

Preparation, Characterization and Study of the Photodecolorization of Mixed-Ligand Binuclear Co(II) Complex of Schiff Base by ZnO

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Abstract: In this work, a new mixed-ligand binuclear Co(II) complex of Schiff base was prepared. Moreover, the characterization of this prepared complex was performed by measurement of melting points, UV-Vis spectra, FT-IR spectra, and magnetic susceptibility measurements, and later compared with metal and ligand solutions. It has been discovered that the Schiff bases with Co(II) ion forms a binuclear complex with a stoichiometry of molar ratio 1:2 from "metal:ligand". The photodecolorization of this complex was done under UV light for ZnO's suspension solution. The results of this photodecolorization showed that the greatest efficiency was obtained with the use of ZnO dose of 300 mg/100 mL and at an initial pH of 7. The decolorization activation energy for this complex is a small value of 11.289 kJ mol⁻¹. Additionally, the thermodynamic study for this reaction is non-spontaneous, endothermic and less random.

Keywords: Schiff base; binuclear Co(II) complex; photodecolorization; ZnO; UV-A light

■ INTRODUCTION

In reality, the metal complexes of Schiff bases play a crucial role in the development of coordination chemistry, which has generated an enormous number of publications, ranging from pure synthetic projects to physicochemical studies [1]. They are important chelating ligands with a variety of active applications [2-3]. These Schiff bases can be employed in catalytic, photochemical biological activities such as antiviral, anticancer and antifungal activities [4], electrochemical processes such as oxidation reactions [5] and agriculture applications [6]. As a result, they are also used as ligands to obtain metal complexes because they have high stability of the coordinating compounds and good solubility in common solvents [7]. The produced metal complexes of Schiff bases can serve as models in the understanding of biological systems [8-9]. The reaction medium affects the kinetics and mechanism of chemical transformations, which is considered one of the key problems of modern physical chemistry. In addition, the polarity of the medium as a solvent effect [10] and the temperature change [11] were extensively researched for organic

compounds under photolysis. However, the photo reaction is helpful in the presence of light for the degradation of the color of organic molecules.

Direct photochemical transformation occurs closely when the energy of light attacks the bonds within an organic compound [12] that absorbs the light and leads to the treatment of effluent water. This process indicates the occurrence of chemical change and leads to the formation of carbon dioxide and treated water [13]. The purpose of this manuscript is to prepare a new mixed-ligand binuclear Co(II) complex of Schiff base and then investigate the characteristics of the components of these compounds by using UV-Vis. spectrometry, FT-IR spectrometry, magnetic measurements, and melting points. Moreover, the photodecolorization of this prepared complex is conducted under distinct circumstances such as ZnO dose, initial pH and the effect of temperature.

■ EXPERIMENTAL SECTION

Materials

All the used chemicals and solvents such as ethanol,

glacial acetic acid, DMSO, ethanol, DMF and other solvents were used in high purity. Benzedrine, salicylaldehyde, cobalt chloride hexa-hydrates [CoCl₂·6H₂O], ethanol, DMF, DMSO, potassium hydroxide and *o*-phenylenediamine were supplied by BDH and Sigma-Aldrich companies. Commercial ZnO was purchased from Fluka Company in 99.5% purity.

Instrumentation

The melting point was measured by melting point apparatus (Stuart-England). FT-IR spectra were recorded in the range of 4000–400 cm⁻¹ as KBr disc with a FT-IR-8000 S-Shimadzu spectrophotometer (Japan). Electronic spectra with methyl formamide (DMF) as a solvent in concentration 1 × 10⁻³ M at room temperature and the concentrations of binuclear Co(II) complex after irradiation were recorded by using a Shimadzu UV-240 UV-visible spectrophotometer (Japan). The magnetic measurements for samples were detected using auto Magnetic susceptibility balance-MSBMKI-USA.

Procedure

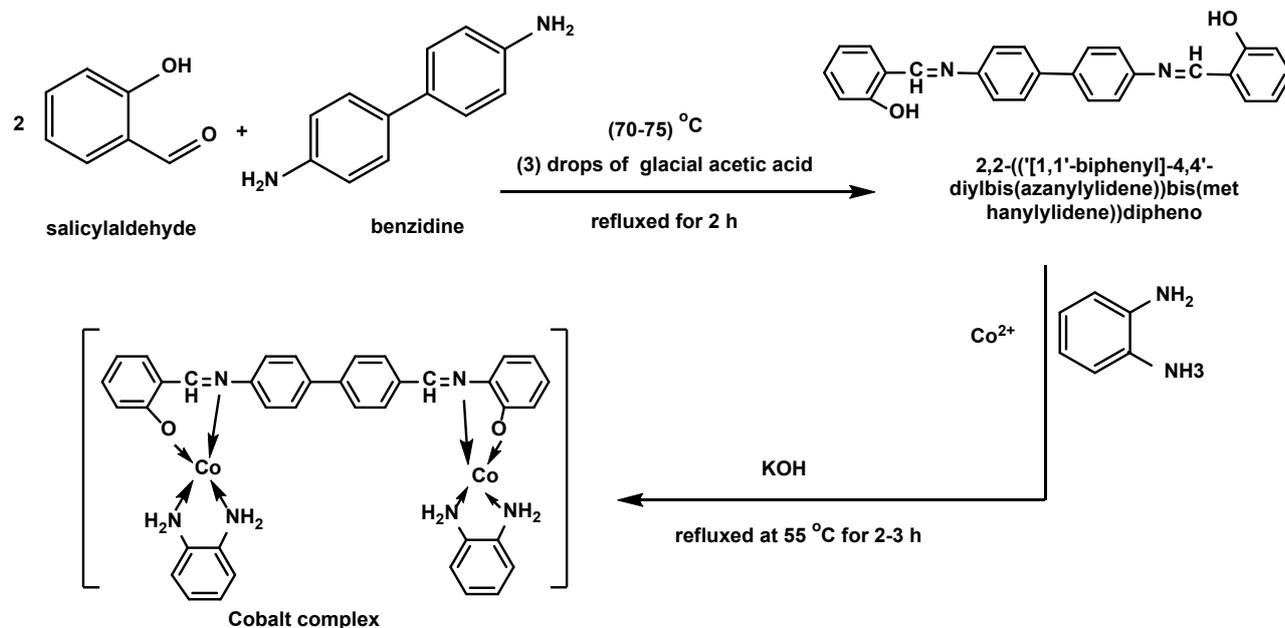
Synthesis of binuclear Co(II) complex

In a round bottom flask with a capacity of 100 mL,

0.5 g (0.00058 mmol) of 2,2-((1,1'-biphenyl)-4,4'-diylbis(azanylylidene)) bis(methanylylidene)) diphenoligand (H₂L) was dissolved in potassium hydroxide-ethanol solution. This solution was mixed with 0.2 g (0.00116 mmol) of *o*-phenylenediamine, and 25 mL of Co(II) ethanol-solution containing 0.0137g (0.00116 mol) [CoCl₂·6H₂O] to produce the mole ratio of H₂L:*o*-phenylene diamine:metal of 1:2:2. The mixture was refluxed with heating at 55 °C for 2–3 h. The final product (greenish brown) was filtered and washed using hot ethanol and lastly dried for 24 h. The melting point for this complex was recorded at 296 °C with the yield 75%, as shown in Scheme 1.

Method of photodecolorization

The photocatalytic decolorization reactions of the binuclear Co(II) complex with ZnO were made by using a homemade photoreactor shown in Fig. 1. This photoreactor consists of a wooden box. This wooden box contains a magnetic stirrer, a fan, a beaker for the reaction and a High pressure mercury lamp-250 Watts (Radium-Germany) as the radiation source, which has a light intensity equal to 1.458 × 10⁻⁷ Ens s⁻¹ by using a chemical actinometric solution [14]. In this work, an



Scheme 1. Schematic diagram for the preparation of the ligand and cobalt complex

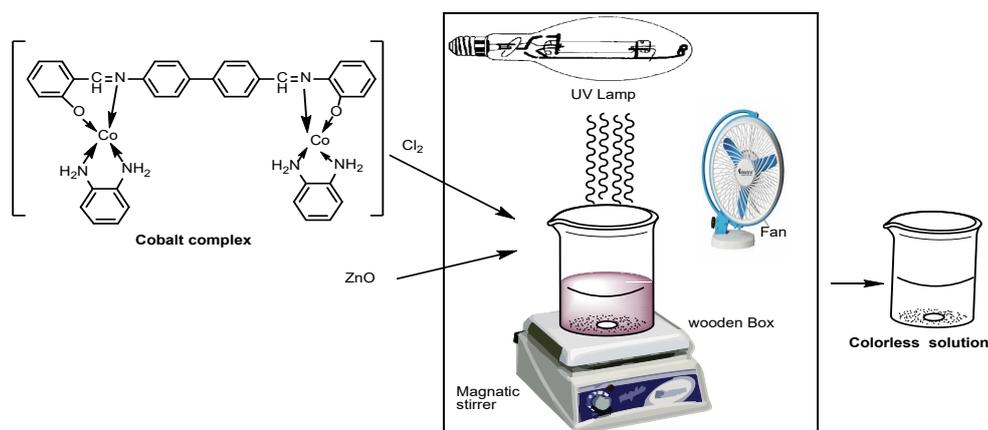


Fig 1. The photo reaction system for the decolorization of the binuclear Co(II) complex

appropriate amount of commercial ZnO was added to 50 mL of binuclear Co(II) complex solution with continuous mixing by a magnetic stirrer.

In the beginning, the dark reaction was carried out for 30 min, when UV-A light illuminated the generated suspension solution. At steady time periods, approximately 3 mL of the formed suspension solution was taken away and centrifuged twice to guarantee the removal of all the fine ZnO catalyst particles at 4000 rpm for 10 min. The absorbance of the residue complex in the solution was recorded by using a UV-Vis spectrophotometer (Shimadzu-UV-240) at 417 nm.

At the low concentration of the studied complex, the rate constant (k_{app}) was explained by Eq. (1), which is based on the Langmuir-Hinshelwood kinetic expression [15].

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app} \cdot t \quad (1)$$

where C_0 is an initial concentration of binuclear Co(II) complex without light (dark reaction) or 0 min of irradiation. C_t is the concentration of the same studied complex at the time of irradiation.

The photodecolorization efficiency (PDE) of binuclear Co(II) complex from aqueous solution is expressed by Eq. (2) [16].

$$PDE = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Physical Properties

Some physical features for H_2L and its complex are

explained in Table 1, including the change in the color and the melting points. The color of the ligand is altered from bright yellow to greenish brown when it is reacting with cobalt ion. In addition, the elevated melting point of the complex compared with the melting point of the ligand indicates the high stability of the complex towards air and light.

FT-IR Spectra

The IR absorption spectrum of the Schiff base for the H_2L in Fig. 2 shows the absence of two absorption bands at 3412 and 3295 cm^{-1} which belongs to $-NH_2$ stretching of benzidine, and $C=O$ absorption band at 1700 cm^{-1} of salicylaldehyde, and the appearance of $C=N$ absorption band at 1618 cm^{-1} . The infrared spectrum of the H_2L ligand appeared as a broad band at (3465 cm^{-1}), which indicated the $-OH$ group [17]. The $\nu(O-H)$ band is absent in the IR spectrum of the Co-complex confirmed by the absence of the $O-H$ bending band for H_2L in the complex of the mixed ligand. Meanwhile, the appearance of the band in the range of 3330–3340 cm^{-1} indicated the presence of the $-NH_2$ group. The absorption band of the $C=N$ group in H_2L appeared at 1618 cm^{-1} [18]. The band of the $C=N$ group was shifted to

Table 1. Physical properties for the ligand H_2L and the binuclear Co(II) complex

Compounds	Color	Melting points (°C)	Yield
H_2L	Bright Yellow	209	90.01%
$[Co_2(OPD)_2L]Cl_2$	Greenish Brown	296	75%

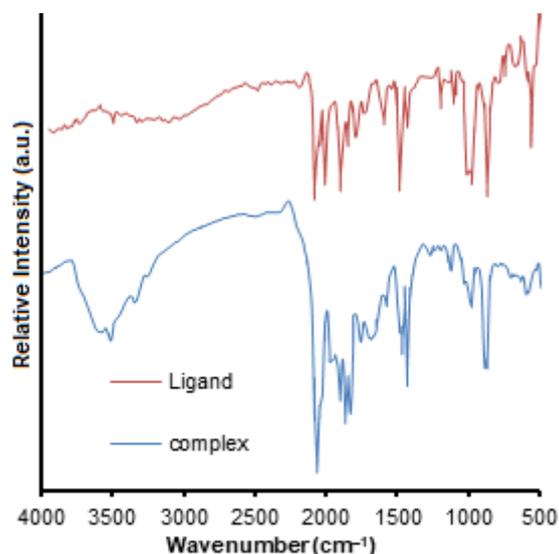


Fig 2. FT-IR spectra of H_2L and $[Co_2(OPD)_2(L)]Cl_2$ complex

lower frequencies because of the coordination with metal ions through the nitrogen atom shown in Fig. 2. The new bands that appeared in the regions, $468.72\text{--}542.02\text{ cm}^{-1}$, may be due to the generation of M–O, and M–N bands [19].

UV-Vis Spectra

Two absorption peaks were displayed in the UV-Vis spectrum of the ligand H_2L as shown in Fig. 3. The first peak at 279 nm (35842 cm^{-1}) was assigned to $\pi\text{--}\pi^*$ electronic transition of the benzene rings. The second peak at 370 nm (27027 cm^{-1}) was attributed to $n\text{--}\pi^*$ electronic transition of the non-bonding electrons (i.e. free electron pair) that is found on the nitrogen in the Schiff base part of the ligand as the transition of the molecular orbital of C=N chromophore [20–21]. Meanwhile the UV-Vis spectrum of the binuclear Co(II) complex shown in Fig. 3 displayed three absorption peaks. The first peak at 272 nm (36764 cm^{-1}) was assigned to the ligand field, while the second peak at 363 nm (27548 cm^{-1}) refers to the charge transfer electronic transition. The third peak was attributed to d-d electronic transition tetrahedral geometry around the central ion Co(II) at 979 nm (10214 cm^{-1}), which mostly observes as a new weak and much broader peak [20].

Magnetic Susceptibility Measurements of Complexes

The magnetic moment of this complex was 5.089 B.M.

This indicates that the generated complexes has tetrahedral form [20], as observed in Table 2.

Photodecolorization Reaction of $[Co_2(OPD)_2(L)]Cl_2$ Complex

Effect of ZnO dose on the decolorization of $[Co_2(OPD)_2(L)]Cl_2$ complex

The effect of ZnO doses in the range of 0.1–0.5 g/100 mL is depicted in Fig. 4 and 5. This study is essential to eschew the excess of the catalyst used, which reduces the efficiency of the photoreaction. The apparent rate constants for the decolorization of binuclear Co(II) complex were raised with increased dose of ZnO with a maximum value of 0.3 g/100 mL, due to the sufficient amount of active sites on the catalyst surface to raise the chance of radical formation [22–23]. On the other hand, the high amount of ZnO induced the decrease of the rate of this reaction due to the reduction of the penetration ability of light into this solution which acts as a screen [24–25]. In Fig. 5, the maximum PDE% was reached at 99.129% after 70 min.

Effect of the initial pH on the decolorization of $[Co_2(OPD)_2(L)]Cl_2$ complex

The study of the initial pH of the aqueous solution

Table 2. Magnetic susceptibility measurements of binuclear Co(II) complex

Complex	Xg $\times 10^{-6}$	XM $\times 10^{-6}$	XA $\times 10^{-6}$	μ_{eff} B.M
$[Co_2(OPD)_2(L)]Cl_2$	13.5	10731.15	11128.15	5.089

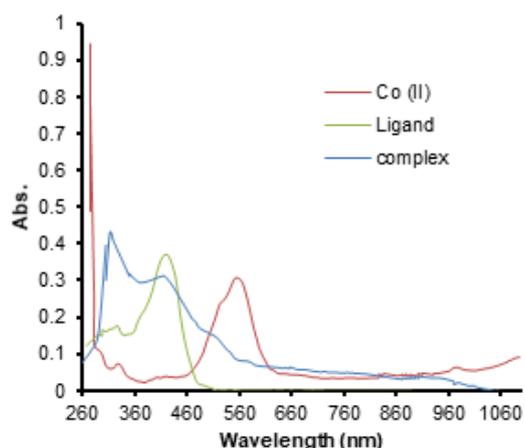


Fig 3. UV-Vis spectra for H_2L ligand, Metal (Co(II)) and complex $[Co_2(OPD)_2(L)]Cl_2$

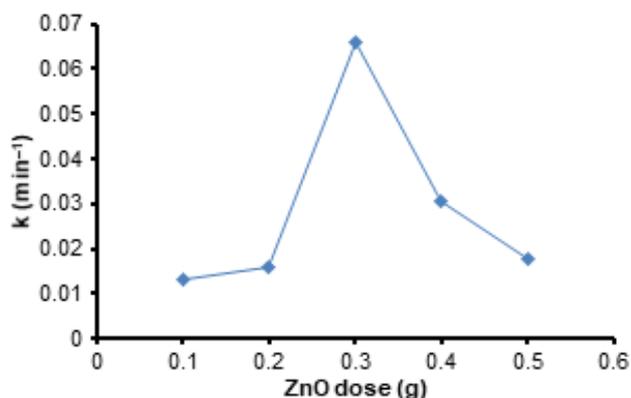


Fig 4. Effect of ZnO dosage on the apparent rate constant of reaction. At conditions: ZnO dosage 0.1–0.5 g/100 mL, binuclear Co(II) complex conc. 25 ppm, initial pH of solution 7.00 and T 311.15 K

for this complex was monitored at a pH range of 3–11, as explained in Fig. 6 and 7. The pH is considered to be a vital factor in increasing the decolorization of this complex because it affects the nature of the complex, and also the nature and surface properties of ZnO, thus affecting the hydroxyl radical generated [26–27]. The maximum decolorization for the binuclear Co(II) complex occurred at pH 7 with maximum PDE% equal to 99.128% at 70 min. In fact, the results demonstrated that when the pH was more or less than pH 7, the rate of decolorization and the PDE% declined, based on the following two causes [27]: At elevated acidic medium,

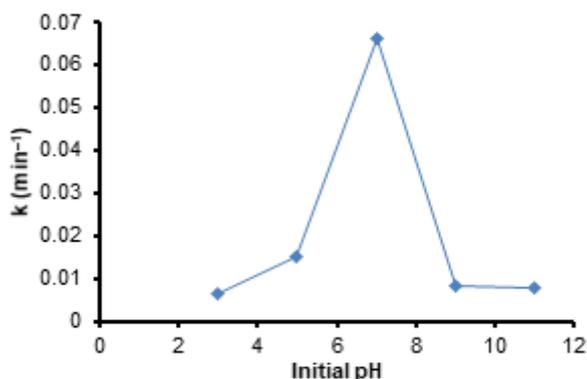


Fig 6. Effect of initial pH of binuclear Co(II) complex solution on the apparent rate constant of reaction. Conditions: ZnO dose 0.3 g/100 mL, binuclear Co(II) complex conc. 25 ppm, initial pH of solution 3–11 and T 311.15 K

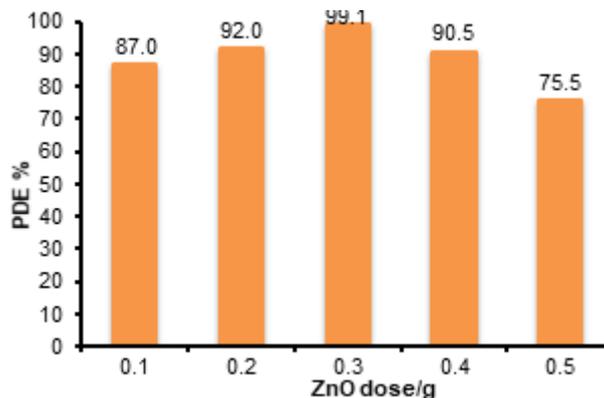
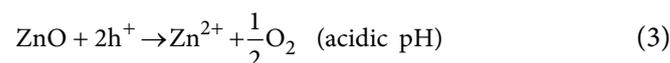
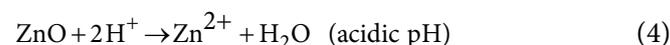


Fig 5. PDE % of binuclear Co(II) complex solution at different ZnO dosage. At conditions: ZnO dosage 0.1–0.5 g/100 mL, binuclear Co(II) complex conc. 25 ppm, initial pH of solution 7.00 and T 311.15 K

ZnO may have undergone photocorrosion and altered to Zn(II) ion [23,28].



or



Inversely, in high basic pH, ZnO can be negatively charged and lead to the decrease in the photocatalytic activity [23,25].



or

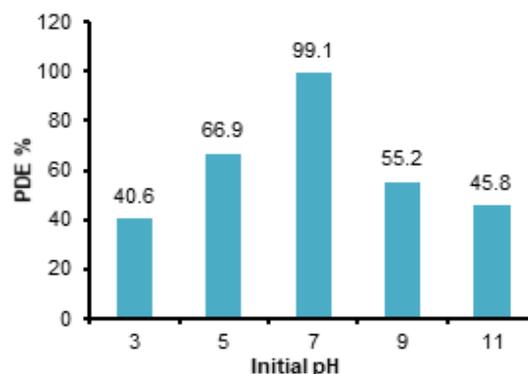
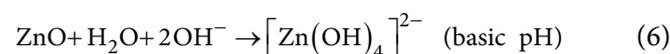


Fig 7. PDE % of binuclear Co(II) complex solution at different ZnO dosage. Conditions: ZnO dose 0.3 g/100 mL, binuclear Co(II) complex conc. 25 ppm, initial pH of solution 3–11 and T 311.15 K.

Effect of temperature on the decolorization of $[\text{Co}_2(\text{OPD})_2(\text{L})]\text{Cl}_2$ complex

At temperatures in the range of 288.15–303.15 K, the results in Fig. 8 and 9 show that the decolorization process for the binuclear Co(II) complex is elevated with raised temperature. The plotted Arrhenius equation (Eq. (7)) [29,23], and Eyring-Polanyi equation (Eq. (8)) [25,30] were demonstrated.

$$\ln k_{\text{app}} = \frac{-E_a}{RT} + \ln A \quad (7)$$

where E_a is activation energy, k is rate constant, R is gas constant, T is the temperature of reaction and A is a frequency constant.

ΔH^\ddagger and ΔS^\ddagger were calculated based on the Eyring-Polanyi equation [25,30-31]

$$\ln\left(\frac{k_{\text{app}}}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \left(\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R}\right) \quad (8)$$

where k_B is a Boltzmann's constant, h is a Plank's constant, R is a gas constant and T is the temperature of the reaction.

The activation energy for the decolorization of the binuclear Co(II) complex is small and equals to 11.289 kJ/mol, which proves this photoreaction is fast speed [32-33] and the reaction is endothermic where the change in enthalpy equals to 8.832 kJ/mol as listed in Table 2. ΔG^\ddagger of the photo reaction was calculated using the Gibbs equation (Eq. (9)) based on the fitting results of the Eyring-Polanyi equation [29-31].

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (9)$$

All fitted factors of the thermodynamics functions and the activation energy are listed in Table 3.

The positive ΔH^\ddagger (endothermic) and positive $\Delta G^\ddagger_{303.15}$ (non-spontaneous) for the decolorization of the binuclear Co(II) complex demonstrated that the transition state between the complex molecules and intermediates (hydroxyl radicals) is a well solvated structure. The negative values of ΔS^\ddagger for the decolorization of the binuclear Co(II) complex species formed is less random than the reactants. These results have similar behavior with other photo reactions observed by several researchers [25,31,34].

Mechanism of the Photodecolorization of $[\text{Co}_2(\text{OPD})_2(\text{L})]\text{Cl}_2$ Complex

The series of redox processes can take place via the presence of ZnO as a suspension in an aqueous solution of $[\text{Co}_2(\text{OPD})_2(\text{L})]\text{Cl}_2$ complex. The best species [16,35] which can decolorize the $[\text{Co}_2(\text{OPD})_2(\text{L})]\text{Cl}_2$ complex are HO and HOO under irradiation by UV-A light, as explained in Fig. 10.

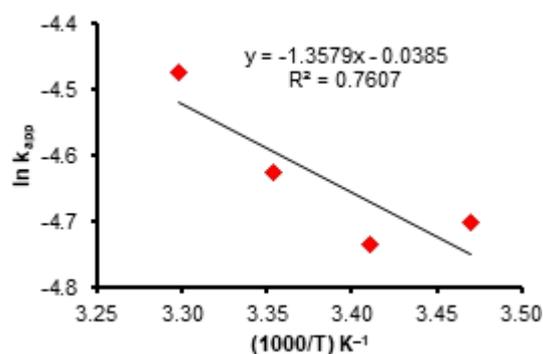


Fig 8. Arrhenius equation plotted at varying temperatures, at 288.15–303.15 K. Conditions: ZnO dose 0.3 g/100 mL, binuclear Co(II) complex conc. 25 ppm, initial pH of solution 7

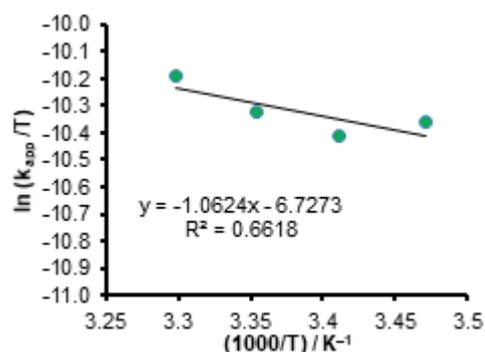


Fig 9. Eyring plot of $(\ln(k/T))$ vs. $1/T$. Conditions: ZnO dose 0.3 g/100 mL, binuclear Co(II) complex conc. 25 ppm, initial pH of solution 7

Table 3. The activation energy and thermodynamic parameters of the decolorization of the binuclear Co(II) complex under UV-A light

Type of lamp	E_a	ΔH^\ddagger	ΔS^\ddagger	$\Delta G^\ddagger_{303.15}$
(UV-A)	kJ mol^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$	kJ mol^{-1}
250 Watt	11.289	8.832	-3.666	9.945

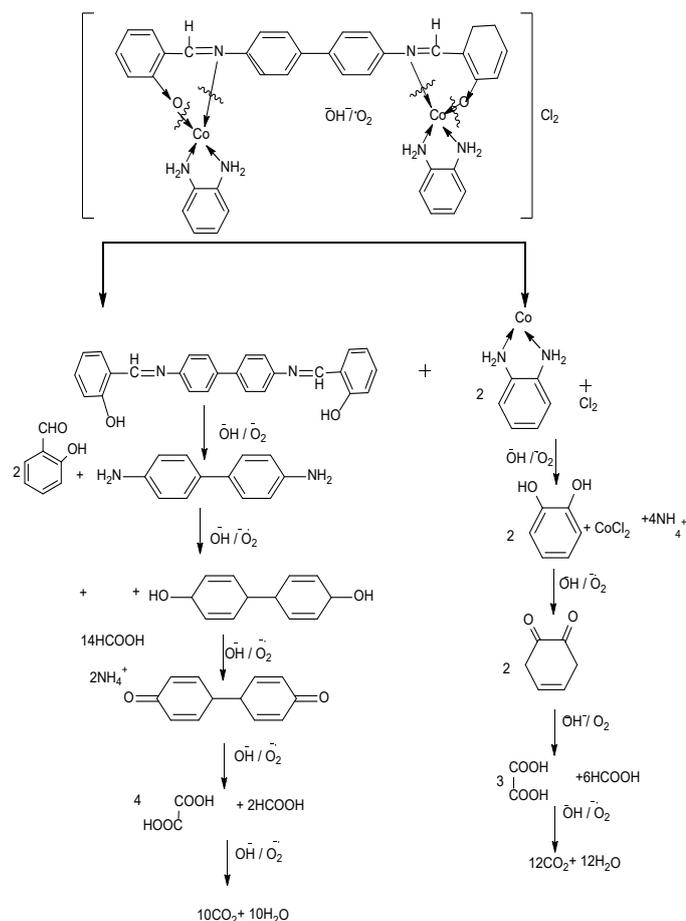


Fig10. Schematic diagram of the suggested mechanism of the photodecolorization of $[\text{Co}_2(\text{OPD})_2\text{L}]\text{Cl}_2$ complex with photocatalyst ZnO

CONCLUSION

The main conclusions are referred to the forming of $[\text{Co}_2(\text{OPD})_2\text{L}]\text{Cl}_2$ complex in the mole ratio of 1:2 “metal:ligand” stoichiometry and with greenish brown color. From FTIR analysis, new bands appeared in the regions, $469\text{--}542\text{ cm}^{-1}$ which may be due to the formation of M-O and M-N bands. The increased melting point is proven to be a binuclear Co(II) complex. In the UV-Visible spectrum, the appearance of the new weak and much broader peak at 979 nm were attributed to d-d electronic transition tetrahedral geometry around the Co(II) central ion. The optimum conditions for photodecolorization of the binuclear Co(II) complex were observed at 300 mg of ZnO/ 100 mL from binuclear Co(II) complex solution, initial pH of 7, with low activation

energy, endothermic, less random and non-spontaneous reaction.

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