

Spectral and Cyclic Voltammetric Studies on Cu (II)-Schiff Base Complex Derived from Anthracene-9(10H)-one

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Abstract: Novel Schiff base chelate of Cu(II) derived from anthracene-9 (10H)-one with (s)-2-amino-5-guanidinopentanoic acid has been synthesized. The ligand and complex were characterized by elemental analysis, molar conductance, magnetic susceptibility and UV,IR, NMR spectroscopic techniques. The redox properties of the ligand and complex were extensively investigated by electrochemical method using cyclic voltammetry (CV). Cyclic voltammetric measurement of Cu(II) complex display quasireversible redox process due to the Cu(II)/Cu(I) process.

Keywords: Schiff base, anthracene-9 (10H)-one, Cyclic Voltammetry

I. Introduction

The complexes of Schiff bases with metal ions are very important in the development of coordination chemistry. These complexes are also known to have anticorrosion properties and biological activities such as antimicrobial, antifungal, and antitumor [1-17]. Copper complexes have played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials [18]. In the present paper we report the synthesis and characterization of Cu(II) complex of Schiff base derived from the condensation of anthracene-9 (10H)-one with (s)-2-amino-5-guanidinopentanoic acid.

II. Experimental

Materials and Methods

All the chemicals used were of analytical grade and solvents used for spectral studies were of spectroscopic grade. Carbon, hydrogen, and nitrogen content of the ligand and its Cu(II) metal complex were determined by microanalysis using Elementar make Vario EL III model CHN analyzer. Molar conductance of the complex at room temperature was measured using a ELICO conductivity meter. Magnetic susceptibility was measured by Sherwood, UK (Mark 1) balance. The UV-visible spectra of the ligand and complex were recorded on a Shimadzu UV-visible-1800 Spectrophotometer using DMSO as solvent. The infrared spectra of the ligand and metal complex were recorded using KBr disc technique in the range 4000-400 cm^{-1} on a Shimadzu model FT-IR Spectrometer (Model IR affinity). ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in DMSO- d_6 for all compounds on a Bruker AMX-400 NMR spectrometer. The cyclic voltammetry studies were carried out in an Ivium compactstat-e electrochemical system with three electrode assemblies which were connected to a personal computer assisted with software "Ivium soft". The three electrode system consisted of glassy carbon (working), platinum wire (counter) and Ag/AgCl (reference) electrodes.

Synthesis of Schiff base ligand

Polynuclear Schiff base (s)-2-(anthracene-9(10H)-ylideneamino)-5-guanidinopentanoic acid (A9Y5GPA) was obtained by the condensation of equimolar mixture of anthracene-9 (10H)-one and (s)-2-amino-5-guanidinopentanoic acid in ethanol. The reaction mixture was refluxed for 5 hours, cooled by keeping overnight to obtain dark coloured compound, filtered, washed and dried.

Synthesis of Cu(II) Schiff base complex

The hot ethanolic solution of anthracene-9(10H)-one (1mM), and (s)-2-amino-5-guanidinopentanoic acid (1mM) were refluxed for 2 hr. To this added cupric acetate (1mM) and refluxed for about 6-7 hours in the presence of sodium acetate (1.0 g). The solution was concentrated, cooled at room temperature for overnight and filtered. The metal complex was dried in a desiccator over anhydrous calcium chloride.

III. Results And Discussion

The analytical data along with some physical properties of the Schiff base and complex are summarized in Table 1. The analytical data show that the metal to ligand ratio is 1:1. The complex is

coloured and non hygroscopic in nature. It is insoluble in water but slightly soluble in organic solvents like ethanol, methanol and DMSO. The very low molar conductance value of the complex in DMSO at a concentration of 10^{-3} M at room temperature was indicative of their non electrolytic nature. The Cu(II) chelate exhibited the magnetic moment 1.38 B.M which is a low value compared to the spin only value 1.73 B.M. This suggests a dimeric square planar configuration facilitating anti-ferromagnetic exchange.

Electronic spectra

The electronic spectrum of the Schiff base A9Y5GPA showed three specific bands around 26400, 33200 and 40616cm^{-1} , characteristic of $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions respectively. Electronic spectrum of the Cu(II) chelate gave a single broad and poorly resolved absorption band around 13880cm^{-1} , characteristic of Cu(II) with D_{4h} symmetry.

Table 1. Microanalytical data of Schiff base and its Cu(II) complex

Complex	Colour	Yield (%)	Mol. wt	M.P ($^{\circ}\text{C}$)	Metal % Found (Calculated)	Elemental Analysis Found (Calculated)		
						C %	H %	N %
A9Y5GPA	Dark	85	265	235	-	68.18 (68.48)	6.03 (6.27)	15.48 (15.97)
[CuLAc] ₂	Bluish Green	72	944	>300	6.44 (6.73)	55.62 (55.94)	4.88 (5.09)	11.26 (11.86)

IR Spectra

The stretching vibration of NH_2 and NH group of the ligand appeared in the region 3425cm^{-1} and 3304cm^{-1} respectively. The asymmetric and symmetric stretching frequencies of the carboxylate groups exhibited respectively at 1656cm^{-1} and 1456cm^{-1} . The IR spectral data of the ligand A9Y5GPA contain a significant absorption frequency at 1595cm^{-1} which may be assigned to the stretching frequency of $\text{C}=\text{N}$ group which upon complexation undergoes red shift by ca. 30cm^{-1} indicating the involvement of azomethine nitrogen in coordination. The asymmetric and symmetric stretching vibrations of COO^- of ligand shifted to lower frequency upon complexation and were appeared at $\approx 1650\text{cm}^{-1}$ and $\approx 1430\text{cm}^{-1}$. The $\Delta\nu$ value ($\nu_{\text{COO}^- (\text{asym})} - \nu_{\text{COO}^- (\text{sym})}$) $\approx 220\text{cm}^{-1}$ are consistent with monodentate carboxylate moiety. Conclusive evidence of bonding of the ligand to the central metal ion is provided by the appearance of bands at the region $520 - 552\text{cm}^{-1}$ and $442 - 467\text{cm}^{-1}$, which can be assigned to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ bands respectively.

^1H NMR and ^{13}C NMR Spectra

The ^1H NMR spectrum of the ligand showed a singlet peak at highly deshielded region (δ 12.2) can be assigned to the carboxylic acid proton. All aromatic protons showed their characteristic resonance peaks between δ 7.40 and 8.35 in the ^1H NMR spectrum. A broad peak at δ 6.97 can be attributed to free NH_2 proton in the ligand. The methylene proton attached to NH group showed a peak at δ 2.45. The CH proton attached to $-\text{N}=\text{C}<$ (azomethine) exhibited a peak at δ 4.46. The ^{13}C NMR spectrum of the ligand exhibited a peak at 182.1 ppm due to the presence of highly electron withdrawing oxygen atoms on the carboxylic group and also due to the π -electron anisotropic effect. The methylene carbon attached to NH group showed a peak at δ 37.66 ppm. The carbon atom of the azomethine moiety resonated at 140.05 ppm. The proton nmr spectrum of the complex was very much complex and peak detection was difficult with respect to each characteristic protons. The NMR spectrum of the complex exhibited significant difference from the spectrum of the ligand A9Y5GPA mainly in two regions. The disappearance of the signal at δ 12.2 due to the acid proton in the ligand, is a clear indication of the coordination of the ligand through the carboxylate group. Similarly, there is a downward shift of the signals due to carboxylic acid and azomethine carbon atoms. This can be attributed to the lowering of electron densities as a result of coordination to the metal ion. The spectral and elemental analysis confirms the general structures of the ligand and complex as shown in Fig.1 and Fig.2 respectively.

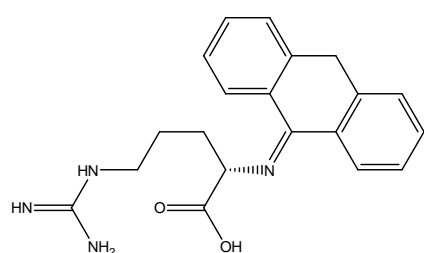


Fig. 1. Structure of Schiff base A9Y5GPA

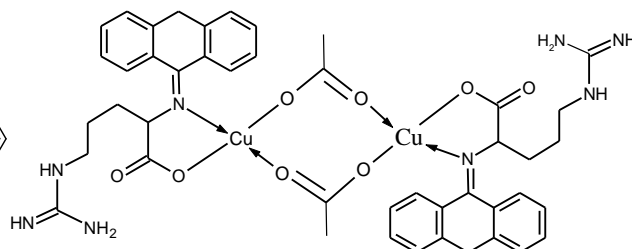


Fig. 2. Structure of Cu(II)- A9Y5GPA complex

CV studies on the Schiff base A9Y5GPA

The electrochemical response of the Schiff base A9Y5GPA was studied by recording the cyclic voltammogram in the potential range +1.0 V to -1.0 V. The Fig.3 shows the CV of A9Y5GPA at a scan rate of 0.1 V/s. It can be observed that there are one cathodic peak represented by A and three anodic peaks represented by B, C and D. The E_p and i_p values of the various peaks are listed in the table 4.2. From the Fig. 3 and Table 2, the electrochemical characteristic of A9Y5GPA can be interpreted as follows.

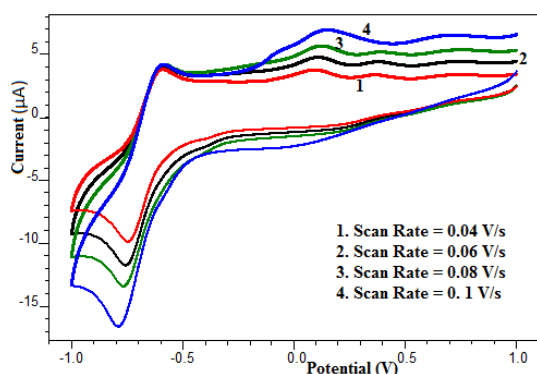


Fig. 3. Cyclic Voltammogram of A9Y5GPA at a scan rate of 0.1 V/s

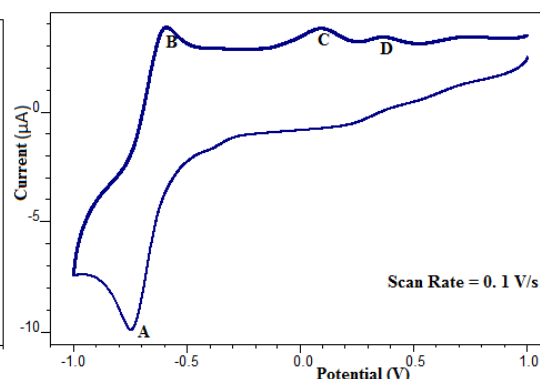


Fig. 4. Cyclic Voltammogram of A9Y5GPA at scan rates 0.04 - 0.1 V/s

The peak A appeared at -0.790 V can be considered due to the two electron reduction process of the azomethine moiety into saturated system. The involvement of two electrons was assumed, since the height of this cathodic peak was significantly higher than the other normal peaks. The two oxidation peaks observed at B and C can be attributed to the two successive oxidation processes of the reduced form of the Schiff base. Thus the original molecule regenerates at a higher oxidation potential 0.390 V. The overall mechanism of the redox process is depicted in the Fig. 5. The third oxidation peak D appeared at 0.142 V in the voltammogram may be due to the involvement of (s)-2-amino-5-guanidinopentanoic acid moiety.

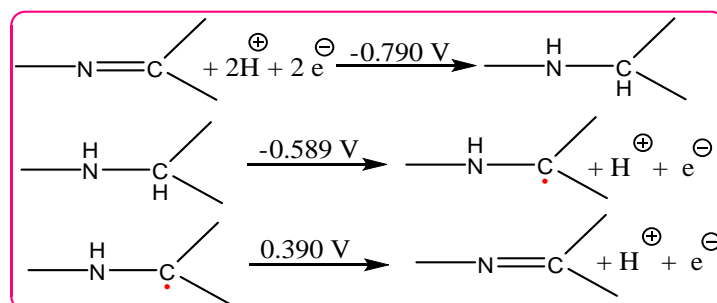


Fig. 5. Mechanism of redox process at azomethine moiety of A9Y5GPA

Table 2. Cyclic Voltammetric data for Schiff base A9Y5GPA

Scan Rate (V/s)	Redox Peak	E_{pa} (V)	E_{pc} (V)	i_{pa} (μ A)	i_{pc} (μ A)
0.04	A	-	-0.747	-	5.03
	B	-0.589	-	3.105	-
	C	0.083	-	0.569	-
	D	0.362	-	0.246	-
0.06	A	-	-0.758	-	5.382
	B	-0.588	-	3.30	-
	C	0.110	-	0.609	-
	D	0.374	-	0.285	-
0.08	A	-	-0.766	-	5.75
	B	-0.585	-	4.172	-
	C	0.120	-	0.871	-
	D	0.388	-	0.197	-
0.10	A	-	-0.790	-	7.08
	B	-0.589	-	4.66	-
	C	0.142	-	0.990	-
	D	0.390	-	0.394	-

CV studies on the Cu(II)-A9Y5GPA complex

Fig. 6 and 7 show the cyclic voltammogram of Cu(II) complex at a scan rate of 0.1 V/s and 0.04-0.1 V/s respectively. The Table3 exhibits the CV data of Cu(II) complex at different scan rates.

Table3. Cyclic Voltammetric data for Cu(II) - A9Y5GPA complex

Scan Rate (V/s)	E_{pa} (V)	E_{pc} (V)	ΔE_p	i_{pa} (μA)	i_{pc} (μA)	i_{pa}/i_{pc}
0.04	-0.507	-0.671	164	0.608	2.687	0.2
0.06	-0.511	-0.685	174	0.675	3.382	0.2
0.08	-0.526	-0.693	167	0.771	3.838	0.2
0.1	-0.528	-0.712	184	0.783	4.605	0.2

The cyclic voltammogram of Cu(II) complex (+1.0 V to -1.0V) at a scan rate of 0.1 V/s shows a quasi-reversible peak in the negative region, characteristic of the Cu(II) \rightarrow Cu(I) couple at $E_{pc} = -0.712$, with associated anodic peak at $E_{pa} = -0.528$ for Cu(I) \rightarrow Cu(II). On comparing the voltammogram of A9Y5GPA and its Cu(II) complex, it is evident that the oxidation peaks appeared in the voltammogram of Schiff base (peaks C and D) was totally disappeared on complexation. The peak separation value also increases with the scan rate, giving further evidence for the quasi-reversible Cu(II)/Cu(I) couple.

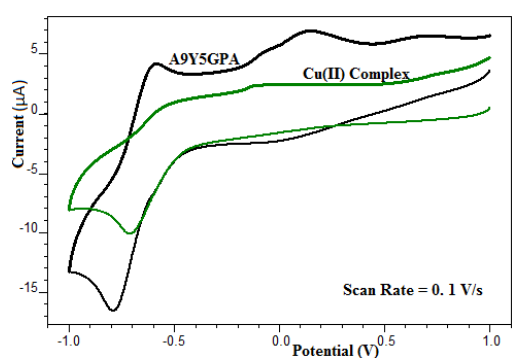
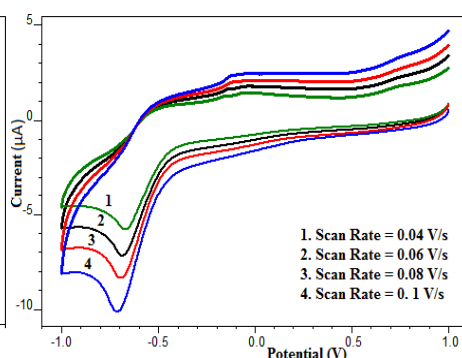
**Fig. 6.** Cyclic Voltammogram of A9Y5GPA and Cu(II) complex at a scan rate of 0.1 V/s**Fig. 7.** Cyclic Voltammogram of Cu(II)-A9Y5GPA complex at scan rates 0.04 - 0.1 V/s**Effect of scan rate and multiple scan on the voltammogram of A9Y5GPA and Cu(II) complex**

Fig.4 shows the cyclic voltammogram of A9Y5GPA at different scan rate. As the scan rate increases, the E_{pc} values are shifted to more negative potentials. For the peaks B, C and D, no counter cathodic peak was observed in the voltammogram. Similarly counter anodic peak was absent for the reduction process designated by 'A' and it may be concluded that the reduction and oxidation process occurred in the potential range -1 to +1 V for the Schiff base A9Y5GPA were irreversible in nature.

The variation of i_p values with the square root of scan rate is depicted in the Fig.8 and 9. The current-scan responses [19, 20] (i_p versus $v^{1/2}$, Randles-Sevcik representation) are straight lines which exhibit slight deviations from linearity. These deviations suggest a change from a diffusion-controlled process to a mixed control process.

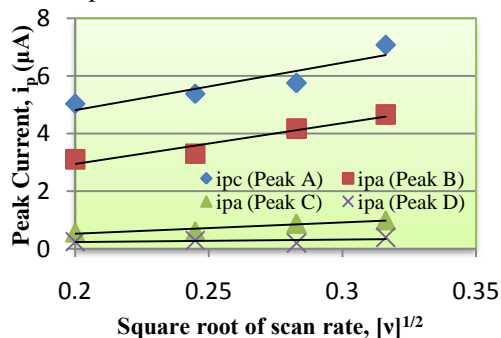
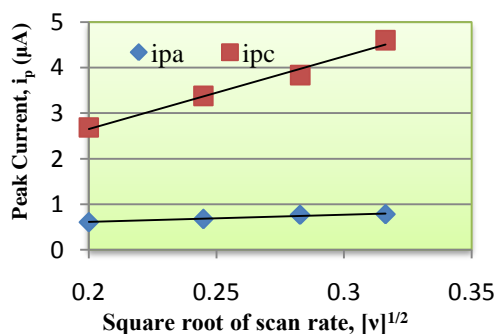
**Fig. 8.** Plot of peak current against square root of scan rate of A9Y5GPA**Fig. 9.** Plot of peak current against square root of scan rate of Cu(II)-A9Y5GPA complex

Fig.10 and 11 represent CV recorded at a scan rate of 0.1 V/s with 5 scan cycles of the ligand and complex respectively. Since all the peaks were appeared in the same position in all the cycles, it is concluded that there is no adsorption of the compound on the glassy carbon electrode surface.

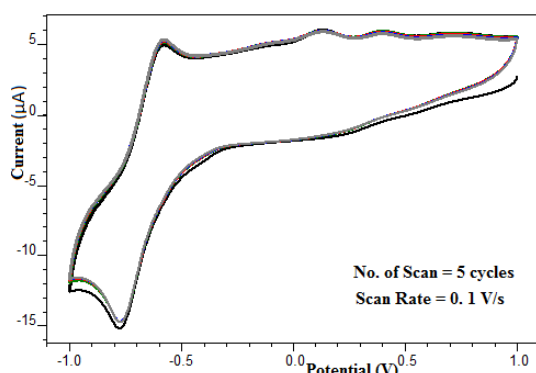


Fig. 10. Cyclic Voltammogram of Schiff base A9Y5GPA with multiple scan cycles

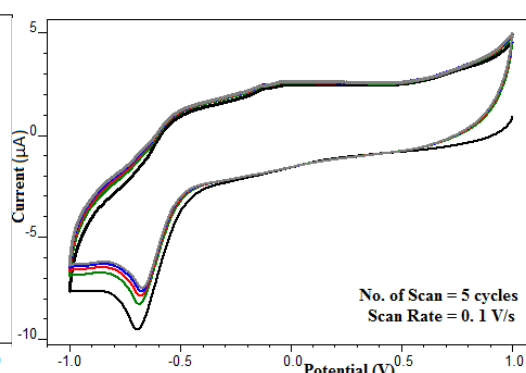


Fig. 11. Cyclic Voltammogram of Cu(II)-A9Y5GPA complex with multiple scan cycles

IV. Conclusion

In the present work, complex of Cu(II) with Schiff base derived from anthracene-9 (10H)-one and (s)-2-amino-5-guanidinopentanoic acid was synthesized and characterised. The Schiff base act as a monovalent bidentate ligand. On the basis of different micro analytical and spectra analytical techniques, the structures of the ligand and complex are proposed. The electrochemical properties of the Cu(II) complex revealed the quasi-reversible one electron transfer redox process.

Reference

- [1]. P. K. Panchal, P. B. Pansuriya, and M. N. Patel, Study on increase in toxicity of Schiff bases on microorganism on chelation with metal, *Toxicological and Environmental Chemistry*, 88(1),2006, 57–64.
- [2]. K.S.Shaju,K.J.Thomas, V.P.Raphael and A.Paul,Synergistic effect of KI on corrosion inhibition of mild steel by polynuclearschiff base in sulphuric acid, *ISRN Corrosion*,2012,doi:10.5402/2012/425878.
- [3]. M. Tümer, E. Akgün, S. Toroglu, A. Kayraldız, and L. Dönbak, Synthesis and characterization of Schiff base metal complexes: their antimicrobial, genotoxicity and electrochemical properties, *Journal of Coordination Chemistry*, 61(18), 2008, 2935–2949.
- [4]. A. Gölcü, M. Tümer, H. Demirelli, and R. A. Wheatley, Cd(II) and Cu(II) complexes of polydentate Schiff base ligands: synthesis, characterization, properties and biological activity, *InorganicaChimicaActa*, 358(6), 2005,1785–1797.
- [5]. M. Tümer, N. Deligonul, and A. Gölcü, Mixed-ligand copper(II) complexes: investigation of their spectroscopic, catalysis, antimicrobial and potentiometric properties, *Transition Metal Chemistry*, 31(1), 2006, 1–12.
- [6]. M. Arif, M. M. R. Qurashi, and M. A. Shad, Metal-based antibacterial agents: synthesis, characterization, and in vitro biological evaluation of cefixime-derived Schiff bases and their complexes with Zn(II), Cu(II), Ni(II), and Co(II), *Journal of Coordination Chemistry*, 64(11), 2011, 1914–1930.
- [7]. K.S.Shaju,K. J.Thomas and V. P.Raphael, Effect of iodide on the corrosion inhibitive behaviour on carbon steel by an azomethine compound derived from anthracene-9(10 H)-one, *Oriental Journal of Chemistry*, 30(2), 2014, 807-813.
- [8]. M. M. Aboaly and M. M. H. Khalil, Synthesis and spectroscopic study of Cu(II), Ni(II), and Co(II) complexes of the ligand salicylidene-2-amino thiophenol, *Spectroscopy Letters*, 34(4), 2001, 498–504.
- [9]. Y. T. Li, C. W. Yan, and X. C. Zeng, Heterobinuclear copper(II)–lanthanoid(III) complexes bridged by N,N'-oxamidobis(benzoato)cuprate(II), *Transition Metal Chemistry*, 26(1-2), 2001,110–115.
- [10]. K. A. R. Salib, A. A. Saleh, S. Abu El-Wafa, and H. F. O. El-Shafiy, Preparation and characterization of novel asymmetrical Schiff-base ligands derived from 2-methyl-7-formyl-8-hydroxyquinoline and their metal complexes, *Journal of Coordination Chemistry*, 56(4), 2003.
- [11]. H. Chakraborty, N. Paul, M. L. Rahman, Catalytic activities of Schiff bases aquo complex of Cu(II) in the hydrolysis of amino acid esters, *Transition Metal Chemistry*, 19, 1994, 524-526.
- [12]. K. S. Shaju, K. J. Thomas, V. P. Raphael, and A. Paul, Electrochemical and surface morphological studies of carbon steel corrosion by a novel polynuclear Schiff base in HCl Solution, *ISRN Electrochemistry*, 2013,dx.doi.org/10.1155/2013/820548.
- [13]. T. D. Bharamagouclar, M.A. Pujar, A.R. Alagawadi, Biological activity of Schiff base and their metal complexes, *Current Science*, 56,1987, 889-890.
- [14]. B. Kołodziej,E. Grech,W. Schilf,B. Kamiński, A. Pazio and K. Woźniak, The NMR and X-ray study of L-arginine derived Schiff bases and its cadmium complexes, *Journal of Molecular Structure*, 1063(24), 2014, 145–152.
- [15]. Z. H. Chohan and C. T. Supuran, Structure and biological properties of first row d-transition metal complexes with N-substituted sulfonamides, *Journal of Enzyme Inhibition and Medicinal Chemistry*, 23(2), 2008, 240
- [16]. M. Arif, M. M. R. Qurashi, M. A. Shad, Metal-based antibacterial agents: synthesis, characterization, and in vitro biological evaluation of cefixime-derived Schiff bases and their complexes with Zn(II), Cu(II), Ni(II), and Co(II), *Journal of Coordination Chemistry*, 64(11), 2011, 1914
- [17]. J.Thomas and G. Parameswaran, Anti tumour and thermo gravimetric studies of transition metal complexes of the Schiff base, anthracene-9-carboxaldehyde thiosemicarbazone, *AsianJournal of Chemistry*, 14(3-4), 2002,1370-1382.
- [18]. R. Katwal, H. Kaur, B. K. Kapur,Applications of Copper-Schiff base complexes: A review, *Scientific Reviews and chemical communications*,3(1), 2013, 1-15.
- [19]. A.D. Kulkarni, S.A.Patil and P.S. Badami, Electrochemical properties of some transition metal complexes: Synthesis, characterization and in-vitro antimicrobial studies of Co(II), Ni(II), Cu(II), Mn(II) and Fe(III) complexes, *International Journal of Electrochemical Science*,4,2009,717-729.
- [20]. S. Zolezzi, E. Spodine and A. Decinti, Electrochemical studies of Cu(II) complexes with Schiff base ligands, *Polyhedron*, 21, 2002, 55.