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A Study of Spectroscopic and Electrochemical Investigations of Novel Coordination Polymer of Bis(Hydrogenphthalato)Copper (II)

Anupama[1]* Dr. Parveen[2]

[1] Research Scholar of OPJS University, Churu, Rajasthan

[2] Associate Professor, OPJS University, Churu, Rajasthan

Abstract – Cu buildings are presumably the most concentrated metal edifices having significance in a wide assortment of fields, for example, catalysis, biomimetics, spectroscopy, attraction, fluid gem, essential coordination science and so on. Progress metal edifices, for example, Cu buildings as impetuses have gotten much consideration in light of their relatively selective organic capacity in living frameworks. Cu (II) buildings have been known for their basic decent variety and practical models for the dynamic focuses of copper containing redox catalysts. The development of a biomimetic sensor is an impressive test in the improvement of diagnostic systems for the assurance of different analytes. However, provides details regarding copper buildings as cathode adjusting specialists is not very many because of the flimsiness caused by the changed structure amid redox process. Thus finding another copper intricate as terminal altering operator for recognition of analytes involves significance. In this paper there is an endeavor to orchestrate a polymeric copper compound shaped from copper (II) chloride and a natural ligand, 4 (2-butoxycarbonyl) benzoic corrosive which was described by UV-Visible, EPR, Cyclic voltametry and X-beam diffraction examines. The compound was tried for superoxide dismutase action and its micellar connection was contemplated by cyclic voltammetrically.

Keywords: spectroscopic, electrochemical investigations, polymer, bis(hydrogenphthalato)copper (ii)

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1. INTRODUCTION

Copper (II) buildings with natural acids and other benefactor ligands exists widely in living life forms, assuming an essential job in a huge scope of concoction and biochemical synergist systems (Pederson and Aust, 1973). In light of the reactant and bioinorganic importance the science of progress metal buildings has gotten extensive consideration. Such edifices are additionally essential because of their potential organic exercises, for example, antibacterial and antimalerial and antitumor (Fridovich, 1978, Handrail and Railing, 1980). As of late a few works have showed up concerning models of copper compounds (Liczmanski, et. al., 1994, Cover, et. al., 1987). This developing enthusiasm for copying the dynamic locales of metalloproteins has a noteworthy commitment to the improvement of new thoughts and patterns in coordination science. The dynamic restricting site of Cu could be connected in very effective and synergist response by utilizing an assortment of coordination potential outcomes, for example, the fluctuation and adaptability of ligands in organically important coordination circle (Burry, et. al., 1989). Since changes in coordination geometry because of the adaptability of the coupling capacity of ligands can prompt a vacant position at the metal particle site, these might be valuable for synergist response to happen (Bijloo, et. al., 1990).

Coordination polymers, that are metal-natural structures, are another class of natural - inorganic half and half materials dependent on metal particles facilitated by natural ligands with all around characterized coordination geometry. The field of coordination polymers has been widely examined in the course of recent decades with an attention on practical material research and gem designing. They have been looked into in the most recent decade due to their multifunctional properties and huge potential applications in numerous fields, for example, catalysis, attractive gadgets, partition, sub-atomic acknowledgment, non-straight optics, hydrogen stockpiling and so on (Bhirud and Srivastava, 2011, Kimura, et. al., 1994). By choosing suitable metal particles and natural linkers, coordination polymers with different structures, for example, 1D chains stepping stool (Oberley & Buettner 1979, Steink_hler, et. al., 1990), 2D matrices (Iakovidou, et. al., 2001) and 3D systems (Patole, et. al., 2001) can be gotten. Polycarboxylic acids speak to supramolecular connectors that can produce vast systems and metal-natural structures (Patole, et. al., 2001). The carboxylate gathering may introduce different coordination modes, prompting the arrangement of mono-atomic, di - atomic, metal-natural systems or coordination polymers (Ferrari, et. al., 2002).On the other hand precious stone building is pulling in enthusiasm from both the engineered courses and the specialty of auxiliary plan (Sun, et. al., 2000). Among the different viable uses of coordination polymer the hydrogen stockpiling presents a genuine logical test to the researchers is as yet an unsolved issue.

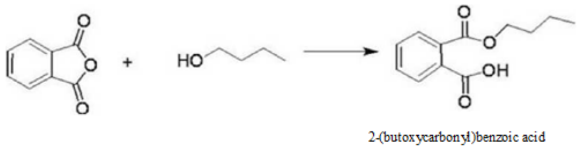
2. METHODOLOGIES

The instrumentation subtle elements and trial systems utilized are given in Chapter 2. The points of interest of synthetics utilized are recorded in area 2.2 of Chapter 2.

2.1. Synthesis:

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, 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 recrystallized from methanol. The synthetic path for the ligand (L) has been shown in scheme 4.1 below



Scheme 1: Synthetic path for the ligand (L)

The yield of the product was found to be 84% and the melting point of the compound is 178 °C.

2.1.2 FTIR analysis of L

FTIR spectrum of L was recorded in KBr pallet. Peaks were observed at 3474.4 cm^{-1} due to u_{O-H} stretching, 1724 cm^{-1} due to $u_{c=o}$ stretching, 1417 cm^{-1} due to aromatic c=c stretching, 1124cm^{-1}& 1293.4 cm^{-1} due to u_{c-o} stretching and 2962.6 cm^{-1} due to u_{C-H} stretching of the aromatic ring. The spectrum has been shown in Figure 1

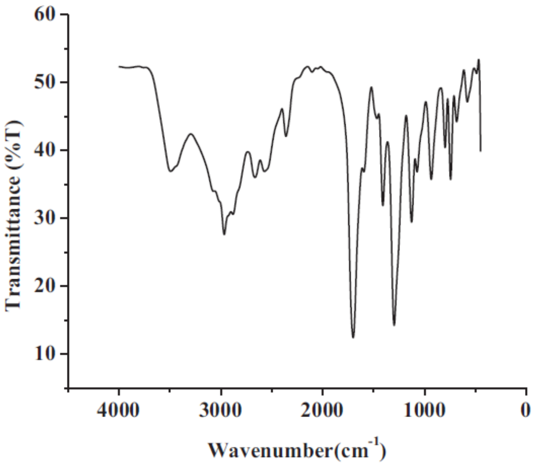


Figure 1: FTIR of L in KBr

2.2.1.2 ^{1}H NMR analysis of L:

^{1}H NMR of L was recorded in CDCl$_3$ on a 300MHz ^{1H} NMR machine. Chemical shift values were reported as 8 in ppm with TMS as standard. The ^{1}H NMR spectrum has been shown in Figure 2. Peaks were observed at 8: 7.99-7.47 (m, 4H), 4.17(m, 2H), 67-1.48(m, 2H), 1.42-1.30(m, 2H), j=7.2 (t, 3H).

2.2.1.1 FTIR examination of L:

FTIR range of L was recorded in KBr bed. Pinnacles were seen at 3474.4 cm-1 because of uO-H extending, 1724 cm-1 due to uc=o extending, 1417 cm-1 because of sweet-smelling c=c extending, 1124cm-1 and 1293.4 cm-1 due to uc-o extending and 2962.6 cm-1 because of uC-H extending of the sweet-smelling ring. The range has been appeared in Figure 1.

2.2.2 Synthesis of the copper (II) complex

To an answer of copper (II) chloride dihydrate (0.170g,1mmol) in methanol (10mL), an answer of 4(2-butoxy carbonyl benzoic corrosive) (0.348 g, 1 mmol) in methanol (10 mL) was included dropwise. The response blend was mixed at room temperature for 2 hours to get a blue shaded accelerate. The accelerate was separated and redissolved in 1:10 (v/v) methanol and water blend. Little blue shaded gems were acquired following 7 days. The precious stones were observed to be reasonable for single gem X-beam diffraction examine. Yield of the item was 70%.

3. RESULTS

3.1 UV/vis spectroscopic investigation

The UV/Vis range of the Cu(II) complex with 4(2 - butoxy carbonyl benzoic corrosive) was recorded in water. The range has been appeared in Figure 3. One expansive retention at 739 nm was seen which is trademark for d-d progress in copper edifices

(Tamboura, et. al., 2002). Another band in the UV area was seen at 393 nm. This progress ought to be expected to intra-ligand n-n* change. Another crest with high annihilation co-proficient was seen at 273 nm which can be ascribed to n-n* progress in benzene ring of the ligand (Tamboura, et. al., 2002).

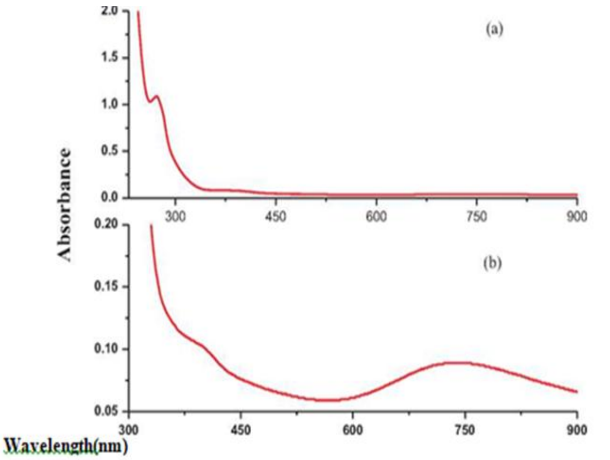
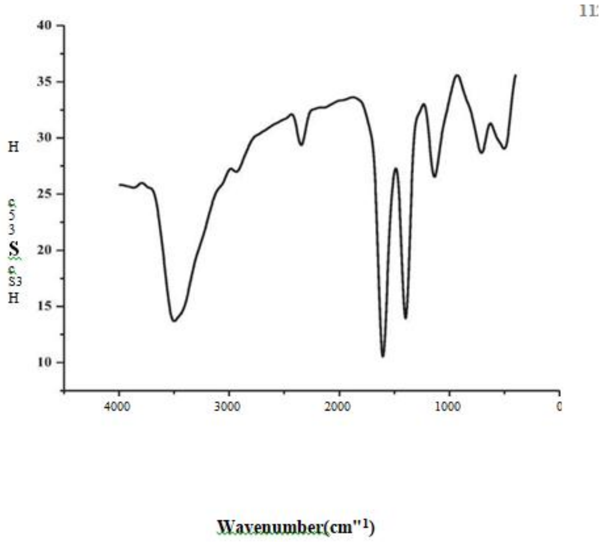


Figure 3. UV/vis spectra of bis(hydrogenphathalato)copper (II) in water when complex concentration is a) 10^{-4} M and b) 10-3M



3.2 FTIR ghastly Study of complex

FTIR range of complex was recorded in KBr bed appeared in figure 4. If there should arise an occurrence of the mind boggling it demonstrates trademark crests because of the ligation of carboxylate in its FTIR range. The pinnacle showing up in the district of 1494-1611 cm-1 can be credited to vasym(COO) vibrations while the crest in the range 1382-1396 cm-1 can be ascribed to vsym(COO) vibrations.

3.3 Single Crystal X-beam investigation of bis(hydrogenphathalato)copper(II)

Basic portrayal of the complex is appeared in Figure 4. Crystallographic information for the complex are introduced in Table 1 whereas chose bond separations and edges are abridged in Table 2. The complex takes shape in the monoclinic P21/c space gathering.

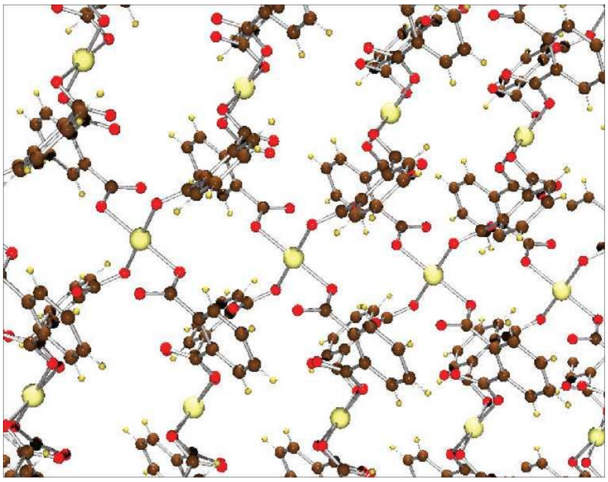


Figure 4 : Structural representation of bis(hydrogenphthalato) copper(II)

Formula	C16 H8 CuO14
M	487.77
crystal system	Monoclinic
space group	P21/c
T,K	296(2)K
X (Mo Ka), A	0.71073 A
a, A	11.0782(11)
b, A	6.6421(7)
C, A	12.1644(12)
a, deg	90
V, A^3	877.40(14)
z	2
F(000)	490.0
-3 **^calcd.** g cm	1.846
Theta range for data collection	3.42 to 39.99 deg.
Completeness to theta = 39.99	94.2 %
Limiting indices	**-20<=h<=19, -9<=k<=12, -21<=l<=19**
Crystal size	0.34 x 0.28 x 0.16 mm

Refinement method	Full-matrix least-squares on F^2
j (Mo Ka), mm^{-1}	1.327
collected reflns	16741
unique reflns	4417
Pint	0.0302
Final R indices [I>2sigma(I)]	R1 = 0.0809, wR2 = 0.1944
R indices (all data)	R1 = 0.1280, wR2 = 0.2376
GOF on F^2	1.064
Extinction coefficient	0.041(12)
Apmax,minj^{Q} A	2.900 and -4.800

$wR_2 = \{E[w(F_0^2-F_c^2)^2] / E[w(F_0^2)^2]\}^{1/2}$ where $w = 1 / [E^2(F_o^2) + (aP)^2 + bP]$ with P is $[2P_C^2 + Max(F_0^2,0)] / 3$

Table 2: Bond lengths [A] and angles [deg] for bis(hydrogenphathalato)copper(II)

Cu(1)-O(3)	1.943(3)	C (7)-O(2M)	1.238(6)	C(3)-C(2)-C(8)	119.9(4)
Cu(1)-O(3)#1	1.943(3)	C (7) -O(4)#3	1.288(4)	C (7)#2-O(4)-	109.4(3)
Cu(1)-O(4)	1.973(3)	C (4)-C(4)	1.382(8)	O(2)-C(8)-O(3)	124.8(3)
Cu(1)-O(4)#1	1.973(3)	O (3)-Cu(1)-O(3)#1	179.999(1)	O (2) -C(8)-C(2)	119.8(4)
C(1)-C(2)	1.391(4)	O(3)-Cu(1)-O(4)	91.04(13)	O (3) -C(8)-C(2)	114.4(4)
C(1)-C(6)	1.398(4)	O(3)#1 -Cu(1)-O(4)	88.97(13)	C (8) -O(3)-Cu(1)	119.3(3)
C(1)-C(7)	1.498(4)	O(3)-Cu(1)-O(4)#1	88.96(13)	C (4) -C(6)-C(1)	120.6(4)
C(2)-C(3)	1.399(6)	O(3)#1-Cu(1)-	91.03(13)	C (2) -C(3)-C(4)	120.4(4)
C(2)-C(8)	1.499(4)	O(4)-Cu(1)-O(4)#1	179.999(1)	O(2M)-C(7)-	123.9(4)
O(4)-C(7)#2	1.287(4)	C (2)-C(1)-C(6)	119.4(4)	O (2 M)-C(7)-C(1)	119.6(4)
C(8)-O(2)	1.241(4)	C (2)-C(1)-C(7)	122.4(3)	O (4)#3-C(7)-C(1)	116.4(4)
C(8)-O(3)	1.284(4)	C (6)-C(1)-C(7)	118.1(3)	C (4)-C(4)-C(3)	119.7(4)
C(6)-C(4)	1.383(7)	C (1)-C(2)-C(3)	119.6(4)	C (4)-C(4)-C(6)	120.3
C(3)-C(4)	1.390(7)	C (1)-C(2)-C(8)	120.4(3)		

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

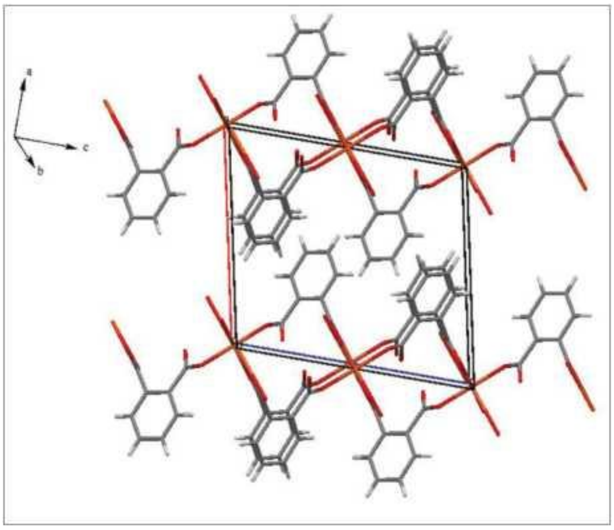


Figure 6. View of bis(hydrogenphathalato)copper(II)with the unit cell.

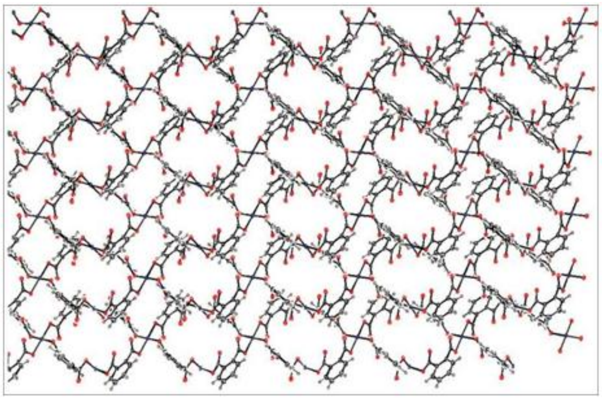


Figure 7: ORTEP (30% probability) of two dimensional structure of bis(hydrogenphathalato) copper (II)

The unit cell structure of the complex has been appeared in Figure 6. The structure demonstrates that the butoxy assemble from the ligand is lost amid the arrangement of the complex and phthalic corrosive goes about as a crossing over ligand in the complex. Each copper (II) particle is facilitated with four phthalate ligands finishing an octahedral structure with six O molecules. Out of the four phthalate two directions to the copper (II) through both O iotas of one carboxylate as chelate. These two chelating carboxylates are observed to be in trans position to one another. Every one of alternate carboxylates (of these two phthalates) ties to another Copper (II) through just a single O particle with the other O dangling as keto gathering. The other two trans coordination locales of the Copper (II) are satisfied via carboxylate O molecules of phthalate of which the rest of the carboxylates chelate to two Copper (II) particles. Along these lines a three dimensional system is produced where each phthalate goes about as an extension between two Copper (II) particles, planning to one Copper (II) by the monodentate carboxylate oxygen and to another Copper (II) by chelating carboxylateThe two trans OCu(II)O points made each by the two O molecules of a chelating carboxylate and the Copper(II) particle were observed to be equivalent which is 43.19o. The other two OCu(II)O points were of esteem 126.81o. Strangely the pivotal Cu (II)- O bonds were not splendidly opposite to the plane of four tropical O iotas from two chelating carboxylates. Every one of the pivotal Cu (II)- O bonds were observed to be tilted marginally towards one of the two tropical chelating carboxylate sets. The OCu(II)O edges including one pivotal O iota and the O particles from one sets of chelating carboxylate are 92.67° and 90.99° while these points with the other combine of carboxylate are 89.01o and 92.67o.

The separation between the two Cu(II) particle bound O molecules having a place two same carboxylate is 2.216 A while the separation between two O iotas (on a similar side of the coordination center) having a place with two diverse carboxylates is 4.22 A.

Henceforth, the tropical O4 center around the Cu (II) particle in the complex is rhombohedral.

The coordination of two carboxylic gatherings of a phthalate to two diverse Copper (II) at long last offers ascend to a polymeric structure. Fig.4.7 demonstrates the two dimensional structure of the polymeric framework. In the three dimensional structure appeared in Fig.4.8 particular gaps has been unmistakably imagined

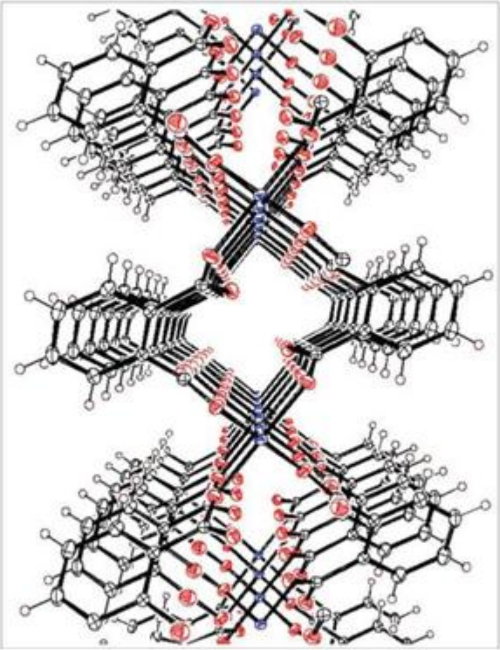


Figure 8: ORTEP (30% probability) representation of complex showing 3 dimensional polymeric structure.

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 Figure 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.

$$g_{iso} = \frac{(g_{\parallel} + 2g_{\perp})}{3}$$

$$G = \frac{(g_{\parallel} - 2.0023)}{(g_{\perp} - 2.0023)} = \frac{4K_{\parallel}^{2}\,\Delta E_{xz}}{k_{\perp}^{2}\,\Delta E_{xy}}$$

The calculated value of g tensor parameter were g_{II} =2.63 and gx = 2.47. Hence g_{II}>gx> 2.0023 which reveals that d $_{x}2_{-}y2$ is the ground state (Liu, et. al., 1997). The value of G was calculated to be 1.34 which means G is less than 4 indicating effective interaction between the copper centers (Tabbi, et. al., 1997).

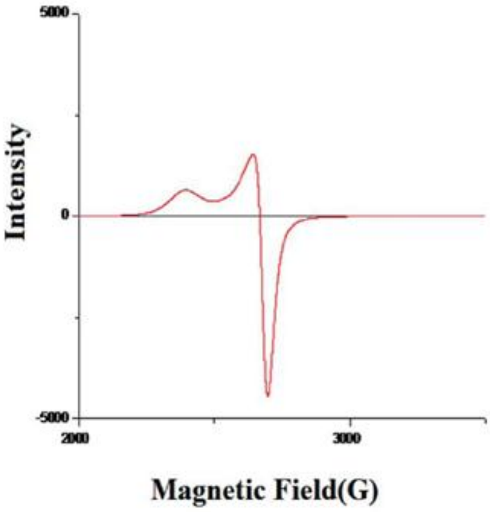


Figure 9: EPR spectrum of bis(hydrogenphathalato) copper(II)

3.5 Cyclic voltammetric investigation of bis(hydrogenphathalato)copper(II):

The cyclic voltammogram of the copper complex was recorded in water utilizing platinum circle as working anode and Ag-AgCl as the reference. One sharp oxidation crest was seen at potential 166.6 mV and one decrease top at potential 44.9 mV. The redox couple ought to be because of Cu (II)/Cu (I) redox process. The cyclic voltammogram has been appeared in Figure 10. The pinnacle potential distinction is 219 mV and redox potential is computed as + 047 mV. From the figure and also the pinnacle potential contrast esteem it tends to be said that a reversible cyclic voltammogram is acquired.

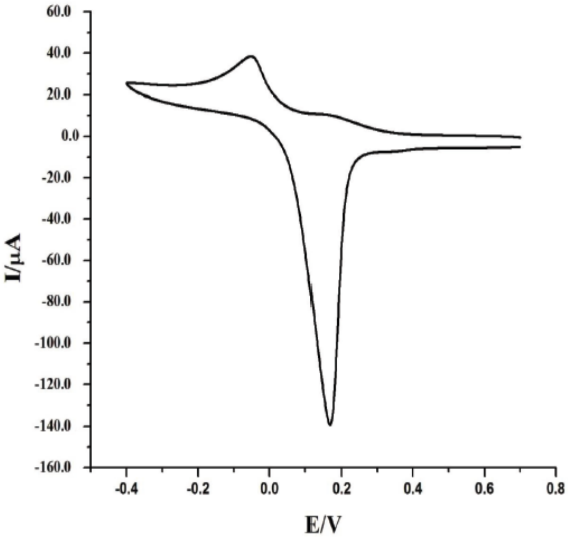


Figure 10: Cyclic voltamogram of bis (hydrogenphathalato)copper(II)

We have additionally recorded cyclic voltammogram of the copper complex in various micellar medium with the end goal to examine the impact of charge nature of the medium on the redox possibilities. The impact of positive and negative charge of the medium given by CTAB and SDS micelles separately together with the impartial micellar medium given by TX-100 on the cyclic voltammogram of the copper complex is clear as appeared in Figure 11. In positive CTAB the oxidation potential was observed to be at 441.3 mV, in negative SDS the oxidation potential was observed to be at 147.4 mV while 143.9 mV was seen at oxidation potential in TX-100 micelle. The high positive potential in CTAB contrasted with that in SDS is because of the way that Cu (II) state will be moderately precarious in positive CTAB contrasted with that in SDS because of electrostatic reason. Henceforth Cu (II) to Cu (I) process is more supported in positive CTAB than in negative SDS and thus considerably higher positive potential was seen in CTAB. TX-100 being nonpartisan the oxidation potential is observed to be in the middle of and near that in SDS

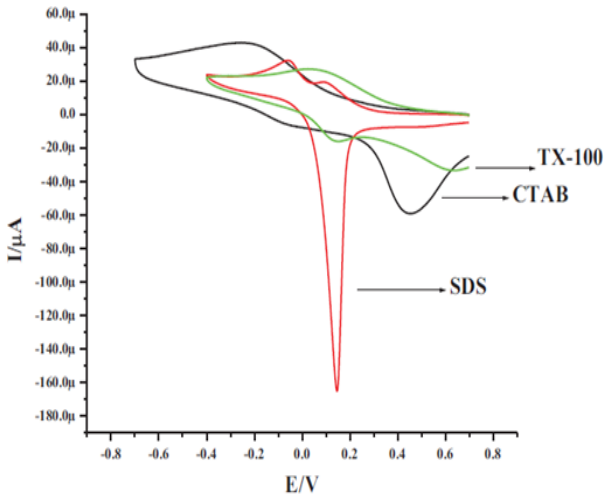


Figure 11: Cyclic voltammograms of bis(hydrogenphathalato) copper (II) in different 1% (w/v) micellar solution using Pt disc as working electrode, Ag-AgCl as the reference and N_aNO_3 (0.1 M) as the supporting electrolyte.

3.6 SOD movement

The SOD action of the compound was tried spectrophotomrtrically by NBT measure strategy utilizing KO2-as the wellspring of superoxide radical however the superoxide scavenging movement of the complex was observed to be extremely poor.

CONCLUSION

A novel polymeric Cu (II) compound was gotten by the response of Cu (II) chloride dry out and 4-(2-butoxycarbonyl) benzoic corrosive. The gem structure of this compound uncovers that in its three dimensional system some particular openings are available which may be useful for future synergist consider.

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Corresponding Author

Anupama*

Research Scholar of OPJS University, Churu, Rajasthan