------ Raf. J. Sci., Vol. 25, No.2 pp. 32-43, 2014------

U.V. Spectroscopic Studies of the Schiff Base N-(o-N-(Methyl-3-ol-2-butenimino)-$\overline{N}$-(o-Toluyl)-1,2- diphenylethandimine and its Complexes with Co(II), Ni(II), Cu(II) and Pd(II): Direct Determination in Absolute Ethanol

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(Received 17 / 4 / 2013 ; Accepted 10 / 6 / 2013)

ABSTRACT

The U.V. Spectra were used for the direct quantification of the Schiff base N-(o-N-(methyl-3-ol-2-butenimino)-$\overline{N}$-(o-Toluyl)-1,2-diphenyl-ethandimine and its complexes with Co(II), Ni(II), Pd(II) and Cu(II) in absolute ethanol at λ= 344 nm for the Schiff base, Co(II), Ni(II) and Pd(II) complexes and at λ = 260 nm for the Cu(II) complex. The direct determination limit was estimated through the plot of the molar concentration against the absorbance and R^2 and R.S.D for each complex were calculated. The method appears to be in a good accuracy and precision.

Keywords: Schiff base, UV spectra, Complexes.

دراسة طيف الأشعة فوق البنفسجية لقاعدة شيف N-اورثو-N-ميثايل-3-أول-2-بيوتين ايمنو-$\overline{N}$-اورثوتولويل 1 ،2-ثنائي فنيل ايثان ثنائي ايمين ومعقداتها مع الكوبلت الثنائي، النيكل الثنائي، النحاس الثنائي والبلاديوم الثنائي. التقدير المباشر في الايثانول المطلق

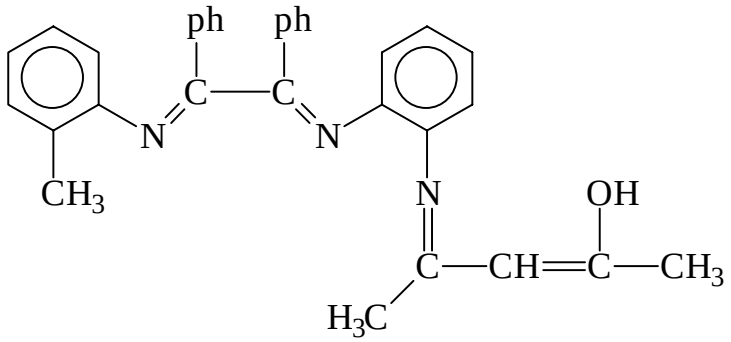
الملخص

يتضمن البحث طريقة مباشرة لتقدير قاعدة شيف N-اورثو-N-ميثايل-3-أول-2-بيوتين ايمنو-$\overline{N}$-اورثوتولويل 1،2-ثنائي فنيل ايثان ثنائي ايمين ومقعداتها مع الكوبلت الثنائي، النيكل الثنائي، البلاديوم الثنائي والنحاس الثنائي في الايثانول المطلق عند الطول الموجي (344nm) لقاعدة شيف ومعقداتها مع الكوبلـت ، النيكل والبلاديوم وعند الطول الموجي (260 nm) لمعقد النحاس ولقد أجريت عملية التقدير المباشـر مـن خلال رسم العلاقة بين التراكيز المولارية والامتصاصات لكل المركبات المعقدة حيث عينت قيم R.S.D, R^2 وان نتائج هذه الطريقة تبدو من خلال نسب الاسترجاع أنها على درجة جيدة من الدقة والتوافقية.

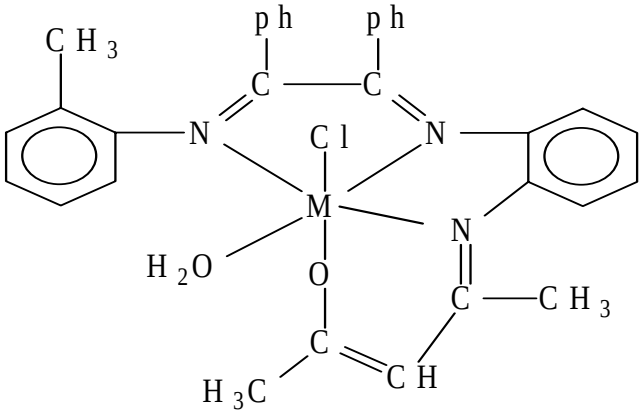
INTRODUCTION

Schiff bases are well known to have antifungal, antitumor and herbicidal activities (Mitu *et al*., 2012), (Pandeya *et al.*, 1999). The complex behavior of Schiff base as ligands with transition metal ions is very useful for bio-inorganic chemists, several complexes of palladium were synthesized and used as anticancer (kalyani *et al*., 2012) and having biological activities (Shanker *et al*., 2009). In recent years, because of the new interesting applications founded in the field of pesticides and medicine, the metal complexes with tridentate O, N, N types of alternative structures have attracted the attention of chemists, various metal complexes with bi- and tridentate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological system and represent interesting models for metalloenzymes as in the complex behavior of Schiff bases with various first series transition metal ions (Singh and Adhikari, 2012). Copper(II) and Cobalt(II) metal complexes were synthesized and characterized and these complexes have shown good antibacterial and antifungal activities (Ahmadi and Amani, 2012). Many researches have been accomplished about the Schiff bases and their complexes with metal ions, of these the synthesis of a new Schiff base compound tetrachloro [5-(5-phenyl-$\overline{3}$-N-ethyl-$\overline{2}$-thiazolene) imino-3-N-ethyl-$\overline{2}$-thion-1, 3, 4- thiadiazole].titanium(IV) and its metal complexes with [Cr(III), Fe(III), Ru(III), Rh(III) and Au(III)] were studied by theoretical treatment and antibacterial activity (Al-Hassani, 2009), the complex- formation reactions between Cu^{2+} , Zn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions with 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio) ethylimino) methyl)-4-bromophenol have been studied by spectrophotometeric and conductmetric methods (Payehghadr *et al*., 2009). The complexes of new Schiff bases derived form Leucine amino acid sodium salt with 3-acetylpridine and sodium acetoacetanilide with Co and Ni were studied by the first and second derivative UV spectra and considered to be a direct method of determination (Al-Nuri *et al*., 2011), and in the pharmaceutical field a Schiff base of a salen-type Schiff bis base presents a good capacity of complexing with Mn(II) and this Schiff bis base was used as a reagent in spectrophotometeric determination of the Mn(II). This method was successfully applied to pharmaceutical products containing Mn(II) cation (Tantaru *et al*., 2002).

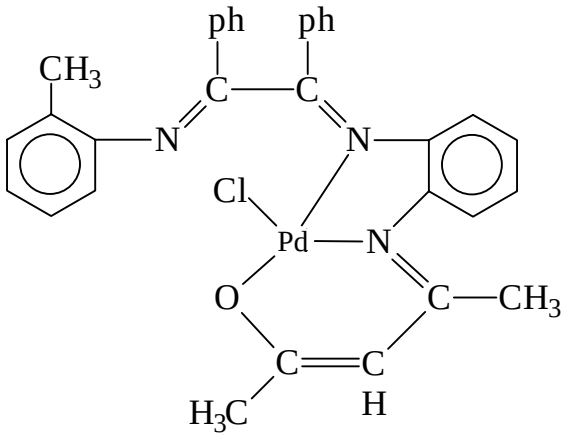
The present work deals with the UV spectroscopic study of a Schiff base N-(o-N-(Methyl-3-oL-2-butenimino)-N-(o-Toluyl)-1,2-diphenylethandiimine) (L_2ac) and their complexes with Co(II), Ni(II), Cu(II) and Pd(II) and their direct quantification by UV spectroscopic technique.

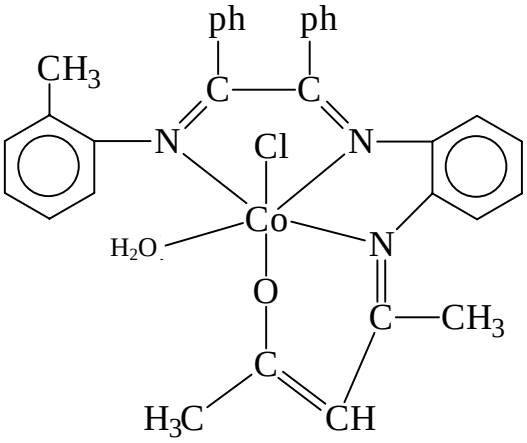


(L_2ac)



M= Ni(II), Cu(II)





Cobalt complex of (L_2ac)

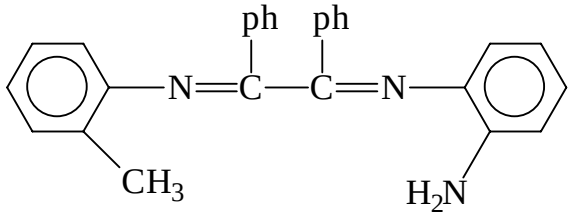
EXPERIMENT

All chemicals used were of reagent grade and obtained from fluka and B.D.H. chemical companies and were used as supplied.

Synthesis of Schiff base (L_2ac) (Al-Thaher, 2011)

A- Preparation of (L_2)

(N-o amino phenyl $\overline{N}$-o-Toluyl-1,2-diphenyl ethan) (1.07 g, 0.01 mole) of ortho methyl aniline was added to a solution of (2.10 g, 0.01 mole) of benzil dissolved in hot absolute ethanol. The reaction mixture was refluxed for two hours then cooled, yellow needle crystals formed, these crystals were dissolved in (10 ml) of hot absolute ethanol and added to the (1.08 g,0.01 mole) of ortho phenylenediimine which was dissolved in (10 ml) of hot absolute ethanol, the mixture was heated under reflux for one hour. On cooling, a dark brown solid was separated which was filtered off, washed with ether and dried.



(L_2)

B- Preparation of the Schiff base ligand (L_2ac)

L_2ac:N-(o-N-(methyl-3-ol-2-butenimino)-$\overline{N}$-(o-Toluyl)-1,2-diphenylethandi-imine

(3.89 g, 0.01 mole) of (L_2) dissolved in (20 ml) of hot absolute ethanol was added to (1.00 g, 0.01 mole) of acetylacetone dissolved in (10 ml) of hot absolute ethanol, the reaction mixture was refluxed, then cooled until precipitate appeared, which filtered off, washed by cold absolute ethanol and dried.

Preparation of Schiff base complexes (Al-Thaher, 2011)

A- Preparation of the solution of palladium salt Na_2 Pd Cl_4:

This solution was prepared by mixing aqueous solution of palladium chloride $PdCl_2$ (0.177 g, 0.001 mole) with (0.116 g, 0.002 mole) NaCl in (5 ml) of distilled water until the $PdCl_2$ is dissolving to obtain the dark red brown solution.

B- Preparation the Ni(II), Cu(II) and Pd(II) complexes of Schiff base (L_2ac):

These complexes were prepared by adding (0.237 g, 0.001 mole) of $NiCl_2.6H_2O$ or (0.170 g,0.001 mol) of $CuCl_2.2H_2O$ which was dissolved in (10 ml) of hot absolute ethanol or the solution of palladium salt in (A) gradually to the solution of (0.472 g, 0.001 mole) of the ligand (L_2ac) which dissolved in (10 ml) of hot absolute ethanol, the reaction mixture was heated under reflux for one hour. On cooling the separated solid was filtered off, washed several times by cold absolute ethanol then dried.

C- Preparation of Co(II) complex of the Schiff base (L_2ac)

The same procedure was repeated as above in (B) using (0.2378 g, 0.001 mole) of $CoCl_2.6H_2O$.

The physical and spectral properties of this complex were measured as shown in Table (1).

Table 1: Physical and spectral properties of Cobalt(II) complex

Compound	Colour	m.p C^o	μ eff. (BM)	Λm $Ohm^{-1}mole^{-1}cm^2$	
Co(II)complex of L_2ac $[Co(L_2ac)(H_2O)Cl]$	Bright gray	126.0	4.77	21.0	
	I.R (KBr) υ(cm^{-1})				
	C=N	C=N	**M-N**	**M-O**	
	1650.79	1596.40	488.26	520.05	

Co(II) complex in absolute ethanol gives the transitions $\upsilon_1$and υ_3 at 9728 cm^{-1} and 18382 cm^{-1} respectively. So the structure of cobalt(II) complex is expected to be distorted octahedral, indeed the magnetic moment value supports this suggestion.

The I.R spectrum of the Co(II) complex exhibits two strong bands at 1650.79 and 1596.40 cm^{-1} assigned for the isomethane (C=N) groups stretching frequencies, the band at 1650.79 cm^{-1} is assigned for the two (C=N) groups from the benzyl part of the ligand while the other band at 1596.40 cm^{-1} may probably due to the conjugated (C=N) with the (C=C) and aromatic ring of the ortho phenylinediimine part to the ligand.

Instrumentation :

All the UV spectra were recorded using UV-Visible spectrophotometer. Shimadzu UV-1650 PC using 1×1×3cm matched quartz cells.

Solution preparation :

Using absolute ethanol as a solvent for all compounds [Schiff base (L_2ac) and its complexes with cobalt, Nickel, copper and palladium]

1. (10^{-3} M) in (25 ml) of Schiff base compound was prepared by dissolving (0.0029 gm).
2. (10^{-3} M) in (25 ml) of Co(II) complex of Schiff base was prepared by dissolving (0.0062 gm)
3. (5×10^{-4}M) in (25 ml) of Ni(II) complex of Schiff base was prepared by dissolving (0.0028 gm)
4. (5×10^{-4}M) in (25ml) of Pd(II) complex was prepared by dissolving (0.0032 gm)
5. (5×10^{-4}M) in (25 ml) from Cu(II) complex was prepared by dissolving of (0.0029 gm)

The other required concentrations for all compounds were prepared form the stock solutions by an appropriate dilution.

RESULTS AND DISCUSSION

The UV spectra for Schiff base compound (L_2ac) and its complexes with Co(II), Ni(II), Pd(II) and Cu(II) are shown in (Fig. 1) and Table (2)

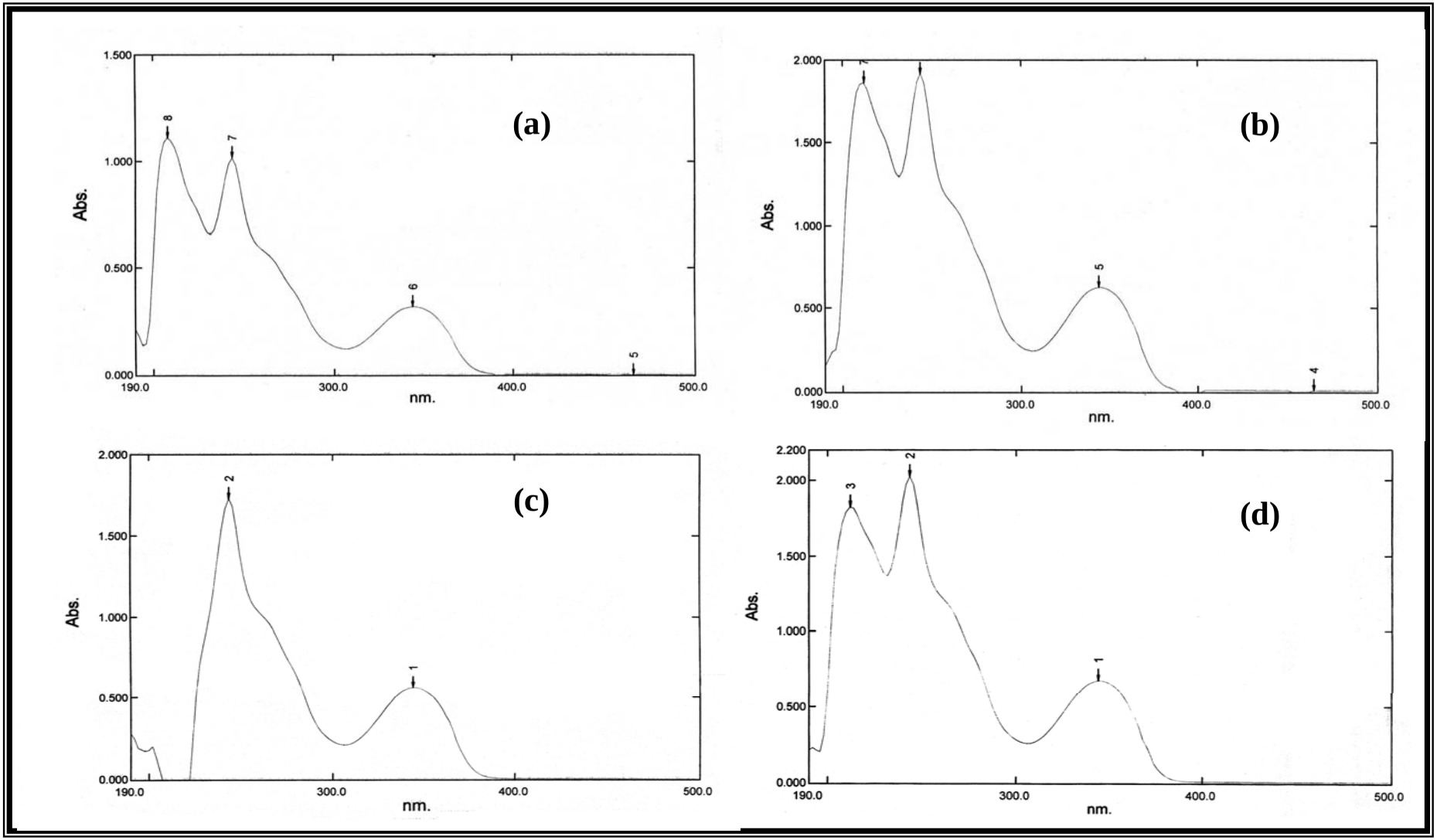


Fig. 1: The UV absorption spectrum of (9×10^{-5} M) of (a) Schiff base (L_2ac), (b) Co(II) complex of (L_2ac), (c) Ni(II) complex of (L_2ac) and (d) Pd(II) complex of (L_2ac) in absolute ethanol

Table 2: The UV absorption for solutions (9×10^{-5} M) of Schiff base (L_2ac) and its complexes in absolute ethanol

Compound	Wavelength (nm)	εmax Litter.mole^{-1}.cm^{-1}
Schiff base (L_2ac)	208.0 244.0 344.0	12311.1 11277.7 3544.4
Cobalt complex of (L_2ac)	212.0 244.0 344.0	20688.8 21300.0 6977.7
Nickel complex of (L_2ac)	244.0 344.0	19233.3 6255.5
Palladium complex of (L_2ac)	212.0 244.0 344.0	20222.2 22466.6 7511.1
Copper complex of (L_2ac)	208.0 260.0	14844.4 10711.1

The absorption at wavelength (344 nm) was chosen for the quantitative determination of the Schiff base as well as its complexes, except for copper (II) (λ = 260 nm) was used.

The UV absorption spectra for the Schiff base and its complexes were recorded at different concentrations at the range (9×10^{-7}M) to (7×10^{-4}M) in absolute ethanol and the absorbance at λ = 344 nm was measured.

The plot of the molar concentrations versus the absorbance of these solutions result in a straight line relationship as shown in (Fig. 2).

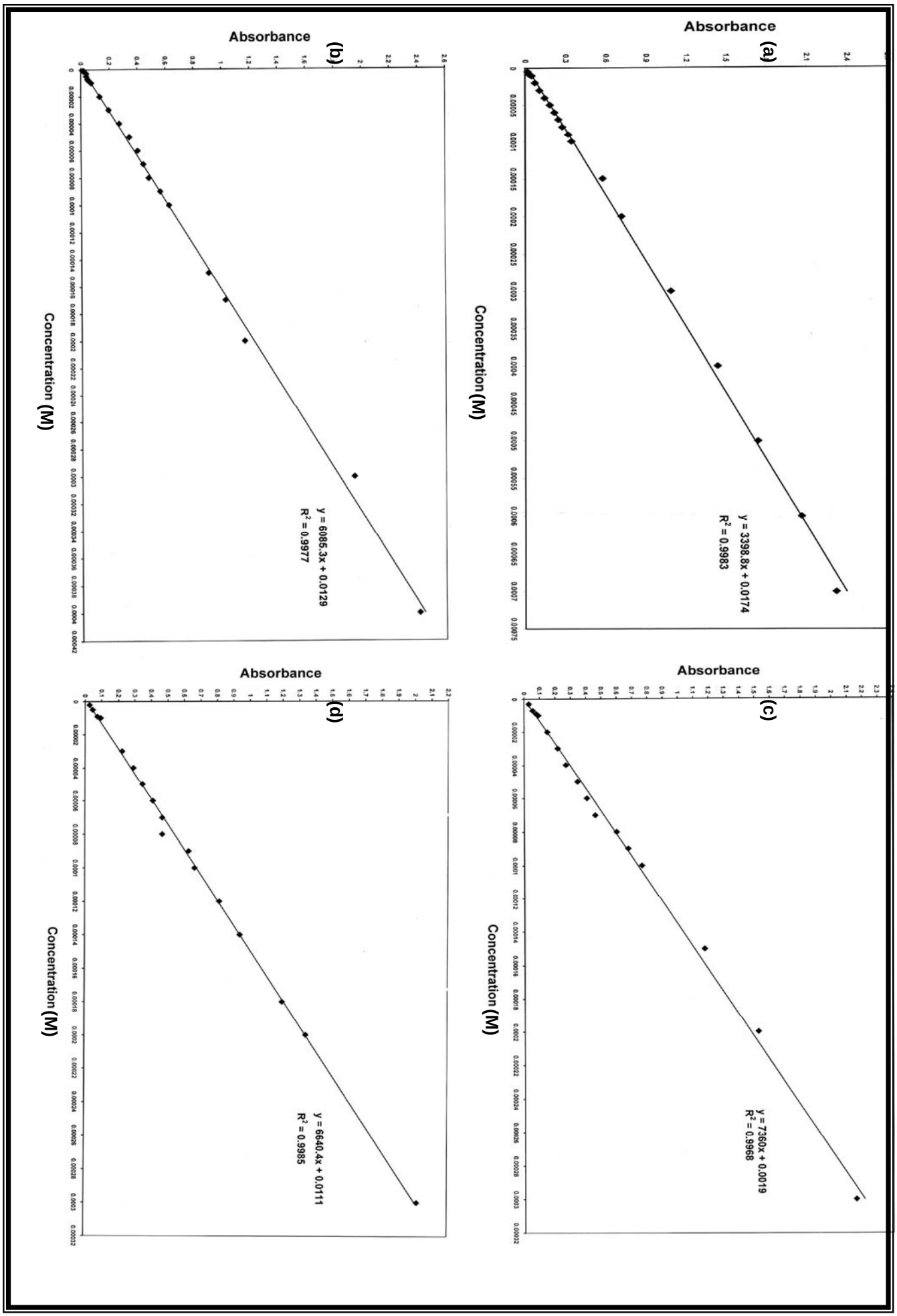


Fig. 2: The relationship between the values of absorbance and molar concentrations in absolute ethanol of (a)Schiff base compound (L_2ac), (b) Co(II) complex of (L_2ac), (c) Ni(II) complex of (L_2ac) and (d) Pd(II) complex of (L_2ac) at (344 nm).

From these relationships, it is clear that the straight line obeying Beer's Lambert law within the range of (5×10^{-6}–7×10^{-4}M) for the Schiff base, (2×10^{-6}–3×10^{-4}M), for the cobalt (II) complex, (9×10^{-7}–4×10^{-4}M) for the nickel(II) complex and (3×10^{-6}-3×10^{-4}M), for the palladium(II) complex. Table (3) and (4).

Table 3: The values of lower and upper determination limits, R^2 and R.S.D for the Schiff base (L_2ac) and its complexes in absolute ethanol

Compound	Lower Determination limits (μg/ml)	Upper Determination limits (μg/ml)	R^2	R.S.D
Schiff base (L_2ac)	0.595	71.40	0.9983	0.33%
Cobalt complex of (L_2ac)	0.497	74.65	0.9985	0.91%
Nickel complex of (L_2ac)	0.208	92.46	0.9977	1.43%
Palladium complex of (L_2ac)	0.782	78.25	0.9968	1.21%

From the results obtained we can find that the determination limits of the Schiff base compound (L_2ac) is in the range (0.595 – 71.40 μg/ml) with R^2 = 0.9983 and Relative Standard Deviation (R.S.D) = 0.33%. It is clear from the results that the complexation of Schiff base compound with the metals [Co(II), Ni(II) and Pd(II)] causes an improvement in the determination range of Schiff base (0.595-41.40μg/ml) and that the Ni(II) complex to have the border range(0.208-92.46 μg/ml), then Co(II) (0.497-74.65 μg/ml) and Pd(II) (0.782-78.25 μg/ml) respectively as shown in Table (3) which means that there is an improvement in the determination range of the Schiff base after complexation which is a favorable results.

Table 4: Accuracy and precision of the method for the direct determination of the compound of (L_2ac) and its complexes in absolute ethanol

Compound	Taken (μg/ml)	Found (μg/ml)	Recovery %	Error
Schiff base (L_2ac)	3.57	3.80	106.4	0.23
	10.71	10.81	100.9	0.10
	71.40	74.97	105.0	3.57
Cobalt complex of (L_2ac)	2.23	2.48	111.2	0.25
	17.41	16.84	96.7	– 0.57
	44.79	43.54	97.2	– 1.25
Nickel complex of (L_2ac)	2.08	2.12	101.9	0.04
	16.18	16.41	101.4	0.23
	69.34	64.72	93.3	– 4.62
Palladium complex of (L_2ac)	2.60	3.13	120.3	0.53
	15.65	15.39	98.3	– 0.26
	52.17	52.17	100.0	0.0

For accuracy and precision of the method, three different concentrations were prepared and the absorbance of each was measured at (λ=344 nm) in absolute ethanol and each solution was measured three times and the results for all compounds [Schiff base and its Co(II), Ni(II), and pd(II) complexes] appear to be in a good precision and accuracy as shown in Table (4).

Copper (II) complex of Schiff base

The UV absorption spectrum of Schiff base copper complex was recorded at different concentrations in absolute ethanol which shows two absorption at (204 and 260 nm) (Fig. 3).

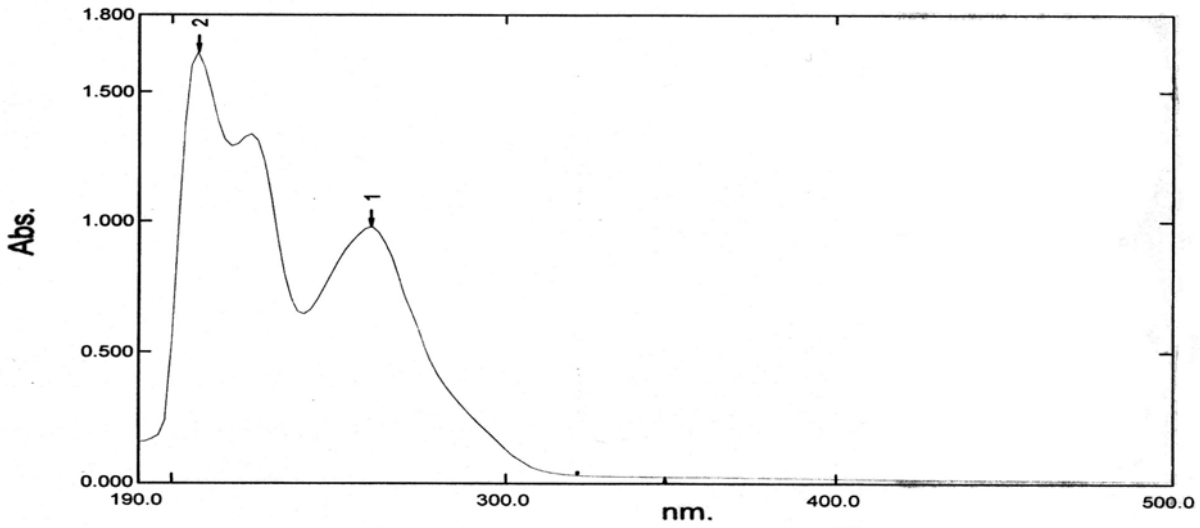


Fig. 3: The UV absorption spectrum of (9×10^{-5} M) of copper(II) complex of (L_2ac) in absolute ethanol

The absorbance at (260 nm) was recorded for a series of different concentration solutions.

The plot of a molar concentration versus the absorbance of the solution result in a straight line relationship obeying Beer's Lambert law at the range of concentration equal (3×10^{-6} – 1×10^{-4}M) (Fig. 4).

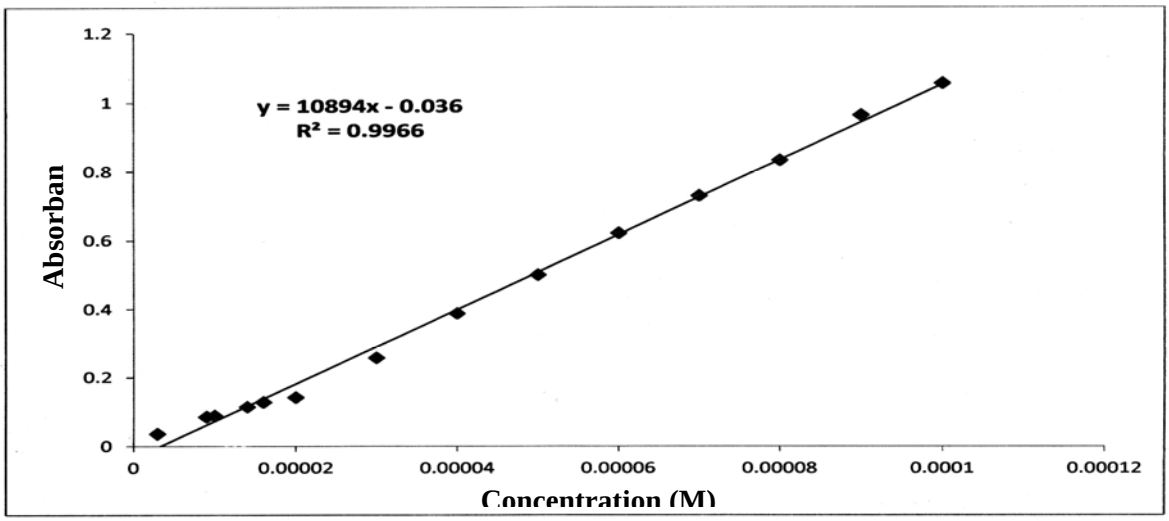


Fig. 4: The relationship between the values of absorbance and molar concentrations for Cu(II) complex of (L_2ac) at (260 nm) in absolute ethanol.

The lower and upper determination limits for the Cu(II) complex of the Schiff base were estimated as shown in Table (5) and (6).

Table 5: The value of lower, upper determination limits, R^2 and R.S.D for Schiff base copper complex in absolute ethanol

Compound	Lower Determination limits (μg/ml)	Upper Determination limits (μg/ml)	R^2	R.S.D
Copper (II) complex of (L_2ac)	0.707	23.599	0.9965	1.2%

Table 6: Accuracy and precision of the method for copper complex of Schiff base in absolute ethanol

Compound	Taken (μg/ml)	Found (μg/ml)	Recovery %	Error
Copper (II) complex of (L_2ac)	2.12	2.19	103.3	0.07
	9.43	8.96	95.0	– 0.47
	21.23	21.00	98.9	– 0.23

From these results, it is clear that the Schiff base Cu(II) complex has a smaller range of the determination limits compared with those complexes with Co, Ni and Pd, which may be attributed to the nature of Cu(II) molecule.

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