



International Journal of ChemTech Research CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.12 No.1, pp 171-177, 2019

# Cobalt (II) complex of (3-Amino-5-[E-(4-ethylbenzaldene)4methyl-2-phenylcyclopetanone): Synthesis, characterization and photocatalytic studies

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**Abstract:** Cobalt(II) complex of 3-Amino-5-[E-(4-ethylbenzaldene)4-methyl-2-phenylcyclo petanone was synthesized and characterized using various spectroscopic techniques. The rate of photocatalytic degradation of methylene blue using prepared metal complexes was carried out under UV light. The complex shows appreciably degraded the methylene blue for 40 mg and further increase dosage the activity reducing. The generation of the hydroxyl radical is responsible for the degradation of dye. The dye has been successfully degraded 61.6% in the presence of cobalt complex.

Key words : Metal complexes, methylene blue, photo catalysis.

# 1. Introduction:

Water pollution is one the world wide problem, which is directly affecting living organisms. The effluents discharged directly or indirectly from industries into water bodies without any prior treatment for removal of toxic compounds leads for water pollution. There is a wide variety of water pollutants, which includes by products & wastage of industries, factories, organic matter, pathogens etc. Water pollution is a burning problem all over the globe, which requires some eco-friendly methods for its purification. Now-a-days, a large amount of waste water having color is generated by many industries like textile, leather, paper, printing, plastic and so on [1]. The presence of dye materials greatly influence the quality of water and the removal of this kind of pollutant is of prime importance. Owing to their complicated chemical structures, dyes are difficult to treat with municipal waste treatment operations [2]. Even a small quantity of dye does cause high visibility and undesirability. Moreover, the color produced by dyes in water makes it aesthetically unpleasant [1]. They can have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time [2]. In addition to that, many dyes are considered to be toxic and even carcinogenic [1, 3, 4]. Now, it has become very important to treat this wastewater.

Methylene blue is a kind of cationic dye (basic dye) containing heterocyclic aromatic chemical compound with the molecular formula  $C_{16}H_{18}N_3SCl$ . This dye is generally classified as a basic dye and cationic species due to the presence of positively charged quaternary nitrogen atoms (as  $NR_3^+$  or  $= NR_2^+$ ). These groups enhance the solubility of dye in water due to their ionic characteristic [5]. Several physical, chemical and biological de-colorization methods such as coagulation/flocculation treatment, biodegradation processes, oxidation methods, membrane filtration and adsorption have been undertaken from time to time for the removal of dyes from industrial effluents [6-9]. However, these methods suffer from many disadvantages, but photocatalytic degradation seems to be the most promising advanced oxidation processes (AOPs) since it is of low cost and less time consuming [10] and is based on the generation of hydroxyl radicals [11, 12], which can be used for nonspecific oxidation of a wide range of organic compounds. AOPs include the classical Fenton reaction as well as its modifications (e.g., light assisted Fenton oxidation or ferrioxalate-photo Fenton oxidation) as well as H<sub>2</sub>O<sub>2</sub>/UV or ozonization [13-17]. However, Fenton's reagent can work only under acidic conditions (pH 2–4), and some dyes are not completely decomposed [18, 19]. Another set of AOP reactions makes use of transition metal ions (mostly Cu) in combination with ligand molecules for the decomposition of hydrogen peroxide and the resulting production of hydroxyl radicals. The main advantage of such systems is the broad substrate specificity and the ability to perform at pH 3–9 [19, 20]. Since, structurally, dyes are double bonded such as -C=C-, -N=N- and heterocyclic compounds, therefore transition metal ions are able to coordinate with most of the organic substances containing this type of bonds [20-23]. This is because of their lenience in change of the oxidation state and presence of unpaired electrons the metal ions react readily with molecular oxygen, thereby mediating oxygenation of other compounds easily [9]. These properties have made use of transition metal complexes for the chemical, biological, photochemical and photo-biological degradation of the organic ligands. So far a number of metal complexes involving degradation of dyes and other pollutants has been reported from time to time [10]. In recent years, 4-aminoantipyrine transition metal complexes and their derivatives have been extensively examined due to their wide applications in biological, analytical and therapeutical fields. Further, they have been investigated due to their diverse biological properties as antifungal, anti-bacterial, analgesic, sedative, anti-pyretic, anti-inflammatory agents and DNA binding properties. Antipyrine Schiff base derivatives can also serve as anti-parasitic agents and their complexes with platinum(II) and cobalt(II) ions have been shown to act as antitumor substances. These properties make us to prepare cobalt(II) complex of 4-aminoantipyrine Schiff base to reduce/remove the methylene blue dye from sewage water.

# 2. Experimental

## 2.1. Materials and methods

4-Aminoantipyrine and 4-ethylbenzaldehyde were of reagent grade purchased from Sigma-Aldrich, Bengaluru. Cobalt(II) chloride (Merck) and Methylene blue (MB) (S D Fine Chem. Limited, Mumbai) were purchased as supplied. All the solvents were used as supplied without further purification.

## 2. 2. Physical measurements

Melting points (accuracy  $\pm 2^{\circ}$ C) were determined in an electrically heated melting point apparatus in an open capillary and are reported as such.Estimation of elements (C, H, N and S) was carried out on a Perkin-Elmer 2400 CHNS elemental analyzer (accuracy  $\pm 0.2 \%$ ). The electronic spectra of the compounds in solution state are recorded on a UV-160 ASchimadzu double beam spectrophotometer in the range 200-1100 nm. The infrared spectra of all the complexes/ligands in solid state in the range of 4000-225 cm<sup>-1</sup> were recorded on a Nocolet Protégé 460 Fourier Transform Infrared spectrometer (used resolution 4 cm<sup>-1</sup>; minimum resolution 0.125cm<sup>-1</sup>) as KBr pellets. About 10 mg of finely powdered sample, thoroughly mixed with even dried spectral grade KBr/polyethylene and pressed into a thin pellet under anhydrous conditions is used for recording IR spectra.system consisted of a glassy carbon (working), platinum wire (auxiliary) and Ag/AgCl (reference). The <sup>1</sup>H- and <sup>13</sup>C{1H}-NMR spectra were recorded on a BrukerSpectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz, respectively.

# 2.3. Synthesis of (3-amino-5-[E-(4-ethylbenzaldene) 4-methyl-2-phenylcyclopetanone) ligand

The ligand was prepared by condensing 4-Aminoantipyrine with 4-ethylbenzaldehyde by following general procedure given in the **Scheme 1**. To a ethanolic solution (40 ml) of 4-Aminoantipyrine (2.033 g,10

mM) added 4-ethylbenzaldehyde (10 mM) and the mixture was refluxed for 4 hrs. The yellow crystalline solid (I) was collected by filtration, washed several times with hot water and dried, then recrystallized from ethanol.



Scheme 1: Synthetic route of Ligand.



Scheme 2: Synthetic route of Metal complexes

## 2.4. Synthesis of Co(II)complex

To a methanolic solution of ligand (2mol) added a solution of cobalt(II) chloride (1mol) in **m**ethanol. The reaction mixture was refluxed for about 30-40 min. on a water bath maintained at  $50-60^{\circ}$ C during which time a solid complex formed was cooled to room temperature, the resulting product was filtered, washed with hot water and finally with diethyl ether and dried in vacuum desiccators over anhydrous CaCl<sub>2</sub>(**Scheme 2**).

## 2.5. Photo catalytic degradation studies

A Photocatalytic activity of metal complexes (MC) on the degradation of methylene blue (MB) in water was examined with and without UV-light. A 300 W high pressure mercury-vapour lamp ( $\lambda$ =320 nm) is a light source. A reaction suspension was prepared by adding metal complexes into 100 mL of aqueous MB solution (10 mg/L), and was allowed to react at ambient condition under stirring. After irradiation, the catalyst was separated by centrifuging and the absorbance of MB was determined by the UV-visible spectrophotometer at the absorption wavelength of 664 nm [24]

Then, percentage degradation of dye was calculated using the following equation.

Percentage Degradation (%) =  $[(A_0 - A) / A_0] \times 100$ 

Where  $A_0$  and A are the initial and final concentration of the dye. The initial and final concentration of the dye was measured at regular intervals using a UV-visible spectrophotometer.

# 3. Results and discussion

The analytical data for the ligand and complexes together correspond well with the formation of ligand its complex. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}NMR spectra of the ligand, recorded in CDCl<sub>3</sub> and the data indicates the formation of Schiff base ligand. Typical <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}NMR spectra of the ligand is shown in Figure 1.



# Figure 1: <sup>1</sup>H- and <sup>1</sup>H{<sup>13</sup>C}NMR spectrum of ligand

In <sup>1</sup>H-NMR spectrum of the ligand, -CH=N- peak is observed at 9.7 ppm (s, 2H)indicating that the proposed Schiff base is formed. It is also evident from the <sup>13</sup>C{<sup>1</sup>H}NMR and IR spectra of the ligand

## 3.1. Characterization of metal complex

Cobalt(II) complex of 3-amino-5-[E-(4-ethylbenzaldene) 4-methyl-2-phenylcyclopetanone have been prepared and characterized. The complexis stable at room temperature, non-hygroscopic, sparingly soluble in methanol, and readily soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The electronic spectra of the complexes have common spectral features. The spectra have one CT band and one d-d band (**Figure 2**) corresponding to octahedral geomentry. The charge transfer may occur due to the migration of electrons from the ligand orbitals to metal orbitals. The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The spectrum of the ligand shows C=O and -C=N bands in the region 1638–1572 cm<sup>-1</sup>, which is shifted to lower frequencies in the spectra of the complexes indicating the involvement of C=O and -C=N nitrogen in coordination to the metal ion. Accordingly, the ligand acts as a bidentate chelating agent, bonded to the metal ion via oxygen group of C=O and nitrogen of -C=N of the Schiff base. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at  $450-400 \text{ cm}^{-1}$  which could be attributed to vM–N respectively.



Figure 2: Electronic spectra of Ligand and its Co(II) complex



Figure 3: A Tentative structure of metal complexes.

Based on analytical and spectral data it is suggested that the tentative structure of the complexes in solid state is shown below (**Figure 3**).

#### 3.2. Photocatalytic Studies

The Photocatalytic degradation of the cobalt complex was evaluated using Methylene Blue dye at room temperature in neutral pH. Degradation of methylene blue was studied with and without the catalyst under UV light irradiation. There was no appreciable degradation with catalyst in dark. So that UV light irradiation was necessary for efficient degradation. Photocatalytic decolorization efficiency of the catalyst was monitored by performing UV-visible spectral studies at different dosage of catalyst. To optimize the amount of catalyst dose, the experiments were conducted by taking catalyst amounts from 20-50 mg (**Fig. 4**). The metal complex (MC) was added into 100 mL of aqueous MB solution (5mg/L), and the solution was stirred for about 15 min. The solution was then exposed to UV light at a distance of 4-5 cm between the liquid surface and the lamp. The solution kept stirring during irradiation. It was observed that the only 22.4% degradation achieved for 20 mg of cobalt complex whereas 61.6% degradation efficiency was achieved with 40 mg of cobalt complex. In general, as increase in the amount of catalyst increases the degradation because it increases the number of active sites on the catalysts surface. Furthermore increase may cause the aggregation of free catalyst and also increased opacity and a decrease in UV light penetration, as a result of increased scattering effect and therefore percentage degradation starts decreasing [25, 26].



Figure 4: Photocatalytic efficiency of MB under ultraviolet irradiation at 10 mg/L initial MB concentration; Catalyst dosage



Fig 5: Photodegradation mechanism of metal complexes.

## 3.4. Mechanism

Metal complex system produced hydroxyl radicals during the catalytic reaction. This is not surprising, since the production of –OH was already confirmed in other metal based AOP systems.

The radicals are strong oxidizing agents that react with dyes and cause their decolorization. The tentative mechanism has been proposed for the degradation of methylene blue in the presence of cobalt complexes and light (**Fig. 5**).

Consider :  $[MLn] + Light \rightarrow [MLn]^* + {}^{3}O_{2} \rightarrow OH^{-1}$ 

 $OH + Dye \rightarrow Oxidative \text{ products } (M \text{ stands } Co(II))$ 

# Conclusion

In present work cobalt(II) complex of ligand derived from 3-amino-5-[E-(4-ethylbenzaldene) 4-methyl-2-phenylcyclopetanone have been synthesized and characterized, structures of the complexes are assigned based on physicochemical and spectral data. The complex is found to be efficient in degradation of dye.

## Acknowledgements

Authors are thanks to Dr. K, R. Prasad, Professor, Department of Organic Chemistry, Indian Institute of Science, Bengaluru for spectral studies.

# References

- 1. Crini G, Bioresour, Technol., 97 (2006) 1061.
- 2. Dash B, Competitive adsorption of dyes (congo red, methylene blue, malachite green) on activated carbon, B.Tech thesis, 2010.
- 3. Mittal A, Malviya A, Kaur D, Mittal J, Kurup L, J. Hazard, Mater. 148 (2007) 229.
- 4. Chen S, Zhang J, Zhang C, Yue Q, Li Y, Li C, *Desalination* 252 (2010) 149.
- 5. Christie R M, Colour Chemistry, Royal Society of Chemistry Paper backs, 2001.
- 6. Anjanyeulu Y, Sreedhara N, Chary D, Suman Raj Samuel, Rev. Environ. Sci. Biotech. 4 (2005) 245.
- 7. SinghRai H, Bhattacharyya M S, Singh J, Bansal T K, Vats P, Banerjee U C, *Crit. Rev. Environ. Sci. Techn.*, 35 (2005) 219.
- 8. Crini G. Badot P M, Crini N M, Torri G, Press universities de Franche-Comte (PUFC), (2007) 16.
- 9. Gimbert F, Crini N M, Renault F, Badot P M, Crini G, J. Hazard.Matter, 157 (2008) 34.
- 10. Lodha S, Jain A, Sharma, and Punjabi, P B, Indonesian J. Chem., 42 (2008)42.

- 11. Khataee A Rand Kasiri M B, J. Mol. Cat. A, 328 (1-2) (2010) 8.
- 12. Kajbafvala A, Ghorbani H, Paravar A, Samberg J P, Kajbafvala E, and Sadrnezhaad S K, *Superlattices and Microstructures*, 51(4) (2012) 512.
- 13. Kuo W G, Water Research, 26(7) (1992) 881.
- 14. D. F. Ollis and H. Al-Akabi, *Photocatalytic Purification andTreatment of Water and Air*, Elsevier, Amsterdam, The Netherlands.
- 15. Arslan I and Balcioglu I A, Dyes and Pigments, 43(2) (1999) 95.
- 16. Arslan I and Balcioglu I A, and Bahnemann D W, Dyes and Pigments, 47(3) (2000)207.
- 17. Herrera F, Kiwi J, Lopez A, and Nadtochenko V, Environ. Sci. Tech., 33(18) (1999) 3145.
- 18. Gregor K H, "Oxidative decolorization of textile waste with advanced oxidation processes," in *Chemical Oxidation: Technologies for Nineties*,
- 19. Eckendfelder W W, BowersA R, and Roth J A, Eds., (1992) 161.
- 20. Nerud F, Baldrian P, Gabriel J, and Ogbeifun D, Chemosphere, 44(5) (2001) 957.
- 21. Verma P, Baldrian P, and Nerud F, Chemosphere, 50(8) (2003) 975.
- 22. Watanabe T, Koller K, and Messner K, J. Biotech.62(3) (1998) 221.
- 23. Gabriel J, Shah V, Nesm'er'ak K, Baldrian P, and Nerud F, Folia Microbiologica, 45(6) (2000) 573.
- 24. MoheyEl-Dein A, Libra JA, Wiesmann U, *Chemosphere*, 52, (2003) 1069.
- 25. Yatmaz H C, Akyol A, Bayramoglu M, Ind. Eng. Chem. Res., 43 (2004) 6035.
- 26. Gupta V K, Jain R, Agarwal S, Nayak A, Shrivastava M, J. Colloid Interface Sci. 366 (2012) 135.

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