



Synthesis, Characterization, Green Catalysis & Computational Studies of a Binuclear Copper(II) Complex Encapsulated in Zeolite Y

¹M. G. Meera, ^{*2}P.Kamatchi Selvaraj ³S.Tamilmani, ⁴B.Viswanathan

¹Research and Development Centre Bharathiar University Coimbatore, Tamil Nadu, India-641 046

²Department of Chemistry Government Arts College for Men (Aut) Nandanam, Chennai, Tamil Nadu, India-600 035

^{3,4}National Centre for Catalysis Research Indian Institute of Technology-Madras Chennai, Tamil Nadu, India-600 035

Email: ¹meerageorge1987@gmail.com, ^{*2}porbal96@gmail.com ³stamilmani89@gmail.com; ⁴bvnathan@iitm.ac.in

[Received: 11th Nov.2014; Accepted:25th Nov.2014]

Abstract — A new symmetric acyclic hydroxo bridged binuclear copper (II) complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ was synthesized in situ from a phenol based binucleating compartmental “end-off” type ligand, viz., 2,6-bis{N-[3-(dimethylamino)propyl]iminomethyl}-4-methylphenol (L). The structure of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ was solved by X-ray crystallography. The crystal structure establishes the presence of a dinuclear copper core with distinct copper sites in a distorted trigonal bipyramidal environment. This complex exhibits quasi-reversible redox processes. The complex was encapsulated in zeolite Y by flexible ligand method. It was characterized by FTIR, UV-DRS and pXRD techniques. The tendency of the heterogenized complex to catalyze the transformation of phenol was studied along with two similar model complexes theoretically by Density Functional Theory calculations. The antimicrobial activity of the complex was also investigated.

I. INTRODUCTION

Synthesis and characterization of new binuclear copper (II) complexes have made an impact on bioinorganic chemistry, since the spectral, electrochemical and magnetic features provide new insight into the structure of naturally occurring dicopper proteins such as hemocyanin, tyrosinase, catechol oxidases, ceruloplasmin etc [1-3]. In physicochemical aspects, these dicopper complexes have noteworthy significance as new inorganic materials capable of exhibiting peculiar magnetic properties, charge separation, multi electron transfer and electron transport and hence these binuclear copper (II) complexes have wealth of applications [4-8].

The contemporary interest in the selective oxidation of phenol to catechol, has been fueled by its utility in nearly every sector of chemical industries including pharmaceuticals, agrochemicals, flavors, polymerization inhibitors, and antioxidants [9]. Worldwide, the catechol production from phenol involves two procedures: (i) ortho-formylation of phenol followed by subsequent oxidation, and (ii) oxidation of phenols to o-quinones and

subsequent reduction of the latter into catechol. These multi step routes are often lengthy, energy-intensive, and generate a large number of oxidized, coupling, and polymerized products [10]. To meet the increasing demand for catechol and to satisfy environmental requirements, considerable efforts have been made for producing catechol by the one-step hydroxylation method using various homogeneous and heterogeneous transition metal complexes [11- 13].

Homogenous catalyst systems i.e., neat inorganic complexes acting as catalysts tend to be destroyed in one catalytic cycle itself. This makes the retrieval and reuse of the catalyst difficult. To avoid this, heterogenization of the solid CuY catalyst is done by immobilizing or anchoring a soluble homogeneous metal complex. These hybrid catalysts offer the advantages of selectivity and controllability owing to the site isolation effect. Metal complexes encapsulated in various zeolites show enhanced catalytic activity. They are known to involve in various catalytic reactions such as dehydrogenation, dehalogenation, cracking, etc.[14 - 17]. There are a number of well-documented examples in which the catalytic activity of the zeolite encapsulated mononuclear complexes are either enhanced or more selective as compared to the same complexes in solution.

Phenol is known to be a common pollutant in the industrial effluents. Although there are many techniques in practice to bring about its mineralization [18], the concept of sustained development has prompted us to design a heterogeneous catalyst by encapsulating the binuclear copper (II) complex in zeolite Y. The present work deals with the synthesis of a binuclear copper complex and its characterization so as to study and compare the changes in its physical, chemical and structural aspects when it is heterogenized by encapsulation in NaY zeolite (Si/Al \approx 2.56). The catalyst prepared was tested for its tendency to facilitate the organic transformation of the pollutant i.e., phenol to more value added products relevant to industries, along with two similar model complexes at the Density Functional level of theory.

II. EXPERIMENTAL SECTION

A. Materials

2,6-Diformyl-4-methylphenol [19] was prepared as per the literature method. 3-(Dimethylamino) propylamine was procured from Sigma Aldrich. All other chemicals and solvents used are of analytical grade and were used as received without any further purification. Tetra(n-butyl)ammonium perchlorate (TBAP) was purchased from Fluka, recrystallized from hot methanol and used as supporting electrolyte in carrying out electrochemical measurements. (Caution! TBAP is potentially explosive; hence, care should be taken in handling the compound). NaY Zeolite (Si/Al \approx 2.6) was obtained from Sud-Chemie India Pvt. Ltd.

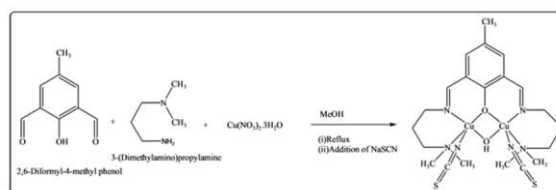
B. Physical Measurements

Elemental analysis was carried out using a Perkin-Elmer 2400 Series CHNS/O Analyser. IR spectrum was recorded using a Bruker TENSOR FT-IR spectrometer in the range 4000-650 cm^{-1} . Electronic spectrum was recorded on a JASCO V-530 spectrophotometer in the range 200-800nm. The single crystal X-ray diffraction study was carried out on a BRUKER Single Crystal Kappa APEXII diffractometer using a Mo $K\alpha$ radiation in the range of $\theta < 2\theta < 25^\circ$. Emission intensity measurement was carried out on a Perkin Elmer fluorescence spectrometer. Electrochemical measurement of the sample was carried out at room temperature using a CHI1200B electrochemical analyzer. Ag/AgCl/KCl electrode was used as the reference electrode, Pt electrode was used as the counter electrode and Glassy carbon electrode was used as the working electrode. TBAP was used as the supporting electrolyte (0.1 M) and the concentration of the solution in DMF was around 10^{-3} M. The sample was deoxygenated prior to the experiments. Powder XRD patterns were recorded on a PHILIPS miniflex diffractometer using a Cu- $K\alpha$ radiation in the range of 5° to 80° .

C. Synthesis

1) Synthesis of binuclear copper complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$: 2,6-Diformyl-4-methylphenol (0.164g, 1mmol) in methanol was slowly added to a solution of 3-(Dimethylamino)propylamine (0.25 mL, 2.0 mmol) in 5 ml of methanol and stirred for 30 minutes. The resulting mixture was refluxed for 10 min. To the yellow ligand solution obtained copper (II) nitrate trihydrate (0.485g, 2 mmol) was added and the mixture was refluxed for another 30 min. The addition of sodium thiocyanate (0.162g, 2 mmol) resulted in the precipitation of light green microcrystals (**Scheme 1**). Single crystals suitable for X-ray diffraction were obtained by recrystallization from acetonitrile. Yield: 0.401g (56%); Anal. for $\text{C}_{21}\text{H}_{32}\text{N}_6\text{O}_2\text{S}_2\text{Cu}_2$. Found (%):

C, 42.59; H, 5.32; N, 14.60. Calc. (%): C, 42.62; H, 5.45; N, 14.20.



Scheme 1. Synthesis of $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ complex.

2) Preparation of Cu(II)-NaY by ion exchange method: Cu-NaY was prepared by exchanging 0.604 g of copper (II) nitrate trihydrate in 50 mL of double distilled water with 1 g of Na-Y (Si/Al=2.56) (Sud-chemie) under stirring. The system is heated under reflux for 6 hours and cooled. The solid is filtered and washed thoroughly with hot demineralised water till the washings are colourless. The solid Cu-Y obtained was dried at 120°C for 24 hours and stored in a desiccator.

3) Synthesis of $[\text{Cu}_2(\text{L})(\text{OH})]$ -Y (A-Y): A solution of 2,6-Diformyl-4-methylphenol (0.164g, 1 mmol) and 3-(Dimethylamino)propylamine (0.25 mL, 2.0 mmol) in 5 ml of methanol was stirred and refluxed for 10 min respectively. Dry Cu-Y (0.5 g) was added in portions to the ligand under constant stirring. The synthesis was carried out under N_2 atmosphere for 48 hours and the resulting mass was soxhlet extracted with acetonitrile and with dichloromethane for 36 hours to remove any uncomplexed ligand or species adsorbed on the surface of the zeolite crystallites. The greenish yellow residue obtained was dried overnight under vacuum (90°C) and stored in a vacuum dessiccator.

III. RESULTS AND DISCUSSION

A. X-ray structure of $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$

Fig. 1 shows an ORTEP diagram of the binuclear copper complex. The complex has a dinuclear copper (II) core bridged by the phenolic oxygen of (L) and a OH group, providing a μ -Hydroxo- μ -phenolato-dicopper (II) core with the Cu—Cu separation of 3.086\AA . The geometry around the metal centres can be best described as distorted trigonal bipyramidal.

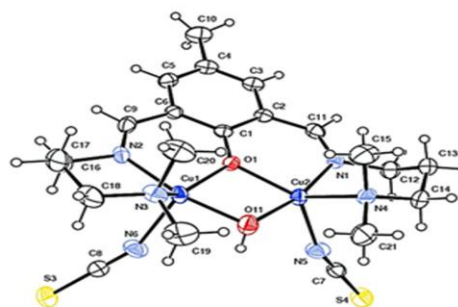


Fig. 1. An ORTEP view of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ with the atom numbering scheme.

B. IR spectra of $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ and $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$ (A-Y)

The complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ shows an absorption band around $3460\text{-}3600\text{ cm}^{-1}$ characteristic of the $\nu(\text{O-H})$ mode of bridging hydroxo group [20]. The IR spectrum of the starting material (2,6-diformyl-4-methylphenol) shows a peak at around 1699 cm^{-1} due to -CHO group. This peak disappears and a new peak appears at around 1636 cm^{-1} which is indicative of the formation of C=N by Schiff base condensation. The appearance of a band in the region $1520\text{-}1560\text{ cm}^{-1}$ suggests the phenoxide bridging with the metal ions. The complex shows a distinct $\nu(\text{CN})$ mode for the NCS-group at 2073 cm^{-1} . This is in harmony with the X-ray crystallographic results indicating that monodentate isothiocyanate groups are involved in co-ordination with the metal centres.

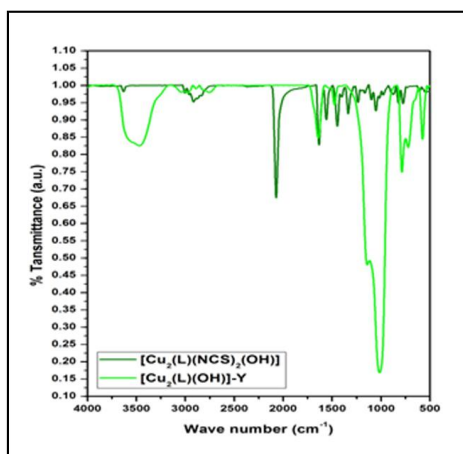


Fig. 2. FTIR Spectra of $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$, $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$

The IR spectrum of (A-Y) shows bands due to surface hydroxyl groups due to νOH , in the range of $3700\text{-}3200\text{ cm}^{-1}$. The bands at (i)767, (ii)810, (ii)990 and (ii)1132 cm^{-1} may be attributed to the lattice (i) symmetric and (ii) asymmetric stretching vibrations [21]. The bands characteristic of the neat complex was observed in the $1650\text{-}1475$ and $3750\text{-}2500\text{ cm}^{-1}$ ranges due to the encapsulation of the complex inside the zeolite walls. Fig. 2 shows the IR spectra of the neat complex and encapsulated complex A-Y.

C. UV-Vis/Diffuse reflectance spectra of $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ and $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$ (A-Y)

Fig. 3 displays the UV-Vis absorption spectrum of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$, recorded in dimethylformamide (DMF) and diffuse reflectance spectrum of the encapsulated complex A-Y. The intense peak at 257 nm may be due to the intraligand charge-transfer transitions (phenyl ring based $\pi\text{-}\pi^*$ transition) involving delocalization throughout the azomethine chromophores. A peak in the range of 370 nm may be

due to phenolate to copper charge transfer transitions (LMCT) [22]. Graph (b) represents very weak d-d transition in the visible region of 710 nm which is characteristic of binuclear copper (II) complexes. It can be seen that the spectrum exhibited by the encapsulated complex is very similar to that of neat complex.

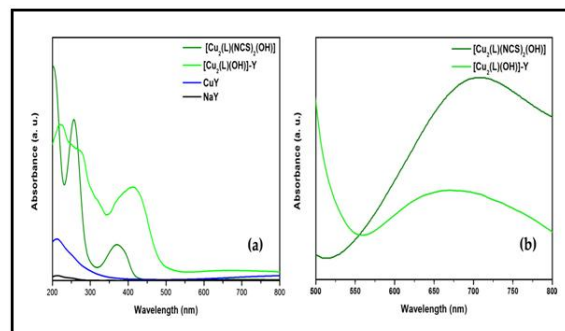


Fig. 3. UV-Vis Spectrum of (a) the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$, $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$, CuY and NaY and (b) d-d transition exhibited by $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ and $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$.

D. Fluorescence Studies of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$

The fluorescence spectrum of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ and its ligand before complexation is shown in Fig. 4. The complex shows an emission band around 475 nm when excited with 370 nm radiation, at room temperature using 0.1 mM samples in DMF. The ligand exhibits an emission band at 508 nm when excited at 424 nm . The fluorescence exhibited by the complex may be due to the intra-ligand transitions ($\pi\text{-}\pi^*$). Similar type of complexes are reported to be used as luminescent probes for biological applications under physiological conditions [23].

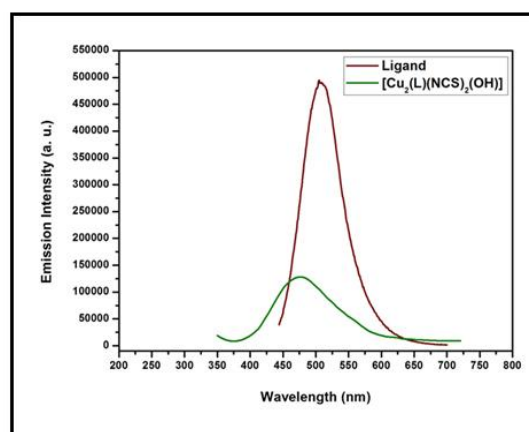


Fig. 4. Fluorescence Spectra of the ligand and its complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$.

E. Electrochemistry

The cyclic voltammogram of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ is shown in Fig. 5. The electrochemical behavior of the complex was studied in the potential range of 0 to -2V by cyclic voltammetry in DMF containing 0.1 M TBAP as the supporting electrolyte. The complex shows two quasi-reversible (one electron transfer) peaks at -0.519 V for the first reduction potential and at -1.282V for the second reduction potential. The first and second redox processes correspond to the redox couples, $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}/\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ respectively [24]. The differences in the peak positions may substantiate the stability of the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ mixed valence state [25]. The larger the separation between the potentials of the first and second redox processes, the greater the stability of the mixed valence species or greater the exchange interaction with respect to the isovalent species [26].

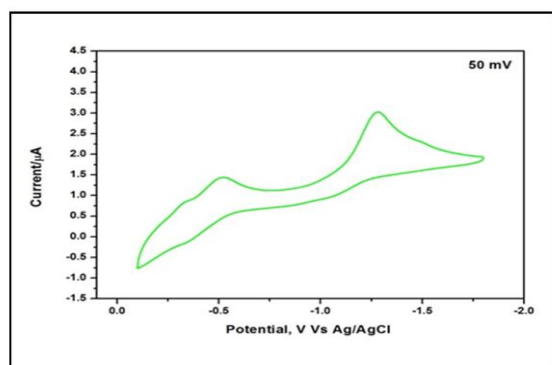


Fig. 5. Cyclic voltammogram of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$

Usually the electronegative nature of the phenoxide ligands influences the redox potential of the complex. The electrochemical data of the complex indicate that it undergoes reduction at highly negative potentials ($E_{\text{pc}}^1 = -0.519$ V; $E_{\text{pc}}^2 = -1.282$ V). The value of the cathodic current is larger than the anodic current which may be due to the probable structural reorganization of the copper coordination sphere due to solvation or chemical changes [27]. In particular, a high peak separation observed between the reduction and the corresponding oxidation peaks in the range of 200-300mV may be due to the stepwise saturation of the unsaturated C=N bonds by the donation of the electrons through the antibonding orbital of the C=N linkage from the filled d orbital of the Cu (I) [28].

D. Powder X-Ray Diffraction

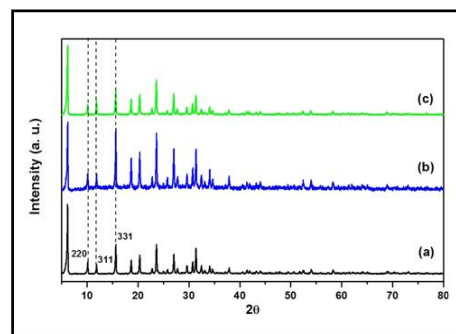


Fig. 6. Powder XRD Patterns of (a) NaY, (b) CuY and (c) $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$.

The powder XRD patterns of (a) NaY, (b) CuY and (c) A-Y were recorded at 2θ values between 5 and 80 degrees (Fig. 6) and it was found that the XRD pattern of A-Y and CuY were similar to that of NaY except for a slight change in the intensity of the peaks and no new crystalline pattern emerges. These facts confirmed that the framework and crystallinity of zeolite were not destroyed during the ion exchange and subsequent encapsulation of the complex within the voids of the zeolite. The relative peak intensities of the 220, 311 and 331 reflections are correlated to the locations of cations. In zeolite-Y, the order of peak intensity is in the order: $I_{331} \gg I_{220} \gg I_{311}$, while in encapsulated complexes, the order of peak intensity became $I_{331} \gg I_{311} \gg I_{220}$. This difference indicates that the ion-exchanged Cu^{2+} , which substitutes at the location of Na^+ , undergoes rearrangement during complexation [29].

E. DFT Studies

DFT calculation using Gaussian 09 (G09) program package was carried out to evaluate the catalytic activity of the encapsulated complex $[\text{Cu}_2(\text{L})(\text{OH})]\text{-Y}$ (A-Y) by comparison with the optimized structures of two similar complexes B-Y and C-Y where the substitution at the diamine moiety is varied. In A-Y, two methyl groups are attached to the nitrogen atoms i.e., $\text{R}=\text{CH}_3$ and $\text{R}'=\text{CH}_3$ whereas in B-Y, $\text{R}=\text{CH}_3$ and $\text{R}'=\text{H}$ substitutes the two methyl groups in A-Y and in C-Y, it is $\text{R}=\text{C}_2\text{H}_5$ and $\text{R}'=\text{C}_2\text{H}_5$ which substitutes the two methyl groups in A-Y. Table 1 shows the calculated energies of the frontier molecular orbitals (HOMO and LUMO), global hardness, (η) and softness (S).

Among all the systems, the HOMO energy of zeolite-Y encapsulated A-Y complex system is good when compared to C-Y but slightly less than B-Y. This indicates that transfer of electrons from the metal centres of A-Y catalyst to the substrate (phenol) is feasible [30].

TABLE I. CALCULATED ENERGY OF HOMO, LUMO, GLOBAL HARDNESS (η), AND SOFTNESS (S).

Sample	Encapsulated complexes			
	HOMO (in eV)	LUMO (in eV)	η (in eV)	S (in eV)
A-Y	-0.1408	-0.0519	0.0444	11.2485
B-Y	-0.1404	-0.0534	0.0435	11.4942
C-Y	-0.1677	-0.0640	0.0518	9.6432

According to the maximum hardness principle, the most stable structure has maximum hardness. The encapsulated complexes with minimum η values will be comparatively less stable and more reactive than their other counterparts. From the above observations, it is expected that the catalyst A-Y might possess higher catalytic efficiency in the conversion of phenol to catechol.

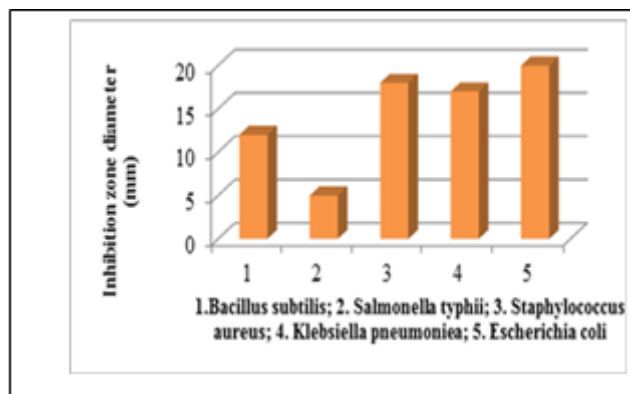
F. Anti-microbial Studies

The test microorganisms, *Bacillus subtilis* MTCC 1133, *Salmonella typhi* MTCC 531, *Staphylococcus aureus* MTCC 96, *Klebsiella pneumoniae* MTCC 530 and *Escherichia coli* MTCC 1687 were used for the evaluation of antimicrobial activity against the complex. Well diffusion method^[9] was adopted to evaluate antibacterial activity against test strains on LB agar (Luria Bertani agar).

A single colony of each test strain was grown overnight in LB broth medium on a rotary shaker (200 rpm) at 35°C. Overnight cultures of the test strains were applied to the sterile LB agar plates and then wells of 4 mm diameters were made using sterile cork borer and each was filled with 25 μ L of the binuclear complex. The plates were then incubated at 30°C for 24 hrs, after which the diameters of inhibition zones were measured to estimate its inhibitory effects. The results are listed in Table 2 and the corresponding graph (Fig. 7) shows the trend in the diameter of the zone inhibition area with different test microorganisms.

TABLE II. ANTI-MICROBIAL ACTIVITY OF THE COMPLEX $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$.

S. No.	Organism name	Inhibition zone diameter (mm)
1	<i>Bacillus subtilis</i> MTCC 1133	12mm
2	<i>Salmonella typhi</i> MTCC 531	5mm
3	<i>Staphylococcus aureus</i> MTCC 96	18mm
4	<i>Klebsiella pneumoniae</i> MTCC 530	17mm
5	<i>Escherichia coli</i> MTCC 1687	20mm

Fig. 7. Graphical representation of the antimicrobial activity of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$.

IV. CONCLUSIONS

A new binuclear Cu(II) complex was synthesized and characterized. The complex was encapsulated in NaY zeolite. The structural and redox processes of the complex were studied. The complex shows a distorted square pyramidal geometry as evidenced by spectral and structural studies. The spectral features of the neat complex agree with the encapsulated complex which confirms the successful encapsulation of the complex within the voids of the zeolite. Electrochemical measurement of the neat complex reveals two quasi-reversible single electron transfer peaks at highly negative potentials. Density Functional Theory calculation suggests that the encapsulated complex A-Y may be highly active in catalyzing the oxidation of phenol to catechol. The antimicrobial activity of the complex $[\text{Cu}_2(\text{L})(\text{NCS})_2(\text{OH})]$ was tested against some test strains of bacteria. The results show that the neat complex was toxic against the bacteria.

V. ACKNOWLEDGEMENT

MGM and Dr. PKS gratefully acknowledge the financial support received from the University Grants Commission, Government of India, New Delhi. They also thank National Centre for Catalysis Research, Indian Institute of Technology, Chennai for providing research facilities.

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