

Crystal Structure and Catalytic Activity of Copper(II) Dafone Complex

Reena¹, Biju.A.R²

¹PRNSS College, Mattanur, reenaprns@gmail.com

²Sir Syed College, Taliparamba; biju.ar@gmail.com

Abstract: A new complex of dafone (4,5-diazafluoren-9-one) with copper, $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$ was synthesised. Its structure was analysed by various spectroscopic methods and confirmed crystallographically. The complex crystallizes in the monoclinic $C2/c$ lattice in which central atom Cu(II) octahedrally coordinated to four nitrogen atoms of two dafone molecules and two oxygen atoms of methanol. Two perchlorate anions and dafone molecules are present in the lattice. Two dafone ligands chelate in *trans*-mode with one shorter Cu—N bond length 1.991 Å and other very longer Cu—N bond length 2.594 Å, which is along the Jahn–Teller axis. The molecular structure of the title complex was optimized using density functional theory (DFT) at the B3LYP/6–311 G(d,p) level. Catalytic activity was studied on the basis of decomposition of hydrogen peroxide and photocatalytic activity was tested on the basis of decomposition of methylene blue dye.

Key words - Dafone, crystallography, Frontier Molecular orbitals, catalyst.

I. INTRODUCTION

4,5- diazafluoren-9-one (dafone), a derivative of 1,10-phenanthroline, is a bidentate ligand having an exocyclic keto group (Henderson et al., 1984). Dafone attracted attention of researchers due to its DNA interaction properties (Pyle et al., 1989). The reactive exocyclic keto function in dafone offers distinct advantages for further derivatization, to yield multinuclear metal complexes having interesting catalytic and biological properties (Kulkarni et al., 2001). Copper(II) exhibits a wide of structural varieties due to various reasons like Jahn-Teller instability of the single hole e_g and steric effect of the ligands (Menon et al., 1994). As compared to phenanthroline and bipyridine only few crystal structures have been reported for the dafone and transition metal

complexes. There are few reports of coordination complex for the structure of the type $[\text{M}(\text{dafone})_2\text{X}_2]$ (M = metal ion, X = anion), which are mainly the Cu(II) complexes like $[\text{Cu}(\text{dafone})_2(\text{NCS})_2]$ & $[\text{Cu}(\text{dafone})_2(\text{NCO})_2]$ (Babu et al., 2011) $[\text{Cu}(\text{dafone})_2\text{Cl}_2]$ (Balagolalakraishna et al., 1992) $[\text{Cu}(\text{dafone})_2\text{Br}_2]$ (Menon et al., 1998), $[\text{Cu}(\text{dafone})_2(\text{SCN})_2]$ (Barbara et al., 2011) and $[\text{Cu}(\text{dafone})_2(\text{NCO})_2]\text{MeCN}$ (Kishore et al., 2011). There is also report of Co(II), $[\text{Co}(\text{dafone})_2(\text{NCS})_2]$ (Shi et al., 1995), Zn(II), $[\text{Zn}(\text{dafone})_2\text{I}_2]$ (Maguire et al., 2009), Ni(II), $[\text{Ni}(\text{dafone})_2(\text{SCN})_2]$ (Barbara et al., 2011), $[\text{Ni}(\text{dafone})_2(\text{NCS})_2]$ (Kishore et al., 2011) and Hg(II) complexes $[\text{Hg}(\text{dafone})(\text{SCN})_2]$ (Barbara et al., 2011). In all the Cu(II) complexes, dafone is coordinated in *trans* position with one shorter Cu—N bond length 1.97–2.03 Å and other very longer Cu—N bond length 2.64–2.79 Å, which is along the Jahn–Teller axis. In both Co and Zn complexes the dafone coordinates in a *cis*-mode, in Co complex the Co—N bond lengths were 2.22 and 2.27 Å, in Zn complex Zn—N bond lengths were 2.17 and 2.46 Å. There is only one report for Mn(II) dafone coordination complex $[\text{Mn}(\text{dafone})_2\text{Cl}_2]$ (Wu & Xu, 2004), in which dafone coordinates to Mn(II) in *cis*-mode.

In our work we have prepared a new complex of dafone(4,5-diazafluoren-9-one) with copper, $\text{trans}[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$. Its structure was analysed by various spectroscopic methods and confirmed by single crystal XRD studies. The molecular structure of the complex was optimized using density functional theory (DFT) at the B3LYP/6–311 G(d,p) level. Catalytic activity of the complex was studied on the basis of decomposition of hydrogen peroxide and photocatalytic

activity was tested based on the decomposition of methylene blue dye.

II. MATERIALS AND METHODS

All chemicals were purchased from Ranbaxy chemicals and Sigma Aldrich and used without further purification. Dafone was prepared using a reported procedure (Henderson et al., 1984).

IR spectra were measured by using a Thermo Nicolet AVATAR 370 DTGS model FT IR Spectrophotometer using the KBr pellets in the 4000-400 cm^{-1} range. Elemental analysis experiment was conducted using an ELEMENTAR Vario EL III CHNS analyser. X-ray diffraction data was collected on a Bruker Kappa APEX2 CCD diffractometer, equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) at 298 K. Data were reduced using Computer programs: APEX2 (Bruker, 2004), SIR92 (Altomare et al., 1994) SHELXL2014/7 (Sheldrick, 2015), Mercury (Macrae et al., 2006), publCIF (Westrip, 2010). The analysis was carried out from department of chemistry, Hyderabad University.

A. Synthesis of $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$

Copper perchlorate (0.370 g, 1.000 mmol) was dissolved in minimum amount of methanol. To this solution dafone (0.728 g, 4.000 mmol) dissolved in minimum amount of methanol was added slowly and kept undisturbed. Bluish green crystals were formed slowly after one week. Yield: 0.4238 g (40.23%). Anal. (%): Calc. for $\text{C}_{46}\text{H}_{32}\text{Cl}_2\text{CuN}_8\text{O}_{14}$: C, 52.39; H, 3.03; N, 10.63; Cu, 6.03. Found: C, 53.78; H, 2.90; N, 9.27; Cu, 7.69. IR (KBr, cm^{-1}): 3464, 3107, 2286, 1964, 1821, 1722, 1592, 1411, 1213, 1074, 1019, 756.0, 724.0 and 621.0. The crystals are stable in air and melt above 280°C.

B. Computational analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are called Frontier Molecular Orbitals (FMO). FMO's decides the optoelectronic properties of the molecule. The molecular structure of the complex was optimized using density functional theory (DFT). DFT calculations were performed for the complex $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$ with computer program Gaussian09 (Frisch et al., 2009), using the basis set B3LYP/6-311 G(d,p) (Becke, 1993).

C. Catalytic activities of copper dafone complex

The catalytic activity of the complex was studied by considering the decomposition of hydrogen peroxide at constant concentration as the model reaction. The ability of

metal complex to catalyse the decomposition of hydrogen peroxide was determined by permanganometric titrations. The metal complex (2×10^{-4} mmol) was mixed with 50ml of 10% H_2O_2 in a beaker at room temperature under constant stirring. The extent of decomposition of hydrogen peroxide at different intervals of time was estimated through permanganometric titration by withdrawing 1ml aliquot of reaction mixture in each 30 minutes and titrating against 0.02M KMnO_4 in presence of 1:5 H_2SO_4 solution. The difference in titre values of permanganate solution before and after the catalysed decomposition was recorded (Gupta & Abdulkadir, 2008), (Hosny, 2007). Percentage decomposition of H_2O_2 can be calculated by the equation, **Percentage decomposition of $\text{H}_2\text{O}_2 = (\text{C}_0 - \text{C}_t / \text{C}_0) \times 100$.**

The percentage decomposition of H_2O_2 is found to increase with time. Metal complex M-L interact with HO_2^- (formed by the decomposition of hydrogen peroxide) to form an intermediate complex $[\text{M-L}(\text{HO}_2)]^-$, which on reacting with another molecule of H_2O_2 to form H_2O and O_2 (Demetgul, 2012).

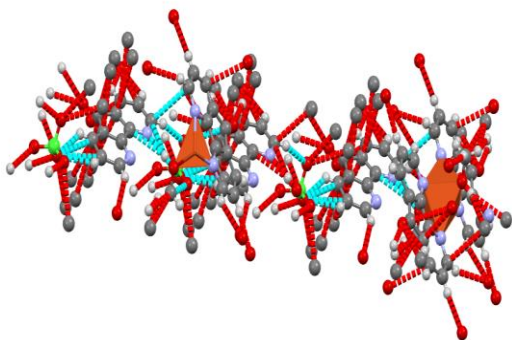
D. Photocatalytic activity

Photocatalytic activity of the prepared complex was carried out using methylene blue dye as the pollutant and UV lamp as the source of radiation. The metal complexes (0.01g) and aqueous solution of methylene blue (70ml) were mixed in a beaker and was equilibrated by constant stirring at room temperature in dark for thirty minutes to allow the adsorption of methylene blue dye, if any, by the complex. The solution is stirred under UV light. The sample was allowed to absorb UV light and 5ml aliquots were taken and filtered at definite time interval of 30minutes. The filtrate was analysed using UV-Visible spectrophotometer. When the reaction mixture was stirred, the complex absorbs UV rays and get excited due to the appropriate band gap. The photogenerated electron hole pairs produce hydroxyl radicals in the system which decolorises the blue colored methylene blue solution (Tabbi et al., 2001), (Verma et al., 2003). The intensity of absorption peak of methylene blue at 663nm gets diminished gradually with extension of the exposure time indicating the degradation of methylene blue dye.

III RESULTS AND DISCUSSION

A. Characterisation of the ligand and the complex

Ligand and complex were characterised by various spectroscopic studies. IR Spectrum of dafone shows three characteristic bands, whose wavelengths corresponding to the stretching vibrations of its three types of bonds: 3304 cm^{-1} ($\nu_{\text{C-H}}$), 1714 cm^{-1} ($\nu_{\text{C=O}}$) and 1461 cm^{-1} ($\nu_{\text{C=N}}$). In

Fig.3. Crystal packing of $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$

D. Refinement

The C-bound H atoms were positioned geometrically and refined using a riding model. Selected geometric parameters are given in Table II.

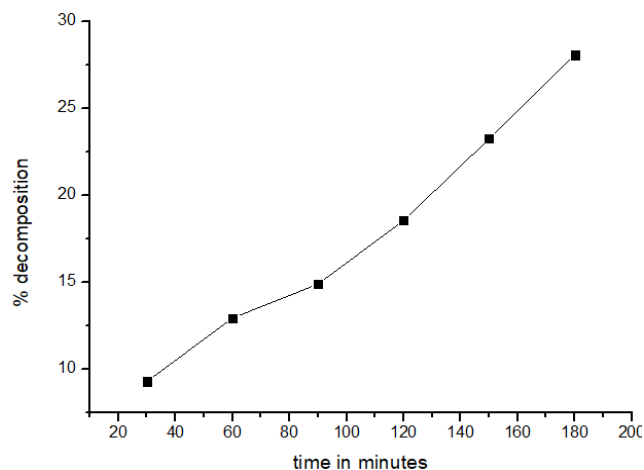
TABLE.II.
SELECTED BOND LENGTH IN Å AND BOND ANGLES IN°

Cu1—N3	1.991	Cu1—N3	2.594	Cu1—O7	1.959
N2—Cu1—N3	80.2	N2—Cu1—O7	89.6		
N2—Cu1—N2	180	N2—Cu1—N3	99.8	N3—	
Cu1—N3	180	O7—Cu1—N3	90	O7—	
Cu1—N2	90.4	O7—Cu1—O7	180		

Symmetry code: (i) $-x+1, y, -z+1/2$.

E. Frontier Molecular orbital studies

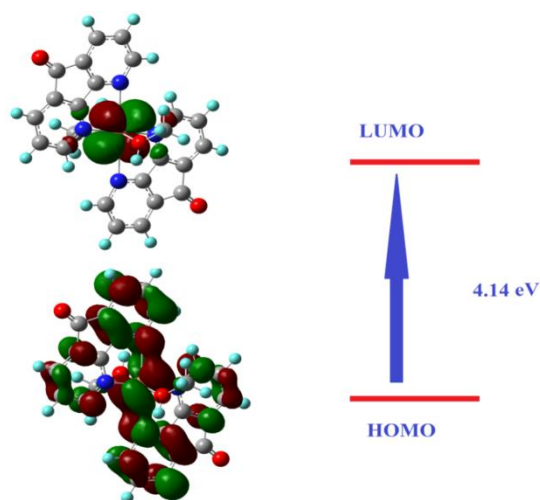
The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are called frontier molecular orbitals (FMOs). The FMOs decides the optoelectronic properties of the molecule. A molecule can be classified into soft and hard depending up on the HOMO-LUMO gap. The molecular structure of the complex was optimized using density functional theory (DFT). DFT calculations were performed for the complex with Gaussian09 by using the basis set B3LYP/6-311 G(d,p). The calculated energy of HOMO and LUMO orbitals of the compound were negative, indicates the stability of the complex. The electron distribution of the HOMO-LUMO orbitals of the title compound is presented in Figure 4

Fig.5. Catalytic action of $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$ on the basis of decomposition reaction of hydrogen peroxide

reaction of hydrogen peroxide and was given in Figure.5. The results shows that, upto 28% of the decomposition reaction was found to be completed within 3hrs in presence of $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$.

Table III Catalytic Activity of
 $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$

Time in minutes	Vol. Of KMnO_4 (mL)	% decomposition
0	76.5	-
30	69.4	9.28
60	66.6	12.94
90	65.1	14.90
120	62.3	18.56
150	58.7	23.27
180	55.0	28.10

Fig.4. Electron distribution of the HOMO-LUMO orbital of $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$

F. Catalytic activities on the basis of decomposition of Hydrogen Peroxide

Percentage decomposition of H_2O_2 against time was given in Table.III. A time-volume graph and time vs % decomposition of KMnO_4 graph was plotted to visualise progress of the decomposition

G. Photocatalytic activity

Intensity vs absorption graph of methylene blue dye in presence of the complex on exposure to UV light was given in Figure.6. The intensity of the absorption peak of methylene blue at 663nm gets diminished gradually with extension of the exposure time indicating the degradation of methylene blue dye and hence support the catalytic property of the complex.

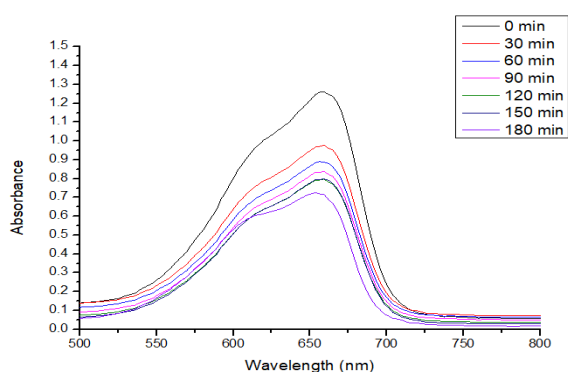


Fig.6. Photodegradation plot of methylene blue dye degradation under UV light using $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$: A- 0min; B-30min; C-60min; D-90min; E-120min; F-150min; G-180min;

IV. CONCLUSION

Complex $[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$ was prepared by solvent based synthesis method using methanol as solvent. Characterisation of ligand and complex were done by elemental analysis and various spectral studies. Structure of the complex was confirmed by Single crystal X-ray diffraction studies and it is octahedral in geometry. Computational analysis of the complex was carried out to find the optimized structure of the complex. The high energy difference (4.14eV) of HOMO and LUMO orbitals of the title compound indicates that the complex is stable. Its catalytic activity was studied by considering decomposition reaction of hydrogen peroxide. Upto 28% of the decomposition reaction was found to be completed within 3hrs in presence of
Institute of Science, BHU Varanasi, India

$[\text{Cu}(\text{dafone})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2(\text{dafone})_2$. It can act as photocatalyst as clear from the photodegradation of methylene blue dye.

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