Chapter 5

5.1 Introduction

Copper (II) complexes with organic acids and other donor ligands exist extensively in living organisms, playing an important role in a vast range of chemical and biochemical catalytic systems[1]. Because of the catalytic and bioinorganic relevance the chemistry of transition metal complexes has received considerable attention. Such complexes are also important due to their potential biological activities such as antibacterial and antimalarial and antitumor [2-7]. In recent years several works have appeared concerning models of copper enzymes [8-10]. This growing interest in mimicking the active sites of metalloproteins has a major contribution to the development of new ideas and trends in coordination chemistry. The active binding site of Cu could be applied in highly efficient and catalytic reaction by using a variety of coordination possibilities such as the variability and flexibility of ligands in biologically relevant coordination sphere [11]. Since changes in coordination geometry due to the flexibility of the binding ability of ligands can lead to an open position at the metal ion site, these may be beneficial for catalytic reaction to occur [12].

Coordination polymers, that are metal-organic frameworks, are a new class of organic–inorganic hybrid materials based on metal ions coordinated by organic ligands with well defined coordination geometry. The field of coordination polymers has been extensively investigated over the past few decades with a focus on functional material research and crystal engineering. They have been researched in the last decade because of their multifunctional properties and tremendous potential applications in many fields, such as catalysis, magnetic devices, separation, molecular recognition, non-linear optics, hydrogen storage etc. [13-19]. By selecting appropriate metal ions and organic linkers, coordination polymers with various structures, such as 1D chains ladder [20-22], 2D grids [23] and 3D networks [24] can be obtained. Polycarboxylic acids represent supramolecular connectors that can generate infinite networks and metal-organic frameworks [25]. The carboxylate group may present various coordination modes, leading to the formation of mono- nuclear, di- nuclear, metal-organic frameworks or coordination polymers [26]. On the other hand crystal engineering is attracting interest from both the synthetic routes and the art of structural design [27-33]. Among the
various practical applications of coordination polymer the hydrogen storage presents a serious scientific challenge to the scientists and is still an unsolved problem.

In this chapter there is an attempt to synthesize a polymeric copper compound formed from copper (II) chloride and an organic ligand, 4 (2-butoxycarbonyl) benzoic acid which was characterized by UV-Visible, EPR, Cyclic voltametry and single-crystal X-ray diffraction studies. The compound was tested for superoxide dismutase activity and its micellar interaction was studied by cyclic voltammetrically.

5.2 Experimental:

5.2.1 Materials and Methods:

The instrumentation details and experimental techniques used are provided in Chapter 2. The details of chemicals used are listed in section 2.2 of Chapter 2.

5.2.2 Synthesis:

5.2.2.1 Synthesis of 4 (2-butoxycarbonyl) benzoic acid (L) and its characterization:

1.48g (10 mmol) phthalic anhydride was taken in a mortar and grinded. To it, 0.91mL (10 mmol) of 1-butanol was added drop wise. The reaction mixture was heated to 60 °C, and 2-3 drops of pyridine was added to it. The reaction mixture was stirred for two hours and cooled to obtain an off-white product which was then recrystallised from methanol. The synthetic path for the ligand (L) has been shown in scheme 5.1 below.

![Scheme 5.1: Synthetic path for the ligand (L)](image-url)
The yield of the product was found to be 85% and the melting point of the compound is 178 °C.

5.2.2.1.1 FTIR analysis of L:

FTIR spectrum of L was recorded in KBr pallet. Peaks were observed at 3475.4 cm\(^{-1}\) due to \(\nu_{O-H}\) stretching, 1725 cm\(^{-1}\) due to \(\nu_{C=O}\) stretching, 1417 cm\(^{-1}\) due to aromatic \(C=C\) stretching, 1125 cm\(^{-1}\) & 1293.4 cm\(^{-1}\) due to \(\nu_{C-O}\) stretching and 2962.6 cm\(^{-1}\) due to \(\nu_{C-H}\) stretching of the aromatic ring. The spectrum has been shown in Fig.5.1

![FTIR of L in KBr](attachment:image.png)

Fig. 5.1 FTIR of L in KBr
5.2.2.1.2 $^1$H NMR analysis of L:

$^1$H NMR of L was recorded in CDCl$_3$ on a 300MHz $^1$H NMR machine. Chemical shift values were reported as $\delta$ in ppm with TMS as standard. The $^1$H NMR spectrum has been shown in Fig.5.2. Peaks were observed at $\delta$: 7.99-7.47 (m, 4H), 4.17(m, 2H), 1.67-1.58(m, 2H), 1.42-1.30(m, 2H), $j$=7.2 (t, 3H).

Fig.5.2 $^1$H NMR of L in CDCl$_3$

5.2.2.2 Synthesis of the copper (II) complex:

To a solution of copper (II) chloride dihydrate (0.170g,1mmol) in methanol (10mL), a solution of 4(2-butoxy carbonyl benzoic acid) (0.358 g, 1 mmol) in methanol (10 mL) was added dropwise. The reaction mixture was stirred at room temperature for
2 hours to obtain a blue coloured precipitate. The precipitate was filtered and redissolved in 1:10 (v/v) methanol and water mixture. Small blue coloured crystals were obtained after 7 days. The crystals were found to be suitable for single crystal X-ray diffraction study. Yield of the product was 70%.

5.3 Results and discussion:

5.3.1 UV/vis spectroscopic study of the complex:

The UV/Vis spectrum of the Cu(II) complex with 4(2–butoxy carbonyl benzoic acid) was recorded in water. The spectrum has been shown in Fig.5.3. One broad absorption at 739 nm was observed which is characteristic for d-d transition in copper complexes [34]. Another band in the UV region was observed at 393 nm. This transition should be due to intra-ligand π–π* transition. Another peak with very high extinction co-efficient was observed at 273 nm which can be attributed to π–π* transition in benzene ring of the ligand [35].
Fig.5.3 UV/vis spectra of bis(hydrogenphthalato)copper(II) in water when complex concentration is a) $10^{-4}$M and b) $10^{-3}$M

5.3.2 FTIR spectral Study of complex:

FTIR spectrum of complex was recorded in KBr pallet shown in fig.5.4. In case of the complex it shows characteristic peaks due to the ligation of carboxylate in its FTIR spectrum. The peak appearing in the region of 1595-1611 cm$^{-1}$ can be attributed to $\nu_{\text{asym}}$(COO) vibrations while the peak in the range 1382-1396 cm$^{-1}$ can be attributed to $\nu_{\text{sym}}$(COO) vibrations.
5.3.3 Single Crystal X-ray study of bis(hydrogenphthalato)copper(II):

Structural representation of the complex is shown in Fig. 5.5. Crystallographic data for the complex are presented in Table 5.1 whereas selected bond distances and angles are summarized in Table 5.2. The complex crystallizes in the monoclinic P21/c space group.
Fig. 5.5: Structural representation of bis(hydrogenphthalato) copper(II)
Table 5.1 Crystal data and structure refinement for bis(hydrogenphthalato)copper(II)

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Formula</td>
<td>C16 H8 Cu O14</td>
</tr>
<tr>
<td>M</td>
<td>487.77</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>T, K</td>
<td>296(2) K</td>
</tr>
<tr>
<td>λ (Mo Kα), Å</td>
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</tr>
<tr>
<td>a, Å</td>
<td>11.0782(11)</td>
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<tr>
<td>b, Å</td>
<td>6.6521(7)</td>
</tr>
<tr>
<td>c, Å</td>
<td>12.1645(12)</td>
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<tr>
<td>α, deg</td>
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</tr>
<tr>
<td>β, deg</td>
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<tr>
<td>γ, deg</td>
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<tr>
<td>V, Å³</td>
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<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>F(000)</td>
<td>490.0</td>
</tr>
<tr>
<td>ρcalcd, g cm⁻³</td>
<td>1.846</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.42 to 39.99 deg.</td>
</tr>
<tr>
<td>Completeness to theta = 39.99</td>
<td>94.2 %</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-20&lt;=h&lt;=19, -9&lt;=k&lt;=12, -21&lt;=l&lt;=19</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.34 x 0.28 x 0.16 mm</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>μ (Mo Kα), mm⁻¹</td>
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<tr>
<td>collected reflns</td>
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<tr>
<td>unique reflns</td>
<td>5417</td>
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Table 5.2: Bond lengths [Å] and angles [deg] for bis(hydrogenphathalato)copper(II)

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Angles</th>
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<tr>
<td>Cu(1)-O(3)</td>
<td>1.943(3)</td>
</tr>
<tr>
<td>Cu(1)-O(3)#1</td>
<td>1.943(3)</td>
</tr>
<tr>
<td>Cu(1)-O(4)</td>
<td>1.973(3)</td>
</tr>
<tr>
<td>Cu(1)-O(4)#1</td>
<td>1.973(3)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.391(5)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.398(5)</td>
</tr>
<tr>
<td>C(1)-C(7)</td>
<td>1.498(5)</td>
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<tr>
<td>C(2)-C(3)</td>
<td>1.399(6)</td>
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<td>C(2)-C(8)</td>
<td>1.499(5)</td>
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<tr>
<td>O(4)-C(7)#2</td>
<td>1.287(5)</td>
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<tr>
<td>C(8)-O(2)</td>
<td>1.241(5)</td>
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<tr>
<td>C(8)-O(3)</td>
<td>1.284(5)</td>
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<tr>
<td>C(6)-C(5)</td>
<td>1.383(7)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.390(7)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1  #2 -x+2, y-1/2, -z+1/2
#3 -x+2,y+1/2,-z+1/2
The unit cell structure of the complex has been shown in Fig.5.6. The structure shows that the butoxy group from the ligand is lost during the formation of the complex and phthalic acid acts as a bridging ligand in the complex. Each copper (II) ion is coordinated with four phthalate ligands completing an octahedral structure with six O atoms. Out of the four phthalate two coordinates to the copper (II) through both O atoms of one carboxylate as chelate. These two chelating carboxylates are found to be in trans position to each other. Each of the other carboxylates (of these two phthalates) binds to another Copper (II) through only one O atom with the other O dangling as keto group. The other two trans coordination sites of the Copper (II) are fulfilled by carboxylate O atoms of phthalate of which the remaining carboxylates chelate to two Copper (II) ions. In this way a three dimensional network is generated where each phthalate acts as a bridge between two Copper (II) ions, coordinating to one Copper (II) by the monodentate carboxylate oxygen and to another Copper (II) by chelating carboxylate.
Fig. 5.7 ORTEP (30% probability) of two dimensional structure of bis(hydrogenphathalato)copper(II)

The two trans OCu(II)O angles created each by the two O atoms of a chelating carboxylate and the Copper(II) ion were found to be equal which is 53.19°. The other two OCu(II)O angles were of value 126.81°. Interestingly the axial Cu (II)-O bonds were not perfectly perpendicular to the plane of four equatorial O atoms from two chelating carboxylates. Each of the axial Cu (II)-O bonds were found to be tilted slightly towards one of the two equatorial chelating carboxylate pairs. The OCu(II)O angles involving one axial O atom and the O atoms from one pair of chelating carboxylate are 92.67° and 90.99° while these angles with the other pair of carboxylate are 89.01° and 92.67°.

The distance between the two Cu(II) ion bound O atoms belonging two same carboxylate is 2.216 Å while the distance between two O atoms (on the same side of the coordination core) belonging to two different carboxylates is 4.22 Å. Hence, the equatorial O₄ core around the Cu (II) ion in the complex is rhombohedral.
The coordination of two carboxylic groups of a phthalate to two different Copper (II) finally gives rise to a polymeric structure. Fig.5.7 shows the two dimensional structure of the polymeric system. In the three dimensional structure shown in Fig.5.8 specific holes has been clearly visualized.

Fig. 5.8: ORTEP (30% probability) representation of complex showing 3 dimensional polymeric structure.
5.3.4 EPR Study of bis(hydrogenphathalato)copper(II):

The X – band EPR spectra of the complex was recorded as the polycrystalline sample at room temperature. The EPR spectrum has been shown in Fig.5.4. The $g_{iso}$ value and geometric parameter $G$ i.e. the measurement of exchange interaction between the copper centers were evaluated by using the expression [36]

$$g_{iso} = \frac{g_{ll} + 2g_{l}}{3}$$

$$G = \frac{g_{ll} - 2.0023}{g_{l} - 2.0023} = \frac{4K_{ll}^{2} \Delta E_{xx}}{K_{ll}^{2} \Delta E_{xy}}$$

The calculated value of $g$ tensor parameter were $g_{ll} = 2.63$ and $g_{l} = 2.47$. Hence $g_{ll} > g_{l} > 2.0023$ which reveals that $d_{x^{2}-y^{2}}$ is the ground state [37]. The value of $G$ was calculated to be 1.34 which means $G$ is less than 4 indicating effective interaction between the copper centers [38].

![EPR spectrum of bis(hydrogenphathalato)copper(II)](image-url)
5.3.5 Cyclic voltammetric study of bis(hydrogenphathalato)copper(II):

The cyclic voltammogram of the copper complex was recorded in water using platinum disc as working electrode and Ag–AgCl as the reference. One sharp oxidation peak was observed at potential 166.6 mV and one reduction peak at potential 54.9 mV. The redox couple should be due to Cu (II)/Cu (I) redox process. The cyclic voltammogram has been shown in Fig 5.10. The peak potential difference is 219 mV and redox potential is calculated as +057 mV. From the figure as well as the peak potential difference value it can be said that a reversible cyclic voltammogram is obtained.

![Cyclic voltamogram of bis(hydrogenphathalato)copper(II)](image)

**Fig.5.10:** Cyclic voltamogram of bis(hydrogenphathalato)copper(II)

We have also recorded cyclic voltammogram of the copper complex in different micellar medium in order to investigate the effect of charge nature of the medium on the redox potentials. The effect of positive and negative charge of the medium provided by
CTAB and SDS micelles respectively together with the neutral micellar medium provided by TX-100 on the cyclic voltammogram of the copper complex is obvious as shown in Fig. 5.11. In positive CTAB the oxidation potential was found to be at 451.3 mV, in negative SDS the oxidation potential was found to be at 147.5 mV while 143.9 mV was observed at oxidation potential in TX-100 micelle. The high positive potential in CTAB compared to that in SDS is due to the fact that Cu (II) state shall be relatively unstable in positive CTAB compared to that in SDS due to electrostatic reason. Hence Cu (II) to Cu (I) process is more favored in positive CTAB than in negative SDS and hence much higher positive potential was observed in CTAB. TX-100 being neutral the oxidation potential is found to be in between and close to that in SDS.

![Cyclic voltammograms of bis(hydrogenphthalato)copper(II) in different 1% (w/v) micellar solution using Pt disc as working electrode, Ag-AgCl as the reference and NaNO₃ (0.1 M) as the supporting electrolyte.](Fig.5.11)
5.4 SOD activity:

The SOD activity of the compound was tested spectrophotometrically by NBT assay method employing KO$_2^-$ as the source of superoxide radical but the superoxide scavenging activity of the complex was found to be very poor.

5.5 Conclusion:

A novel polymeric Cu (II) compound was obtained by the reaction of Cu (II) chloride dehydrate and 4-(2-butoxycarbonyl) benzoic acid. The crystal structure of this compound reveals that in its three dimensional network some specific holes are present which might be helpful for future catalytic study.
5.6 References: