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Research Article

COPPER(II) THIOCYANATE COMPLEXES : SYNTHESIS, SPECTROSCOPIC STUDY AND ELECTROCHEMISTRY OF COPPER(II)-BIS NAPHTHYLAZO IMIDAZOLE/BENZIMIDAZOLE/PYRIDINE THIOCYANATE COMPLEXES.

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Abstract

Reaction of copper perchlorate hexahydrate $[Cu(H_2O)](OClO_4)$ with NaaiR´ in CH_2Cl_2 medium following ligand addition leads to $[Cu(NCS)_2(NaaiR^{/})_2]$ and $[Cu_2(\text{--}NCS)_2(NaaiR^{/})_2]$, 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex]. 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 voltammogram also 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

Metal-based antitumor drugs play a relevant role in antiblastic chemotherapy. Cis-platin is regarded as one of the most effective drugs, even if severe toxicities and drug resistance phenomena limit its clinical use. Therefore, in recent years there has been a rapid expansion in research and development of novel metal-based anticancer drugs to improve clinical effectiveness, to reduce general toxicity and to broaden the spectrum of activity.

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 [1-4]. 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 [5-9]. Azo-conjugated metal complexes exhibit unique properties upon light irradiation in the area of photon-mode high-density information storage photoswitching devices [10-13]. 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. 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 [14-26]. 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 [27-33]. 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. 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 [34-40]. 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 [41-49].

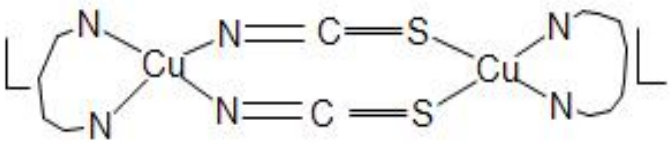
Materials and Methods

Material and instrumentation

Published methods were used to prepare Naphthylazoimidazole /benzimidazole/ pyridine [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 $\sim 10^{-3}$ 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).

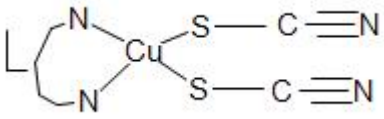
Preparation of the complexes

Synthesis of different copper thiocyanate bridge complex



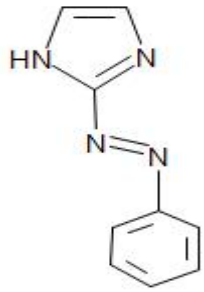
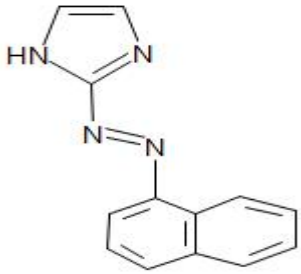
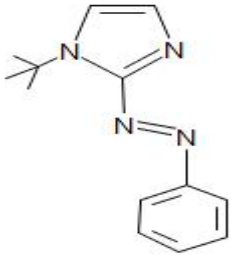
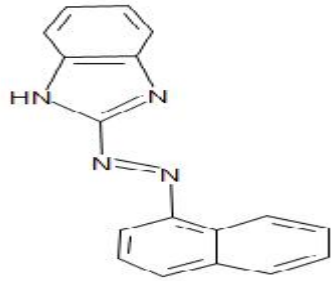
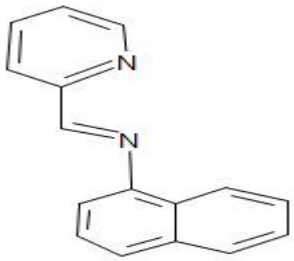
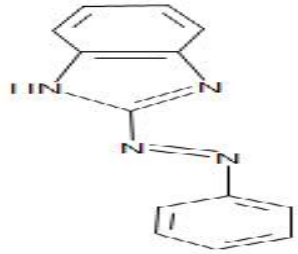
Where **L =PAIM(1)/NAIM(3)/MePAIM(5)/NABEN(7)/αNAiPY(10)/PABEN(12)**

Synthesis of different copper thiocyanate complex



Where **L =PAIM (2)/NAIM (4)/MePAIM (6)/NABEN (8)/αNAiPY (9)/PABEN (11)**

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

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

Synthesis of the compoud 1. 0.1g=0.00058 mole Phenyl azo imidazole(PAIM) +1 equivalent i.e 0.0988g copper chloride($CuCl_2$)+ 1 equivalent i,e 0.04702g sodium thiocyanate (NaSCN), 0.1g i,e 0.00058mole phenyl-azo imidazole (PAIm) was dissolved in acetone solvent. A straw yellow colour was obtained.Then 0.0988g of copper chloride ($CuCl_2$) i.e 1 equivalent was added into this solution which changed the colour to deep green.Now 0.04702g i.e 1 eqv of sodium thiocyanate (NaSCN) was added into the mixture and the colour changed to light green. 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 charecterisation analysis of the compound.

Characterisation of the compound 1: CHN calculation of the above compound [$C_{20}H_{16}N_{10}S_2Cu_2$], gives Calc(found): C, 40.87 (40.9), H, 2.74 (2.7), N, 23.83(23.9); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2177, ESI/MS Spectroscopic data, 587.6 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 2: 0.1020g=0.00059 mole phenyl azo imidazole (PAIM) + 1 equivalent=0.1005g copper chloride(copper chloride) +2 equivalent of sodium thiocyanate i.e 0.0956g NaSCN, 0.1020g i,e 0.00059 mole PAIm was

dissolved in acetone solvent.A straw yellow colour was instantly observed. In this solution.0.1005 g of $CuCl_2$ i.e 1 equivalent was added.The colour of the solution changed to deep green.Now 0.0956g i.e2 eqv of NaSCN was added into the mixture and the colour change was observed.It was light green in colour. The whole mixture was stirred for 12 hours.after the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another charecterisation analysis of the compound.

Characterisation of the compound 2: CHN calculation of the above compound [$C_{11}H_8N_6S_2Cu_1$], gives Calc(found): C, 37.54 (37.5), H, 2.29 (2.2), N, 23.88(23.8); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2186, ESI/MS Spectroscopic data, 351.9 [M^+], Proton n.m.r.Spectroscopic data, ^1H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 3. 0.1688g napthyl azo imidazole (NAIM) i.e. 0.00076 mole+1 equivalent copper chloride i.e. 0.13086g $CuCL_2$ +sodium thiocyanate (NaSCN) 0.0616g=1eqv. , 0.1688g i.e. 0.00076 mole napthyl azo imidazole was dissolved in acetone solvent. The colour was changes to deep brown.In this solution 0.13086 g of $CuCl_2$ i.e. 1 equivalent was added which intensified the brown colour. Into this solution 0.0616g i.e. 1 eqv of NaSCN was added into the mixture and the colour changes to red. The whole mixture was stirred for 12 hours. 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 [$C_{28}H_{20}N_{10}S_2Cu_2$], gives Calc(found): C 48.89(48.8), H, 2.92 (2.9), N, 20.36(20.4); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2177, ESI/MS Spectroscopic data,687.7 [M^+], Proton n.m.r.Spectroscopic data, ^1H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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: Napthyl azo imidazole (0.1590g =0.00072 mole) + copper chloride (0.12398g=1eqv) + sodium thiocyanate (0.11674g=2eqv), 0.1590g i.e. 0.00072mole Napthyl azo imidazole (NAIM) was dissolved in acetone solvent which give a brown colour solution. In this solution 2 equivalent i.e. 0.1239g of CuCl2 was added which intensified the brown colour.Now0.11674g i.e2 eqv of sodium thiocyanate(NaSCN) was added into the mixture and the colour changes to red. The whole mixture was stirred for 12 hours. 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 [$C_{15}H_{10}N_6S_2Cu_1$], gives Calc(found): C, 44.82 (44.8), H, 2.50 (2.5), N, 20.90 (20.9); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2183, ESI/MS Spectroscopic data, 401.9 [M^+], Proton n.m.r.Spectroscopic data, ^1H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 compoud 5. 1-methyl phenyl azo imidazole (MePAIM 0.0846g =0.00045 mole) + copper chloride ($CuCl_2$0.0767g=1eqv) + sodium thiocyanate (NaSCN 0.0364g=1eqv), 0.0846g i.e. 0.00045mole 1-methyl phenyl azo imidazole (MePAIM) was dissolved in acetone solvent .The colour of the solution was deep yellow. Now .0.0767g of CuCl2 (1 equivalent) was added into this solution which changes the colour to greenish yellow. Then 0.0364g i.e 1 eqv of sodium thiocyanate was added into the mixture and the colour changes to reddish brown.The whole mixture was stirred for 12 hours. 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 [$C_{22}H_{20}N_{10}S_2Cu_2$], gives Calc(found): C, 42.91(42.9), H, 3.27 (3.2), N, 22.75 (22.7); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2195, ESI/MS Spectroscopic data, 615.68 [M^+], Proton n.m.r.Spectroscopic data,

^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 6. MePAIM (0.1141g =0.00061 mole) + $CuCL_2$ (0.10399g=1eqv) + NaSCN (0.0989g=2eqv), 0.1141g i.e. 0.00061 mole MePAIM was dissolved in acetone solvent which changed the colour to deep yellow. Now 0.10399 g of CuCl2 i.e. 1 equivalent was added into this solution after which the colour was changed to greenish yellow. Now 0.0989 i.e. 2 eqv. of NaSCN was added into the mixture and stirred the mixture gently. The colour changed into brown.The whole mixture was stirred for 12 hours. 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 $C_{12}H_{10}N_6S_2Cu_1$, gives Calc(found): C, 39.38 (39.3), H, 2.75 (2.7), N, 22.96 (22.9); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2182, ESI/MS Spectroscopic data, 365.9 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 7.Napthyl azo benzimidazole (NABEN 0.116g =0.00043mole) +copper chloride ($CuCL_2$ 0.0733g=1eqv) + sodium thiocyanate (NaSCN 0.03486g=1eqv), 0.116g i.e. 0.00043 mole NABEN was dissolved in acetone solvent which was a brown colour solution. Now 0.0733 g of CuCl2 i.e. 1 equivalent was added into this solution that intensified the brown colour. Then 0.0348g i.e. 1 eqv of NaSCN was added into the mixture and the colour changed to reddish brown. The whole mixture was stirred for 12 hours. 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 $[C_{36}H_{24}N_{10}S_2Cu_2]$, gives Calc(found): C, 54.88 (54.8), H, 3.07 (3.1), N, 17.77 (17.8); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2191, ESI/MS Spectroscopic data, 787.8 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 8. Napthyl azo benzimidazole (NABEN 0.0090g =0.00003 mole) +copper chloride ($CuCL_2$ 0.0051g=1eqv) + sodium thiocyanate NaSCN (0.0048g=2eqv), 0.0090g i.e. 0.00003 mole NABEN was dissolved in acetone solvent which was a brown colour solution. Now0.0051 g of CuCl2 i.e. 1 equivalent was added into this solution which changed the colour to deep brown. Then 0.0048g i.e2 eqv of NaSCN was added into the mixture and the colour change was observed.the whole mixture was stirred for 12 hours.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 8: CHN calculation of the above compound $[C_{19}H_{12}N_6S_2Cu_1]$, gives Calc(found): C, 50.48 (50.5), H, 2.67 (2.6), N, 18.59 (18.6); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2188, ESI/MS Spectroscopic data, 452 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 9. Alpha napthyl azo pyridine (αNaiPY0.0651g =0.00028mole) + $CuCL_2$ (0.0477g=1eqv) + NaSCN (0.0454g=2eqv), 0.0651g i.e. 0.00028 mole of αNaiPY was dissolved in acetone solvent. It was a yellow colour solution. Now 0.0477g of $CuCl_2$ i.e. 1 equivalent was added into this solution which changed the colour to greenish yellow. Now 0.0454g i.e2 eqv of NaSCN was added into the

mixture and the colour change was observed. It was a reddish brown colour. The whole mixture was stirred for 12 hours.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 9: CHN calculation of the above compound [$C_{18}H_{12}N_4S_2Cu_1$], gives Calc(found): C, 52.47 (52.4), H, 2.93 (2.9), N, 13.59 (13.6); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2182, ESI/MS Spectroscopic data, 411.9 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 10. α-NaiPY (0.0737g =0.00032mole) + $CuCL_2$ (0.0545g=1eqv) + NaSCN (0.02594g=1eqv), 0.0737g i.e. 0.00032 mole of αNaiPY was dissolved in acetone solvent. It was a yellow colour solution .Now 0.0545g of CuCl2 i.e. 1 equivalent was added into this solution. That changed the colour to greenish yellow. Then 0.0259g i.e1 eqv of NaSCN was added into the mixture and the colour change was observed. It was a deep brown colour. The whole mixture was stirred for 12 hours. After the completion of the reaction it was filtered & filtrate was collected for crystal tube setting and for another characterization analysis of the compound.

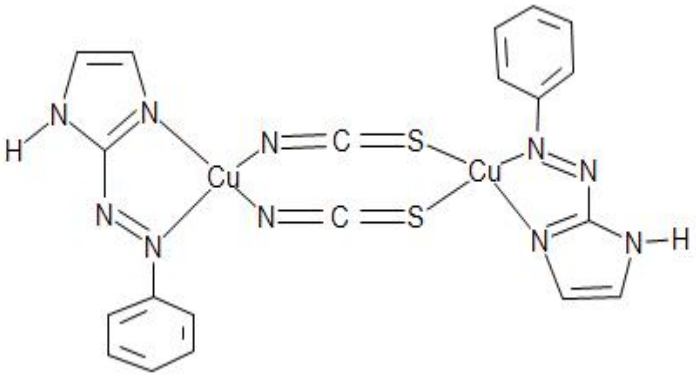
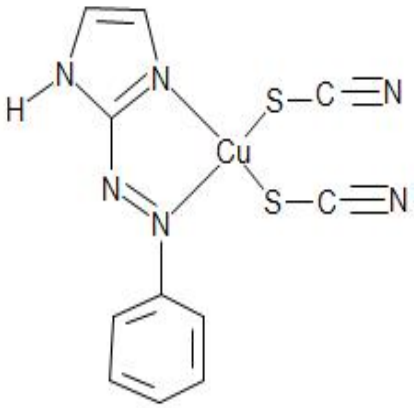
Characterisation of the compound 10: CHN calculation of the above compound [$C_{34}H_{24}N_6S_2Cu_2$], gives Calc(found): C, 57.69 (57.6), H, 3.41 (3.4), N, 11.87(11.9); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2189, ESI/MS Spectroscopic data, 707.8 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 11. Phenyl azo benzimidazole **(**PABEN 0.1186g =0.00053mole) + $CuCl_2$ (0.0903g=1eqv) +NaSCN (0.0859g=2eqv), 0.1186g i.e. 0.00053 mole PABEN was dissolved in acetone solvent which make the solution to light yellow. Now 0.0903g of $CuCl_2$ i.e. 1 equivalent was added into this solution that changed the colour to reddish yellow. Then 0.0859g i.e2eqv of NaSCN was added into the mixture and the colour change was observed. It was a dark brown colour. The whole mixture was stirred for 12 hours. 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 11: CHN calculation of the above compound [C_{15}H10N6S2Cu1], gives Calc(found): C, 44.82 (44.82), H, 2.50 (2.5), N, 20.90(20.9); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2180, ESI/MS Spectroscopic data, 401.9 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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 12. Phenyl azo benzimidazole PABEN 0.1207g =0.00054mole) + $CuCl_2$ (0.09206g=1eqv) +NaSCN (0.04378g=1eqv), 0.1207 i.e. 0.00054mole PABEN was dissolved in acetone solvent Which was a light yellow in colour.Now 0.09206 of CuCl2 i.e. 1 equivalent was added into this solution that changed the colour to reddish yellow. Then 0.0437g i.e1 eqv of NaSCN was added into the mixture and the colour change was observed.It was a reddish brown colour the whole mixture was stirred for 12 hours. 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 12: CHN calculation of the above compound [$C_{28}H_{20}N_{10}S_2Cu_2$], gives Calc(found): C, 48.89 (48.9), H, 2.92 (2.9), N, 20.36(20.3); IR Spectroscopic data, ν(N=N) 1370 ν(C=N) 1590, ν(S=C=N) 2196, ESI/MS Spectroscopic data, 687.73 [M^+], Proton n.m.r.Spectroscopic data, ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 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).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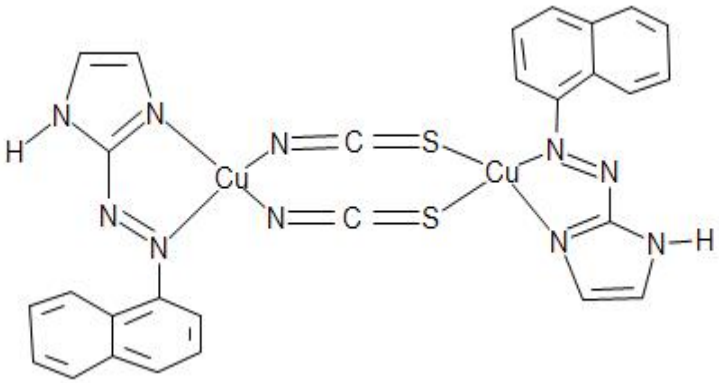	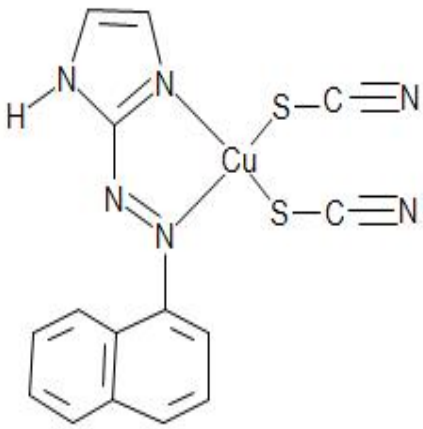
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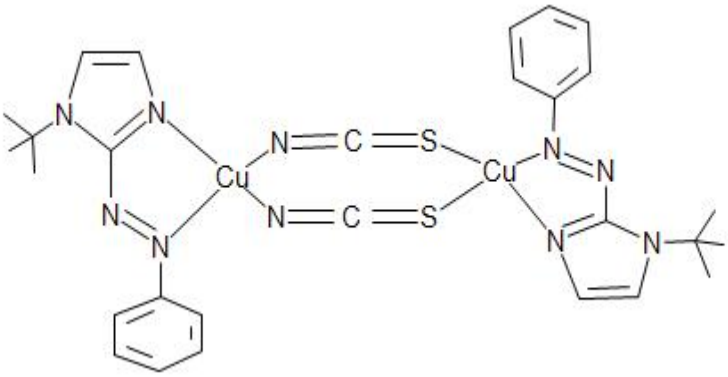	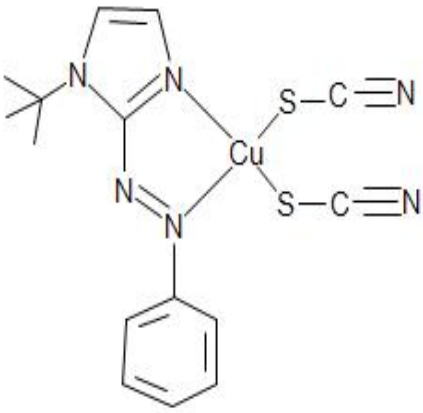
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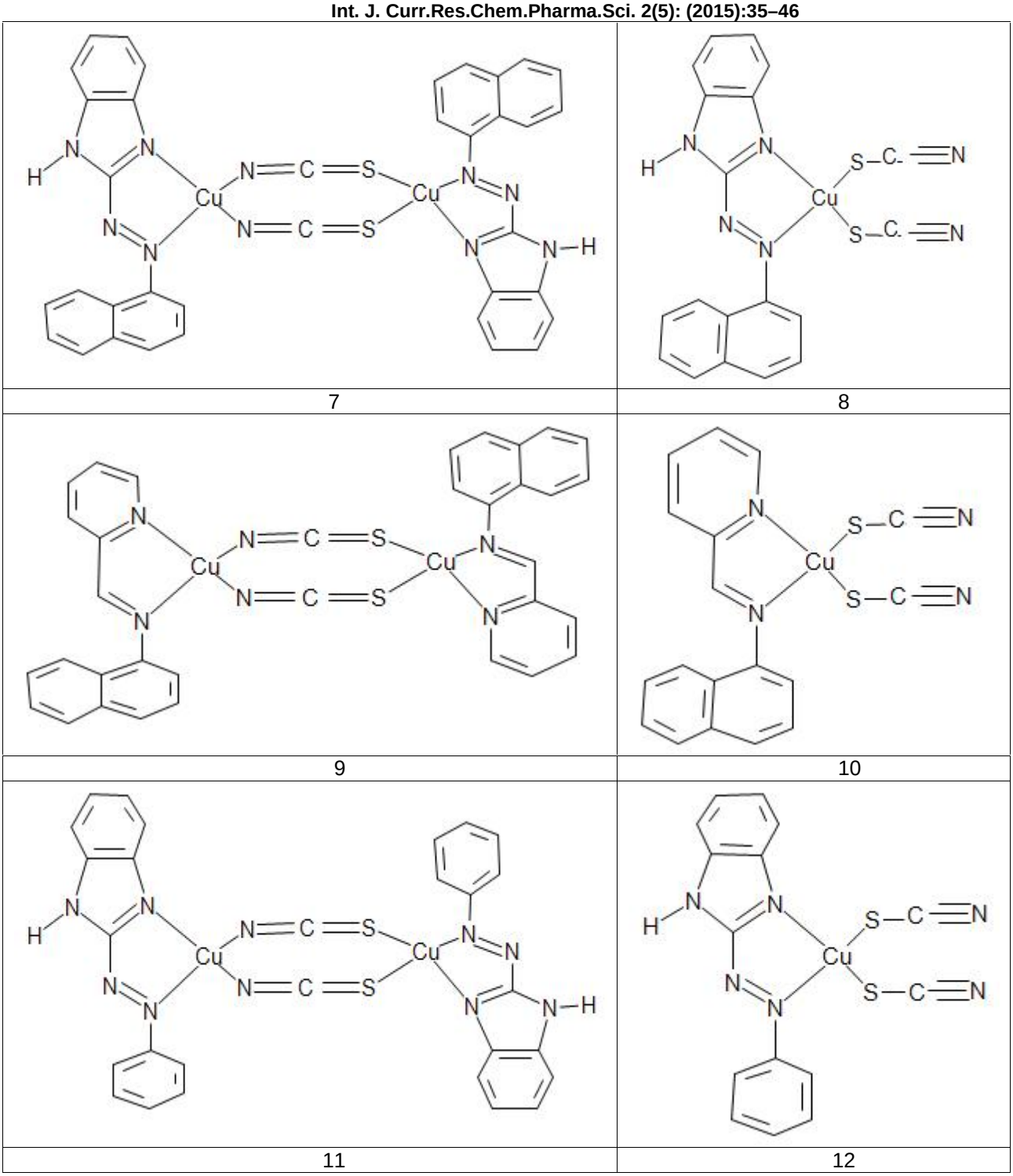

Fig. 1: Reaction scheme and all the mononuclear and binuclear complexes of copper from complex 1 to complex 14, $[Cu(NCS)_2(NaaiR^{/})_2]$ and $[Cu_2(\text{--}NCS)_2(NaaiR^{/})_2]$, [$NaaiR^{/}$ = naphthyl-azo imidazole /benzimidazole /pyridine = $C_{10}H_4$-N=N- / C_3H_2-NN-1-$R^{/}$, (R imidazole) / 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex].

Results and Discussion

Synthesis and formulation

Reaction of copper perchlorate hexahydrate $[Cu(H_2O)](OClO_4)$ with NaaiR in CH_2Cl_2 or acetone medium following ligand addition leads to $[Cu(NCS)_2(NaaiR^{/})_2]$ and $[Cu_2(\text{--}NCS)_2(NaaiR^{/})_2]$, $NaaiR^{/}$ = 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex]. were prepared by removing H_2O, with NaaiR under stirring at 343-353 K in MeOH solution in poor yield (35-40%). The composition of the complexes is supported by microanalytical results. The red orange complexes are soluble in common organic solvents viz. acetone, acetonitrile, chloroform, dichloromethane but not soluble in H_2O, methanol, ethanol. The voltammogramalso shows a small anodic peak at 0.2 V, possibly due to the Cu(I)/Cu(0) couple.

Spectral studies

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.

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 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 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.

The ^{1}H n.m.r. spectra, measured in CD_2Cl_2, of $[Cu(NCS)_2(NaaiR^{/})_2]$ and $[Cu_2(\text{--}NCS)_2(NaaiR^{/})_2]$, $NaaiR^{/}$ = 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex] 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 $[Cu(NCS)_2(NaaiR^{/})_2]$ and $[Cu_2(\text{--}NCS)_2(NaaiR^{/})_2]$, $NaaiR^{/}$ = 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex]. 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.

Electrochemistry

Cyclic voltammogram of the complexes and data are collected in Experimental Section. Copper(I) complexes, $[Cu(NCS)_2(NaaiR^{/})_2]$ and $[Cu_2(\text{--}NCS)_2(NaaiR^{/})_2]$, $NaaiR^{/}$ = 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex] as N,N$^{/}$-chelator, where N(imidazole) and N(azo) represent N and N$^{/}$, respectively; R$^{/}$ = H(*a*), Me (*b*), N_3 = monodentate azide linkage, --N_3 = azide bridged binuclear complex], show a quasireversible oxidative response at 0.4 V which may be referred to Cu(II)/Cu(I) [all the figures are in SI] . 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 voltammogramalso 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 and binuclear azide bridzed complexes, [Cu$(NCS)_2$(NaaiR$^{/}$$)_2$] and [$Cu_2$(--NCS$)_2$(NaaiR$^{/}$$)_2$], NaaiR$^{/}$ = 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*), NCS = thiocyanide linkage, --NCS = thiocyanide bridged binuclear complex], 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,** Project Title: GOLD(I) & GOLD(III) ARYLAZOIMIDAZOLE (N, N DONAR) & OXO COMPLEXES : SYNTHESIS, STRUCTURE, SPECTRAL STUDY, ELECTROCHEMISTRY AND CHEMICAL REACTIVITY). Department of Science and Technology (DST) is thanked for financial support to S Sau.

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