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RESEARCH ARTICLE

Synthesis, Spectral and Structural Studies of Some Copper(II) Complexes of *N,N´*-Bis(2-methyl-*N*-methylbenzimidazolyl)hexanediamide Ligand

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Abstract: Pentacoordinated copper(II) complexes were synthesized from tetradentate ligand *N,N´*-bis (2-methyl-*N*-methylbenzimidazolyl)hexanediamide. Characterization has been done on the basis of elemental analysis, electronic spectra, IR studies, conductance data, magnetic properties, EPR and x-ray studies for the complexes. From analytical data, the stoichiometry of the complexes has been found to be 1:1 metal to ligand ratio. IR spectra and x-ray studies show that the ligand behaves tetradentate through two benzimidazolyl nitrogen and two amide oxygen atoms. The fifth coordination site of the metal is occupied by the anion from metal salt solution.

Keywords: Copper(II) complex, Ligand, Crystal structure, Spectral studies

Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups[1-2] and it is multiplied many fold when the ligand has biological importance[3-4]. Benzimidazoles are involved in a great variety of biological processes. Some of their polyfunctional derivatives have been proven to possess antibacterial, fungicide and anti-hermitic activity[5-8]. Therefore substituted benzimidazoles have attracted the interest of various research group, especially since it has been reported that the influence of the substitution at 1,2 and 5-positions is very important for their pharmacological effect[9].

A large number of pentacoordinated copper(II) complexes were reported in literature. Complex $[Cu_2^{II}(NMEDTB)(NO_3)_3]NO_3.4H_2O$[10] crystallizes in space group C2/c with a 19.159Å, b=15.907 Å, c = 16.816 Å, β = 109.57°, V = 4829.0 Å^3, Z = 4. Structure consists of binuclear $[Cu_2^{II}(NMEDTB)(NO_3)_3]^+$ cation having C_2 symmetry, a disordered nitrate ion and disordered water molecules. Each copper ion is in a square pyramidal coordination geometry with two equatorial benzimidazole nitrogen atoms, one equatorial amine nitrogen atom, one equatorial oxygen atom of a monodentate coordinating nitrate ion and one axial oxygen atom of a nitrate ion which is bridging to the axial position of the other copper ion in the cation.

Mono and dihydrate 1:1 Cu(II) complexes with N_2S_2 donor ligand 1,7-bis(*N*–methyl-benzimidazol–2′–yl)–2,6–dithiaheptane (bmdhp)[11] consists of $[Cu(bmdhp)(H_2O)]^{2+}$ ion and perchlorate counter ions with Cu(II) ion in a coordination environment, intermediate between trigonal bipyramidal and square pyramidal ($\tau = 0.48$). X–ray crystal structure of [Cu(BBIDH) Br]Br[12] (where BBIDH= 1.6–bis(*N*–benzimidazol–2–yl) –2,5–dithiahexane) shows that the Cu(II) is in a trigonal bipyramidal coordination geometry with two axial imidazole nitrogen atoms and two thioether S atoms and a Br^- ion in the equatorial plane. The EPR of the solution of the complex indicate a change in the coordination geometry. Two dinuclear compounds $[Cu_2(benzimidazole)_5Br_3]Br{\cdot}4H_2O$ and $[Cu_2(Benzimidazole)_5\ Cl_3]Cl{\cdot}4H_2O$ were reported by Tosik *et. al.* These compounds are isostructural and consist of pairs of copper(II) ions in a distorted trigonal bipyramid geometry sharing an edge with two equatorial halide ions, the axial positions are occupied by the nitrogen atoms from four benzimidazole ligands[13-14].

Structural data of most of the complexes shows that the bulky nature of the ligand prevents the complex from adopting a perfectly trigonal bipyramidal or square pyramidal geometry. Often the geometries are intermediate between trigonal bipyramidal ($\tau = 1$) and square pyramidal ($\tau = 0$). The metal ion generally moves out of the basal plane, changing the bond angles from predicted values. The distortion of coordination geometries is desired as these impart interesting properties to the complex required in their catalytic activity.

Our aim had been to prepare ligating systems which are more close to the basic units possessed by life *i.e.*, proteins or in a deeper sense amides. Along with amide groups, the present ligand also contains two additional benzimidazole donors. The incorporation of two bulky benzimidazole moieties, apart from mimicking the imidazole function in proteins, will cause steric crowding on copper, which may help to induce unusual coordination geometries and hence interesting spectral and redox properties.

Experimental

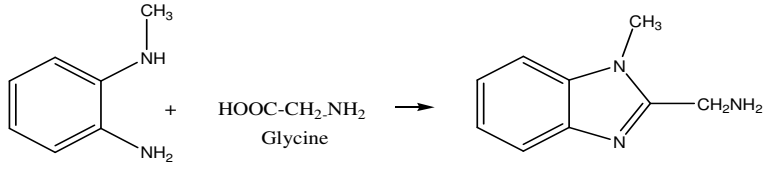
Freshly distilled solvents were employed for all synthetic work. All the chemicals were of AR grade. Carbon, hydrogen and nitrogen were estimated microanalytically on Perkin Elmer 2400 (IEES) from microanalytical laboratory of RSIC, CDRI Lucknow. Metal copper was analysed in all the complexes by chelatometric titration with EDTA. Electronic spectra were recorded on a Beckman DU–64 UV/VIS Spectrophotometer. IR spectra were recorded in the solid state as KBr pellets on a Perkin Elmer FTIR–2000 Spectrometer. Magnetic susceptibilities of complexes were determined using Guoy's magnetic balance having a semimicrometer balance (Model C Meltov Zoric type H16) at 298 K at IIT, Roorkee. Cyclic voltammetric measurements were carried out using a BAS CV 50W electrochemical analyzing system. Cyclic voltammograms of all the complexes were recorded in 2:8 DMSO: Acetonitrile solutions, with 0.1 M $NaClO_4$ as supporting electrolyte. X–band EPR spectra were recorded on a VARIAN E–12 spectrometer with a variable temperature liquid nitrogen cryostat at IIT, Madras. ^1H NMR spectra were recorded on 300 MHz Bruker–Spin instrument. X–ray diffraction data for [CuCl(GMBHA)]Cl was collected by standard methods using graphite monochromated Mo x–radiation at CDRI Lucknow.

Synthesis of ligand *N,N′*-bis(2-methyl-*N*-methylbenzimidazolyl)hexandiamide (GMBHA)

Step I

Glycine *N*-methylbenzimidazole dihydrochloride was prepared following the procedure reported by Cescon and Day[15]. A solution of 12.2 g (0.1 mol) of *N*–methyl-*o*-phenylenediamine and 11.25 g (0.15 mol) of glycine in 100 mL of 5.5 N HCl was refluxed for

30 h. The solution was allowed to stand overnight in cold and the green crystalline product obtained was filtered off. It was recrystallized from ethanol with the aid of decolorizing carbon. The resulting white product was dried in air.



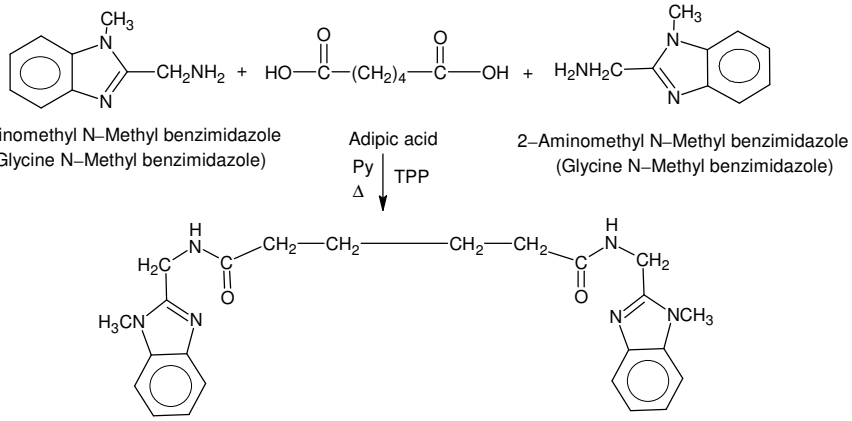
N-methyl-o-phenylenediamine Glycine N-methylbenzimidazole

Scheme 1

The product was analyzed by melting point, IR and UV spectral studies. M.P.: 265 °C; Yield: 14.5 g (62%); IR (cm^{-1}, KBr): 1630, 1488, 1430, 1220, 1008, 887, 770. λ_{max}nm (methanol): 280, 272, 245.

Step II

The ligand *N,N´*-bis(2-methyl-*N*-methylbenzimidazolyl)hexanediamide (GMBHA) was prepared as follows[16]: To a solution of adipic acid (1.67 g, 11.4 mmol) in pyridine (20 mL) a solution of glycine–*N*–methylbenzimidazole dihydrochloride (5.32 g, 22.8 mmol) in pyridine (30 mL) was added. The reaction mixture was then heated slowly on a water bath at a temperature of 40 °C and to it triphenyl phosphate (7.08 mL, 22.8 mmol) was added dropwise over a period of 15-20 minutes. The reaction mixture was simultaneously stirred. When the addition of triphenyl phosphate was complete, the temperature of the reaction mixture was slowly raised up to 75 °C and the clear solution was stirred for one hour. A white solid resulted, which was filtered off, washed with chloroform and recrystallized with EtOH-H_2O (1:2) mixture.



N,N´-Bis(2-methyl N-methyl henzimidazolyl)hexanediamide)

Scheme 2

Characterization of the ligand was done using elemental analysis, UV, IR and ^{1}H NMR spectral studies. M.pt.: 278 °C; Yield: 2.1 g (41.1%); Anal. (%) Found (Calc.): C 63.93(64.0); H 6.54(6.66); N 18.53(18.66); UV (in methanol) $\lambda_{max,}$ nm (log ε): 214 (4.58), 279 (3.68), 272 (3.68), 243 (3.67); IR (KBr pellets, cm^{-1}): 3296(s) ($\upsilon_{N\text{-}H\ amide}$), 3434(s) ($\upsilon_{O\text{-}H\ water}$), 1005(s) ($\upsilon_{N\text{-}CH3\ benzimidazole}$), 1635(s) ($\upsilon_{C=O\ amideI}$), 1539(s) ($\upsilon_{C\text{-}N\ amideII}$), 1448(s) ($\upsilon_{C=N\text{-}C=C}$), 739(s) ($_{benzene\ ring\ vibrations}$); ^{1}H NMR ($d_6$ DMSO) δ ppm: 1.65 (quin., 4H), 2.26 (t, 4H), 4.54 (d, 4H), 7.15–7.49 (m, 8H), 8.44 (t, 2H $_{amide\ NH}$), 10.48 (s, 3H–CH_3).

Preparation of copper(II) salt solutions

Copper(II) salts [$CuCl_2.2H_2O$, $Cu(NO_3)_2.3H_2O$, $Cu(ClO_4)_2.2H_2O$] solutions were prepared by dissolving the 'AR' salt in methanol. The strength of solutions was determined iodometrically.

Synthesis of copper(II) complexes

All the metal complexes were prepared by mixing equimolar solution (0.5 mmole) of metal salt and GMBHA (0.5 mmole) in 1:1 ratio in methanolic solution. The resulting solutions were stirred for an hour after which the volume was reduced on water bath. The solutions were allowed to cool for 24 hours when green colored precipitates separated out. The precipitates were separated from the reaction mixture by filtration, washed with methanol and dried in vacuum desiccator over $CaCl_2$. The complexes were analysed for the following compositions

[Cu(GMBHA)Cl]Cl. $H_2O.CH_3OH$

M.f.: $CuC_{24}H_{28}N_6O_2Cl_2.H_2O.CH_3OH$; Yield: 200 mg (64.8%); Anal. (%) Found (Calc.): C 48.49 (48.65); H 5.51 (5.51); N 13.52 (13.62); Cu 10.20 (10.30) ; UV (in methanol) $\lambda_{max,}$ nm(log ε): 756 (2.05), 277 (4.28), 270 (4.30), 243 (2.52); IR (KBr pellets, cm^{-1}): 3395(m) ($\nu_{O-H\ water}$), 3209(s) ($\nu_{N-H\ amide}$), 1005(s) ($\nu_{N-CH3\ benzimidazole}$), 1604(s) ($\nu_{C=O\ amideI}$), 1560(m) ($\nu_{C-N\ amideII}$), 1452(m) ($\nu_{C-N-C=C\ benzimidazole}$), 745(s) ($_{Benzene\ ring\ vibration}$); Λ_M: 75 $\Omega^{-1}cm^2mol^{-1}$

Cu(GMBHA)NO_3]NO_3.CH_3OH

M.f.: $CuC_{24}H_{28}N_8O_8.CH_3OH$; Yield: 210 mg (64.4%); Anal. (%) Found (Calc.): C 45.44 (46.04); H 4.90 (4.91); N 17.15 (17.19); Cu 9.72 (9.74); UV (in methanol) $\lambda_{max,}$ nm(log ε): 775 (1.94), 277 (4.28), 270 (4.30), 243 (2.51); IR (KBr pellets, cm^{-1}): 3230(m) ($\nu_{N-H\ amide}$), 1007(s) ($\nu_{N-CH3\ benzimidazole}$), 1604(s) ($\nu_{C=O\ amide\ I}$), 1500(m) ($\nu_{C-N\ amide\ II}$), 1445(b) ($\nu_{C=N-C=C\ benzimidazole}$), 1384(b) ($\nu_{O-N-O\ symm}$), 821(b) ($\nu_{O-N-O\ antisymm}$), 749(m) ($_{Benzene\ ring\ vibration}$); Λ_M: 85 $\Omega^{-1}cm^2mol^{-1}$.

[Cu(ClO_4)(GMBHA)]ClO_4.0.25CH_3OH

M.f.: $CuC_{24}H_{28}N_6O_{10}Cl_2.0.25CH_3OH$; Yield: 180 mg (51%); Anal. (%) Found (Calc.): C 41.30 (41.42); H 4.10 (4.12); N 11.80 (11.95); Cu 8.98 (9.04); UV (in methanol) $\lambda_{max,}$ nm (log ε): 762 (2.19), 278 (4.32), 270 (4.35), 243 (2.52) ; IR (KBr pellets, cm^{-1}): 3244(b) ($\nu_{N-H\ amide}$), 1005(s) ($\nu_{N-CH3\ benzimidazole}$), 1603(s) ($\nu_{C=O\ amideI}$), 1538(m) ($\nu_{C-N\ amideII}$), 1445(s) ($\nu_{C=N-C=C\ benzimidazole}$), 1100(m) and 1080(m) ($\nu_{O-Cl}$), 743(m) ($_{Benzene\ ring\ vibration}$), 625(s) ($\nu_{ClO4}$); Λ_M: 92 $\Omega^{-1}cm^2mol^{-1}$. *Safety Note! Caution!* Perchlorate salts of metal complexes are potentially explosive when shocked or heated[17].

Results and Discussion

The complexes were prepared through direct reaction of the metal salt solutions $CuCl_2.2H_2O$, $Cu(NO_3)_2.3H_2O$, $Cu(ClO_4)_2.2H_2O$, with the ligand *N,N´*-bis(2-methyl-*N*-methylbenzimidazolyl) hexanediamide (GMBHA) in (1:1) molar ratio. The analytical data of the complexes also show that all the metal chelates have 1:1 metal to ligand stoichiometry.

The electronic spectra of copper(II) complexes were recorded in methanol solvent. Two peaks in the range 270-285 nm are observed in free ligand as well as in all the complexes which have been assigned to intraligand π-π* transition of benzimidazole group[18]. The bands show enhanced absorption in complexes as indicated by their extinction coefficients.

In IR spectra, shift in amide I band due to C=O group and increase/decrease in amide II band due to C-N group in the ligand are indicative of the coordination of the amide through carbonyl oxygen in the complexes[19-24]. In all the complexes, the $\upsilon_{C=O\ amide\ I}$ band decreases while $\upsilon_{C\text{-}N\ amide\ II}$ band shifts as compared to the ligand. The shift of amide NH bands indicates hydrogen bonding either with the solvent molecules or with the exogenous anionic ligand in the complexes[19-20]. In chloride complex, a broad band in the 3300-3500 cm^{-1} region is due to $\upsilon_{(O\text{-}H)}$ indicating the presence of water molecule. The nitrate complex shows bands at 1384 and 821 cm^{-1} due to $\upsilon_{O\text{-}N\text{-}O\ (symm)}$ and $\upsilon_{O\text{-}N\text{-}O\ (antisymm)}$ stretching of the coordinated nitrate group[25-27]. A split band for perchlorate complex at 1100 and 1080 cm^{-1} is assigned to ν_{O-Cl} stretching of perchlorate group and indicates the coordination of perchlorate ion[26-27], while a sharp band at 625 cm^{-1} arises due to the presence of ionic perchlorate[28-30].

X-ray diffraction shows that complex $[CuCl(GMBHA)]Cl.H_2O.CH_3OH$ consists of a discrete complex cation and a chloride ion. In the cation, the coordination environment around the copper atom is penta−coordinate consisting of two benzimidazolyl nitrogen atoms, two amide carbonyl oxygen atoms and a chloride ion (Figure 1). The structure has the appearance of a trigonal bipyramid in which equatorial positions are occupied by a Cl atom and amide carbonyl oxygen atoms O(1) and O(2) and the axial positions by benzimidazole imine nitrogen atoms N(1A) and N(1B).

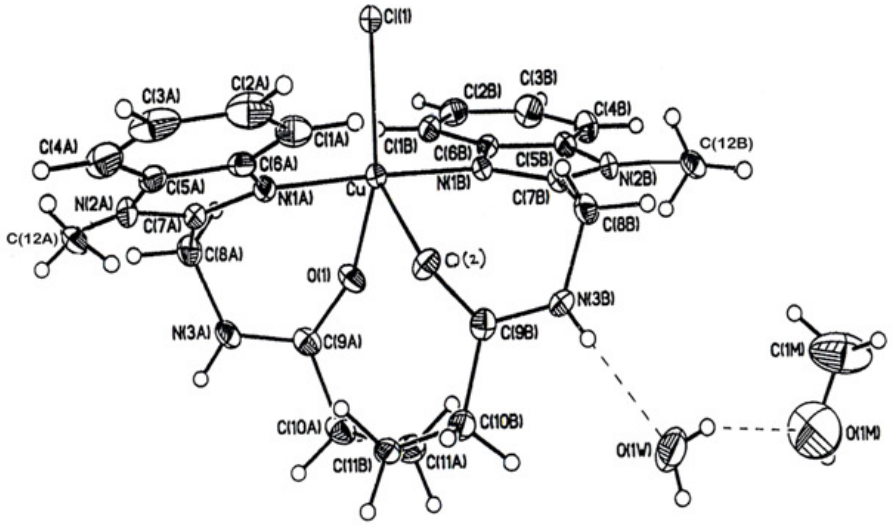


Figure 1. ORTEP projection of $[CuCl(GMBHA)]Cl.H_2O.CH_3OH$ showing atomic numbering scheme

Cu–N bond distances of 1.967Å (Cu–N(1A)) and 1.977Å (Cu–N(1B)) are in the range found for similar benzimidazole and imidazole ligated compounds (Table 1). A large number of trigonal bipyramidal complexes containing axially bound imidazole/benzimidazole nitrogen atoms are available[11,12,18, 31,] in literature which report Cu–N bond lengths as 1.951 and 1.945 Å, 1.950 Å, 1.94 and 1.93 Å, 1.961 and 1.968 Å.

The geometric parameter τ is applicable to five coordinated structures as an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal (τ=1) and square pyramidal (τ=0). The complex $[CuCl(GMBHA)]Cl.H_2O.CH_3OH$ has τ value of 0.591 indicating a strong distortion from perfect TBP. One complex reported in literature, [31]

$[Cu(bbtb)(H_2O)](ClO_4)_2$ (where bbtb = 1,2–bis(benzimidazol–2′–ylmethyl– thio)benzene has τ value 0.64 near to our system. The observed Cu–Cl(1) bond length is in similar range as that observed for similar[32-34] five coordinated Cu(II) compounds with Cu–Cl bond lengths 2.241 Å, 2.391 Å and 2.364–2.421 Å. An interesting network of hydrogen bonding appears to stabilize the lattice structure. The crystal consists of layers of [CuCl (GMBHA)]$Cl.H_2O.CH_3OH$ stacked over each other, held together by NH_{amide}----OH_{water}----O_{CH3OH} interactions.

Table 1. Selected bond lengths (Å) and bond angles (°) for [CuCl(GMBHA)] $Cl.H_2O.CH_3OH$

Bond lengths			
Cu-N(1A)	1.967(3)	Cu-N(1B)	1.977(3)
Cu-O(1)	2.111	Cu-O(2)	2.166(3)
Cu-Cl(1)	2.3082(12)		
Bond angles			
N(1A)-Cu-N(1B)	176.89(13)	N(1A)-Cu-O(1)	92.12(12)
N(1A)-Cu-O(2)	87.41(12)	N(1B)-Cu-O(1)	84.77(12)
N(1B)-Cu-O(2)	92.87(13)	N(1A)-Cu-Cl(1)	91.51(10)
N(1B)-Cu-Cl(1)	90.92(10)	O(1)-Cu-Cl(1)	141.46(10)
O(2)-Cu-Cl(1)	123.28(9)		

All the complexes display a quasi-reversible redox wave (Figure 2-4) due to the Cu(II)/Cu(I) process. Anodic shifts in $E_{1/2}$ values indicate the retention of the anion in the coordination sphere of Cu(II). The $E_{1/2}$ values vary anodically in the order

$$ClO_4^- < Cl^- < NO_3^-$$

This indicates that bound nitrate destabilizes Cu(II) state while bound perchlorate stabilizes it.

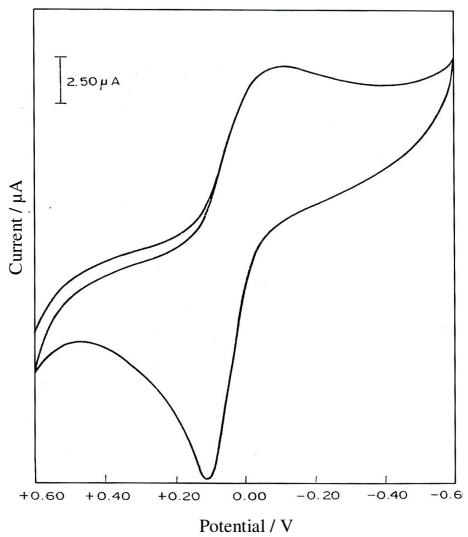


Figure 2. Cyclic voltammogram of [Cu (GMBHA)Cl]Cl in 2:8 DMSO:CH_3 CN solution at scan rate 100 mV/s

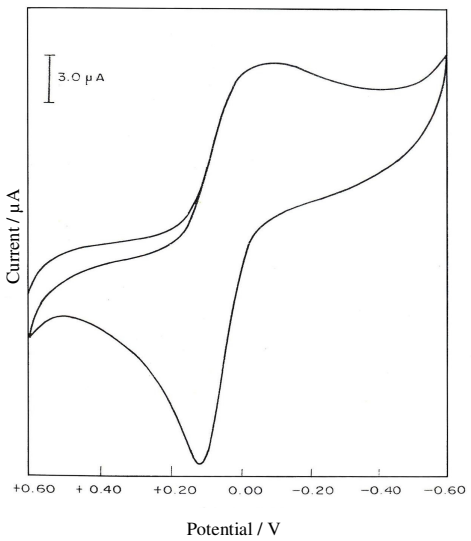


Figure 3. Cyclic voltammogram of [Cu (GMBHA)NO_3 NO_3 in 2:8 DMSO:CH_3CN solution at scan rate 100 mV/s

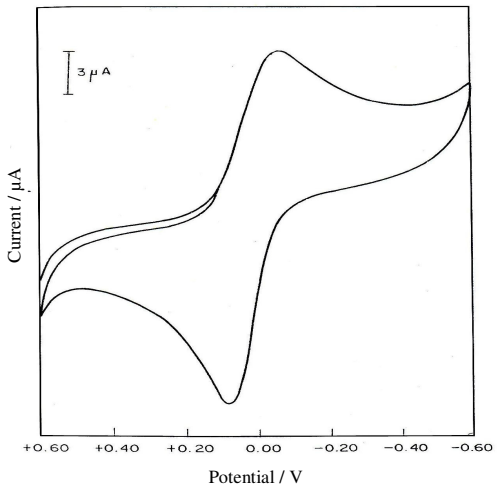


Figure 4. Cyclic voltammogram of $[Cu(GMBHA)ClO_4]ClO_4$ in 2:8 DMSO:CH_3CN solution at scan rate 100 mV/s

Binding of amide carbonyl oxygen apparently has a destabilizing effect on Cu(II), leading to relatively high anodic redox potential for this series of complexes. Conductance data was obtained for the copper complexes in 2:8 DMSO:CH_3CN solvent system at concentration 0.001 M. The molar conductance value is high for chloride, nitrate and perchlorate complexes indicating that all the complexes behave as true electrolytes.

Magnetic moments were measured at 25 ^oC. For all the copper(II) complexes, the magnetic moments were (1.90-2.04) B.M., suggesting the presence of one unpaired electron. X–Band EPR spectra of the Cu(II) complexes were recorded in DMSO at liquid nitrogen temperature (Table 2). Spectra typically indicate a $dx^2–y^2$ ground state ($g_{\|} > g_{\perp} > 2.0023$).

Table 2. X–Band EPR data of Cu(II)–GMBHA complexes in DMSO

Complexes	$g_{\|}$	$g_{\perp}$	$A_{\|}$ (G)	$g_{\|}/A_{\|} \times 10^{-4}$	α^2
[CuCl(GMBHA)]Cl	2.27	2.07	145	156	0.65
$[Cu(NO_3)(GMBHA)](NO_3)$	–	2.07	–	–	–
$[Cu(ClO_4)(GMBHA)](ClO_4)$	2.28	2.11	120	190	0.55

The factor $g_{\|}/A_{\|}$ reflects the distortion of coordination geometry. Higher the value of this factor, greater is the distortion. This is because when the geometry is no longer planar, the interaction of $dx^2–y^2$ ground state orbital with ligand orbitals is lowered and thus repulsion between unpaired electron in $dx^2–y^2$ orbital and ligand electrons decreases. As a result this unpaired electron is now more delocalized and couples with the copper nucleus to a lesser extent. Hence the coupling constant is low. $g_{\|} / A_{\|}$ allow the order $ClO_4^- > Cl^-$ indicating the distortion of coordination geometry is more in perchlorate complex than in chloride complex. For $[Cu(NO_3)(GMBHA)](NO_3)$ an isotropic signal was obtained in DMSO solution. The α^2 ranges from 0.55–0.65 indicating considerable amount of covalent character in Cu–Ligand bond.

Conclusion

Chloride complex was found to possess distorted trigonal bipyramidal geometry. X-ray diffraction and IR studies of copper(II) complexes of ligand GMBHA with different exogenous

anions show that the benzimidazole nitrogen atoms are coordinated to Cu(II) and unexpectedly amide carbonyl oxygens are involved in coordination to Cu(II) to give otherwise less favourbale seven membered chelate rings rather than coordination of amide nitrogen to give more favourable five membered chelate ring.

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