

# Comparative study of bis-chelate M(II) complexes (M = Ni, Cu, Zn) as new heterogeneous photocatalysts for degradation of methylene blue under visible light

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Abstract Three tetrahedral coordination compounds formed from Ni(II), Cu(II), and Zn(II) transition-metal ions with ON-donor, (2-aminophenol) ligand (L), were synthesized and characterized by Fourier-transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–Vis) absorption spectroscopy, elemental analysis, and magnetic susceptibility measurements. The magnetic properties revealed that the NiL<sub>2</sub> and CuL<sub>2</sub> complexes were paramagnetic while the ZnL<sub>2</sub> complex was diamagnetic. Also, photodegradation of methylene blue as model organic pollutant by the synthesized complexes was studied based on an oxidation process under visiblelight irradiation. The results showed that the photocatalytic activity of the Cu complex was greater compared with the Ni and Zn complexes, with degradation efficiency of 100, 85, and 60 %, respectively, after 30 min of irradiation in this condition. Thus, the Cu (bis-chelate) complex is more efficient, produces higher yield, is easily produced, and represents a more stable heterogeneous photocatalyst for degradation of organic dyes such as methylene blue.

**Keywords** Visible light · Methylene blue · Heterogeneous catalyst · Photodegradation · Bis-chelate complexes · NO-donor ligand

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# Introduction

Organic dyes are one of the most important classes of organic pollutant found in wastewater. Elimination of organic pollution is a significant challenge [1]. Different methods have been developed to remove pollutants from wastewater [2]. In recent decades, degradation of organic pollutants by photochemical processes has become a very interesting research topic as it represents an effective, green, and easy approach for removal of organic contaminants from water [3–6].

Generally, semiconductor compounds have been used for this purpose. TiO<sub>2</sub>, ZnS, and ZnO have been widely applied as semiconductor photocatalysts [7–11]. However, to date, few coordination compounds have been used in this context. Complexes such as [Mn(III)–SALEN–Schiff base] [12], ferric and ferrous oxalate [13], iron(III)–phenolate [14], [(Ph<sub>3</sub>Sn)<sub>4</sub>Fe(CN)<sub>6</sub>] [15], copper(II) porphyrin–TiO<sub>2</sub> [16], and complexes of Ni(II) and Co(II) with NO-donor Schiff-base ligand [17] have been reported as photocatalysts for degradation of organic dyes in recent years.

In most previous works, the photocatalytic process was performed under ultraviolet radiation, which is a major disadvantage of such photooxidation systems, because ultraviolet radiation is dangerous and not economically affordable. Therefore, in a bid to develop a photooxidative system that is cheaper, safer, more efficient, and compatible with green chemistry concepts, researchers are now applying special attention to this area.

In this work, three [M(II) (bis-chelate)] complexes formed by complexation of Cu(II), Ni(II), and Zn(II) transition-metal ions with an NO-donor ligand were synthesized and characterized, and their catalytic activity compared for photodegradation of methylene blue as model organic pollutant with  $H_2O_2$  under visible-light irradiation.

# Experimental

## General

All materials were of commercial reagent grade, purchased from Merck and Fluka chemical companies, and used without any purification.

## Synthesis of complexes

To a solution of 2-aminophenol as ligand (2 mmol) in EtOH (10 mL) was added  $Et_3N$  (2 mmol) under reflux conditions for 1 h. This solution was then added to a solution of M(CH<sub>3</sub>COO)<sub>2</sub> salt where M is Cu, Ni or Zn (1 mmol) in EtOH (10 mL). The reaction mixture was stirred to reaction completion under reflux conditions for 24 h. After completion of complex formation, a colored substance was obtained. The solid product was filtered off and washed with EtOH and  $Et_2O$ . The solid product was put into a vacuum oven at 40 °C for 24 h (yield = 85–95 %). The

products were characterized by FTIR spectroscopy, UV-Vis spectroscopy, and elemental (CHN) analysis.

## **Characterization techniques**

IR spectra were recorded from pressed KBr discs using a PerkinElmer RXI FTIR instrument. Electronic absorption spectra were recorded on an Specord 205 UV–Vis spectrophotometer (Analytik Jena) in the range of 200–900 nm.

## Photocatalytic activity

Photocatalytic experiments were carried out using a homemade photoreactor with 400-W metal-halide lamps for visible irradiation, two computer fans to cool the photoreactor cabinet, and magnetic stirring with circulating water to cool the reaction mixture. The distance between the solution surface and light source was about 25 cm [10].

In a typical experiment (Fig. 1), 10 mL aqueous MB at initial concentration of  $1 \times 10^{-5}$  M was placed in a 25-mL round-bottomed flask. Photocatalyst (0.01 g) was added with 1 mL H<sub>2</sub>O<sub>2</sub> (30 %), and the suspension was stirred for 30 min in the dark at room temperature to ensure establishment of adsorption–desorption equilibrium. The lamp was then turned on while the suspension was magnetically stirred. At fixed intervals of time, 4 mL of sample was withdrawn and centrifuged, and the supernatant transferred to a spectrophotometer cell for measurement of the absorbance of MB at 900 to 500 nm.

## **Results and discussion**

## Synthesis of bis-chelate complexes

As shown in Scheme 1, one equivalent of bis-chelate metal complex was synthesized by complexation of one equivalent of metal ion with two equivalents



Fig. 1 Photodegradation process



Scheme 1 Synthesis root for bis-chelate complexes

of NO-donor ligand in alcoholic solution under basic condition. Each ligand has one negative charge in the coordination site as a result of removal of a phenolic hydrogen by an organic base. Therefore, the complex was precipitated by neutralizing the negative charge of the two ligands and the 2+ charge of the metal ion.

## **IR** spectra

The IR spectra of all the complexes and ligand were similar, as shown in Fig. 2; some important vibration bonds are presented in Table 1. However, they showed a weak split band at around  $3300 \text{ cm}^{-1}$ , which can probably be attributed to  $-\text{NH}_2$  stretching of the amine group of the ligand. All complexes showed the expected phenyl C=C (around 1590 cm<sup>-1</sup>), phenolate (Ph–O) (about 1290 cm<sup>-1</sup>), and C–H



Fig. 2 FTIR spectra of all complexes

Compound	-NH <sub>2</sub>	C=C <sub>(Arom)</sub>	Ph–O	С–Н	M–N	M–O
Ligand (LH) [18]	3306	1612	1288	752	_	_
Cu(L <sub>2</sub> )	3254	1548	1290	742	592	530
$Ni(L_2)$	3268	1596	1288	750	650	438
$Zn(L_2)$	3300	1598	1294	750	618	532

Table 1 Some stretching and bending vibrations of complexes and ligand

(around 740 cm<sup>-1</sup>) stretching bands in their spectrum. The positions of these bands were very similar in all complexes and similar to that of the ligand [18]. The band found at around 600 and 500 cm<sup>-1</sup> for all complexes can be attributed to metal–N and metal–O bond sequences, providing strong evidence that the metal ions were loaded at the NO-coordination site.

#### **Elemental analysis**

The results of elemental (CHN) analysis of the complexes are presented in Table 2. The experimental data are in accordance with calculated data for the bis-chelate metal complexes.

### **Electronic absorption spectra**

The electronic absorption spectra of the three complexes and the ligand were measured in acetonitrile solution (Fig. 3).

The data are summarized in Table 3. The electronic absorption spectra of all the complexes and ligand showed an intense band at around 400 nm, attributed to charge transfer of metal ion to ligand (MLCT), while the bands at around 200 and 300 nm are attributed to  $\pi \rightarrow \pi^*$  transition of  $\pi$  system of ligand. The Cu and Ni complexes, in contrast to the Zn complex, exhibited absorption bands in the 550–1050 nm region, which can be attributed to d–d transitions of copper(II) and nickel(II) ions in Td environment [19].

Complex	Chemical formula (color)	$FW (g mol^{-1})$	%C	%H	%N	C/N
CuL <sub>2</sub>	$C_{12}H_{12}CuN_2O_2$	279.78	51.51	4.32	10.01	5.15
	(green)		(51.21)	(4.11)	(9.89)	(5.18)
NiL <sub>2</sub>	C <sub>12</sub> H <sub>12</sub> NiN <sub>2</sub> O <sub>2</sub>	274.93	52.42	4.40	10.19	5.14
	(brown)		(52.30)	(4.48)	(10.09)	(5.18)
ZnL <sub>2</sub>	$C_{12}H_{12}ZnN_2O_2$	281.62	51.18	4.29	9.95	5.14
	(yellow)		(51.02)	(4.06)	(9.86)	(5.17)

Table 2 Results of elemental (CHN) analysis of complexes (found)



Fig. 3 UV-Vis spectra of ligand and the complexes in CH<sub>3</sub>CN

<b>Table 3</b> Electronic spectraldata for complexes in	Compound	$\lambda_{\max}$ (nm)		
acetonitrile solution	_	$n \to \pi^*, \pi \to \pi^*$	Charge transfer	d-d transition
	CuL <sub>2</sub>	208, 238, 270	435	565, 645
	NiL <sub>2</sub>	206, 237, 274	420	590, 820, 1045
	$ZnL_2$	212, 234, 288	450	_
	Ligand	212, 234, 286	_	_

#### Magnetic behavior

The magnetic properties based on spin only for all complexes are presented in Table 4. The results reveal that the NiL<sub>2</sub> and CuL<sub>2</sub> complexes were paramagnetic while the  $ZnL_2$  complex was diamagnetic.

Table 4 Magnetic moment results							
Complex	$\mu_{S(experimental)}$ , BM	$\mu_{S(\text{theoretical})}, BM$	n <sup>a</sup> <sub>(experimental)</sub>	n <sub>(theoretical)</sub>			
				Td	SP		
CuL <sub>2</sub>	1.629	1.73	$0.91 \approx 1.0$	1	1		
NiL <sub>2</sub>	2.951	2.83	$2.1 \approx 2.0$	2	0		
$ZnL_2$	0.46	0	$0.1 \approx 0.0$	0	0		

Table 4 Magnetic moment results

<sup>a</sup>n is the number of single electrons



Fig. 4 Electronic configuration of three complexes in two proposed structures, viz. tetrahedral (Td) and square planer (SP)

Figure 4 shows the electronic configuration of the three complexes for two proposed structures, viz. tetrahedral (Td) and square planer (SP). Each complex has 1, 0, and 0 single electrons in the SP structure, but in the Td structure, each complex has 1, 2, and 0 single electrons for Cu(II), Ni(II), and Zn(II) ion, respectively. The experimental magnetic moment results show that all the complexes had Td or distorted-Td structure, because the number of single electrons of the Cu, Ni, and Zn complexes was 0.91, 2.1, and 0.1, respectively. The magnetic moment of the Zn complex was not significant, so we can ignore it.

#### Photodegradation

#### Adsorption-desorption equilibrium

The absorption peak of an organic dye will be decreased due to some adsorption onto the surface of the photocatalyst solid phase. Thus, the initial mixture for the photoreaction must be allowed to reach adsorption–desorption equilibrium in dark condition before measurements. The electronic absorption spectrum of the organic dye is useful for detection of this equilibrium. Therefore, the variation of the absorption of MB at  $\lambda_{max}$  (around 670 nm) was recorded at 5, 10, 20, 30, 40, and 50 min in dark condition as shown in Fig. 5. The absorption peak decreased from



Fig. 5 Variation of absorption of MB at  $\lambda_{\text{max}}$  (around 670 nm) recorded at 5 to 50 min in dark condition

0 to 30 min, but after 30 min remained almost fixed. Thus, after 30 min, the concentration of MB was at equilibrium.

#### Photocatalytic activity

First, the reaction mixture was allowed to equilibrate in the dark for 30 min before the visible irradiation lamp was switched on. When the solution had reached adsorption–desorption equilibrium (denoted 0 min in spectrum), the 400-W metal-halide lamp was switched on. For decoloration studies, the decrease in absorption peak at 500–800 nm was monitored.

Initially, experiments were carried out in presence of either visible light, complex or  $H_2O_2$  alone and complex/visible light or complex/ $H_2O_2$  together; neither of these treatments had an effect on the absorption maximum of the dye solution and caused no decoloration. However, decoloration of the dye occurred when subjected to visible light in presence of  $H_2O_2$ , probably due to production of hydroxyl radicals, which could in turn react with the dye and lead to dye degradation [20].

Figures 6, 7, and 8 show the decrease of the absorption peak at 500–800 nm in the photodegradation process. According to these figures, the Cu complex degraded the dye in 30 min, while the Zn and Ni complexes decolorized the solution in 45 and 105 min. Thus, the copper complex is an effective compound for photodegradation of methylene blue under visible-light irradiation.

The degradation efficiency (% DE) was calculated as the percentage photodegradation of MB using

$$\%$$
DE =  $(1 - C/C_0) \times 100\%$ 

where C and  $C_0$  are the equilibrium concentration of methylene blue after and before visible-light irradiation.



Fig. 6 Time-dependent decrease of absorption pick of MB by  $[\rm CuL_2]$  complex under visible light/H\_2O\_2 within 30 min



Fig. 7 Time-dependent decrease of absorption pick of MB by  $[NiL_2]$  complex under visible light/H<sub>2</sub>O<sub>2</sub> within 105 min



Fig. 8 Time-dependent decrease of absorption pick of MB by  $[ZnL_2]$  complex under visible light/H<sub>2</sub>O<sub>2</sub> within 45 min

In previous study, it was reported that the %DE of MB was less than 10 after 100 min of visible-light irradiation only [10].

Figure 9 shows a plot of the change of %DE as a function of irradiation time for MB dye in presence of each photocatalyst, revealing percentage degradation efficiency after 30 min of about 60, 85, and 100 % for the Ni(II), Zn(II), and Cu(II) complex, respectively. The photocatalytic activity of the complexes lay in the following order: Cu(II) > Zn(II) > Ni(II). These results demonstrate that the MB dye was degraded much more quickly in presence of the Cu(II) complex compared with the other complexes. This result can be attributed to the influence of the nature of the metal cation used, with Cu being a more active metal cation than Zn, and Zn more than Ni [21–23].

The same result regarding the different activities of copper and nickel complexes was observed previously [24]. This different reactivity of the metal complexes is illustrated by the tentative mechanism shown in Scheme 2. First, the metal complex system is excited under visible-light irradiation, and hydroxyl radicals are produced



Fig. 9 Degradation efficiency of  $ML_2$  (M = Cu, Ni, Zn) complexes versus reaction time



Scheme 2 Tentative photodegradation mechanism of metal complex



Fig. 10 Structural change of metal complexes in reaction condition

by interaction between the excited complex and hydrogen peroxide and water, during the photocatalytic reaction. The radicals are strong oxidizing agents that react with the dye and cause its decolorization. The metal complexes have different activity due to differences in electron-hole  $(e^-/h^+)$  separation and recombination.

Also, it seems that the photocatalytic activity can be attributed to the geometrical and electronic structures of the complexes (Fig. 10). In the basic geometrical structure (before reaction), Cu(II) has a single electron, whereas nickel and zinc have no single electrons. This difference in the number of single electrons can influence the photocatalytic activity.

The reaction mixture includes more species, including solvent ( $H_2O$ ),  $H_2O_2$ , and methylene blue. Also, the square-planar metal complexes have two coordination sites, above and below the molecular plane. Therefore, the reaction components can coordinate to these sites and a structural change occurs from the square planar to



Fig. 11 Relationship between  $-\ln(C/C_0)$  and irradiation (visible light) time for kinetic data versus degradation rate of MB by complexes

octahedral geometry. In the structure with octahedral geometry, Cu(II) has d<sup>9</sup> electron configuration and tetragonal deviation. The ninth electron is far from the nucleus in the tetragonal deviation, thus having potential for excitation, whereas  $Zn^{2+}$  has no single electrons while Ni<sup>2+</sup> has two single electrons. In general, according to the explanation above, the role of electrons and the geometric structure of the catalysts could be important factors in the reactivity of these complexes.

#### Kinetics of photocatalytic degradation of MB

The dependence of the photocatalytic reaction rate on the concentration of organic pollutant can be well described by the Langmuir–Hinshelwood kinetic model [10]:

$$r = \mathrm{d}C/\mathrm{d}t = kKC/(1 + KC).$$

This equation can be simplified to a pseudo-first-order equation:

$$\operatorname{Ln}(C_0/C) = kKt = k't,$$

where *r* is the oxidation rate of dye (mg/L h<sup>-1</sup>),  $C_0$  is the initial concentration of dye (mg/L), *C* is the concentration of dye (mg/L) at irradiation time *t*, *k* is the reaction rate constant (h<sup>-1</sup>), and *K* is the adsorption coefficient of dye onto catalyst particles (L/mg).

To determine whether the reaction rate was consistent with such a first-order reaction under different conditions,  $\ln(C/C_0)$  is plotted versus reaction time for the different photocatalysts in Fig. 11. As shown, a good linear relationship was found between  $\ln(C/C_0)$  and t in the initial reaction step. This indicates that the latter equation indeed describes the photocatalytic rate of the dye.

# Conclusions

Cu, Ni, and Zn metal-ion complexes with NO-bidentate chelate ligands were prepared and used as photocatalysts for degradation of aqueous solution of methylene blue. The complexes were stable under visible-light irradiation and more efficient as photocatalysts. The Cu bis-chelate complex was more efficient than the Ni or Zn complex for removal of the organic pollutant from water under visiblelight irradiation. This degradation system represents an efficient method because it is environmentally friendly, economical, and a chemical process for removal of organic pollution.

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