Photodegredation of Cobalt (II) and Nickel (II) Complexes with Schiff Base in Dimethyl Sulphoxide (DMSO) Solvent.

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الخلاصة

تم في هذا البحث دراسة التجزئة الضوئية لمعقد ثنائي كلورو بس ن [(4- آزو بنزين 3- هيدروكسي انيلينو) 2- هيدروكسي بنزيليدين] كوبلت (II) (المعقد A1) وثـائي كلورو ن [(4- آزو بنزين 3- هيدروكسي انيلينو) 2- هيدروكسي بنزيليدين] نيكل (II) (المعقد A2). لقد شخصت هذه المعقدات بأستخدام الطرائق الطيفية كالاشعة تحت الحمراء والفوق البنفسجية – المرئية ودرست حركيات تفكك هذه المعقدات ضـوئيا في درجة حرارة 25 م° باستخدام ثنائي مثيل سلفوكسايد كمذيب ووجد أن تفاعل التجزئة الضـوئية هو مـن المرتبـة الاولى وثم تم قياس ثابت السرعة النوعي للتجزئة الضوئية (kd) وبدرجة حرارة 25 م° من خـلال متابعـة التغير في امتصاصية مطيافية الاشعة فوق البنفسجية المرئية وبطـول مـوجي (397 nm = λ) للمعقد A1 و(393nm = λ) للمعقد A2 فكانت تساوي (0.07×10^{-2} min^{-1} ، $k_d = 2.92 \times 10^{-2}$) للمعقد A1 و A2 على التوالي .
تم تعيين نـاتج الكم لتفاعل التجزئـة الضـوئية فـي هـذه الدراسـة وكـان يسـاوي (3.542×10^{-1} ، 4.23×10^{-1}) للمعقد A1 و A2 على التوالي .

ABSTRACT

Photodecomposition of Dichlorobis N [4-Azo benzene 3-hydroxy Anilino] 2-hydroxy benzilidene] Cobalt(II) (Complexe A1) and Dichloro N[4-Azobenzene 3-hydroxy Anilino] 2- hydroxy benzilidene] Nickel(II) (Complex A2) have been performed at (397 nm and 393 nm) for complex A1 and A2 respectively in dimethyl sulphoxide at 25 C°. The absorbance spectrum for these complexes have been recorded with the time of irradiation inorder to examine the Kinetics of photodecay. The specific rate constant (k $_d$)for the first order reaction have been calculated and found to be ($0.07*10^{-2}$ min^{-1}) for complexe A1 and (k $_d$= $2.92 * 10^{-2}$ min^{-1}) for camplexe A2. the primaey Quantum Yields (Ø) has also been calculated and found to be ($4.233 *10^{-1}$; $3.543*10^{-1}$) for complex A1 and A2 respectively.

INTRODUCTION

The photochemistry of coordination compounds has become an increasingly popular technique for controlling and tuning the reactivity of transition metal complexes and organo metallic compounds as well rather uncommon reaction pathways can be initiated by electronic excitation of diverse spectroscopic states of these compound besides stoichiometric electron – transfer, dissociation, substitution as well as rearrangement reactions induced by light [1]. 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 [1,2] .Photodecomposition of schiff bases complexes are among the most photoreactive metal complexes known[3] . synthesis of metal complexes has led to preparation of molecular systems that have varying degrees of control over the primary and secondary coordination spheres around the thermal ions [4]. [5]Turankaya Yazicilar study synthesis, spectroscopic and thermal properties of some 4(dimethyl amine)benzalden- metal complexes (V,Cr,Co,Ni, Cu,Zn,Cd,Hg,Mn)the relation ship between thermal stability and the structure of complexes was discussed. The photochemistry of cobalt (III) complexes has been the subject of considerable study in recent years. During the irradiation a noticeable color change in the solutions occurred , consistent with a change in the coordination sphere of the metal ion[5] .

In this work we used two complexes of cobalt and Nickel derived for the ligand N [4- Azo benzene 3- hydroxy Anilino] 2- hydroxy benzilidene for studying the photodegredation in DMSO solvent. Photodecomposition of schiff bases complexes is similar to metal carbonyl complexes , the photodegredation of cobalt and Nickel complexes in (DMSO) solvent was perfomed .

Complex (A_1) :   [Co ($C_{19}H_{15}N_3O_2$)$_2$Cl$_2$]

Complex (A_2) :   [Ni ($C_{19}H_{15}N_3O_2$)Cl$_2$]

MATERIALS AND METHODS

Chemicals (a) potassium ferrioxalate hydrate $K_3[$ Fe $(C_2O_4)_3]$ .3H$_2$O actinometer was perepared by the method reported by Hatchard and Parker[6] . The photolysis apparatus used is shown in fig (1).

 (b) Two complexes (A_1 and A_2) was prepared as reported earlier[7] .

 (c) The DMSO used was of spectroscopic grade

Apparatus
i. The photolysis apparatus shown in fig (1) consist of medium pressure mercury lamp (150w) (λ=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 dimethel 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} .

iv. The acidity (pH) of the solution before and after irradiation were measured by (Multi 740/pH-meter).

Procedures

The photoexperiments wer carried out in (35 ml) pyrex cell with two holes in itsupper section for the passage of gas and for sampling processes. 150W medium pressure mercury lampwas used as a radiation source**.**Aknown concentration $(3 \times 10^{-4}$ M)of the complex was introduced in to 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 ($I_\circ$) was carried out by using standard method of potassium ferrioxalate actinometry [6] .

$$I_\circ = \frac{A\ V_1}{\varepsilon \varnothing_\lambda\ V_2\ t}$$

where $I_\circ$ 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 , $\varnothing_\lambda$ 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).
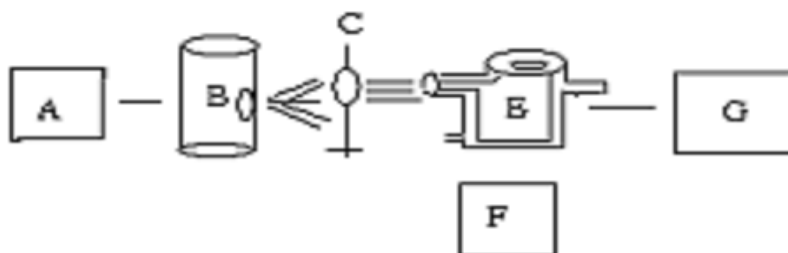

Fig -1 : Shematic digram of the experimental apparatus for photolysis of complexes :
(A) power supply Unite (B) medium pressure mercury Lamp MPML (C) Lenses; (D) Filter (365 nm) ; (E) quartz cell ; (F) magnetic stirrer. (G) circulating water thermostat.

Result and Discussion

The spectra of cobalt and Nickel complexes

Uv-Vis spectra for the named complexes have been found to contain absorption bands around 397 nm as shown in fig (2) as a represantive example.
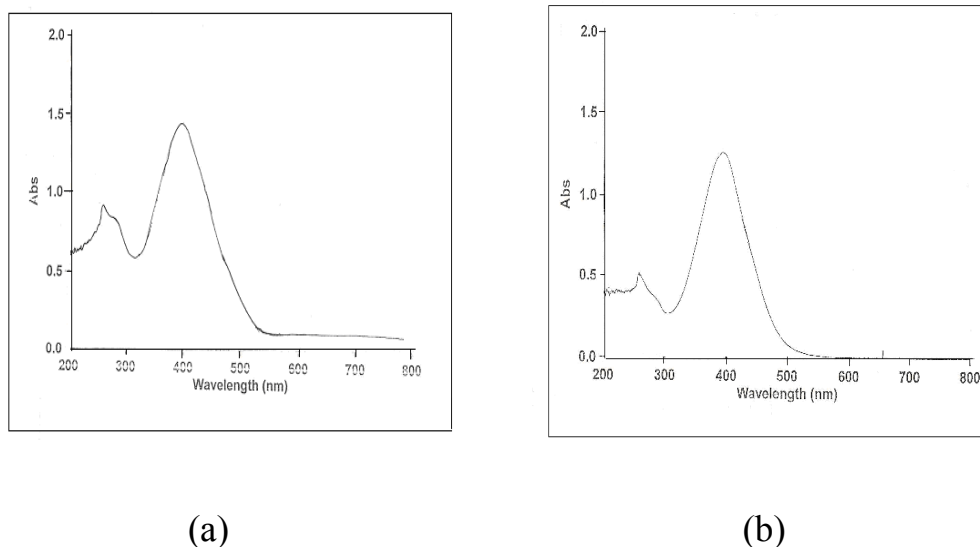
(a)   (b)

Fig -2 : Electronic spectra of (a) [Co (C$_{19}$H$_{15}$ N$_3$O$_2$)$_2$ Cl$_2$]
(b) [Ni (C$_{19}$H$_{15}$N$_3$O$_2$)Cl$_2$]

The ε Values are ($0.25*10^4$; $0.102*10^4$)L.mol^{-1}.cm^{-1} for complex A$_1$ and A$_2$ respectively the band at (20161 cm^{-1}) due to ^{4}T$_1$g (F) ^{4}A$_2$g(F)

transition and at (23201 cm^{-1}) duo to ^{4}T$_1$g (F) $\longrightarrow$ ^{4}T$_1$g (P) transition . The spectrum of [Co (C$_{19}$H$_{15}$ N$_3$O$_2$)$_2$ Cl$_2$] in dimethyl sulphoxide showed ^{4}T$_1$g(F) ^{4}A$_2$g(F) and ^{4}T$_1$g(F) ^{4}T$_1$g(P) transitions indicative of ctahedral geometry . Electronic absorption for complex (A$_2$) shows three band transition at

(15974 cm^{-1}) due to ^{1}A$_1$g $\longrightarrow$ ^{1}A$_2$g
(22988 cm^{-1}) due to ^{1}A$_1$g $\longrightarrow$ ^{1}B$_1$g
(26525 cm^{-1}) due to ^{1}A$_1$g $\longrightarrow$ ^{1} Eg
and (33898 cm^{-1}) due to charge transfer (C.T) transition which supported the squer planer structure[8,9] .
the changes in absorbanse during photolysis were measured for different irradiation periods of time at (397nm) for complex(A$_1$) and (393nm) for complex(A$_2$) inorder to study the kinetics of the photodecay of complexes in solution fig (3) .
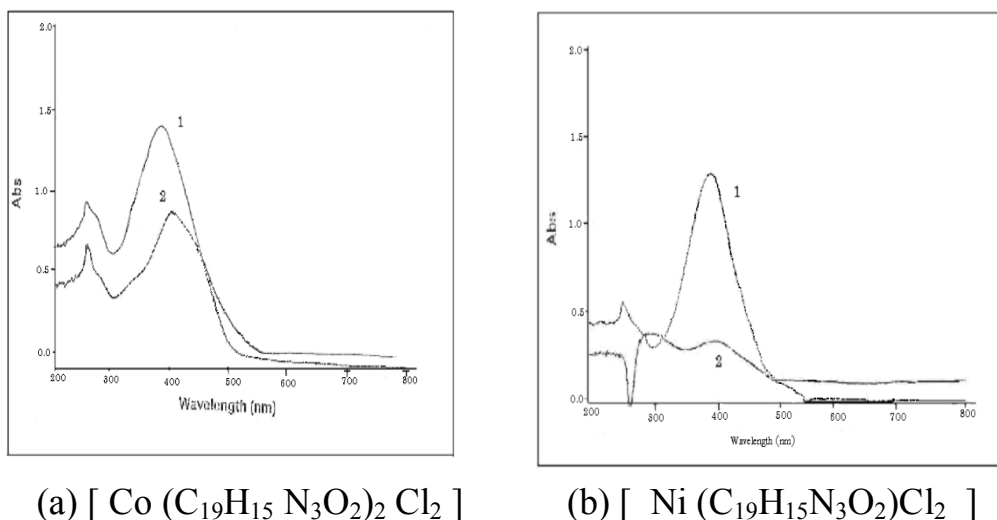
(a) [Co $(C_{19}H_{15}N_3O_2)_2 Cl_2$]   (b) [Ni $(C_{19}H_{15}N_3O_2)Cl_2$]

Fig-3 : Electronic spectra of (a) complex A_1 (b) complex A_2 spectra changes at 397 nm accompany change in irradiation on time in dimetheyl sulphoxide solvent at 298 K° . (1) 0 ; (2) 3 hr.

The spesific decomposition rate constant of each complex (k_d) was determined after examining the order of reaction of these compounds. The spectra of the complex [Co($C_{19}H_{15}N_3O_2)_2Cl_2$] treated kinetically by plotting the curve between (A_t-A ∞) versus irradiation time and ln (A_t-A ∞) versus irradiation time table(1) Only the plot of ln(A_t-A ∞) with irradiation time gives straight line fig (4) which indicates that the reaction is first – order . the (k_d) of decomposition of this complex was determined by the following first – order equation :-
ln(A_t-A ∞) = ln(A_o-A ∞) − k_d t .
The value of k_d for this complex is (7 x 10^{-4} min^{-1}) ; photolysis of other complex (A_2) have been perfomed in a similar manner. (Fig 3(b)) show the change in Uv-Vis spectra with time of irradiation . On irradiatin of the complex (A_1) in dimethyl sulphoxide the color changes gradually from red orange to pale orange and the absorbance intensity of all bands is decrease with time of irradiation in the region 200-800 nm. all photochemical change in these complexes are reactively similar and simple. the new mixed ligand cobalt(III) and nickel (II) complexes of the type [M(bpy)$_2$qbdp]($pF_6)_n$.xH_2O(where M=Co(III) or Ni(II) , bpy= 2.2○-bipryidine , qbdp = Quinolino[3,2-b] benzodiazepine , n= 3 or 2 and X= 5 or 2) have been synthesized and characterized . the DNA binding properties of these two complexes were studied by M.C.Prabhakara [10].S.AL-saleh found that the hydrolysis of carbaryl at different pH solutions follow first- order reaction kinetic [11] and S.M.Aliwi found that the photooxidation reaction of CN ion on TiO_2 surface follow first order relation ship . the specific rate constants and then the photooxidation rates were measured [12] .

Table -1 : Absorbance of complex [Co(C$_{19}$H$_{15}$N$_3$O$_2$)$_2$Cl$_2$] at different time

Time (min)	Abs.	(A$_t$-A ∞)	Ln (A$_t$-A ∞)
0	1.457	0.547	- 0.6033
30	1.447	0.537	-0.6217
60	1.436	0.526	-0.641
90	1.429	0.519	-0.654
120	1.405	0.495	-0.703
150	1.404	0.494	-0.7052
180	0.910	0	----------
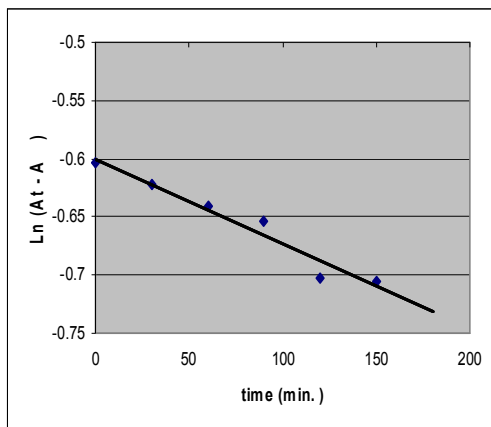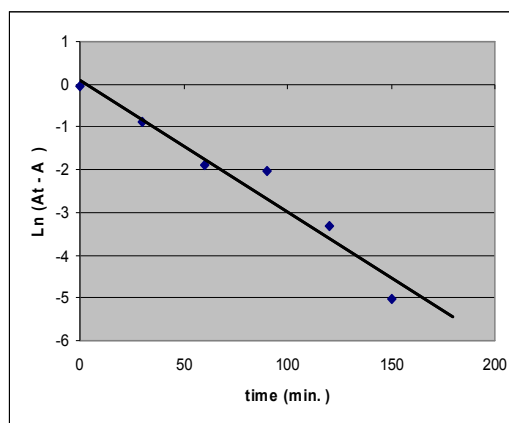
a   b

Fig-4 : Variation of neutral Logarithm of Absorpance with irradiation time of (a) complex A$_1$ and (b) complex A$_2$ in (DMSO) solvent using (MPML) at 298 K° .

Determination of apperant quantum Yield (Ø)

The determination of apperant quantum yield (Ø) has been done for cobalt and nickel complexes after the determination of absorbed light intensity I $_{abs.}$ and incidence light intensity I$_◦$ as follows :-

$$I_{abs.} = I_◦ (1- e^{-\varepsilon c l})$$

$= 9.40 \times 10^{-7} (1 - e^{-0.25 \times 104 \times 1 \times 3 \times 10^{-4}})$
$= 9.40 \times 10^{-7} (1- e^{-0.75})$
$= 9.40 \times 10^{-7} \times 0.5277 = 4.960 \times 10^{-7}$ $\quad$ Ein . I^{-1}.S^{-1} $\quad$ for complex (A$_1$)

$$Ø = \frac{Rate}{I_{abs}} = \frac{k_d [C]}{I_{abs}}$$

$$= \frac{7 \times 10^{-4} \times 3 \times 10^{-4}}{4.960 \times 10^{-7}} = 0.423 = 4.233 \times 10^{-1} \text{ for complex (A}_1)$$

The value of Ø for complex (A$_2$) = 3.543 x 10^{-1}

[11] Alison and Ghiggino found that apperant quantum yield for the cobalt complexes $[Co^{III}(3)Cl_2]4H_2O$ where 3 is 6- (anthracen-9-ylmethyl)).1,4,8,11-tetraazacyclotetradecane. are in the range (0.01-0.68).

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 two peaks appearing at (237-273 ; 1543 cm^{-1} (v.w)) due to M –Cl and (N =N) bands also we show disappearance band at (1600 cm^{-1} ; 324-360 cm^{-1}) indicated to scission of (C= N) and (M –   N) bands (for complex A_1) , which clearly show that the complex have been photodecomposed to metal chloride . the difference between (fig 6) before irradiation and Fig (5) after irradiation for example (complex A_1) shows that there is complete degradation of this complex metal chloride and stable ions via a series of secondary reactions . the acidity of the final photolysis which was increased with time of irradiation , the initial alkali was at (pH = 8.17) and the final was at (3.27)

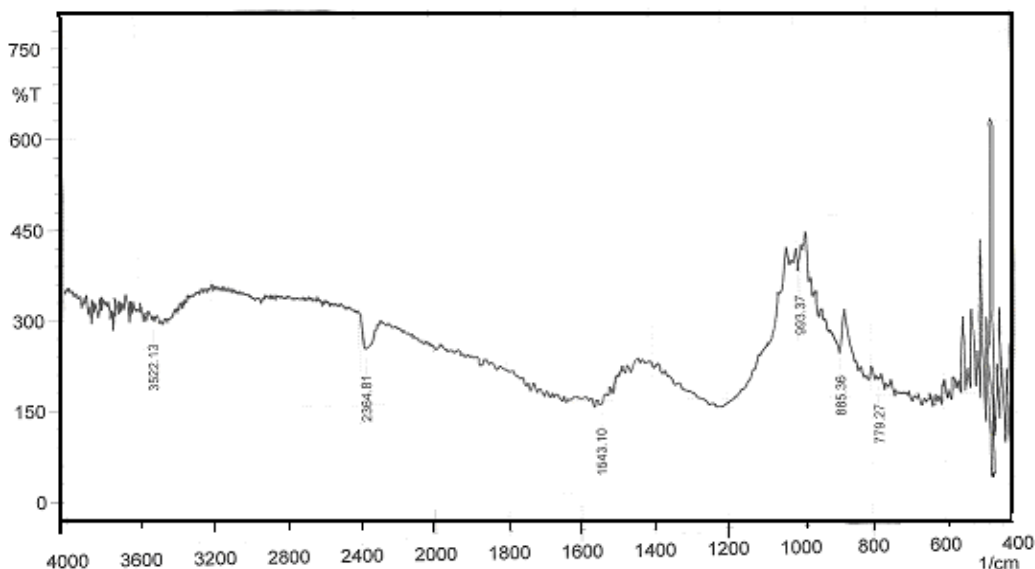All these final photoreactions have been suggested without proposing the exact primary process.

Fig -5 : IR spectrum of complex $[Co(C_{19}H_{15}N_3O_2)_2Cl_2$] at 298 K $^{\circ}$ after photolysis.
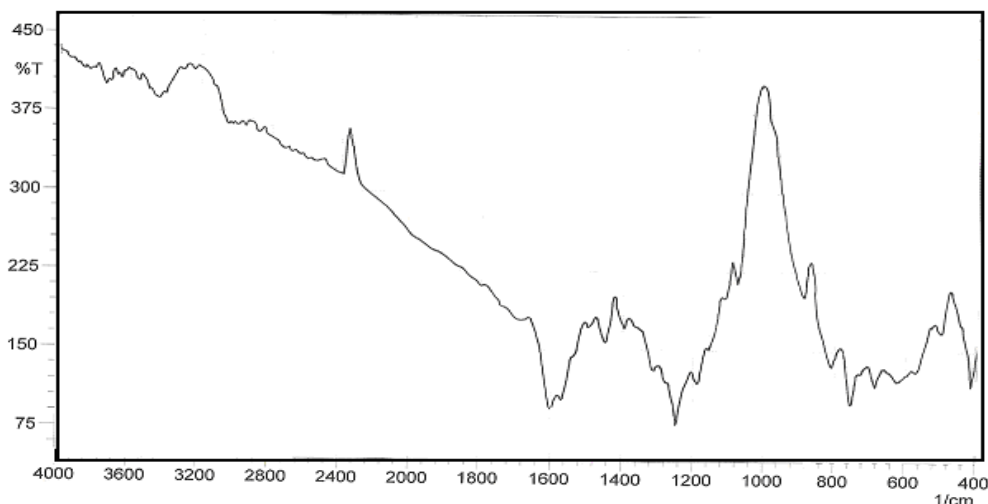
Fig -6 : IR spectrum of complex [Co(C$_{19}$H$_{15}$N$_3$O$_2$)$_2$Cl$_2$] at 298 K ° before photolysis.

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