

Photodegradation of Schiff Bases Copper(II) Complexes in Dimethyl Sulphoxid (DMSO)

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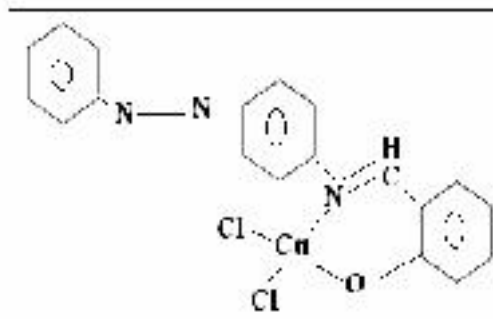
Abstract

Photodecomposition of dichlorobis N [4-Azo benzene aniline)2-hydroxy benzilidene] Copper (II) (Complex A₁) and dichloro N[2-Azo 3- sulphonic -2- naphthol) 6- carboxylic 2- hydroxy benzilidene] copper (II) (Complex A₂), have been performed at $\lambda = 373$ nm for complex A₁ and at $\lambda = 358$ nm for complex A₂ in dimethyl sulphoxide at 25°C. The absorbance spectrum of these complexes have been recorded with time of irradiation in order to examine the kinetics of photodecay. The apparent rate constant (K_d) for the first order reaction has been calculated and found to be $1.1 \times 10^{-2} \text{ min}^{-1}$ for complex A₁ and $2.34 \times 10^{-2} \text{ min}^{-1}$ for complex A₂. The primary quantum yields (Φ) has also been calculated and found to be 2.810×10^{-1} and 0.2765×10^{-1} for complex A₁ and A₂ respectively .

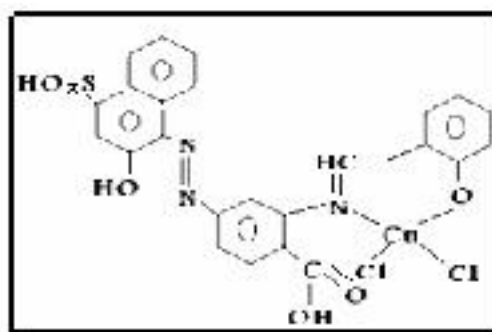
Introduction

Copper is a metal that has a wide range of applications due to its good properties . It is used in electronics, for production of wires , sheets , tubes , and also to form alloys. The use of inorganic inhibitors as another native to organic compounds that are based on the possibility of degradation of organic compounds with time and temperature[1]. Long – lived , photochemically generated excited states of the second and third row transition metal complexes usually feature significant triplet character and often are based on internal charge transfer [2]. Schiff bases form stable complexes with metals that perform important role in biological systems. They find also wide application in analytical chemistry since they allow simple and inexpensive determinations of several organic and inorganic substances. Some Schiff bases complexes were found to be very effective catalysts for hydrolytic cleavage or transesterification of RNA phosphate diester back bone. Therefore metal complexes of Schiff bases attained a prominent place in coordination chemistry [3,4]. Photodecomposition of Schiff bases complexes are among the most known photoreactive metal complexes [5]. Schiff bases are condensation products of an amine and a ketone or aldehyde, with $R_2C=NR$ as their general formula they, contain heteroatoms and π electrons that enable bonding with copper [1,5]. Marjorie and Joseph have studied toxicity of copper to larval pimephales promelas in the presence of photodegraded natural dissolved organic matter [6]. The photodegradation of copper complexes in (DMSO) solvent was performed.

In this work, we used the following copper complexes as examples for studying the photodegradation in DMSO solvent.



Complex(A₁) dichloro bis N [(4- Azo benzene 3- hydroxy Anilino) 2- hydroxy benzilidene] copper (II) . [Cu (C₁₉H₁₅N₃O)Cl₂]



Complex (A₂) dichloro N [(2-Azo – 3-sulphonic-2-naphthol) 6- carboxylic aniline -2-hydroxy benziliden] copper(II). [Cu (C₂₄H₁₇N₃O₇S)Cl₂]

Photodegradation of molybdenum(II) and tungsten(II) carbonyl complexes with triazole, benzimidazole, and oxadiazole acetylenic derivatives have been studied previously[5]. In this paper the Kinetic and mechanism of degradation have been established. Copper is necessary for the formation of blood cells, connective tissue and it is also involved in producing the skin pigment melanin [7].

Experimental techniques

Chemicals

(a) potassium ferrioxalate hydrate K₃[Fe (C₂O₄)₃] .3H₂O actinometer was prepared by the method reported by Hatchard and Parker[9].

(b) Two complexes (A₁ and A₂) were prepared as reported earlier[8]. The ligand L₁ (2 mmole, 0.63 g) that was dissolved in ethanol (10 ml) was added to ethanolic solution (10 ml) of (1.05 mmole, 0.17 g) of CuCl₂.2H₂O with stirring the mixture was refluxed for 2 hr, the products were recrystallized from ethanol and dried under vacuum.

(c) The DMSO used was of spectroscopic grade

Apparatus

- I) The photolysis apparatus consist of medium pressure mercury lamp 150w, $\lambda=365$ nm supplied by PHYWE ltd .was used as light source.
- II) UV-Vis spectral absorption bands were obtained using Pye-unicam(8800) spectrophotometer at 25 C°. using dimethyl sulphoxide (DMSO) as a solvent in quartz photochemical cell.
- III) IR spectra were obtained using Pye-unicam SP3 -300 infrared spectrophotometer for the range (4000-200) cm^{-1} but for the ligands were recorded on KBr discs with a Pye-unicam SP3 -100 infrared spectrophotometer for the range 4000- 600 cm^{-1} .
- IV) The acidity (pH) of the solution before and after irradiation was measured by (Multi 740/pH-meter).

procedures

The photoexperiments wer carried out in (35 ml) pyrex cell with two holes in its upper section for the passage of gas and for sampling processes. 150W medium pressure mercury lamp was used as a radiation source. A known concentration (1.5×10^{-6} M) of the complex was introduced into the cell after treatment with oxygen for 20 min. the cell was closed tightly and the absorption spectra were recorded between 200-800 nm. The measurement of the incident light (I_0) was carried out by using standard method of potassium ferrioxalate actinometry [9].

$$I_0 = \frac{A V_1}{\epsilon \phi_{\lambda} V_2 t}$$

where I_0 is the incident light intensity , A; the absorption at 510 nm . V_1 the final volume (25 ml) ; ϵ the extinction coefficient = slope of calibration curve , ϕ_{λ} the quantum yield = 1.21 at 365 nm , V_2 the volume taken from irradiation solution (1 ml) and t ; the time of irradiation of actinometer solution (s).

Results and Discussion

The spectra of copper complexes .

UV-Vis. spectra for the complexes have shown absorption bands around 373 nm (Fig 1) . The ϵ values are 0.043×10^6 and $0.009 \times 10^6 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ for the complexes A_1 and A_2 respectively, the band at 34129 cm^{-1} is due to charge transfer (C.T) transition from ($L \rightarrow M$) and at 23255 cm^{-1} is due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition . Electronic absorption for complex (A_2) shows band at 34482 cm^{-1} which is due to C.T transition from ($L \rightarrow M$) and at 24813 cm^{-1} which is due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition , Table (1) , which supports the squar planar structure. The changes in absorbance during photolysis were measured for different irradiation periods of time at 373 nm for complex A_1 and 358 nm for the complex A_2 in order to study the kinetics of the photodecay of complexes in solution (Fig .2). The specific decomposition rate constant of each complex (K_d) was determined after examining the order of reaction of these compounds. The spectra of the $[\text{Cu}(\text{C}_{19} \text{H}_{15} \text{N}_3 \text{O}) \text{Cl}_2]$ were treated kinetically by plotting the curve between ($A_{\infty} - A_t$) and $\text{Ln}(A_{\infty} - A_t)$ versus irradiation time (Fig.3) . Only the plot of $\text{Ln}(A_{\infty} - A_t)$ with irradiation time gives straight line which indicates that the reaction is first – order. The K_d of decomposition of this complex was determined by the following first – order equation ,

$$\text{Ln}(A_{\infty} - A_t) = \text{Ln}(A_0 - A_{\infty}) - K_d t.$$

The value of K_d for this complex is $1.1 \times 10^{-2} \text{ min}^{-1}$; photolysis of other complex (A_2) has been performed in a similar manner . Fig 2(b)) shows the change in Uv-Visb. Spectra with time of irradiation . On irradiation of the complex A_1 in dimethyl sulphoxide, the color changes

gradually from pale yellow to colorless and the absorbance intensity of all bands increases with time of irradiation in the region 200-600 nm, all photochemical changes in these complexes are reactively similar and simple. Although we believe that the solvent (DMSO) undergoes photolysis during irradiation, but this fact does not affect the change in the spectra of the complex.

Determination of apparent quantum yield (Φ)

The apparent quantum yield (Φ) for copper complexes was determined after the determination of the absorbed light intensity I_{abs} and incidence light intensity I_0 as follows :-

$$I_{\text{abs.}} = I_0 (1 - e^{-\epsilon c l})$$

$$= 9.40 \times 10^{-7} (1 - e^{-0.043 \times 10^6 \times 1.5 \times 10^{-6}})$$

$$= 0.5875 \times 10^{-7} \text{ Ein} \cdot \text{L}^{-1} \cdot \text{S}^{-1} \text{ for complex } A_1$$

$$\Phi = \frac{\text{Rate}}{I_{\text{abs}}} = \frac{K_d [C]}{I_{\text{abs}}}$$

$$= \frac{1.1 \times 10^{-2} \times 1.5 \times 10^{-6}}{0.587 \times 10^{-7}} = 2.810 \times 10^{-1}, \text{ for complex } A_1$$

The value of Φ for complex $A_2 = 0.2765 \times 10^{-1}$

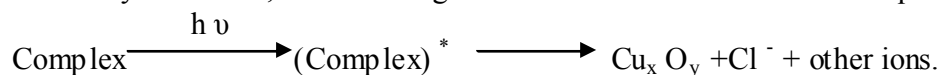
Alias (10) found that apparent quantum yield for carbonyl complexes are in the range of 8.3 to 12.1×10^{-4} .

Luetal have investigated several factors affecting the photocatalytic degradation of (DDVP) using a glass photo reactor coated with TiO_2 and 20 W black-light tungsten fluorescent tube [11]. They found that the quantum yield for the destruction of DDVP was 2.67%.

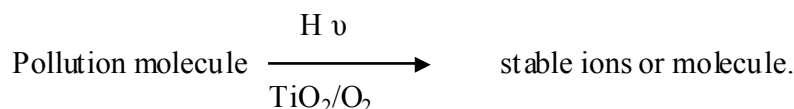
Qualitative Analysis of photolysis products

It is essential to examine the final products of photolysis in order to set up the mechanism. Infrared (IR) spectra have been recorded for the final photoproducts of these reactions. Fig 5 shows that there is only one peak appearing at 470 cm^{-1} due to $\text{M}-\text{O}$ band, also the band at 247 , 1625 , 1560 cm^{-1} were disappeared indicated to scission of $\text{Cu}-\text{Cl}$, $(\text{C}=\text{N})$ and $(\text{N}=\text{N})$ bands respectively, which clearly shows that the complex has photodecomposed to metal oxide (for complex A_1). The difference between

(Fig.4) before irradiation and (Fig.5) after irradiation, for example complex A_1 indicates that there is a complete degradation of this complex metal oxide and stable ion via a series of secondary reactions, the following is a well known chemical reaction equation (6).



Analysis for NO_3^- have also been done by using classical analytical method, positive (brown-ring) has been detected depending on the number of nitrogen atom in the complex [12]. The acidity (pH) of the final photoproduct also was measured by during the photolysis which was increased with time of irradiation. The initial pH=9.8 and the final pH was at 3.2, all these final photoreactions have been suggested without proposing the exact primary process. . Hussein [13] found that photodegradation of dichlorovos (DDVP) under UV-150 W illumination in the presence of TiO_2 in oxygen atmosphere, gives an increase in the formation of Cl^- ions and conductivity, but a decrease in pH. These types of reactions have an application in environmental degradation or mineralization of polluted water [14].



References

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Table (1): UV-Visible bands of copper complexes in DMS O

complex	Absorbance band cm ⁻¹	Transition	Geometry
[Cu(C ₁₉ H ₁₅ N ₃ O)Cl ₂]	34129 23255	C.T ${}^2E_g \rightarrow {}^2T_{2g}$	Squar planar
[Cu(C ₂₄ H ₁₇ N ₃ O ₇ S)Cl ₂]	34482 24813	C.T ${}^2E_g \rightarrow {}^2T_{2g}$	Squar planar

Table(2): Absorbance of complex [Cu(C₁₉H₁₅N₃O)Cl₂] versus irradiation time

Time (sec.)	Abs. 373nm	(A _∞ - A _t)	Ln (A _∞ - A _t)
0	0.062	0.013	- 4.342
1800	0.066	0.009	- 4.710
3600	0.069	0.006	- 5.11
5400	0.0672	0.007	- 4.853
7200	0.071	0.004	- 5.52
9000	0.073	0.002	- 6.214
10800	0.075	0	-----

Table (3): IR bands of the Ligand and complexes cm⁻¹

No.Complex	compound	ν(C=N)	ν(N=N), C=C	ν(OH)	M-Cl	M-N	M-O	ν(CO)
L ₁	C ₁₉ H ₁₅ N ₃ O	1600	1560	3200	-	-	-	-
L ₂	C ₂₄ H ₁₇ N ₃ O ₇ S	1610	1532	3300	-	-	-	1720
A ₁	[Cu(L ₁)Cl ₂]	1625	1560	-	247- 271	334- 364	470	-
A ₂	[Cu(L ₂)Cl ₂]	1618	1533	3242	235- 260	322- 340	470- 520	1720

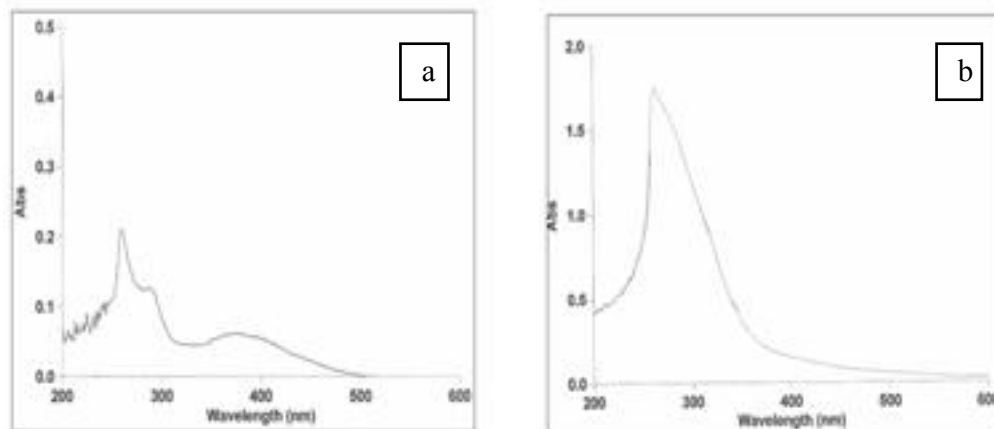


Fig (1): Electronic spectra of (a) $[Cu(C_{19}H_{15}N_3O)Cl_2]$.
 (b) $[Cu(C_{24}H_{17}N_3O_7S)Cl_2]$.

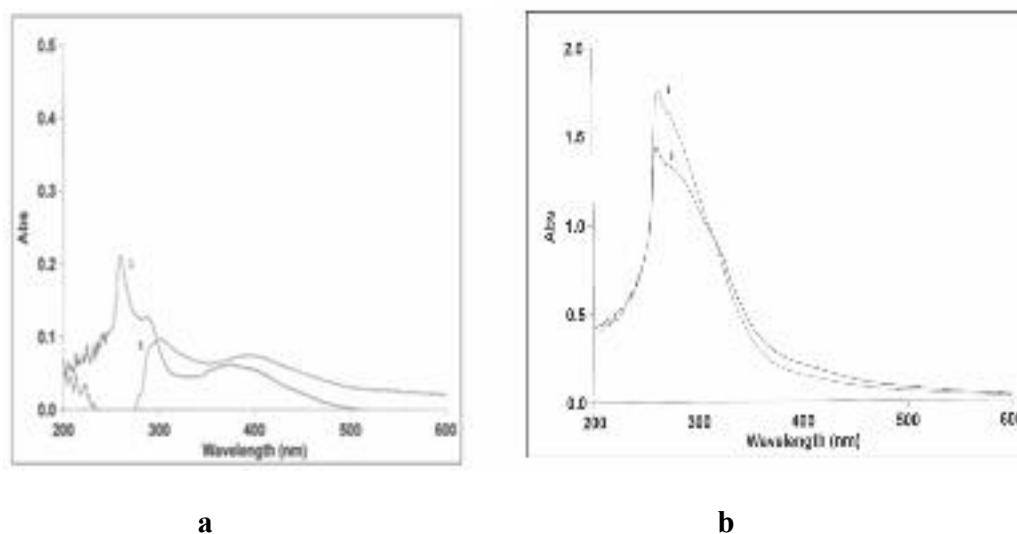
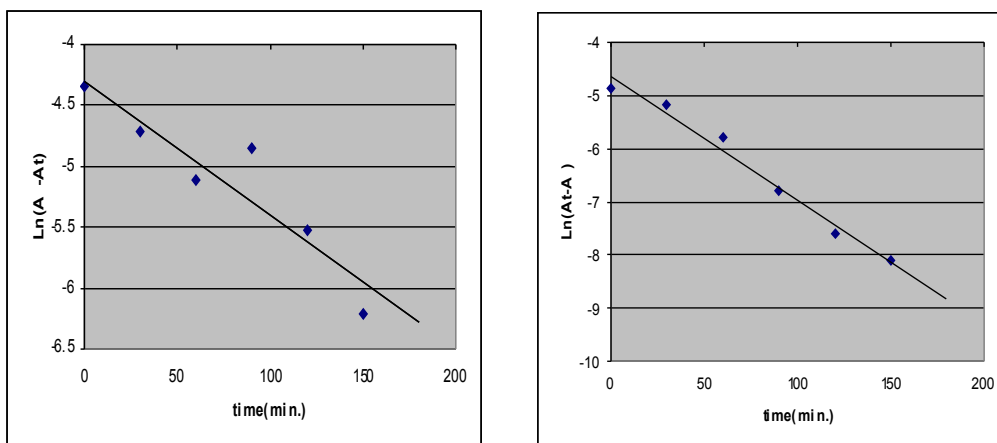


Fig. (2): Electronic spectra of (a) complex A_1 (b) complex A_2 changes at 373 nm accompany change in irradiation time in dimethyl sulphoxide solvent at 298 K° (1) 0 , (2) 3 hr.



a

b

Fig.(3): Variation of natural logarithm of absorbance with irradiation time of (a) complex A₁ and (b) complex A₂ in dimethyl sulphoxide solvent at 373 nm (complex A₁) and 358 nm (complex A₂), using MPML Lamp at 298 K°.

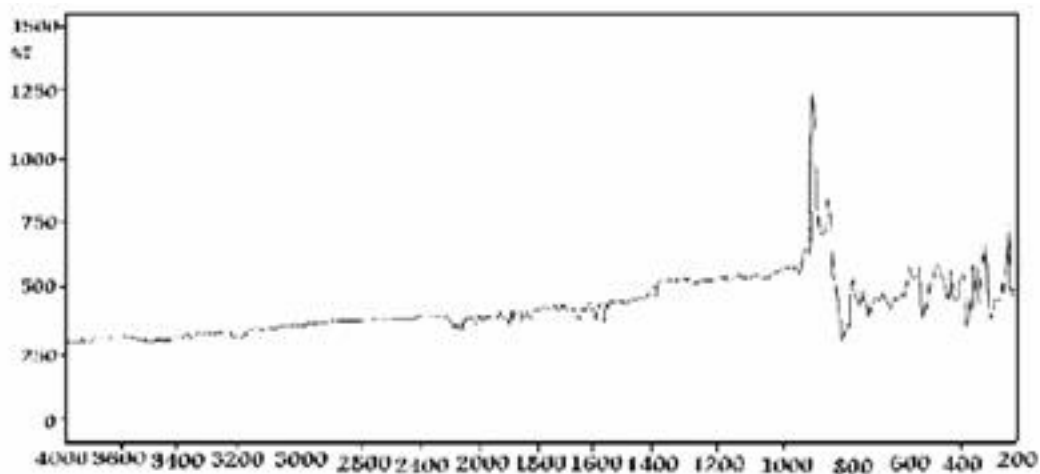


Fig.(4): IR spectrum of [Cu(C₁₉H₁₅N₃O)Cl₂] at 289 K° before photolysis.

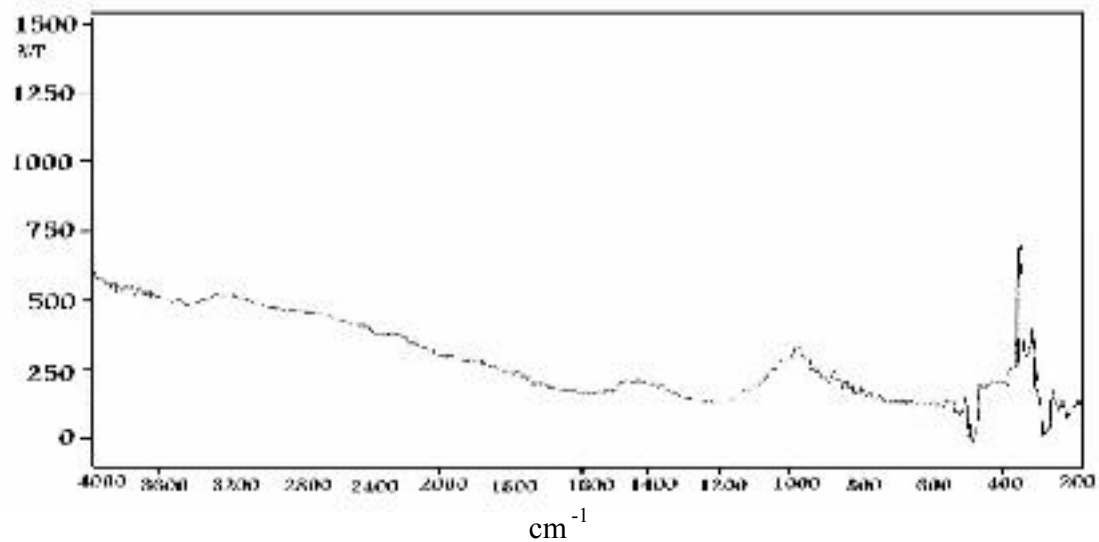


Fig.(5): IR spectrum of $[\text{Cu}(\text{C}_{19}\text{H}_{15}\text{N}_3\text{O})\text{Cl}_2]$ at 289 k° after photolysis.

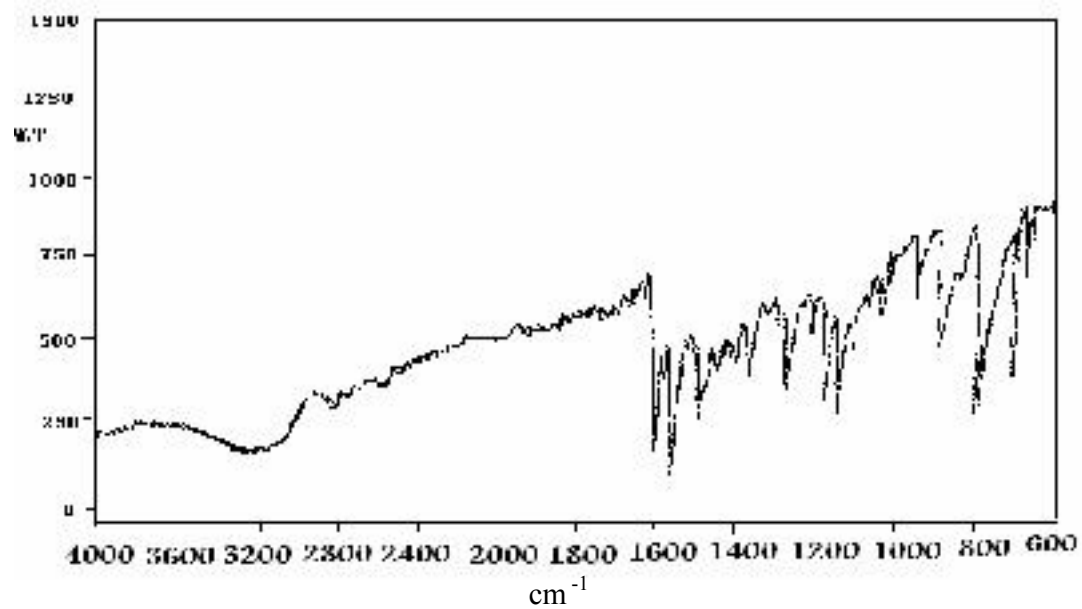


Fig.(6): a IR spectrum of $L_1 = \text{C}_{19}\text{H}_{15}\text{N}_3\text{O}$

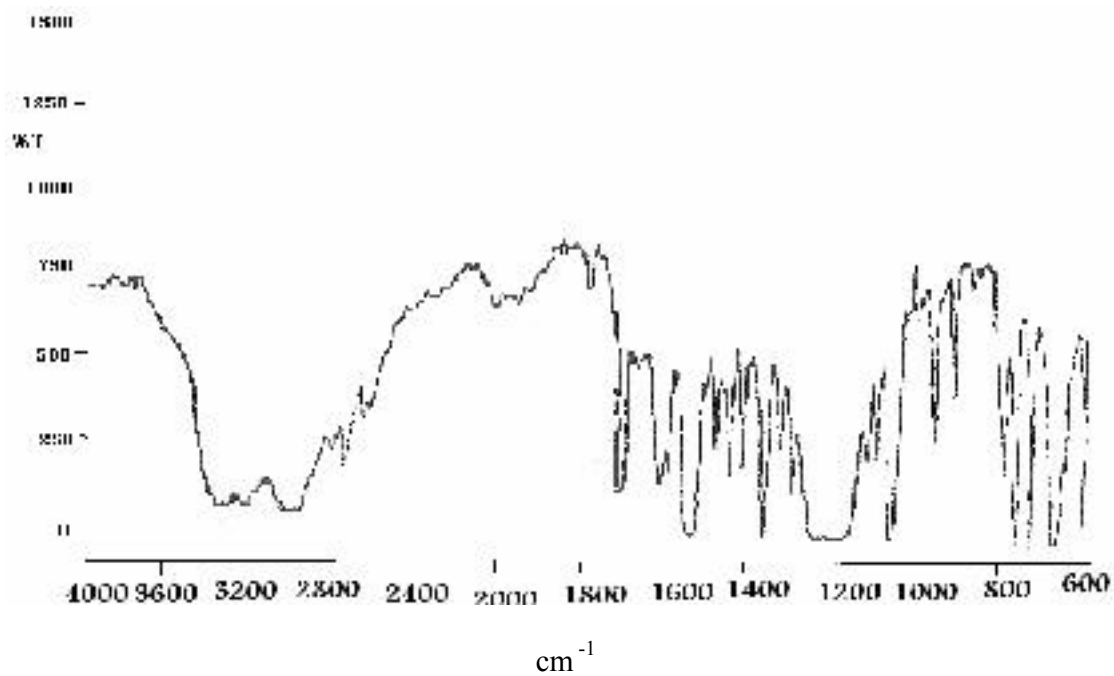


Fig.(6): b IR spectrum of L₂= C₂₄H₁₇N₃O₇S

التجزئة الضوئية لمعقد النحاس (II) مع قواعد شف في مذيب ثنائي مثيل سلفوكسايد (DMAO)

اسماء جميل علي اللامي

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الخلاصة

تم في هذا البحث دراسة التجزئة الضوئية لمعقد النحاس (II) مع ثنائي كلورو [N-4-أزو بنزين 1-نيلين 2-هيدروكسي بنزليدين] المعقد (A₁) وثنائي كلورو N [(2-أزو بنزين 3-سلفونك 2-نفثول) 6-كربوكسيلك 2-هيدروكسي بنزليدين] المعقد (A₂). شخص هذين المعقدين بأستخدام الطرائق الطيفية مثل الاشعة تحت الحمراء وال فوق البنفسجية - المرئية. درست حركية تفكك هذين المعقدين ضوئيا في درجة حرارة 25 °C في مذيب ثنائي مثيل سلفوكسايد ووجد أن تفاعل التجزئة الضوئية هو من لمرتبة الاولى ومن ذلك قيس ثابت السرعة النوعي للتفكك الضوئي (K_d) من خلال متابعة التغير في امتصاصية الاشعة فوق البنفسجية المرئية وبطول موجي 373 nm للمعقد A₁ و 358 nm للمعقد A₂، فكانت تساوي $1.1 \times 10^{-2} \text{ min}^{-1}$ ، 2.34×10^{-2} للمعقدين A₁ و A₂ على التوالي. عين ناتج الكم لتفاعل التجزئة الضوئية وكانت تساوي 2.810×10^{-1} و 0.2765×10^{-1} للمعقدين A₁ و A₂ على التوالي.