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Study of the Degradation of Dyes by a Mononuclear Copper Complex Forming a Zigzag Chain

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Abstract. The titled mononuclear complex [Cu(L)] with the formally tetradentate schiff base ligand, [N,N'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropan-2-ol] has been synthesized and characterized using IR spectroscopy and elemental analysis. Cristal structure has been determined by XR diffraction that reveals the pseudo octahedral complex geometry and the use of hydroxo bridges between two neighbor units to form a 1D coordination polymer. The use of this complex as a catalyst for the degradation of two textile dyes: crystal violet (CV) and methylene blue (MB), in the presence of the appropriate amount of H_2O_2 and a UV light source has given very good results with yields exceeding 90% after 50 minutes.

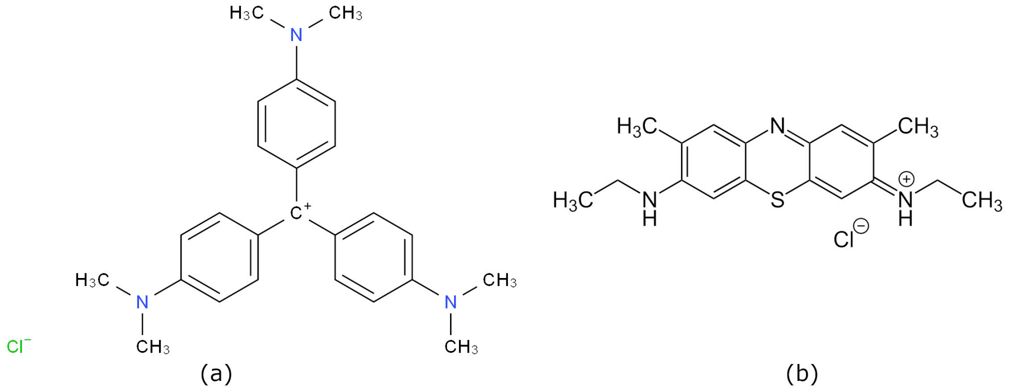
Introduction

Condensation reactions between carbonyl compounds and diamines have provided one of the most important and widely studied classes of chelating ligands. Schiff bases derived from aromatic or aliphatic diamine and phenolic aldehydes have proved to be the source of tetradentate ligands [1-3] for many transition metal complexes [4-6].

Depending on the intended application and area of interest, the formulas and structures of Schiff base compounds change. Indeed, we find homometallic complexes with different nuclearities, which depending on the size of the desired active sites, can be formed either with transition metals [7-8], or with larger cations, generally lanthanides [9]. In addition, hetero-metallic complexes are very diverse. They essentially come from the association of a 3d element with a 4f element [10-12], an alkaline earth metal [13] or an alkali metal [14]. These complexes in general are very popular because of their numerous catalytic [15-16], magnetic [17-19], and biological [20-26] properties.
Photocatalysis is a field of chemistry that deals with chemical reactions that occur in the presence of light and photocatalysts [27-30]. This technique is effective in wastewater treatment and has helped a lot to effectively degrade organic pollutants such as textile dyes, especially since this technique is environmentally friendly and cost-effective. Several studies have recently been conducted in this direction [31-34].

The main objective of our work is to study the catalytic efficiency of a mononuclear copper Schiff base complex on the degradation of two industrial textile dyes, crystal violet (CV) and methylene blue (MB). We are specifically interested in homogeneous photocatalysis including photo-Fenton [35]

In this paper, we report the synthesis of the complex resulting from the reaction of a symmetric Schiff base ligand namely N,N'-bis(2-hydroxy-3-méthoxybenzylidene)-1,3-diaminopropan-2-ol, with nitrate copper and the characterization by IR spectroscopy and elemental analysis. Single crystal XR diffraction is used to establish the structure of resulted Cu (II) complex unit and the chain obtained in polymer form. The same complex was used as a catalyst in the photodegradation of Crystal Violet (CV) and Methylene Blue (MB) dyes, the results are very promising.



(a) (b)

Fig. 1 Structure of (a) Crystal violet, (b) Methylene blue

Experimental Section

Materials. All starting materials; o-vanillin, Copper nitrate, Triethylamine (NEt3) including solvents Methanol (MeOH), Dimethylformamide (DMF) and Acetonitrile were of reagent grade and were used without further purifications.

Synthesis. A mixture of 1,3-diaminopropan-2-ol (1 mmol, 90mg) and o-vanillin (2 mmol, 304 mg) in Methanol (MeOH) was stirred for 30 min. Copper nitrate (1 mmol, 199.5 mg) was added followed by an excess of NEt3 dissolved in MeOH. The resulting green solution was mixed for 3 hours. It was then filtered and left to evaporate at room temperature. After 24 hours single green crystals suitable for X-ray Diffraction were formed on the surface of the solution.

Physical measurements. IR spectra were recorded on Perkin Elmer spectrum two spectrometer in the 4000 - 400 cm^{-1} range with the samples as KBr pellets. UV-vis measures were recorded on JENWAY 7300 spectrometer.

Crystallography. X-ray diffraction data of the single crystal were collected at 150 K on an APEXII Bruker-AXS diffractometer equipped with a CCD-LDI-APEX2 detector using a radiation type Mo-Kα (λ = 0.71073 Å). The structure was solved by a dual-space algorithm using the SHELXT program [36], and further refined by full-matrix least-squares methods based on F^2 using SHELXL [37]. A final refinement on F^2 2038 unique reflections and 139 converging parameters at $\omega R(F^2) = 0.1009$ ($R(F) = 0.0405$)) for 1536 reflections observed with $I > 2\sigma(I)$.

Results and Discussion

IR. The free ligand spectrum, C=N shows a band at 1633 cm^{-1} which is shifted to 1620 cm^{-1} for the complex indicating the participation of this group in coordination to the metal ion [39]. The shift of the phenolic C-O band from 1337 cm^{-}1 in the ligand to 1221 cm^{-1} in LCu confirms its role in the complex formation [40]. The bands between 3477 and 3447 cm^{-1} were attributed to (O-H) ; 3054 cm^{-1} to (C-H) ; 1441 cm^{-1} to (C-N) and at 1549 cm^{-1} to (C=C) stretching.

Elemental analysis. [C19 H22 Cu1 N2 O6] calculated: C 52,10; H 5,06; N 6,40 and found: C 51,96; H 5,16 and N 6,33.

X-ray Crystal structure. The title complex is a molecule in which a copper atom is linked by six atoms; two nitrogen and four oxygen; forming an octahedral geometry as shown in Fig. 2. Interatomic distances and angles are given in table 3. Equatorial bonds Cu1-N11 and Cu1-O1

(2.014(3) and 1,9529(19) respectively are clearly shorter than apical ones Cu1-O14 and Cu1-O15 (2,572(2) and 2,71(3) Å respectively). The chelating angles observed around the metal are a little different from 90°: 85.69° (5) and 95.31° (4). The angle O14 Cu1 O15 (174.93° (5)) deviates slightly from 180°. This difference in bond lengths and angles around the copper valence indicates its pseudo-octahedral geometry. The four atoms of the equatorial plane are coplanar because of symmetry with a dihedral angle close to zero.

The cupric ion is out of a plane (N11O1N11O1) at a distance of 0.0198 Å. The distance N11-O1 (via Cu1) is equal to 3.9669 (2) Å. The significant elongation along the O14 ... O15 axis (5.280 (3) Å) can be attributed to the Jahn-Teller effect. Except for hydrogen, all other atoms were anisotropically refined. No disorder was observed in the asymmetric unit; Fig. 2; where the whole atoms occupation is 100%.

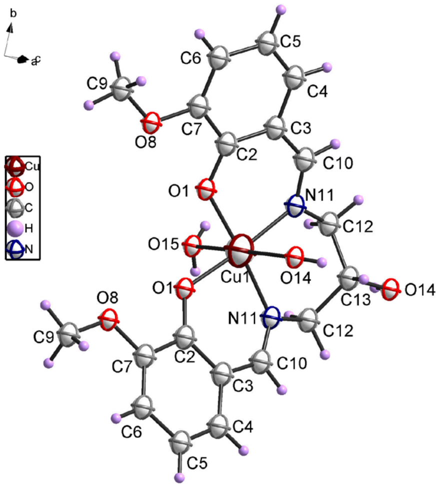


Fig. 2 DIAMOND plot of LCu asymmetric unit. Thermal ellipsoids are drawn at the 30% probability level.

Table 1 Crystallographic data of LCu

Chemical formula	$C_{19}H_{22}CuN_2O_6$
M_r	437.92
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	150
a, *b*, *c* (Å)	10.5990 (6), 22.8447 (14), 7.3098 (3)
V (Å^3)	1769.93 (16)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.28
Crystal size (mm)	0.32 × 0.27 × 0.11
Data collection	
Diffractometer	APEXII Bruker-AXS
Absorption correction	Multi-scan [Sheldrick, G.M. (2014). *SADABS* Bruker AXS Inc., Madison, Wisconsin, USA]
T_{min}, T_{max}	0.743, 0.869
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7252, 2038, 1536
R_{int}	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.111, 1.03
No. of reflections	2038
No. of parameters	139
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.18, −0.59

This material forms a one-dimensional zigzag chain where the cupric ion in each asymmetric unit is linked to the adjacent unit through the aliphatic alcohol oxygen of the diamine to form a linear chain (Fig. 3). The distance between two successive copper atoms Cu-Cu is 6.489Å. Selected lengths and angles are presented in table 3, respectively.

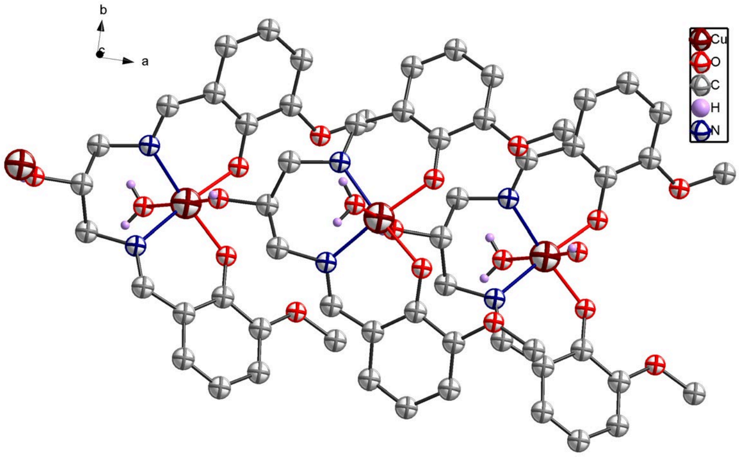


Fig. 3 Diamond plot showing one chain of LCu.

Each chain consists of the previously described copper entities associated through intermolecular hydrogen bonds established between neighboring asymmetric units in addition to dative bonds forming also one-dimensional chains. These connections take place between the oxygen atom of water molecule O15 and the methoxy oxygen atom O8 through H15, then the oxygen atom of the alcohol O14 and the oxygen of water O15 through H14, see table 2.

Table 2 Hydrogen bonds geometry [Å ,°]

Donor—H—Acceptor	D-H	H...A	D...A	D-H...A
O14 - H14 .... O15	0.78(6)	2.08(7)	2.800(5)	153(7)
O15 - H15 .... O8	0.76(3)	2.02(3)	2.703(2)	149(3)

Table 3 Selected bonds and angles (Å, °)

Selected bonds			Selected angles			
Cu1	N11	2.014(3) Å	O1	Cu1	O1	174.94(9)
Cu1	O1	1.9529(19) Å	O1	Cu1	N11	124.6(3)
N11	C12	1.483(4)	O1	C2	C3	119.2
C7	O8	1.364(3)Å	C5	C4	H4	109.5
C2	C3	1.416(4)	O8	C9	H9C	109.5
C9	H9A	0.9800 Å	H9A	C9	H9C	128.4(3)
O8	C9	1.421(3)	N11	C10	C3	99(5)
O14	H14	0.78(6)	C13	O14	H14	106(5)
C10	N11	1.279(4)	H15	O15	H15	174.94(9)

Photocatalytic activity. With an aim to investigate the photo-catalytic capacity of the catalyst LCu in the degradation of industrial dyes, Crystal violet and methylene blue were used as substrates and optimization studies were conducted to determine the optimum degradation parameters.

As mentioned above in the paper, we worked with a photo-Fenton like process, as shown in figure 4. Charge transfer between metal (3d) and ligand through oxygen or nitrogen (2p) plays an important role in the mechanism of dye photo-degradation.

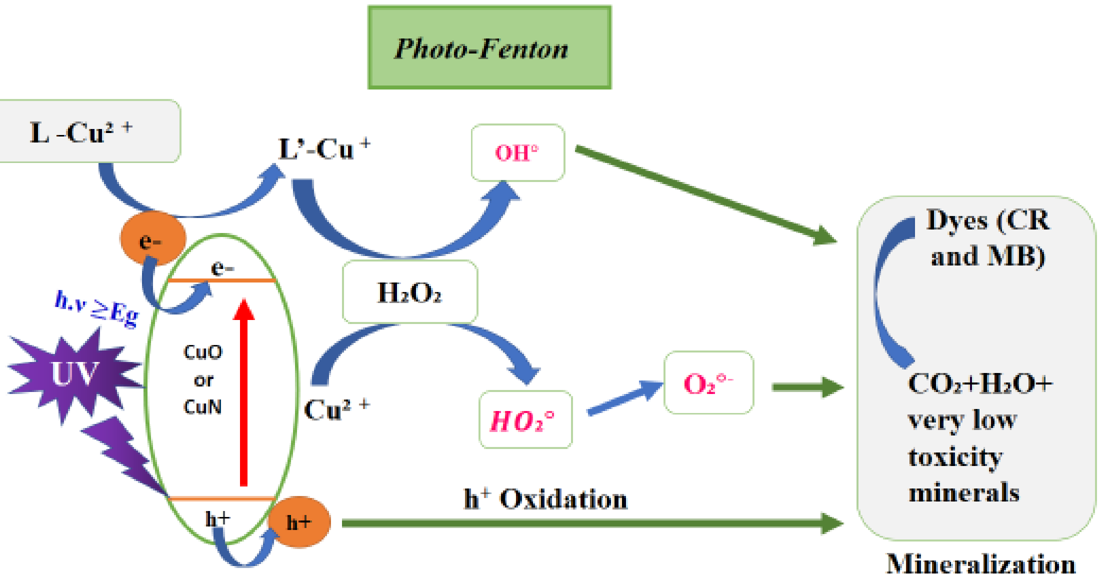


Fig. 4 Possible photo-catalytic mechanism for degradation of CV and MB dyes by LCu complex.

Crystal violet. A series of experiments were conducted to determine the optimum parameters for the degradation of crystal violet with LCu. To determine the optimal hydrogen peroxide quantity the degradation reaction of crystal violet (15 ppm) was conducted with different volumes of 3% H_2O_2 with a catalyst concentration of 15 ppm in a total volume of a solution of 300 ml (pH= 6) under UV radiation (λ= 254 nm) at room temperature. As it's shown in Fig. 5, the best results are obtained (99.45 % degradation) with a (volume) of H_2O_2 equal to 1.5 ml after 30 min. Subsequently, the effect of catalyst quantity was studied in the same manner as before, while using the optimum H_2O_2 volume previously determined. Fig. 6 shows that the best results are obtained with a catalyst concentration equal to 6 mg and 20 min of reaction time. However to confirm the synergic effect of UV radiation and hydrogen peroxide on the degradation process with the catalyst, two experiences were conducted one without the UV radiation and the other in the absence of H_2O_2, the degradation rates were 24.78 % and 65% respectively. An additional experience was carried out in the same latter reaction conditions except UV wavelength was 365 nm and the results of this experiment showed no significant degradation only 19.7 %. Thus, the optimum parameters for the degradation of crystal violet with LCu are: 6 mg of catalyst, 1.5 ml of H_2O_2 (3 %) and 20 min of reaction time.

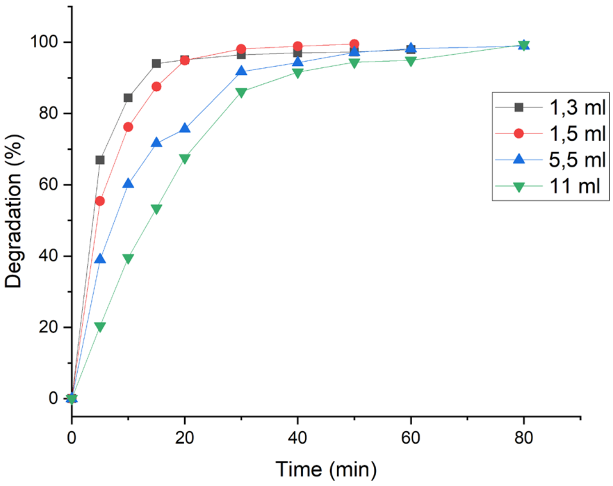


Fig. 5 Effect of hydrogen peroxide quantity on the degradation of crystal violet (15 ppm), catalyst (15 ppm), pH = 6, room temperature.

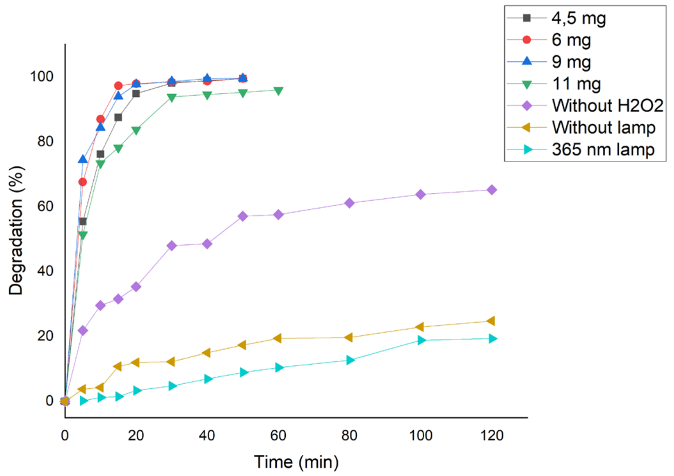


Fig. 6 Catalyst concentration effect on the degradation of crystal violet at pH = 6 and room temperature.

Methylene blue. Similarly with the other dye in search of optimum degradation parameters experiments were carried out. Aiming to determine the optimal hydrogen peroxide quantity the degradation reaction of methylene blue (15 ppm) was conducted with different volumes of 3% H_2O_2 with a catalyst concentration of 15 ppm in a total volume of a solution of 300 ml (pH = 6) under UV radiation (λ= 254 nm) at room temperature. Fig. 7, reveals that the best results are obtained (98.46 % degradation) with a volume of H_2O_2 equal to 2.25 ml after 50 min of reaction. Afterward, an investigation of the catalyst quantity effect on the degradation reaction was carried what in similar reaction conditions, while using the optimum H_2O_2 volume previously determined. Results are represented in Fig. 8. It’s evident that the best results are obtained with catalyst concentration equal to 4.5 mg and 120 min of reaction time. The synergetic effect of UV radiation and hydrogen peroxide on the degradation process along the catalyst is visible (Fig. 8), we notice that degradation rates in the experiences without the UV radiation and the other in the absence of H_2O_2, were 7.14 % and 67% respectively. Another experience was carried out in the same latter reaction conditions with a different UV wavelength (λ= 365 nm) and the results of this experiment showed no significant degradation of only 29 %. Hence, the optimum parameters for the degradation of crystal violet with LCu are: 4.5 mg of catalyst, and 2.25 ml of H_2O_2 (3 %) in a relatively short reaction time.

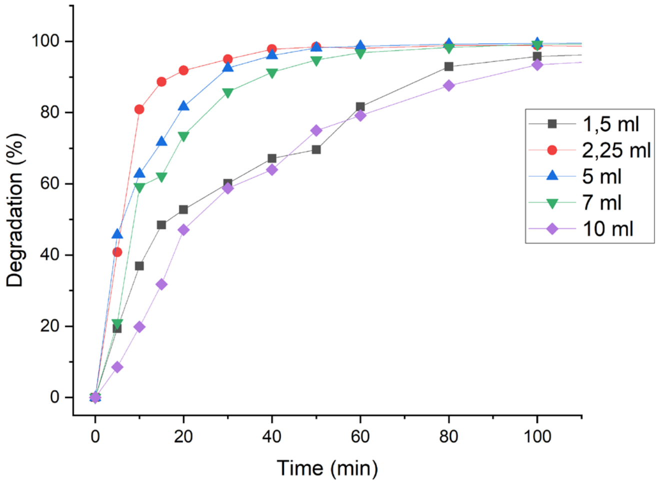


Fig. 7 Effect of hydrogen peroxide quantity on the degradation of Methylene blue (15 ppm), catalyst (15 ppm), pH = 6 and room temperature..

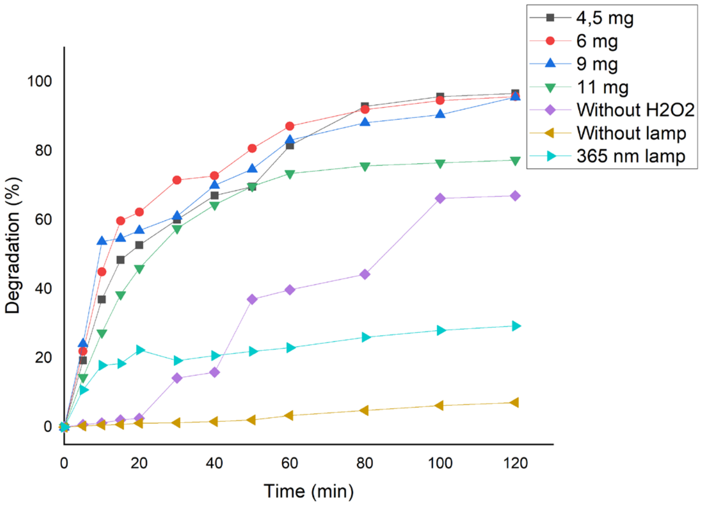


Fig. 8 Catalyst concentration effect on the degradation of Methylene blue at pH = 6 and room temperature.

The results obtained from optimization studies reveal that our copper complex indeed can successfully catalyze the degradation of CV and MB two dyes of different structures and different classes, our compound is as effective as other recently published Schiff base catalysts [35,41]. As a perspective, we plan to replace the UV lamp with sunlight if the gap energy of the catalyst is appropriate [42].

The results also highlight the capacity and potential of the complex making it an efficient candidate in the pool of similar catalytic agents for the degradation of industrial textile dyes.

Conclusion

The complex LCu was synthesized and characterized using FT-IR and elemental analysis, single crystal of the complex were isolated, and its structure was later determined using XRD.

Catalytic efficiency of the LCu complex in the degradation of industrial textile dyes was investigated. The results of the photo-catalytic study experiments, prove that LCu possesses a significant photo-catalytic capacity in the degradation of crystal violet and methylene blue. The optimum parameters of the degradation reactions were determined for both of the dyes. The catalyst turned out to be very efficient while using very low quantities of hydrogen peroxide H_2O_2 (3 %) and fast acting with a short reaction time to achieve around 98% to 99% degradation. The sum of the results of this study reveal that LCu could be a very promising catalyst in the field of environment and the photodegradation of industrial dyes.

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