 1. Preparation steps of DCPAC ligand of azo dye based on curcumin.



Scheme 2. Preparation of Pd(II) complex for DCPAC ligand of azo dye based on curcumin.

DCPAC ligand and the [Pd(DCPAC)$_2$] formula of Pd(II) complex.

Reaction of Pd(II) with DCPAC ligand in ethanol under reflux led to high yield Pd(II) complex and the results of the (C, H, N) elemental analyses of the synthesized Pd(II) complex were in good accord with what the proposed formula demanded.

^{1}H NMR spectrum of DCPAC ligand as shown in Fig. 2, was exhibited many signals related to O–H 9.7 ppm [9,10]. The signals exhibited at 3.91 and 3.3 ppm due to O–CH_3 and D_2O of solvent respectively. The aromatic protons exhibited in the range of 6.55–7.91 ppm. The chemical shifts of OH groups showed at 9.7(2H, s) and the singlet signal at 6.1 ppm due for the proton of curcumin between the carbonyl groups, which disappeared in the signals of palladium complex. The protons of 2 and * showed at 6.7 ppm with j-coupling equal to 15.8 Hz and the protons of 3 and 3* showed at 7.7 ppm with j-coupling equal to 15.4 Hz. The complex of palladium (II) was characterized by nuclear magnetic resonance spectroscopy (H NMR1) It showed a wide band at a chemical displacement (9.12 ppm) belonging to the O–H group. It is also noted that the proton signal has disappeared at position 1, and the complex also showed signs of aromatic and ethylene protons at a chemical displacement of (7.71–6.42 ppm), as well as a singlet signal at a chemical displacement of (7.81 ppm) belonging to a proton at position 9 in the phenyl group. A signal at 3.83 ppm chemical displacement belongs to the O–CH_3 groups, another

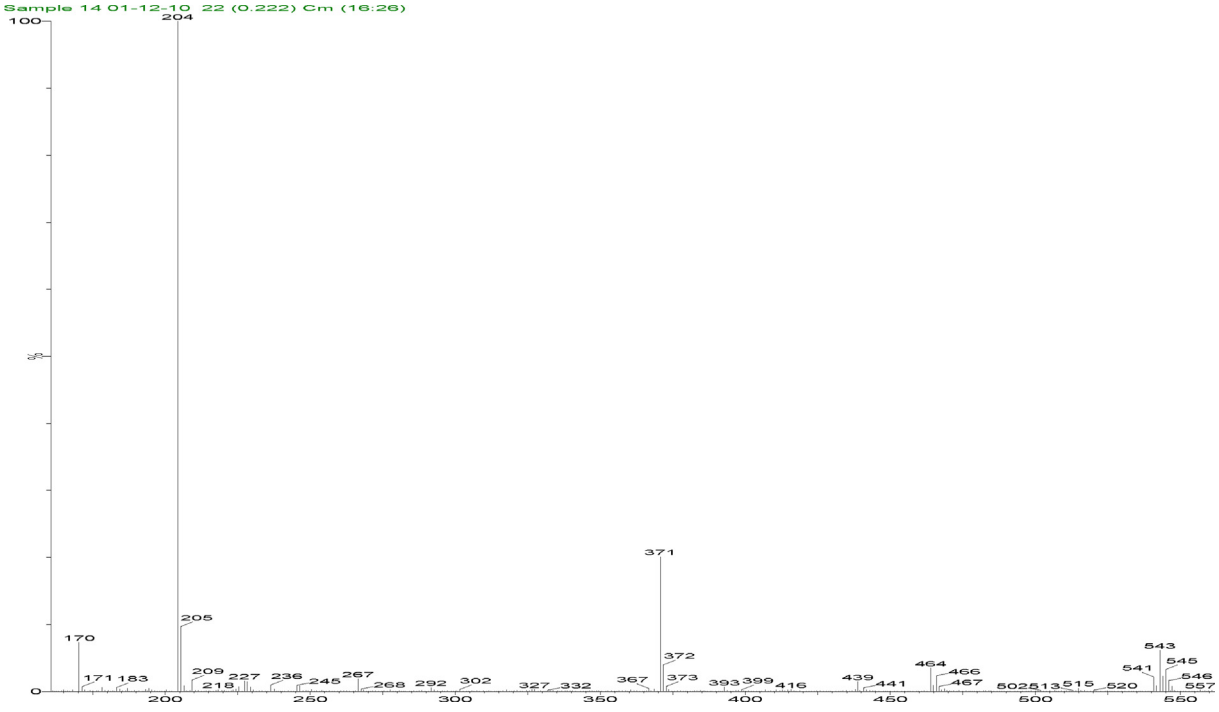


Fig. 1. Mass spectrum of DCPAC ligand of azo dye based on curcumin.

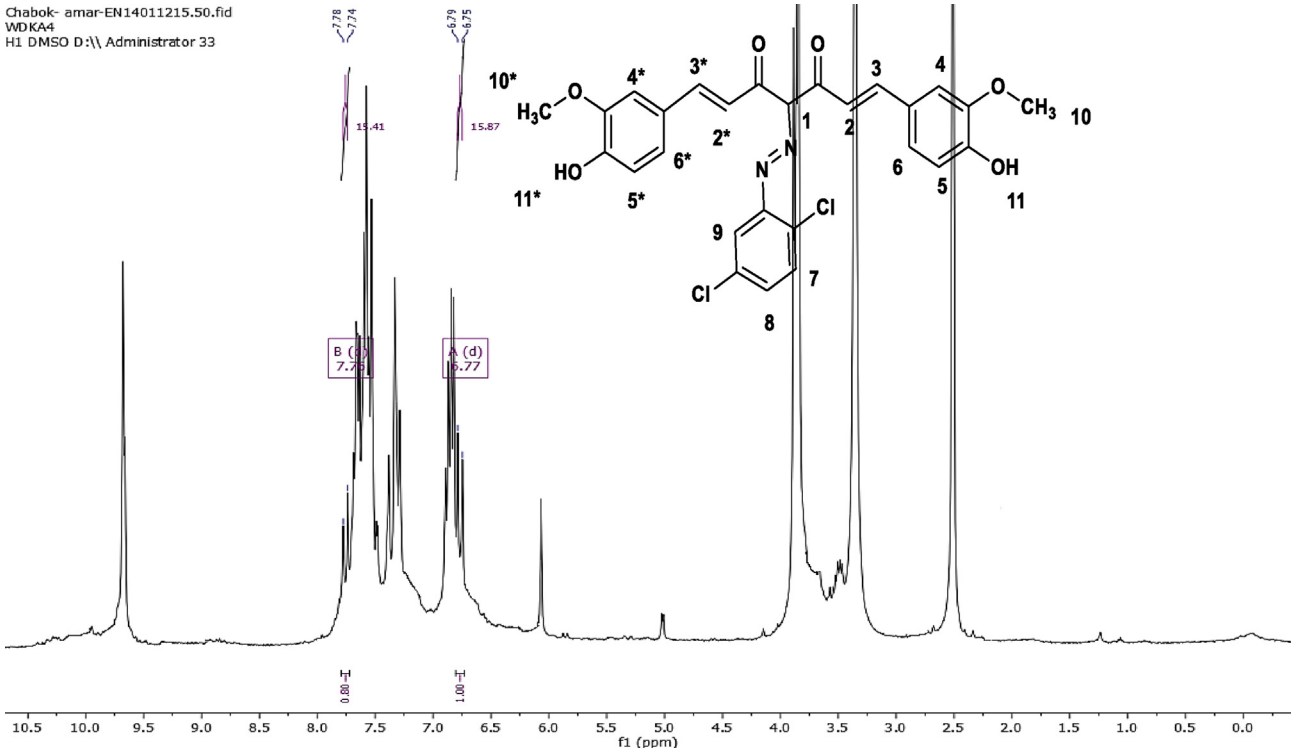


Fig. 2. ^{1}HNMR spectrum of DCPAC ligand of azo dye based on curcumin in DMSO d6 solvent.

Table 1. The important vibrations of DCPAC ligand and it Pd(II) complex.

Compound	OH	CH aliphatic	CH aromatic	C=O	C=C	N=N	Ph- O	C−Cl	M-O
DCPAC ligand	3401	3050	2936, 2843	1627	1511	1428	1272	817	
Pd(II) complex	3441	3089	2947, 2837	1585	1513	1429	1274	815	550

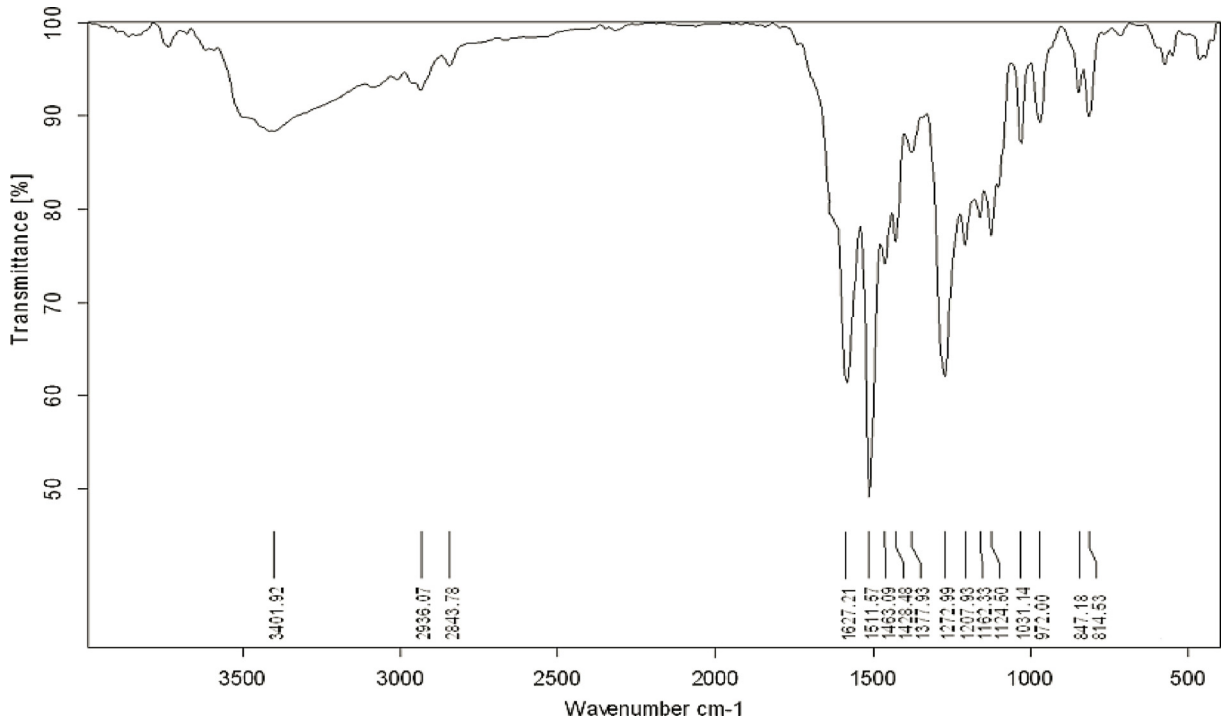


Fig. 3. Infrared spectrum of DCPAC ligand.

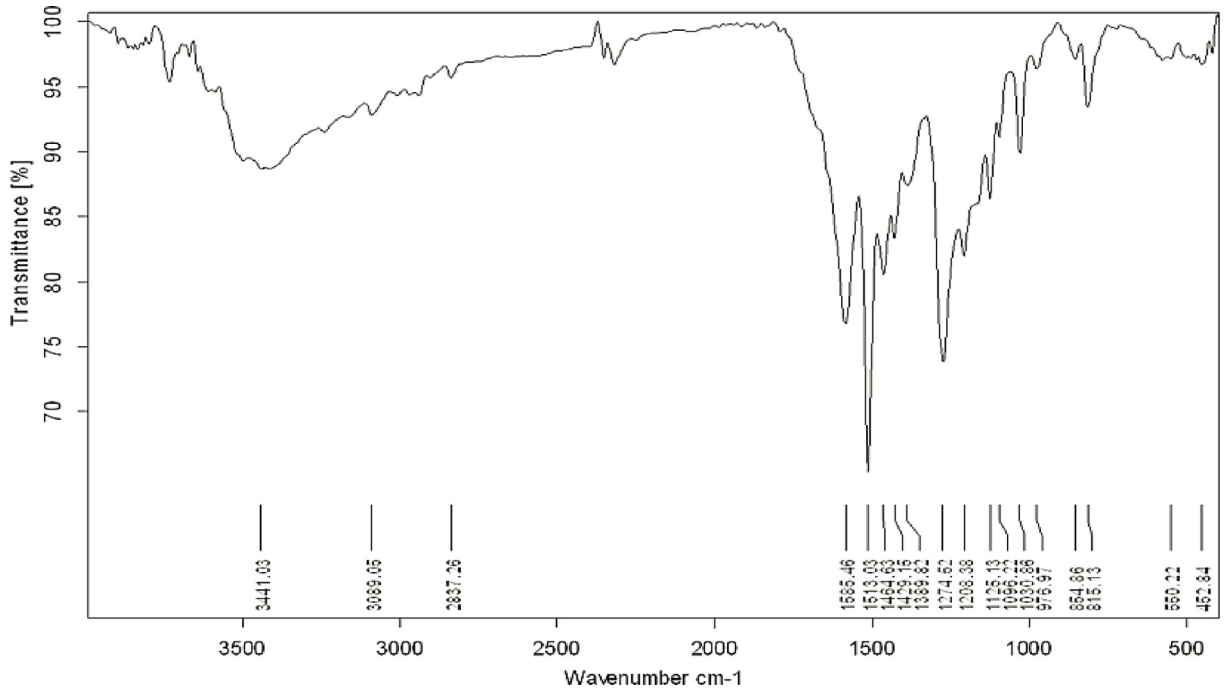


Fig. 4. Infrared spectrum of Pd(II) complex for DCPAC ligand.

signal at (3.33 ppm) refers to D_2O, and a signal at 2.51 ppm refers to DMSO-d6.

3.1. Infrared spectra

The important function groups of the DCPAC ligand and its Pd(II) complex were investigated by infrared spectroscopy. The infrared spectra of the DCPAC ligand and its Pd(II) complex were done by using KBr disc. Their significant bands are summarized in Table 1, and Figs. 3 and 4 represent their IR spectra respectively. The DCPAC ligand showed many diagnostic peaks, which were included in the table, and among the important groups that appeared in the (DCPAC) ligand spectrum is the O–H group of curcumin, which appeared at 3401 cm^{-1}, which did not suffer a change in the complex [11,12]. That indicates on its presence and not participating in the process of coordination in the case of palladium complex. As well as other groups such as CH aromatic at 3050 cm^{-1} and CH aliphatic at 2936 and 2843 cm^{-1} [13–16] and a group of C=C at 1511 cm^{-1} [17,18]. The ph-O vibration showed at 1272 cm^{-1} in addition to the CH bending

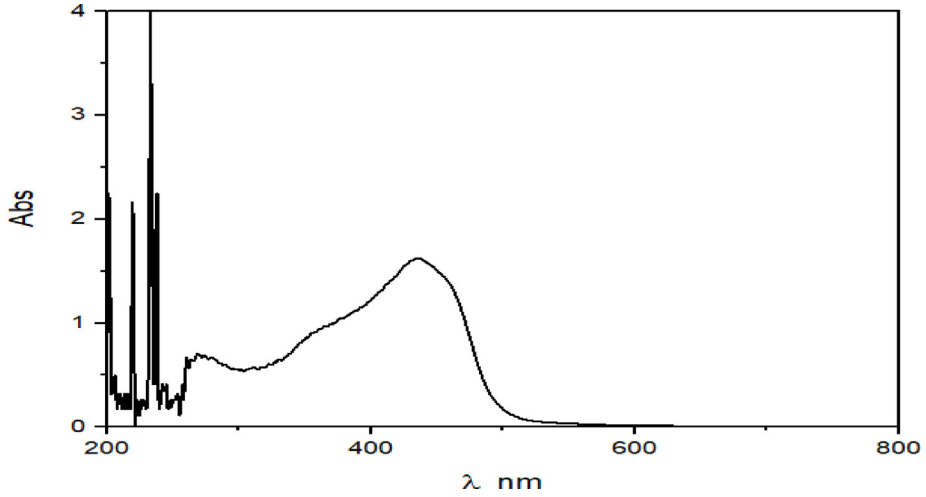


Fig. 5. UV–Visible spectra of DCPAC ligand.

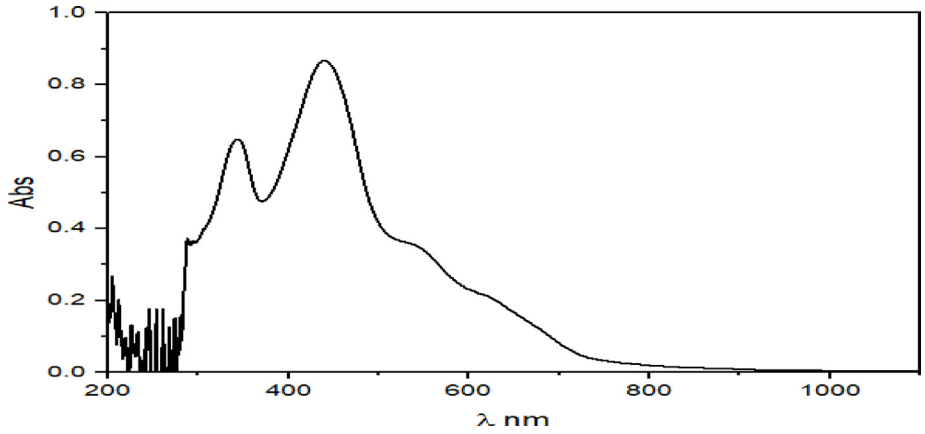


Fig. 6. UV–Visible spectra of Pd(II) complex.

of aliphatic at1031 cm $^{-1}$ as well as CH bending of aromatic at 814 cm^{-1}, which in turn did not suffer a change after the consistency of the ligand to the palladium metal ion in the prepared complex [19,20]. The (DCPAC) ligand showed an absorption of N=N at 1428 cm^{-1}, which did not suffer a change in the location and intensity in the spectrum of the palladium complex which indicates its inconsistency with the metal ions in the complexes [21,22]. The ligand also showed absorption of the C–Cl group at 816 cm^{-1} [23]. The ligand (DCPAC) showed an absorption of C=O at 1627 cm^{-1}, which suffered a change in location and intensity in the palladium complex spectrum, which indicates its consistency with the metal ions in the complex, as its frequency decreased by 42 cm^{-1} under coordination [24].

3.1.1. Electronic transitions of (DCPAC) ligand and Pd (II) complex

Electronic transitions measurements were conducted in dimethylsulfoxide at room temperature. UV–Vis spectra of DCPAC ligand and Pd (II) complex were listed within Figs. 5 and 6 respectively. The DCPAC ligand showed bands at 376 nm and 436 nm. These bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively [25–28]. The Pd(II) complex spectrum exhibited bands at 554 nm and 680 nm due to ($^1A_{1g}$) → ($^1T_{2g}$), ($^1A_{1g}$) → ($^1T_{1g}$) transitions respectively. These bands represent pretty accurately with the square planar shape of the Pd(II) ion [29–32].

4. Detection of the hidden fingerprints

Fingerprints are invisible to the naked eye at the scene of the event, which are called latent embodies (LEPS), which can be exploited as important

Fig. 7. Showing the latent fingerprint by the [Pd(DCPAC)$_2$]Cl complex on the aluminum surface.

Fig. 8. Showing the latent fingerprint by complex [Pd(DCPAC)$_2$] complex on a glass surface.

Fig. 9. Showing the latent fingerprints by the standard black powder on the glass.

evidence In many cases in crimes, which requires a special photographic process in order to be understood by security men [33]. The most common method for identifying fingerprints is powder dust. Number of azo dyes were used to detect fingerprints. Fingerprints consist of a group of ridges called friction ridges. Each ridge includes a pore, which is associated with the sweat glands under the skin. Fingerprints leave an effect on anything you touch as a result of this resulting sweat. The process of chemical manifestation of fingerprints depends on the interaction of chemicals with the components of the sweat secretions of the skin [34]. The ligand (DCPAC) and complex Pd(II) were taken and ground well, dried and placed on the surfaces to be fingerprinted. The powder of the material was spread with a special brush for this purpose over the fingerprints. The Pd(II)complex showed high effectiveness in showing latent fingerprints on smooth surfaces such as glass and smooth surfaces such as aluminium, where it showed positive results through the appearance of fingerprints clearly and with high stability and contrast which are depicted in Figs. 7–9 respectively.

5. Conclusion

Through this work, we synthesized and characterized new azo ligand (DCPCAC) and Pd(II) complex. The (DCPAC) ligand is bidentate and the Pd(II) complex is square planar. The palladium complex (II) has high effectiveness and stability in detecting latent fingerprints on different surfaces compared with that standard (black powder).

Funding

This research received no specific grant from any funding agency in the public or commercial.

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