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Research Article

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Copper (II) 2-2' bipyridine complexes: Synthesis, Spectroscopic study and Electrochemistry of Copper (II)-bis naphthylazo imidazole/benzimidazole/pyridine bipyridine Complexes.

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Abstract

Reaction of copper chloride $CuCl_2$ with NaaiR$^{´}$ in acetone medium following ligand addition leads to [Cu(NaaiR$^{/}$)bpy]Cl_2 where NaaiR$^{/}$ = naphthylazo imidazole /benzimidazole /pyridine = -$C_{10}H_4$-N=N- / -C_3H_2-NN-1-R$^{/}$, (R = imidazole) / -C_7H_4-NN-1-H (Benzimidazole), / -C_3H_4-N-(Pyridine), abbreviated as -N,N$^{/}$-chelator, where -N(imidazole) and -N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*)]. The ^{1}H NMR spectral measurements suggest the molecular structure of bis chelated complex with the protons at the aromatic region and naphthyl protons at higher ∂ value. ^{13}C NMR spectrum suggest the molecular skeleton. The voltammogramalso shows a small anodic peak at 0.2 V, possibly due to the Cu(I)/Cu(0) couple.

Keywords: Copper(II), Naphthylazoimidazole, NMR, IR, ESIMS.

Introduction

The variety of metal ion functions in biology has stimulated the development of new metallodrugs other than Pt drugs with the aim to obtain compounds acting via alternative mechanisms of action. Among non-Pt compounds, copper complexes are potentially attractive as anticancer agents. Actually, since many years a lot of researches have actively investigated copper compounds based on the assumption proposal that endogenous metals may be less toxic.

It has been established that the properties of copper-coordinated compounds are largely determined by the nature of ligands and donor atoms bound to the metal ion. In this review, the most remarkable achievements in the design and development of copper(I, II) complexes as antitumor agents are discussed *(Yu Wang, et al., 2012, Christopher S. Letko, et al., 2012, Moriya, Shingo Tominaga, Takayoshi Hashimoto, et al., 2012,).* Special emphasis has been focused on the identification of structure-activity relationships for the different classes of copper(I,II) complexes. This work was motivated by the observation that no comprehensive surveys of copper complexes as anticancer agents were available in the literature. Moreover, up to now, despite the enormous efforts in synthesizing different classes of copper complexes, very few data concerning the molecular basis of the mechanisms underlying their antitumor activity are available. This overview, collecting the most significant strategies adopted in the last ten years to design promising anticancer copper(I,II) compounds, would be a help to the researchers working in this field. Copper(II) and copper(I)-diimine complexes (diimine function) have attracted much research interest in the realm of science and technology. Cu(II) prefers distorted octahedral(six coordinate), square pyramidal (five coordinate) or square planar (tetra coordinate) while Cu(I) demands, in general, tetrahedral geometry. The redox change Cu(II), Cu(I) or vice versais associated with structural change which requires large reorganization energy *(Alexey Potapov, et al., 2012, Nadia Marino, et al., 2012,Pampa M. Guha, et al., 2012,L. Choubrac, et al., 2012, Rathinasabapathi Prabhakaran, et al., 2012, Kaushik Ghosh, Pramod Kumar, et al, 2012).* In fact this energy has been utilized by biochemical pro-cesses. Thio ether donors destabilize Cu(II) state elevating the Cu(II), Cu(I) redox potentials which includes structural flexibility in the stabilization of Cu(I) state. The electronic property of thio ether containing ligands may be controlled by incorporating substituents in the conjugated framework of the ligand system. Incorporation of photochromic molecules into organic or hybrid organic–inorganic materials leads to the development of very effective devices for optical data recording and storage. Azo-conjugated metal complexes exhibit unique properties upon light irradiation in the area of photon-mode high-density information storage photoswitching devices *(P. Byabartta, et al., 2001, P. Byabartta, et al., 2001, P. Byabartta, et al., 2002., P. Byabartta, et al., 2002, P. Byabartta, et al., 2001, P. Byabartta, et al., 2003,).* The proposed curative properties of Cu-based non-steroidal anti-inflammatory drugs (NSAIDs) have led to the development of numerous Cu(II) complexes of NSAIDs with enhanced anti-inflammatory activity and reduced gastrointestinal (GI) toxicity compared with their uncomplexed parent drug. These low toxicity Cu drugs have yet to reach an extended human market, but are of enormous interest, because many of today's anti-inflammatory drug therapies, including those based on the NSAIDs, remain either largely inadequate and/or are associated with problematic renal, GI and cardiovascular side effects. The origins of the anti-inflammatory and gastric-sparing actions of Cu-NSAIDs, however, remain uncertain. Their ability to influence copper metabolism has been a matter of debate and, apart from their frequently reported superoxide dismutase (SOD)-like activity in vitro, relatively little is known about how they ultimately regulate the inflammatory process and/or immune system. Furthermore, little is known of their pharmacokinetic and biodistribution profile in both humans and animals, stability in biological media and pharmaceutical formulations, or the relative potency/efficacy of the Cu(II) monomeric versus Cu(II) dimeric complexes. The following review will not only discuss the etiology of inflammation, factors influencing the metabolism of copper and historical overview of the development of the Cu-NSAIDs, but also outline the structural characteristics, medicinal and veterinary properties, and proposed modes of action of the Cu-NSAIDs. It will also compare the SOD, anti-inflammatory and ulcerogenic effects of various Cu-NSAIDs. If the potential opportunities of the Cu-NSAIDs are to be completely realized, a mechanistic understanding and delineation of their in vivo and in vitro pharmacological activity is fundamental, along with further characterization of their pharmacokinetic/ pharmacodynamic disposition. Elesclomol (N1 dimethyl-N,-di(phenyl carbonothio-yl) malonohydrazide, 1) is a novel small molecule anticancer drug candidate that is discovered and originated from our lab. It exhibits strong antitumor activities against a broad range of cancer cell lines including MDR (multi-drug resistance) cell lines. It is believed that elesclomol exerts its anticancer activity via the induction of reactive oxygen species (ROS) in cancer cells, which results in apoptosis. Recent biological data support the hypothesis that elesclomol generates ROS via its chelation with copper(II) and redox cycling of copper(II). The data suggest that elesclomol obtains copper(II) outside the cell –from serum as well as from purified ceruloplasmin the primary copper-binding protein in blood–and requires copper(II) for its cellular entry and cytotoxicity. On the other hand, copper(II) complexes are of continuing interest for their potential applications as molecular imaging agents *[(Bojan Kozlevčar, et al., 2012, Santokh S. Tandon, et al., 2012, Peter Comba, et al., 2012, Patrick Frank, et al., 2012, Xiaolin Zhang, Xu Jing, et al., 2012, Ping Cui, Lijun Ren, et al 2012,Renata E. H. M. B. Osório, et al., 2012, A. C. Tsipis, et al., 2012, Nóra V. Nagy, et al., 2012, Thao T. Vo, et al., 2012,)].* They were investigated as anticancer agents for their capability to induce the formation of ROS and to inhibit roteasome activities in cancer cells. Recent publications on elesclomol prompt us to communicate our earlier results in the synthesis, crystallographic characterization, and the electrochemical property measurements of the elesclomol copper(II) complex.

A series of copper(II) complexes with 2-methylbenzimidazole, 2-phenylbenzimidazole, 2-chlorobenzimidazol, 2-benzimidazolecarbamate, and 2-guanidinobenzimidazole was prepared, and their cytotoxic activity was evaluated against PC3, MCF-7, HCT-15,HeLa, SKLU-1, and U373 cancer cell lines, showing that [Cu(2-chlorobenzimidazole)Br] and [Cu(2-benzimidazolecarbamate)Br] had significant cytotoxic activity *(Daniel L. Reger, et al., 2012, Sandrine Perruchas, et al., 2012, Linda Tjioe, et al., 2012, Alexander M. Willcocks, et al., 2012, Diego La Mendola, et al., 2012, Almudena Gallego, et al., 2012, Sabrina Turba, et al., 2012, Mingfeng Yu, Jason R. Price, et al., 2011, Gernot Nuss, Gerald Saischek, et al., 2011, Jacob R. Holm-Jørgensen, et al., 2011).* These results showed that the cytotoxic activity was related to the easy displacement of halides from the coordination sphere of the metal. The copper complexes, of 2-methyl-1H-benzimi-dazole-5-carbohydrazide and 2-methyl-N-(propan-2ylidene)-1H-benzimidazole-5-carbohydrazide displayed cytotoxicity against A549 (ICM) tumor cell lines. A series of copper(II) complexes of tri- or tetra-dentate bis(2 methylbenzimidazolyl) amine ligands (has been prepared and fully characterized in solution as well as in the solid state. All ligands acted as tridentate donors toward the cupric ions through one central amine and two benzimidazole N atoms in the solid state. The complex [Cu (a square-pyramidal coordination water ligand and a bridging perchlorate group defined the distorted octahedral environments of complexe *(Apurba Kalita, et al., 2011, Takamitsu Fukuda, et al., 2011, Kayla M. Miller, et al., 2011, José M. López-de-Luzuriaga, et al., 2011, Marco G. Crestani, et al., 2011, Mihail Atanasov, et al., 2011, Amien M. Murphy, et al., 2011,).* The copper complex, had presumably a square-pyramidal coordination geometry, with an additional thioether group attached to the central N atom in the axial position. The antiproliferative activity screening revealed that was endowed with the lowest inhibitory effect, indicating that an additional substituent on the central nitrogen was necessary for eliciting cytotoxic activity. The authors speculated that the nearly planar arrangement of the two benzimidazole units and the cupric ion was not a requirement for biological activity. Interestingly, and had a significant inhibitory effect on K562 cancer cells compared to the low toxicity exhibited against healthy bone marrow cells *(Gengwen Tan and Hongping 2011, Pratik Verma, et al., 2011, Priscila P. Silva, et al., 2011, Sethu Ramakrishnan, et al., 2011, Michelle T. Ma, et al., 2011, Rémi Maurice, et al., 2011, Sujit Sasmal, Sohini Sarkar, et al., 2011, Cristina Núñez, et al., 2011, Sonia Pérez-Yáñez, et al., 2011).* The synthesis and structures of two copper(II) complexes with a benzothiazole sulfonamide ligand, [Cu((py), and [Cu((en) (-2-(4-methylbenzothiazole) toluene sulfonamide, py = pyridine, en = ethylenediamine), were described, exhibit eda square-planar geometry, and displayed a distorted octahedral array, showed different coordination modes: through the benzothiazole N in and through the sulfonamide N in. The ability of the complexes to cleave CT-DNA was studied in vitro through ascorbate activation and tested by monitoring expression of the yEGFP gene containing the RAD54 reporter. Both were found to cleave DNA in vitro, and was found to be more effective ininhibiting Caco-2 and Jurkat T cell growth. There are several copper(II) compounds involving a 1,2,4-triazole moiety (Triazoles, Tetrazoles, and Oxazoles) that show a wide range of biological and pharmacological activities. The Cu(II) complex [Cu( )Cl emerged from a number of triazolemetal-based compounds] screened for their cytotoxicity in human cancer cells. It was found that, by inhibiting caspase-3, impaired execution of the apoptotic program, thus addressing the cells to alternative death pathways, such as paraptosis. Gene expression profiling of the human fibrosarcoma. HT1080 cells showed that upregulated genes involved in theunfolded protein response (UPR) and response to heavy metals. The cytotoxic effects of the complexes were associated with inhibition of the ubiquitin-proteasome system and accumulation of ubiquitinylated proteins in a manner dependent on protein synthesis. The occurrence of the UPR during the induced death process was shown by the increased abundance of spliced XBP1 mRNA, transient eIF2 α phosphorylation, and a series of downstream events, including attenuation of global protein synthesis and increased expression of ATF4, CHOP, BIP, and GADD34. Synthesized two novel chloro-bridged and bromo-bridged 1,2,4-triazol e-based Cu(II) complexes, [Cu= 3,5-bis{[bis(2-methoxyethyl)-amino]methyl}-4H-1,2,4-triazol-4-amine)]. The apparent CT-DNA binding constant (for complexes, respectively) *(Oliver Kluge, et al., 2011, Charles J. Simmons, et al., 2011, Giuseppa Ida Grasso, et al., 2011, Oottil Mayasree, et al., 2011, Daniel L. Reger, et al., 2011, Linda Tjioe, et al., 2011, Li-Pei Wei, et al., 2011).* Furthermore, both compounds displayed efficient oxidative cleavage of supercoiled DNA in the presence of external activating agents. Coordination of monodentate 5-amino-2-tert-butyltetrazole via the endo cyclic N4 atom to the Cu(II) ion produced the five-coordinated [Cu(Cl] complex end owed with low cytotoxic activity against HeLa cells. Analogously, the octahedral copper(II) complex of 3,5-bis(2 pyridyl)-1,2,4-oxadiazole showed moderate cytotoxicity against HepG2and HT29 cells (Takayoshi Suzuki, et al., 2011, Dariusz Matoga, et al., 2011,). Cell morphological changes were observed by light microscopy, and an apoptotic death was proposed. The interaction of the cationic species with native DNA indicated that the copper complex was a DNA groove binder with binding constant *(Bojan Kozlevčar, et al., 2012, Santokh S. Tandon, et al., 2012, Peter Comba, et al., 2012, Patrick Frank, et al., 2012, Xiaolin Zhang, Xu Jing, et al., 2012, Ping Cui, Lijun Ren, et al 2012,Renata E. H. M. B. Osório, et al., 2012, A. C. Tsipis, et al., 2012, Nóra V. Nagy, et al., 2012, Thao T. Vo, et al., 2012*).

Materials and Methods

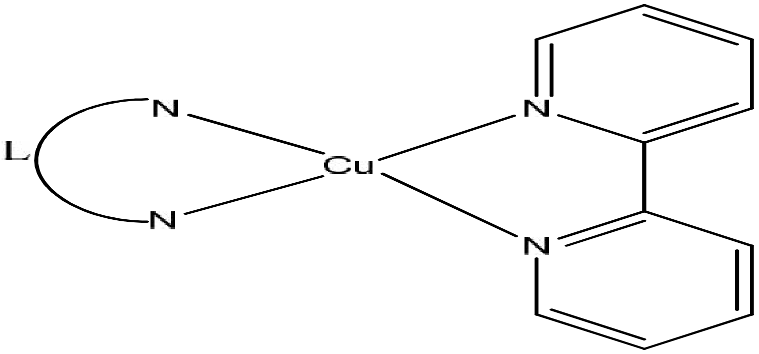
Material and instrumentation

Published methods were used to prepare Naphthylazoimidazole /benzimidazole/ pyridine (Byabartta Prithwiraj, Sau Somnath, et al., 2014 ; Byabartta Prithwiraj, 2014,Byabartta Prithwiraj,2014,Byabartta P., Santra P.K., Misra T .K., Sinha C. and Kennard C.H.L. et al., Polyhedron,2001, Byabartta p., Jasimuddin Sk., Mostafa G ., Lu T.-H. and Sinha C. et al., Polyhedron ,2003, Venkanna Avudoddi , et al., 2014,Huang Xin , et al .,2014, Loganathan Rangasamy , et al., 2014, Kang Kai [1-11]. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^{1}H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using $SiMe_4$ as internal reference, $CFCl_3$ (external ^{19}F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} M in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled

250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE).

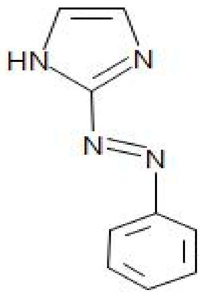
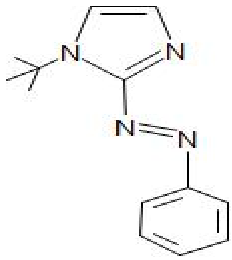
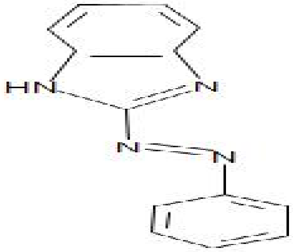
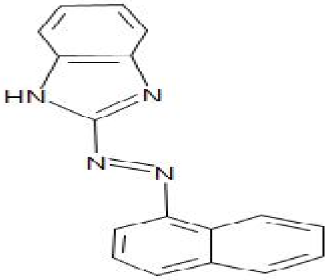
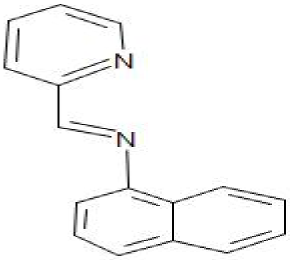
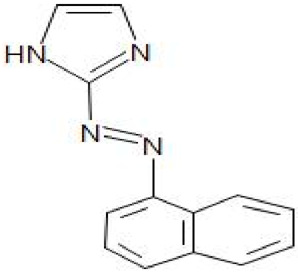
Preparation of the complexes

Synthesis of different copper bipyridine complexes



Where L =PAIM (1)/NABEN (2)/Me- PAIM (3)/αNAiPY (4)/PABEN (5)/NAIM (6)

Structure of the ligands :(N, N donar ligand)

		
Phenyl azo imidazole(PAIM)	**Me-Phenyl azo imidazole(MePAIM)**	**Phenyl azo benzimidazole(PABEN)**
		
Napthyl azo benzimidazole(NABEN)	**α Napthyl azo pyridine(αNaiPY)**	**Napthyl azo imidazole(NAIM)**

Synthesis of the compound 1. The ligand napthyl azo imidazole (NAIM) was obtained by literature method. Now0.1g i.e. 0.00045 mole of napthyl azo imidazole (NAIM) was taken in a small conical flask and 50 ml of acetone solvent added into the flask. An orange colour solution was obtained. Then 0.077g copper chloride was added in it & instantly a deep orange colour was obtained. Finally 0.071g bpy was added into the reaction mixture. A deep green colour ppt was obtained instantly. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 1: CHN calculation of the above compound $[C_{23}H_{18}N_6Cu_1Cl_2]$, gives Calc(found): C, 53.86 (53.86), H, 3.53 (3.54), N,16.38(16.38); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 512.86 [M^+], Proton n.m.r.Spectroscopic data, ^1H, ppm, 7.23(d, J = 8Hz, H(7, 13), 7.55(t, J=6.5Hz, H(8,12), 7.27(d, J=6Hz, H(9,11), 7.01(d, J=5Hz, H(4),7.11(d,J=8.0H(5),8.01(d,J=8.0,H(a-a'),7.89 (t,J=8.0 H(b-b'),7.91(t,J=8.0,H(c-c'), 7.81(d,J=8.0,H(d-d') UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

Synthesis of the compound 2. The ligand phenyl-azo-imidazole (PAIM) was obtained by literature method. It was a yellow colour ligand. Now 0.1075g i.e. 0.00062mole of phenyl azo imidazole (PAIM) was taken in a small conical flask and 50 ml of acetone solvent added into the flask. A yellow colour solution was obtained. Then 0.1057g copper chloride was added in it & instantly a deep green colour was obtained. Finally 0.0968 g bpy was added into the reaction mixture. A light colour solution was obtained instantly. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 2: CHN calculation of the above compound [$C_{19}H_{16}N_6Cu_1Cl_2$], gives Calc(found): C, 49.30 (49.31), H, 3.48 (3.49), N, 18.15(18.15); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data,462.81[M^+], Proton n.m.r.Spectroscopic data, ^1H, ppm, 7.45(d, J = 8Hz, H(7, 13), 7.29(t, J=6.5Hz, H(8,10), 6.29(d, J=6Hz, H(9), 7.08(d, J=5Hz, H(4),7.13(d,J=8.0H(5),8.02(d,J=8.0,H(a-a'),7.91(t,J=8.0 H(b-b'),7.96(t,J=8.0,H(c-c'),7.85(d,J=8.0,H(d-d') UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

Synthesis of the compound 3. Phenyl azo imidazole was synthesized by literature method. It was then methylated by using a strong base sodium hydride and methyl iodide which was take place at the protonated nitrogen atom of imidazole ring. Now 0.1461g i.e. 0.00078 mole of 1-methyl phenyl-azo imidazole (MePAIm) was taken in a small conical flask and 20ml of acetone solvent added into the flask. An orange colour solution was obtained. Then 0.1329 g copper chloride was added in it & instantly a dark orange colour was obtained. Finally 0.1218 g 2-2'bpy was added into the reaction mixture. An orange red colour was persists throughout the reaction. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 3: CHN calculation of the above compound [$C_{20}H_{18}N_6Cu_1Cl_2$], gives Calc(found): C, 50.37 (50.3), H, 3.80 (3.8), N, 17.62(17.6); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 476.84 [M^+] Proton n.m.r.Spectroscopic data, ^1H, ppm, 7.25(d, J = 8Hz, H(7, 13), 7.54(t, J=6.5Hz, H(8,12), 7.29(d, J=6Hz, H(9,), 7.08(d, J=5Hz, H(4),7.12(d,J=8.0H(5),8.01(d,J=8.0,H(a-a'),7.89 (t,J=8.0 H(b-b'),7.91(t,J=8.0,H(c-c'),7.81 (d,J=8.0,H(d-d') 1.5(s, N-Me); , UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

Synthesis of the compound 4. The ligand napthyl azo benzimidazole was obtained by literature method. Now0.0137g i.e. 0.00005 mole of napthyl azo benzimidazole (NABEN) was taken in a small conical flask and 50 ml of acetone solvent added into the flask. A yellow colour solution was obtained. Then 0.00852g copper chloride was added in it & instantly a deep yellow colour was obtained. Finally 0.00781g bpy was added into the reaction mixture. A light green colour ppt was obtained instantly. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 4: CHN calculation of the above compound [$C_{27}H_{20}N_6Cu_1Cl_2$], gives Calc(found): C, 57.60 (57.61), H, 3.58 (3.58), N, 14.92(14.92); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 562.93 [M^+], Proton n.m.r.Spectroscopic data, ^1H, ppm, 7.29(d, J = 8Hz, H(7,13)), 7.59(d, J=6.5Hz, H(8,12)), 7.28(m, 9,11-H), 7.03(d, J=6Hz, H(4)), 7.15(d, J=5Hz, H(5), 7.08(d, J=5Hz, H(4),7.12(d,J=8.0H(5),8.05(d,J=8.0,H(a-a'),7.92 (t,J=8.0 H(b-b'),7.93(t,J=8.0,H(c-c'),7.85(d,J=8.0,H(d-d') UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

Synthesis of the compound 5. The ligand αNaiPYwas obtained from the diazocoupling reaction of αNapthyl amine and pyridine 2 carboxaldehyde. It was a brick red colour ligand. Now 0.0546g i.e. 0.00024 mole of αNaiPY was taken in a small conical flask and 50 ml of acetone solvent added into the flask. A brick red colour solution was obtained. Then

0.0409g copper chloride was added in it & instantly a dark red colour solution was obtained. Finally 0.0374g bpy was added into the reaction mixture. An orange red colour solution was obtained instantly. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 5: CHN calculation of the above compound $[C_{26}H_{20}N_4Cu_1Cl_2]$, gives Calc(found): C, 59.72(59.72), H, 3.85 (3.86), N, 10.71(10.72); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data,522.89$[M^+]$, Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 7.28(d, J = 8Hz, H(7,13), 7.54(d, J=6.5Hz, H(8,12), 7.26(m, 9,11-H), 7.05(d, J=6Hz, H(4), 7.16(d, J=5Hz, H(5), 7.08(d, J=5Hz, H(4),7.12(d,J=8.0H(5),8.02(d,J=8.0,H(a-a'),7.88(t,J=8.0 H(b-b'),7.92(t,J=8.0,H(c-c'),7.83(d,J=8.0,H(d-d') UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

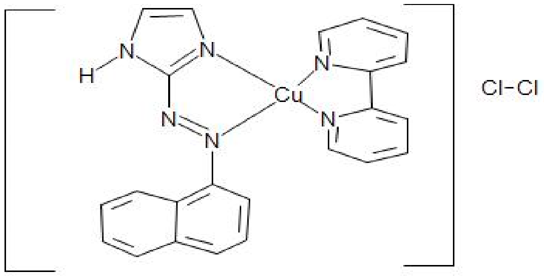
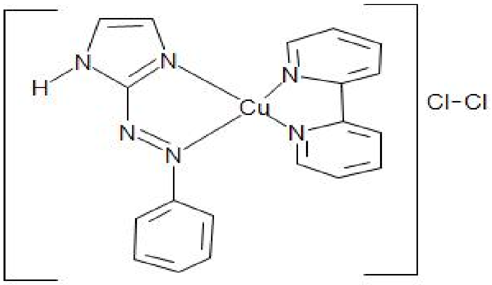
Synthesis of the compound 6. The ligand phenyl azo benzimidazole (PABEN) obtained by literature method. Now0.0165g i.e. 0.00007mole of phenyl azo benzimidazole (PABEN) was taken in a small conical flask and 50 ml of acetone solvent added into the flask. A yellow colour solution was obtained. Then 0.0119g copper chloride was added in it & instantly a deep yellow colour was obtained. Finally 0.0109g bpy was added into the reaction mixture. A light green colour ppt was obtained instantly. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 6: CHN calculation of the above compound $[C_{23}H_{18}N_6Cu_1Cl_2]$, gives Calc(found): C, 53.86 (53.87), H, 3.53 (3.54), N, 16.38(16.38); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1594, ESI/MS Spectroscopic data, 512.87 $[M^+]$, Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 7.24(d, J = 8Hz, H(7,13)), 7.55(d, J=6.5Hz, H(8,12)), 7.28(m,9,-H), 7.04(d, J=6Hz, H(4)), 7.09(d, J=5Hz, H(5), 7.08(d, J=5Hz, H(4),7.11(d,J=8.0H(5),8.01(d,J=8.0,H(a-a'),7.88(t,J=8.0H(b-b'),7.92(t,J=8.0,H(c-c'),7.87(d,J=8.0,H(d-d') UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

Synthesis of the compound 7. The ligand napthyl azo imidazole was synthesized by literature method. It was then methylated by using a strong base sodium hydride and methyl iodide which was take place at the protonated nitrogen atom of imidazole ring. Now0.1464g i.e. 0.00062mole of 1-methyl napthyl-azo imidazole (MeNAIm) was taken in a small conical flask and 20ml of acetone solvent added into the flask. An orange red colour solution was obtained. Then 0.1060 g copper chloride was added in it. Finally 0.0968g bpy was added into the reaction mixture. An orange red colour colour was persists throughout the reaction. The whole mixture was stirred for 12 hours and after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

Characterisation of the compound 7: CHN calculation of the above compound $[C_{24}H_{20}N_6Cu_1Cl_2]$, gives Calc(found): C, 54.70(54.7), H, 3.82 (3.81), N, 15.95(15.95); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ESI/MS Spectroscopic data, 526.89 $[M^+]$, Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 7.25 (d, J = 8Hz, H(7,13), 7.55(d, J=6.5Hz, H(8,12), 7.22(m, 9,11-H); 7.02(d, J=5Hz, H(4),7.13(d,J=8.0H(5),8.02(d,J=8.0,H(a-a'),7.90(t,J=8.0 H(b-b'),7.93(t,J=8.0,H(c-c'),7.84(d,J=8.0,H(d-d') 1.5(s, N-Me); UV-Vis Spectroscopic data, (λ nm), 244(10500), 280(8160), 282(8200), 295(600),(sh); Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] ligand reduction -0.56 (100);

Structure of different copper phenanthroline complexes: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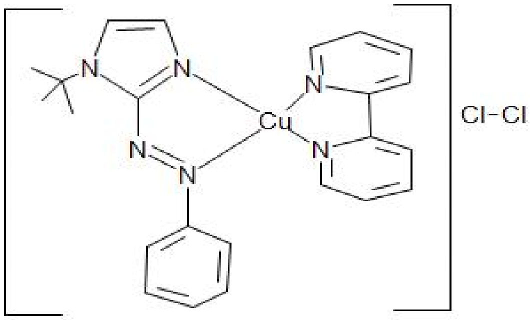	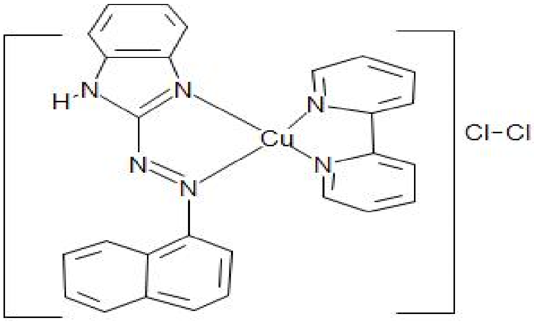
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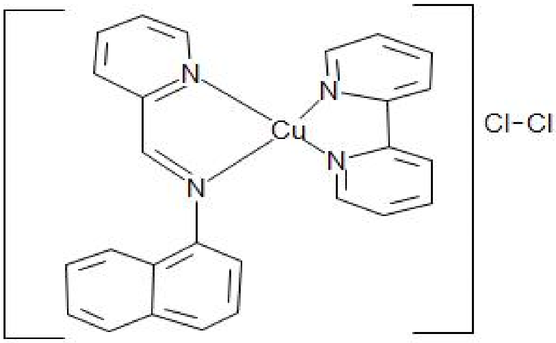	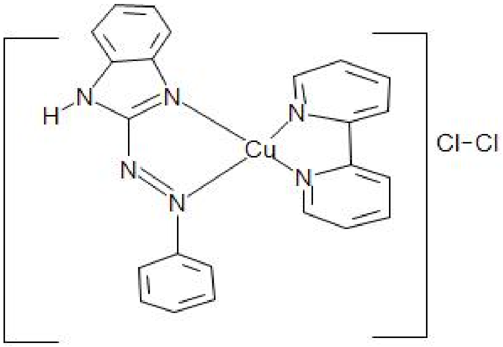
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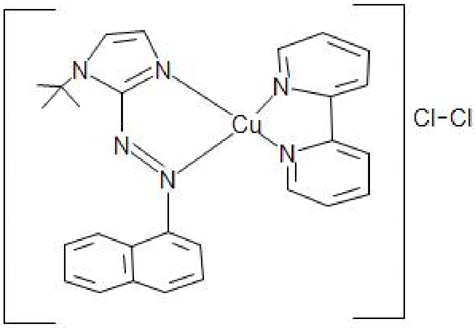	
7	

Fig. 1: Reaction scheme and all the mononuclear complexes of copper from complex 1 to complex 7, [Cu(bpy)(NaaiR$^{/}$)], [NaaiR$^{/}$ = naphthyl-azo or phenyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-R$^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,N$^{/}$-chelator, where N(imidazole) and N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*),]

Spectral studies

I.r. spectra of the complexes, show a 1:1 correspondence to the spectra of the chloro analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm^{-1} with concomitant loss of ν(Cu-Cl) at 320-340 cm^{-1}. They are assigned to ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively.

The ESI mass spectrum of a 1:1, MeCN:H_2O solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly. Population of gas phase ions generated by ESI often closely reflects that in solution.

The electronic spectra of the complexes exhibit multiple high intense transitions in 450–250 nm along with a weak transition at 700–710 nm. In free ligand, the intra-ligand charge transfer, n–p*and p–p*, appear at 370–380 and 250–260 nm, respectively. Low energy weak transition at 700–710 nm (Fig. 2) may be referred to d–d band. Copper(II)–azo-heterocycle and azide bridzed heterocycles show the MLCT transition involving d(Cu) --- p* (Naphthylazoheterocycle) at longer wavelength (>400 nm). It is due to efficient p-acidity of the ligands. On comparing with copper(II) complexes of 1-alkyl-2-(ary-lazo)imidazoles, pyridyl-thioazophenolates and other pyridylthioether ligands the transitions at 430 nm is assigned to MLCT [d(Cu) --- p* (naphthyl-azo-imidazole)] and, the band at 370 nm may be a mixture of S(thioether)--Cu(II)) and ligand centered p–p* transitions (Fig. 2).

The ^{1}H n.m.r. spectra, measured in CD_2Cl_2, of [Cubpy(NaaiR$^{/}$)] [NaaiR$^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-R$^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,N$^{/}$-chelator, where N(imidazole) and N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*), were unambiguously assigned on comparing with [Cu(H_2O)] and the free ligand (NaaiR$^{/}$). Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The aryl protons (7-H—11-H) of (*7-9)* are downfield shifted by 0.1-0.7 ppm as compared to those of the parent derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9)-position. The aryl protons 7-(7$^{/}$-) and 11-(11$^{/}$-)H resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution phase.

The ^{13}C NMR spectrum, measured in CD_2Cl_2, provides direct information about the carbon skeleton of the molecule [Cu(NaaiR$^{/}$)bpy]Cl_2 where NaaiR$^{/}$ = naphthylazo imidazole /benzimidazole /pyridine = -$C_{10}H_4$-N=N- / -C_3H_2-NN-1-R$^{/}$, (R = imidazole) / -C_7H_4-NN-1-H (Benzimidazole), / -C_3H_4-N-(Pyridine), abbreviated as -N,N$^{/}$-chelator, where -N(imidazole) and -N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*)]. The non-protonated carbon atoms at C(2) and C(6) of the naphathylazoimidazole moiety is shifted farthest downfield in the spectrum. The carbon atom adjacent to the benzimidazole, naphthyl, molecule in the complex resonance at a lower field resulting of the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The methyl carbon atom of the imidazole ring resonate at 30 ppm, resonably compare to the other carbon atoms resonance.

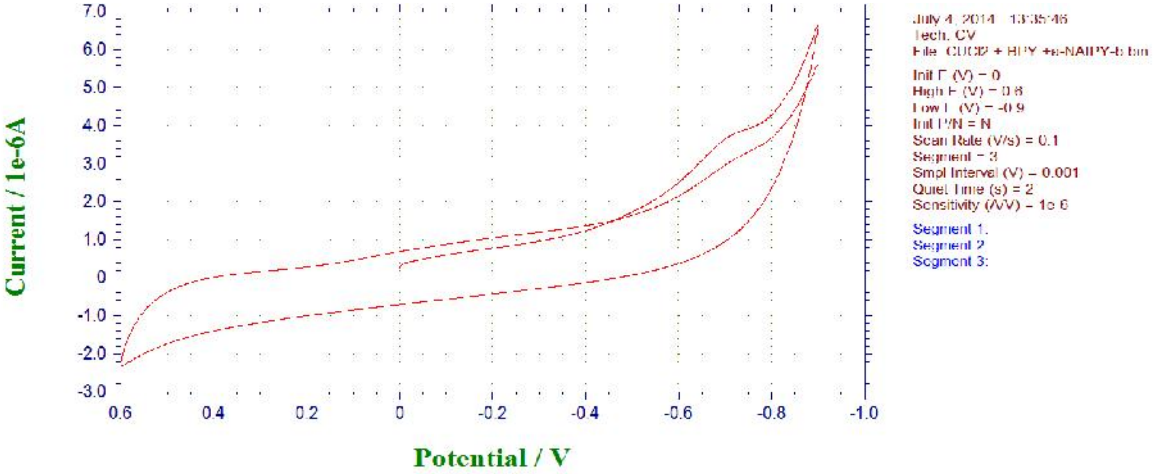

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FIGURE 2: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 5 (above one)

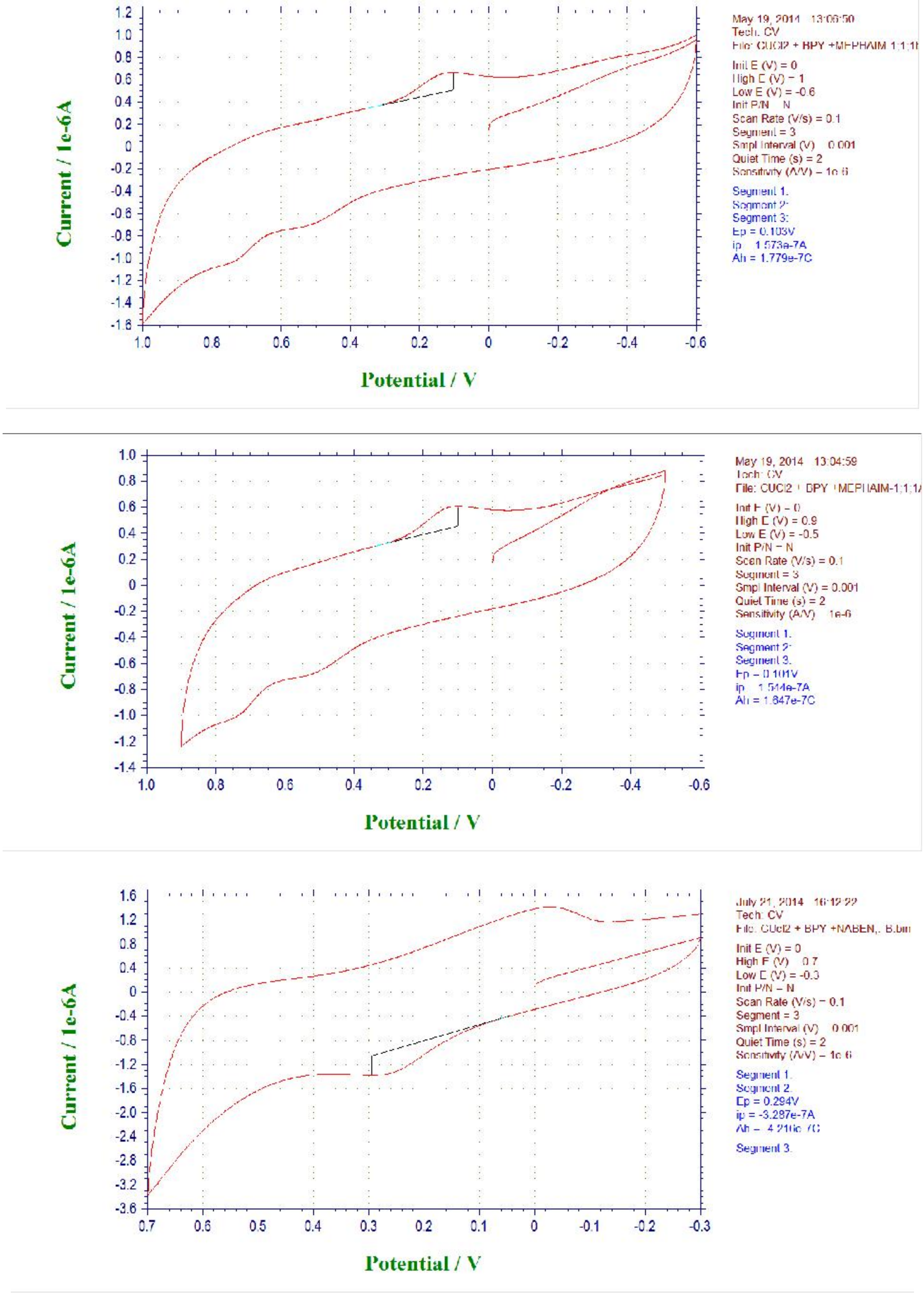

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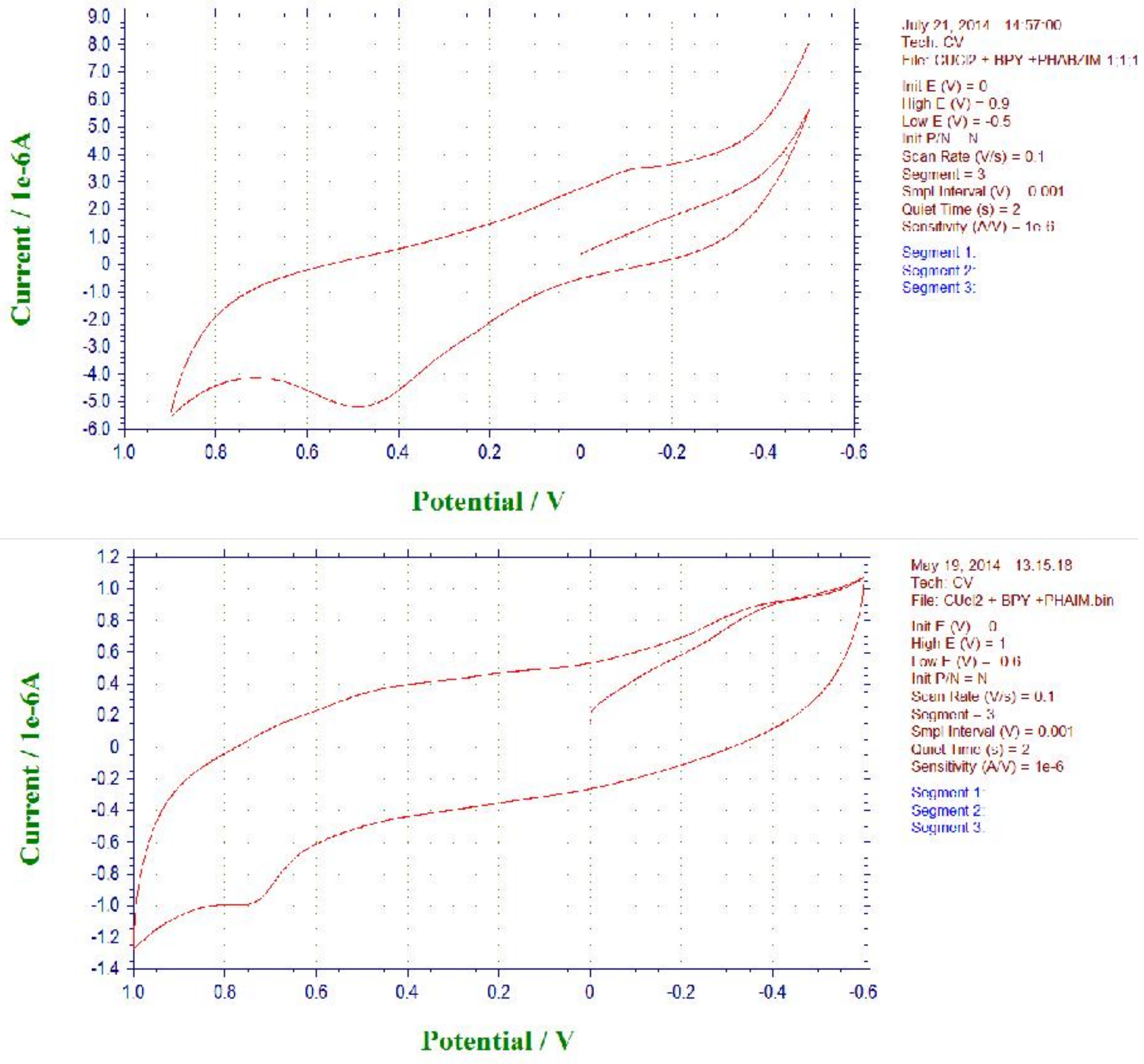
FIGURE 3: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 3 (above two) and 4 (below one)



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Quiet Time (s) = 2
Sensitivity (A/V) = 1e-6

FIGURE 4: Electrochemistry or Cyclic Voltammetric data ($E_{1/2}$ (V) (E_p(mV) [Solvent MeCN, Supporting Electrolyte, Bu_4NClO_4 (0.1 M), scan rate 50 mVs^{-1}, Pt disk working electrode, Pt wire auxiliary electrode, referance electrode SCE at 298 K] of complex 6 (above one) and 2 (below one)

Electrochemistry

Fig. 2, Fig. 3 and Fig. 4 shows representative cyclic voltammogram of the complexes and data are collected in Experimental Section. Copper(II) complexes, [Cu(NaaiR$^{/}$)bpy]Cl_2 where NaaiR$^{/}$ = naphthylazo imidazole /benzimidazole /pyridine = -$C_{10}H_4$-N=N- / -C_3H_2-NN-1-R$^{/}$, (R = imidazole) / -C_7H_4-NN-1-H (Benzimidazole), / -C_3H_4-N-(Pyridine), abbreviated as -N,N$^{/}$-chelator, where -N(imidazole) and -N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*)] , show a quasireversible oxidative response at 0.4 V which may be referred to Cu(II)/Cu(I). An irreversible response is observed at 1.0 V that may be assigned to the oxidation of water present in solvent. On scanning to+ ve direction up to 1.8 V we observe an irreversible response E pc at 0.4 V and a quasireversible response at 1.1 to 1.3 V. They may be assigned to reduction of azo group [(–N@N–)/(–N@N–)] of the chelated ligands. The voltammogram also shows a small anodic peak at 0.2 V, possibly due to the Cu (I)/Cu (0) couple. The reduced Cu (0) is absorbed on the electrode surface as evidenced from the narrow width of the anodic response with a large peak current. In case of [Cu of the couple at 0.4 V is largely dependent on scan rate and increases from 100 mV at remains almost constant and also the values when the voltammogram is scanned at slow scan rates (10–50 mV s^{1}). This observation suggests low heterogeneous electron-transfer rate constant which has been influenced by the applied potential. In general, the electrochemical reduction of copper(II) complexes is associated with change in coordination geometry. Solution structure of copper(II) complex shows square pyramidal or trigonal bipyramidal which upon reduction rearranges fast to tetrahedral geometry via bond rupture and bond formation. Two couples at ca.0.5 and 1.2 V are assigned to azo reduction. The quasireversibility of the couples are noted by peak-to-peak separation.

Conclusion

This work describes the isolation of a novel series of copper(II) azo-imine mononuclear complexes, [Cu(bpy)(NaaiR$^{/}$)], [NaaiR$^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-R$^{/}$, (R imidazole) / C_7H_4-NN-1-H (Benzimidazole), / C_3H_4-N-(Pyridine), abbreviated as N,N$^{/}$-chelator, where N(imidazole) and N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*), bpy = bidentate 2-2$^{/}$ bipyridine ligand, and their spectral and elemental characterisation. The complexes were well characterised by NMR, IR, UV VIS, CV, Mass spectroscopy. The voltammogramalso shows a small anodic peak at 0.2 V, possibly due to the Cu(I)/Cu(0) couple.

Acknowledgments

Department of Science and Technology (DST) is thanked for financial support. (FAST TRACK Grand No. **SERB/F/4888/2012-13 Dated 30.11.2012, No. SR/FT/ CS-102/2009**. Department of Science and Technology (DST) is thanked for financial support to **Somnath Sau**.

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