Synthesis, Spectral Characterization and Quantum Chemical Calculations on Pyridine Cyclodiphosph(V)Azane Derivative and Its Cu(II) Complex

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Novel dioxocyclodiphosph(V)azane of *o*-aminopyridine (H₂L), was prepared and their coordinating behavior towards the transition metal ion Cu(II) was studied. The structures of the isolated products are proposed based on elemental analyses, IR, UV–Vis., ¹H NMR, ³¹P NMR, mass spectra, effective magnetic susceptibility measurements and thermogravimetric analysis (TGA). The coordination polyhedra of the eight donor atoms about both Cu(II) atoms are best described as distorted dodecahedral. Computational studies have been carried out at the DFT-B3LYP/6-31G(d) level of theory on the structural and spectroscopic properties of L and its binuclear Cu(II) complex. Different tautomers of the ligand were optimized at the *ab initio* DFT level. Keto-form structure is about 30.450 kcal/mol more stable than the enol form (taking zpe correction into account). Simulated IR frequencies were scaled and compared with that experimentally measured. TD-DFT method was used to compute the UV-VIS spectra which show good agreement with measured electronic spectra.

Keywords: dioxocyclodiphosph(V)azane; o-aminopyridine copper (II) complex; B3LYP; TD-DFT.

1. INTRODUCTION

In recent years, the structural feature of four-membered N_2P_2 ring compounds in which the coordination number of P varies from three to five have attached considerable attention [1,2]. Heterocycles with P–C, P–N, P–O, and P–S bonds, in addition to their great biochemical and commercial importance [3,4], play a major role in some substitution mechanisms heterocycles had been found to be potentially carcinostatics [3] among other pharmacological activities. The

introduction of tervalent P centers in the ring enhanced the versatility of the heterocycles in complexing with both hard and soft metals. Since the tervalent P centers could stabilize transition metals in low oxidation states [3,4], such complexes could be potential homogeneous or phase-transfer catalysts in various organic transformations [3]. There is considerable current interest in compounds containing spiro and ansa organic P rings [5]. Although the ammonolysis of some 1,3-diaryl-2,4dichlorocyclodiphosph(V)azans had been investigated in some detail, little was known about the interaction of hexachlorocyclodiphosph(V)azanes with bifunctional reagents. The reaction of bifunctional reagents with cycloidphosph(V)azanes could give rise in principle to four types of structures named spiro, ansa, cross-linking, and only one functionality attached, while the other remains free. Spiro, ansa, and cross linking structures of phosphazanes were now well studied spectroscopically, and crystallographically The reaction synthetically, [5]. of hexachlorocyclodiphosph(V)azanes with amino compounds, active-methylene-containing compounds, and bifunctional reagents had been investigated in some details [6,7]. Sulfonamides were the oldest class of antimicrobials and were still the drug of choice for many diseases such as cancer and tuberculosis [8]. Cyclophosphamide and its derivatives were examples of phosphorus compounds which were one of the most effective anticancer agents with proven activity against a large variety of human cancers [9]. Hexachlorocyclodiphosph(V)azanes of sulfonamides and their complexes had been prepared [6,10–12]. In continuation to our interest to prepare hexachlorocyclodiphosph(V)azane of sulfa drugs [13], the present paper aims chiefly to prepare dioxocyclophosph(V)azane of oaminopyridine H₂L. The behaviour of this ligand toward copper (II) ion was studied. The characterization of the prepared compounds was performed using different physicochemical methods.

2. EXPERIMENTAL

Melting points (°C, uncorrected) were determined in open capillaries on a Gallen Kemp melting point apparatus. Elemental analysis (C, H, N and P) were performed on Carlo Erba 1108 Elemental Analyzer. The bromrine content was determined by the Schöninger method, Analysis of the copper complex started with decomposition of the complex with concentrated nitric acid. The resultant solution was diluted with distilled water, filtered to remove the precipitated ligand. The solution was then neutralized with aqueous ammonia solution and the metal ions titrated with EDTA. The infrared spectra were recorded on a Shimadzu FT-IR spectrometer using KBr disks. Electronic spectra were recorded for solution of the ligand, L in DMF, and for the metal complexes as Nujel Mull on a Jasco UV–VIS spectrophotometer model V-550-UV–V1S. ¹H NMR spectra (in CDCl₃) were recorded on Bruker Ac-300 ultra-shield NMR spectrometer at 300 MHz, using TMS as internal standard. Electron impact Mass Spectra were recorded on a Shimadzu Gc-Ms-Qp 5000 instrument. ³¹P NMR spectra were run, relative to external H₃PO₄ (85%), with a Varian FT-80 spectrometer at 36.5MHz. The mass spectrum of H₂L ligand was performed using a Shimadzu-Ge-Ms-Qp 100 EX mass spectrometer using the direct inlet system. The molar conductance measurement was carried out using a Sybron-Barnstead conductometer. Magnetic susceptibility of copper complex was measured at room temperature using the Faraday method with a Cahn-Ventron RM-2 balance standardized with HgCo(NCS)₄. Thermogravimetric analysis was performed under a nitrogen atmosphere using a Shimadzu TGA–50H with a flow rate of 20 ml min⁻¹.

2.1 Syntheses

2.1.1. Synthesis of ligand (H_2L)

The solid of 2–aminopyridine (0. 2 mol; 18.8 g) was added in small portions to a well stirred solution of the 1,3–(di–o–pyridyl)–2,4–(dioxo)–2',4'–dichlorocyclodiphosph(V)-azane (0.1 mol; 34.9 g) in 100 ml acetonitrile over a half–hour period. After the complete addition, the reaction mixture was heated under reflux for 10 h with continuous stirring. After the completion of the reaction (HCl gas ceased to evolve), the reaction mixture was cooled to room temperature and the solid obtained was filtered, then washed several times with acetonitrile and dry diethyl ether to give crystalline 1,3–(di–o–pyridyl)–2,4–(dioxo)–2',4'–bis(2–iminopyridine)cyclodiphosph(V)azane (H₂L).

2.2. Syntheses of copper complex

The copper complex was prepared by adding dropwise a hot aqueous (60°C) solution (100 mL) of CuBr₂ (4.46 g; 0.02 mol) to a solution of H₂L (4.64 g; 0.01 mol) in tetrahydrofuran (THF) (50 mL) while stirring continuously. After complete addition of the CuBr₂ solution, the reaction mixture was heated under reflux for about 18 h under dry conditions. The complex obtained was filtered, washed with diethylether, and THF and then dried in vacuo.

3. COMPUTATIONAL METHODS

All quantum chemical calculations were performed using the Gaussian09 and Gaussian03 suite of programs [14, 15]. Geometry optimization of the ligand have been performed using the *ab initio* Density Functional Theory (DFT) at the B3LYP functional [15-18] in conjunction with the 6-31G(d) basis set. For each stationary point, we carried out a force constant harmonic frequency calculation at the same levels to characterize their nature as minima or transition states and to correct energies for zero-point energy and thermal contribution. The Frequencies are scaled by a factor of 0.98. The vibrational modes were animated using the ChemCraft program [19]. Natural charges were computed within full Natural Bond Orbital analysis, using NBO implemented in Gaussian 09 [15]. The vibrational modes were examined by using the ChemCraft program [20]. Because of the large size of the binuclear copper complex and also the unavailability of the Cu element database in the G09 package, molecular mechanics have been used to optimize the binuclear Cu complex structure.

4. RESULTS AND DISCUSSION

4.1. The ligand

4.1.1. Experimental studies

The novel dioxocyclophosph(V)azane of o-aminopyridine (H₂L) is prepared and subjected to elemental analyses, mass and IR spectral analyses. The results of elemental analyses(C, H, N) with molecular formula and the melting point are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula and the melting point is sharp indicating the purity of the prepared Schiff base.

Table 1. Elemental analyses, melting points, colours and composition of ligand (H_2L) and its corresponding copper(II) complex.

Compd. No.	[M.p.	Color	Elementa	l analyses	Found (Calc.), %		
M.F. (M.Wt)] (°C)		Cu	С	Н	Ν	Р	Br
H_2L	223	White	-	51.69	3.88	24.02	13.29	-
$C_{20}H_{18}N_8O_2P_2$ (464.10)				(51.73)	(3.91)	(24.13)	(13.34)	
$C_{20}H_{16}Br_2Cu_2N_8O_2P_2$	>300	Dark	16.92	32.06	2.15	14.86	8.18	21.24
(749.24)		green	(16.96)	(32.06)	(2.15)	(14.96)	(8.27)	(21.33)
$[Cu_2LBr_2]$								

The structure of H_2L is also confirmed by UV, IR, ¹H, ³¹P NMR and mass spectroscopic data, which will be discussed in detailed manner with metal complexes latter.

The UV spectrum (Figure 1a) of the ligand in DMF solvent showed absorption band at 272 nm, which are due to the electron delocalization within the four membered ring of the dimeric structure for the ligand [14]. The IR spectrum for the ligand H₂L (Figure 2a), showed the characteristic bands of v(P–Cl), v(P–N), v(SO₂), v(C=N) and v(NH) which are summarized in Table 1.



Figure 1. Electronic spectrum of (a) Ligand (H₂L) and (b) Cu(II) complex.



Figure 2. IR spectrum of (a) Ligand (H₂L) and (b) Cu(II) complex.

Table 2. Characteristic IR bands^a of the ligand (H_2L) and its Cu(II) complex [Cu₂LBr₂].

Ligand (H ₂ L)	[Cu ₂ LBr ₂]	assignments
3275br	_	v(NH)
3160m	_	v(P–NH)
1366m	1333m (1366.0) vs	v(C–N)
-	288w (286.3)	v(Cu–O)
-	365m (356.5)	v(Cu–N)
1225m	1225m (1022)	v(P–N) _{cyclic}
1000m	1008m (997.0)	v(P–N) _{linear}
1013m	1012m (1001.5)	v(P–N–P)
815m	813m (807.5)	v(N–P–N)
1296m	1296m (1310.0)	v(P=O)

Where br = broad, s = strong, m = medium, w = weak

^a computed frequencies are given between parentheses.

The ¹H NMR spectrum (Figure 3) of the ligand H₂L revealed its formation by the presence of– NH proton signal at $\delta = 5.37$ ppm. This is further supported by the appearance of stretching vibration band v(NH) imine at 3364 cm⁻¹. Also, the ¹H NMR of the ligand exhibits signals at δ 6.47-7.23 (m, 16H, pyridine) ³¹P NMR of the ligand (Figure 4) records a signal at $\delta = 25.79$ ppm, which supports the phosphazo four membered ring[14].



Figure 3. (a) ¹H NMR spectrum for H_2L ligand in DMSO. (b) ¹H NMR spectrum for H_2L ligand in DMSO+D₂O.



Figure 4. ³¹P NMR spectrum for H₂L ligand.

The electron impact mass spectrum of the free ligand (Figure 5a), confirms the proposed formula by showing a peak at 550 u corresponding to the ligand moiety $[(C_{24}H_{20}N_6O_6P_2)]$ atomic mass 550 u]. The series of peaks in the range, i.e. 67, 76, 93, 124, 134, 216, 432, 448 and 464 u, etc., may be assigned to various fragments and their intensity gives an idea of stability of fragments. The mass spectrum of the ligand (H₂L) shows the fragmentation pattern in Fig. 6.



Figure 5. Mass spectrum of (a) Ligand (H₂L) and (b) Cu(II) complex.

4.1.2. Computational studies

Since single crystal x-ray structure for the novel dioxocyclophosph(V)azane of *o*aminopyridine ligand is not available, quantum chemical calculations were utilized to find the geometry optimized structures for the H₂L at B3LYP/6-31G(d) quantum mechanical method. Fig. 7 shows the optimized structure of the H₂L at B3LYP/6-31G(d). An inspection of the resulting structure easily shows two close contacts H-bonding interactions. Table S1 in the supplementary material presents computed geometrical parameters of L. Although the system is big (32 non-hydrogenic atoms) the optimization process goes smoothly till reached a local minimum after 29 steps as shown in Figures 8 and 9. Figure S1 and S2 in the supplementary material present the structure of the ligand H_2L , showing the atom symbols and atomic numeration respectively. Since dispersion energies do not play a considerable role in these types of structure, electron correlations are not so important consequently DFT methods would provide a good quality structures. The P_2N_2 ring is almost planar and P-N bonds in the ring are not of equal length. The average bond length is 1.754 Å. The exocyclic phosphorus-nitrogen groups have exo orientation relative to the phosphazane ring.



Figure 6. Fragmentation of the mass spectrum of the H₂L ligand.

The phosphoimino bonds are much shorter than P–N distances in the P_2N_2 ring (1.743 vs. 1.792 Å) which confirms the multiple PN connection in P=N-pyridine derivative. Our structural data given in

Table S1 in Supplementary material agrees well with the available x-ray data on P_2N_2 ring-containing compounds [21,22].



Figure 7. The optimized structure of the H_2L at B3LYP/6-31G(d).



Figure 8. The optimization pass way of the H_2L at B3LYP/6-31G(d).



Figure 9. The optimization steps vs deviation from targeted minimum.

Simulated IR spectra of H_2L were calculated at the level B3LYP/6-31G(d). Fig. 10 displays the simulated IR spectra for the keto tautomer scaled by 0.97 as a scale factor [23]. Inspection of the calculated frequencies shows that they agree with the experimentally measured IR spectra Fig.2a and Table 2. The vibrational frequencies were animated with ChemCraft to assign frequencies to their normal modes. The C=N stretching frequency measured as a medium peak around 1622 computed as a very strong peak at 1648.





Figure 10. Simulated IR spectrum of (a) keto-form of H₂L and (b) Cu(II) complex.

The electronic spectrum of L in DMF showed absorption bands at 274 nm regions which is due to intra ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions involving molecular orbital of the pyrimidine ring. DT-DFT calculations were done for the free ligand in the molecular gas state. The UV spectrum of L keto-form is shown in Fig. 1. The UV-VIS data is given in Figure 11. It shows a sharp band at 232 nm.



Figure 11. Simulated uv-vis spectrum of keto-form of H₂L.

Natural charges (Table 3) were computed within full Natural Bond Orbital analysis, using NBO implemented in Gaussian 09 [15]. Positive and negative charges are accommodated on some centers of the H₂L molecule. Positive charges are found on O, P, H and some C atoms. The highest positive charge is found on O (2.453), and the next highest charge is found on P (1.607). On the other hand, negative charges are on N and some C atoms. The highest negative is found on N (-1.121).

Atom	Charge	Atom	Charge	Atom	Charge
P1	1.603	N23	-1.123	H45	-0.225
N2	-1.122	N24	-1.127	H46	-0.294
P3	1.608	C25	-0.192	H47	0.256
N4	-1.143	C26	-0.313	H48	0.273
C5	0.123	C27	-0.203	H49	0.286
C6	-0.202	C28	-0.202	H50	0.256
N7	-1.204	C29	2.355		
N8	-1.123	H30	-0.873		
C9	-0.198	O31	2.422		
C10	-0.202	O32	2.543		
C11	2.351	H33	-0.424		
C12	-0.943	H34	0.273		
N13	-1.122	H35	-0.513		
C14	-0.873	H36	0.571		
C15	0.412	H37	-0.493		
C16	-0.374	H38	-0.322		
C17	0.573	H39	-0.941		
C18	-0.563	H40	-0.904		
C19	0.281	H41	-0.219		
C20	-0.542	H42	-0.287		
C21	-0.513	H43	-0.214		
C22	-0.323	H44	-0.213		

Table 3. Computed natural charge of all atoms in the H₂L



Figure 12. The electrostatic potential of the H_2L .

The electrostatic potential of the H_2L molecule as presented in Figure 12 also is in support with this argument.

Possibility of keto-enol tautomerism has been taken into account. The enol structure was computed and optimized at the same level. The keto structure is more stable than the enol form by about 31.576 kcal/mol. This difference is reduced to 30.446 kcal/mol if zpe correction has been taken into consideration. This large difference permits separable isomers. This allows tautomerization prior to complexation.

4.2. Characterization of copper(II) complex

4.2.1. Elemental analysis of the complex

The results of elemental analyses, Table 1 are in good agreement with those required by the proposed formulae.

4.2.2. IR spectra and mode of bonding

The IR spectra of the free ligand and copper complex (figure 2b) were obtained in the range $4000-400 \text{ cm}^{-1}$ and $400-200 \text{ cm}^{-1}$ (Table 2). The IR spectrum of the ligand shows a broad band at 3275 cm^{-1} , which can be attributed to v (NH) [14,24] group. This band disappears in copper complex, which can be attributed to the involvement NH in coordination. The broad bands observed at 1623 and 1596 cm⁻¹ are assignable to v(C=C) and v(C=N) of the pyridine ring, respectively. The band at 3198 cm⁻¹ are attributable to v(NH) mode, respectively. The weak band observed at 574 cm⁻¹ assigned to inplane ring deformation mode of the pyridine[25]. In the IR spectrum of the complex, IR band is observed at 345 cm⁻¹ which is attributed to the *v*(Cu–N) stretching vibration [26,27]. The computed frequencies are supporting the measured ones (Figure 13). Computed frequencies are given with the measured ones in Table 2. It is obvious that the computed frequencies agree well with the observed ones.

4.2.3. Computational studies

Because of the large size of the binuclear Cu complex and also the unavailability of the Cu element database in the G09 package, molecular mechanics have been used to optimize the binuclear Cu complex structure. Figure 13 shows the optimized structure of the binuclear Cu complex. The ligand behaves a tridentate from the enolic structure. The complex appeared in a square-planar structure. Coordination occurs from N where Cu-N bond length is 2.245. The Cu-Br of the coordinated bromide is a slightly longer (2.244 Å).



Figure 13. Optimized structure of the Cu(II) bi-nuclear complex at B3lyp/6-31G(d).

4.2.4. Molar conductance

The molar conductance value for the binuclear copper(II) complex (3.65 Ω^{-1} cm² mol⁻¹) in CHCl₃ solution suggests that the complex is non-electrolytic in nature[28].

4.2.5. Magnetic moments and electronic spectra

Copper(II) complex show room temperature magnetic moment 2.04 B.M., corresponding to one unpaired electron[29].

The visible spectrum of copper complex (Figure 1b) shows two absorption bands at 662 nm and 518 nm assignable to ${}^{2}B_{1}\rightarrow{}^{2}B_{2}$ and ${}^{2}B_{1}\rightarrow{}^{2}E$ transitions respectively, which indicates the possibility of square planar geometry of the metal complex [30]. TD-DFT calculations were performed to simulate the UV-VIS spectra of the Cu complex. This calculation results in 3 electronic transitions at 606.86, 575.97 and 518.82 nm. These values are comparable with the above mentioned observed bands of the square planner complex.

4.2.6. EPR spectrum of copper complex

The EPR spectrum of the Cu(II) complex was recorded in DMSO at 300 and 77 K (Fig. 14). The observed spectral parameters show $g_1(2.23) > g_{\perp}(2.10) > ge(2.0023)$ which is the characteristic of an tetrahedral geometry [31] The observed value for the exchange interaction parameter for the Cu(II) complex (G = 2.3) suggests that the significant exchange coupling is present and the misalignment is appreciable. The observed value of α^2 (0.82) of the complex is less than unity, which indicates the covalent character [32]. The orbital reduction factors K₁ and K_{\perp} estimated from the expression, K₁ =(g₁-2.0023) $\Delta E/8\lambda$, K_{\perp} = (g_{\perp}-2.0023) $\Delta E/2\lambda$, λ = -829 cm⁻¹ (spin–orbit coupling constant for the free ion). In case of a pure σ -bonding K₁ \cong K_{\perp} 0.78 whereas K₁ < K_{\perp} implies considerable in-plane π -bonding while for out of π bonding K₁ > K_{\perp}. For this complex, K₁ > K_{\perp} indicating poor in–plane π -bonding which is also reflected in β^2 values.



Figure 14. EPR spectrum of [Cu₂LBr₂] at 300 K in DMSO.

4.2.7. Thermal analysis

The TGA/DTA curves (Fig. 15) of the copper complex $[Cu_2LBr_2]$, reveal that the decomposition process proceeds via two main endothermic stages. The first step at 343 °C, is responsible for the elimination of four pyridine rings with mass losses 23.42% (calcd. 24.13%). The second event is a composite one with two mutually overlapping peaks at 422 and 458 °C. The mass loss for the second event amounts to 36.30% (calcd. 35.99%). The thermal decomposition proceeds with the formation of Cu as residue.

The kinetics parameters (Table 4) are calculated by using Coats–Redfern [33] and Horowitz– Metzger methods [34]. In [Cu₂LBr₂] complex, the values of activation energy increase on going from one thermal stage to another for a given complex, indicating that the rate of decomposition decreases in the same order. While, the values of the free activation energy ΔG^* increase significantly for the subsequent decomposition stages of a given complex. This is due to increasing the values of T ΔS^* significantly from one-step to another, which override the values of ΔH^* . This may be attributed to the structural rigidity of the remaining complex after the expulsion of one of the coordinated anions or water molecules, as compared with the precedent complex, which require more energy, T ΔS^* for its rearrangement before undergoing any compositional change. The positive ΔH^* values mean that the decomposition processes are endothermic.



Figure 15. TGA, DTG and DTA curves of [Cu₂LBr₂].

Table 4. Kinetic parameters, $(E^*, \Delta H^*, \Delta G^*, kJ/mol)$, A (s^{-1}) and ΔS^* (J/K mol); determined using Coats–Redfern method and Horowitz–Metzger methods of the copper(II) complex under study.

Complex	Decomp.	Coat	Coats–Redfern					Horowitz–Metzger				
	range	E*	А	ΔS^*	$\Delta \mathrm{H}^{\boldsymbol{*}}$	ΔG^*	E*	А	ΔS^*	$\Delta \mathrm{H}^{\boldsymbol{*}}$	ΔG^*	
[Cu ₂ LBr ₂]	30–91	23	3×10^{5}	-144	17	62	28	2×10^{5}	-134	22	64	
	91–215	34	2×10^{5}	-148	29	93	39	2×10^{5}	-142	33	96	
	215-350	56	2×10^{5}	-152	51	134	66	2×10^{5}	-132	62	144	
	350–512	174	3×10^{6}	-122	171	253	181	4×10^{6}	-127	182	264	
	725-862	292	7×10^{6}	-126	282	418	302	2×10^{7}	-118	302	432	

4.2.8. FAB mass, SEM, powder XRD and structural elucidation

The mass spectrum of Cu(II) complex (Figure 5b) shows a molecular ion peak (M+) at m/z 794 (28%), respectively, suggesting the complex to be dimeric, confirming the stoichiometry of the metal to ligand ratio to be 2:1 in copper complex system.

Fig. 16 depicts the SEM photographs of the synthesized ligand H_2L and $[Cu_2LBr_2]$ complex. The morphology and particle size of (a) the ligand H_2L and $[Cu_2LBr_2]$ complex have been illustrated by the scanning electron micrography (SEM). It was noted that there is a uniform matrix of the synthesized complexes in the pictograph which leads to believe that it is a homogeneous phase material. An ice rock like shape is observed in the ligand H_2L with the particle size of 5 µm. However $[Cu_2LBr_2]$ complex is an ice sponge shaped morphology with 5 µm particle size.



Figure 16. SEM photographs of (a) H₂L ligand and (b) Cu(II) complex.

Single crystal of the complex could not be prepared to get the XRD and hence the powder diffraction data was obtained for structural characterization. An X-ray powder pattern of one representative complex [Cu₂LBr₂] has been given in Figure 17 along with the prominent data. The peak broadening at lower angle is more meaningful for the calculation of particle size; therefore the size of the particle has been calculated using Debye–Scherrer formula [35] using reflection from the XRD pattern. Debye–Scherrer formula is given by $D = 0.94\lambda/\beta Cos\theta$, where D is the size of the particle, λ is the wavelength of X-ray, β is the full width at half maximum (FWHM) after correcting the instrument peak broadening (β is expressed in radians,) and θ is the angle. The size of the particles has been found to be 32–33 nm. The size for the representative complex was obtained 15.0 nm and on this basis it could be concluded that the complex [Cu₂LBr₂] is a nano-sized complex of copper(II) with

an square-planar structure. The observed X-ray pattern of the free ligand sample studied in the present investigation indicates amorphous nature (Fig. 17a).



Figure 17. Powder XRD spectrum for (a) H₂L ligand and (b) [Cu₂LBr₂] complex.

4.2.9. Cyclic voltammogram of [Cu₂L₂Br₂]

The cyclic voltammogram (Table 5; Fig.18) of the copper (II) complex in DMSO solvent, recorded at room temperature shows one step reduction cathodic peak for Cu(II) \rightarrow Cu(0) at $E_{pc} = [-0.753 \text{ V}]$. In the anodic side, the direct oxidation of Cu(0) \rightarrow Cu(II) is observed at $E_{pa} = [0.057 \text{ V}]$. The reversibility of the copper(II)/copper (0) couple was checked by varying the scan rates with peak potentials. From Table 5 it is observed that E_{pc} and E_{pa} value changes with the scan rate and ΔE_p values increase with increasing scan rate and is found to be more than 400 mV. The difference in the value of $E_{pa} - E_{pc}$ is ΔE_p which is larger than the value required for a reversible process (59 V) indicating that reduction of Cu(II) at silver electrode is not only diffusion controlled but also by electron transfer kinetics. These observations indicate that the electron transfer process is irreversible [36].

complex	Scan rate (mV)	$E_{\rm pc}({ m V})$	$E_{\rm pc}({ m V})$	$\Delta E_{\rm p}({ m V})$	
[Cu ₂ LBr ₂]	100	-0.755	0.058	0.813	
	150	-0.724	0.149	0.873	
	200	-0.719	0.205	0.924	

Table 5. Redox potential of the copper(II) complex.



Figure 18. Cyclic voltammogram of [CuL₂.Cl₂] at 100 mV/s scan rate.

On the basis of spectral, thermal and magnetic studies, a plausible structure for the complexes is established in which copper(II) is situated in an square-planar environment.

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