632 **RESEARCH PAPER** OCTOBER, 632–635 JOURNAL OF CHEMICAL RESEARCH 2006

An unusual square planar *open-lock* shaped copper(II) metallaligand obtained from a hexadentate amine–amide–phenol ligand

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The copper(II) complex, [Cu(LH$_{-2}$)] (**4**), asymmetrically coordinated by the tetradentate part of, 1,8-bis(2-hydroxybenzamido)-3,6-diazaoctane (L) is reported. Its structure involves a 1-D infinite chain that utilises hydrogen bonding between coordinated side amide carbonyl oxygen and uncoordinated metallaligand amide nitrogen atoms. Further complexation reaction of the metallaligand with [Cu(bpy)(MeOH)$_2$](ClO$_4$)$_2$ gives [Cu$_2$(LH$_{-4}$)(bpy)] (**5**).

Keywords: hexadentate, amide coordination, metallaligand, copper(II) complex, crystal structure

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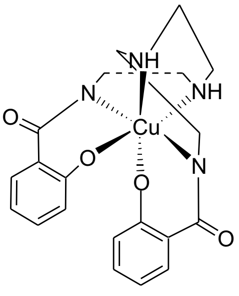
Copper is an essential trace element which forms an integral component of many enzymes.[1] Copper complexes are involved in the process of copper transport in humans.[1,2] Synthesis and characterisation of new copper(II) complexes of acyclic polydentate give complexes of newer structural and functional types. Mononuclear compounds are mostly obtained when the denticity of the ligand matches the coordination number of the ligand. In suitable reaction conditions and in presence of other exogenous nucleating ligands polynuclear complexes may be isolated from the solution. Recently, we reported[3] that a hexadentate amine–imine–phenol ligand can give a tetrahedral tetracopper(II) complex through helical binding of two ligands around four copper ions. Copper(II) when bound to a polydentate ligand adopts a variety of coordination geometries, from distorted square-planar, flattened tetrahedral, and distorted square-pyramidal to distorted octahedral as observed in many crystal structures reported to date.[4-7] The present hexadentate amine–amide–phenol ligand (L, Scheme 1) can bind one copper(II) ion in four possible ways (**1**–**4**). Out of all these possibilities only **4** is obtained exclusively. The amide–amide association complex is most frequently encountered in molecular recognition studies[8] and can develop supramolecular assembly of metal-containing hydrogen-bonded architectures. Herein similar intermolecular coordinated-uncoordinated amide-amide association is observed from the two amide ends of the ligand. The involvement of H-bond capable atoms in the ligand forms an extended H-bonded network throughout the crystal. Complex **4** can be used as an effective bidentate metallaligand (Fig.1) for the controlled synthesis of the new type of dinuclear complex [Cu$_2$(LH$_{-4}$) (bpy)] (**5**).



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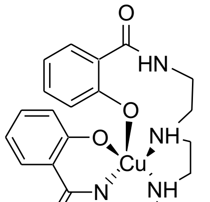

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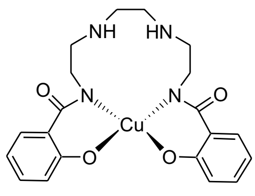

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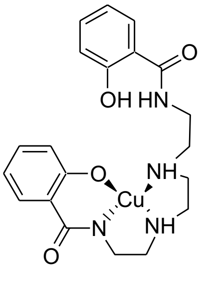

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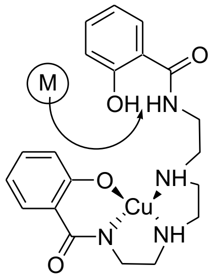

Fig. 1 Structure of Cu(II)-based metallaligand **4** showing donor sites for further metal ion coordination.

The potentially hexadentate, but functionally tetradentate, salicylamide ligand of triethylenetetramine, L was prepared in 80% yield in a single pot condensation reaction of trien with ethylsalicylate in a 1 : 2 molar ratio. ^{1}H and ^{13}C NMR spectral assignments for L are consistent with the proposed formulation of the ligand. The IR spectrum of the ligand shows peaks around 1590 cm^{-1}, which are characteristic of imine C=O functions. The amide NH stretching frequency was observed at 2850 cm^{-1}. In the proton NMR spectrum the amide NH resonance was observed as a broad signal at about $\delta = 8.17$ ppm.

The complex **4** has been obtained by treating the ligand with cupric(II) acetate monohydrate in aqueous methanol in air. Further coordination reaction of **4** was studied by its reaction with [Cu(bpy)(MeOH)$_2$](ClO$_4$)$_2$,[9] in 1 : 1 mole ratio in methanol, which leads to the formation of a novel dinuclear complex, [Cu$_2$(LH$_{-4}$)(bpy)] **(5)**. Room temperature conductivity measurement in DMF identified it as a charge neutral complex confirming the deprotonation of all the dissociable protons in L. In this molecule the hexadentate ligand is shared between two copper ions in tetradentate and bidentate fashion. In its FT-IR spectrum, the absence of NH and OH bands in complex **5** further confirm that both the amide nitrogen and the phenolic oxygen of the metallaligand are deprotonated. All the solution measurements reported in this work were made in dimethylformamide. We were unable to grow X-ray quality single crystal of **5** to confirm the proposed structure.

The complex [Cu(LH$_{-2}$)] belongs to a new class of metallaligand that uses a pendant bidentate ligand site to function as a building block for higher nuclearity homo- and heterometallic-complexes. The ligand used in this work L, is a potentially hexadentate tetrabasic H-bond-forming amine-amide-phenol ligand having three different types of donor atom to bind copper(II) ion. Two amide groups present in the ligand function both as a H-bond donor (–NH–) and

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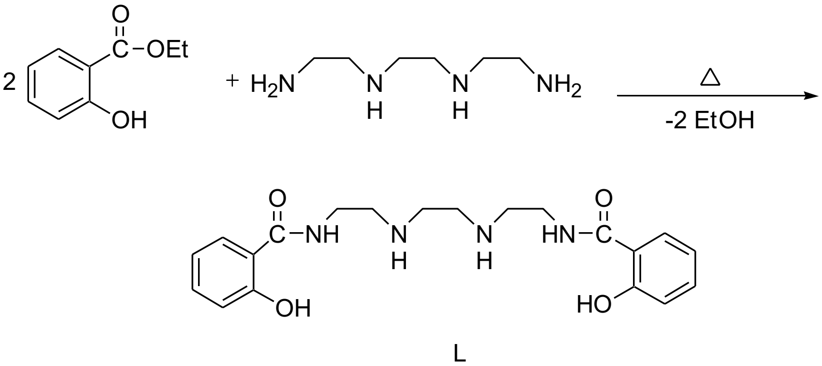

Scheme 1

acceptor (>C=O). A $Cu_4\{\mu_4\text{–}O\}$ complex as obtained by us recently[3] was not obtained with this ligand, neither does it give the mononuclear octahedral complex (**1**). Only a few octahedral complexes of copper(II) are known with acyclic hexadentate ligands.[10-13] Two other possible mononuclear complexes **2** and **3** are not obtained here, of which **3** is non-metallaligand type $CuO_2N(amide)_2$ complex. Complex **4** bears a pendant bidentate amido-phenolate group which is not involved in coordination and we anticipated that certain reactions centred at these functionalities might lead to systems available for further assembly by complexation. This has been demonstrated by the reaction of the complex **4** with $[Cu(bpy)(MeOH)_2](ClO_4)_2$.

Complex **4** crystallises as light pink crystals that belong to the orthorhombic crystal system, space group $P\ 2_12_12_1$. The crystal structure determination revealed that crystals of **4** consist of neutral $[Cu(LH_{-2})]$ species. Although L is a potentially hexadentate ligand, the copper(II) complex is formed from a tetradentate terminal chelation of the ligand. One nitrogen atom and one oxygen atom from the phenol-2-carboxamido moiety O(1) and N(1) and the two central secondary amines N(2) and N(3) form the square plane (Fig.2).

Thus, one of the two phenol-2-carboxamide groups remains uncoordinated. The $Cu\text{–}O_{phenol}$ bond length Cu–O(1) = 1.855(12)Å is comparable to those observed in other four coordinate complexes.[3] For the Cu basal plane the $Cu\text{–}N_{amide}$ distance 1.887(15) Å lies close to the reported value,[14] and is considerably shorter than the average $Cu\text{–}N_{amine}$ (1.990 Å) which is consistent with the stronger donor ability of the deprotonated amido-nitrogen compared to the amine nitrogen.[14-18] This amido-bond length is well within the range of $Cu\text{–}N_{amido}$ distances noted in similar complexes.[19,20] The pendent metallaligand part of **4** is responsible for longer Cu(1)–N(3) distance (2.005(19) compared to Cu(1)–N(2) distance 1.976(14)). Finally the carbon–amine nitrogen bond distances, averaging 1.456 Å, lie close to the reported values.[12] In the crystalline structure, the complex $[Cu(LH_{-2})]$ has a superstructure based on two C=O···HN intermolecular hydrogen interactions between the oxygen atom O(2) of the coordinated salicylamide group and the uncoordinated amido NH [N(4)] of the neighbouring molecule; the distance C=O···HN being 2.790 Å. This N···O distance is in the range of other known amide–amide hydrogen bonded dimmers.[21] Two intermolecular hydrogen interactions thus stabilise the polymeric chain structure. The third intramolecular hydrogen interaction is between the oxygen atom of the uncoordinated carboxy group of salicylamide and protonated phenol at O(3)···O(4) = 2.461 Å. Within the H-bonded superstructure the Cu···Cu distance is 4.264 Å (Fig. 3). Both coordinated and uncoordinated amide moieties are arranged trans (–NH– and >C=O) with respect to the amide bond, and neighbouring neutral metallaligands are linked by amide-amide N–H···O hydrogen bonds into 1-D chains. The –NH– group of the uncoordinated part of the ligand can only function as an H-bond donor, whereas both coordinated and uncoordinated >C=O groups are H-bond acceptors. The whole complex structure resembles an open-lock geometry.

The molar conductivity (Λ_M) value of **4** in dimethylformamide (12 $\Omega^{-1}lit^2mol^{-1}$) indicates the non-electrolyte nature of the complex and the deprotonation level of the ligand (LH_{-2}). The FT-IR spectrum of **4** shows a broad strong band at 3430 cm^{-1} and a sharp band at 2857 cm^{-1} for uncoordinated phenol (ν_{OH}) and amide (ν_{NH}) groups. The sharp band at

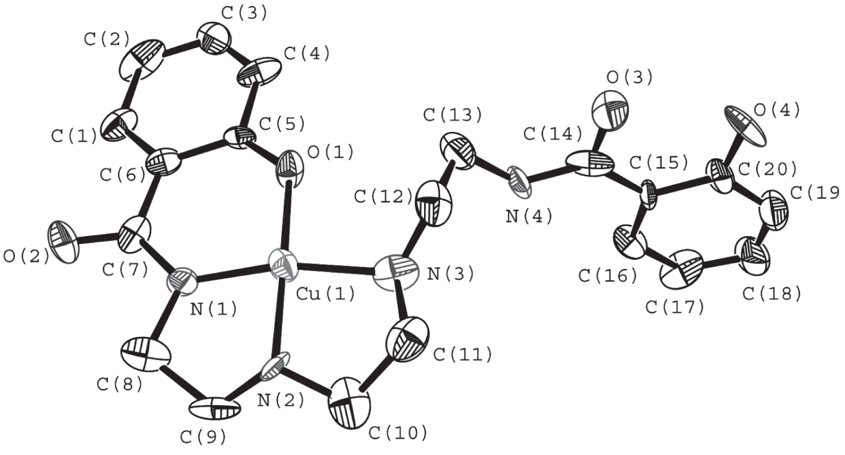

Fig. 2 Labelled ORTEP view of $[Cu(LH_{-2})]$ with atom numbering scheme and thermal ellipsoids drawn at 50% probability level.

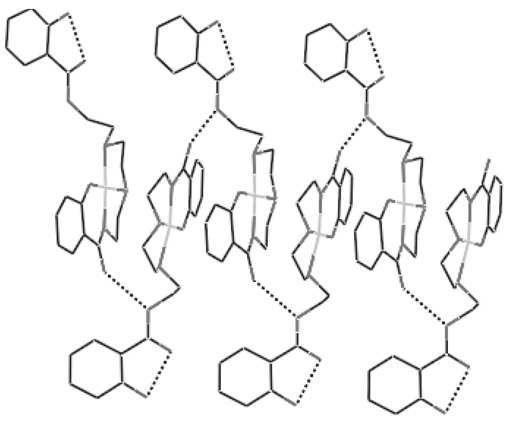

Fig. 3 Hydrogen bonding 1-D chain of Cu(II) metallaligand (**4**) in the solid state. Dotted lines indicate hydrogen bonding.

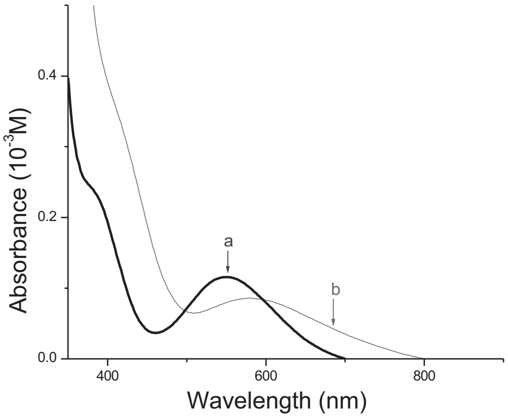

Fig. 4 Room-temperature UV-visible spectra of [Cu(LH$_{-2}$)] (a) and [Cu(LH$_4$)Cu(bpy)] (b) in dimethylformamide (conc. = 1.0 × 10^{-3} mol l^{-1} in each case).

3234 cm^{-1} is assignable to amine (ν_{NH}) groups. These bands are also present in the ligand. The $\nu_{C\text{-}O}$ stretching vibration for the amide carbonyl group is obtained at 1646 cm^{-1}. The $\nu_{C\text{-}O(phenolic)}$ stretching vibration is located at 1334 cm^{-1} as an intense band. The amide N–H (ν_{NH}) and phenol O–H (ν_{OH}) bands, which were present in the metallaligand **4**, are absent in complex **5**.

The position of d–d transitions gives information on the ligand field and the coordination geometry around the metal ion. For a square planar coordination geometry, the energy of the d–d transition depends on the nature of the four donor atoms lying in the square plane. The electronic absorption spectra in the visible region of pink DMF solution of the title compound was examined and found to obey Beer's law in the concentration range 1 × 10^{-3} to 1 × 10^{-5} mol dm^{-3}. The solution contains the mononuclear [Cu(LH$_{-2}$)] species and displays a broad d–d absorption band centred at 550 nm (ε = 111 l mol^{-1}cm^{-1}). A LMCT band is obtained as a shoulder at 390 nm (ε = 242 l mol^{-1}cm^{-1}) due to the phenolate → Cu^{II} transition. Another intense band is observed at 240 nm (ε = 1535 l mol^{-1}cm^{-1}). The band at 240 nm can be assigned to an intraligand n or π to π^* charge transfer transition also present in ligand.

The ability of the amine–amide–phenol ligand L to stabilise the trivalent copper oxidation state was investigated by cyclic voltammetry in dimethylformamide solution at a glassy carbon working electrode. A quasi-reversible one-electron response is observed at $E_{1/2} = +0.69$ V *vs* SCE (ΔEp, 110 mV; supporting electrolyte is tetraethylammonium perchlorate, TEAP) at 298 K for Cu^{II} → Cu^{III} oxidation. The suggestion that the redox process is metal centred is based on the CV of the "free" ligand L which shows no characteristic voltammogram in the experimental potential range. The observation of a lower potential compared to other non-phenolate amide ligands is consistent with the role of phenolate coordination in stabilising the higher (here trivalent copper) oxidation states.[20]

The room temperature magnetic moment values for the mononuclear and dinuclear complexes are 1.94 and 1.68 μ_B/Cu respectively, corresponding to the 3d^9 configuration. A diamagnetic correction of 278.46 x 10^{-6} cgsu per complex, as calculated from the Pascal's constants,[22] was used.

Powder X-Band (9.7857 GHz) EPR spectra were collected for the complex both at room temperature (300K) and 123K. One isotropic signal at g_{iso} = 2.05 (peak-to-peak width 320 G) is obtained at these temperatures. In frozen DMF solution (123 K) the $g_{\parallel}$ is obtained at 2.19 (average g values of 2.40, 2.24, 2.10, and 2.02) ($A_{\parallel}$, 187 x 10^{-4} cm^{-1}) and $g_{\perp}$ at 1.95. When the solution is frozen at 123 K a spectrum typical of an axially symmetric monomeric copper(II) complex exhibiting a tetragonal geometry, with $g_{\parallel} > g_{\perp}$ and a $d_{x^2-y^2}$ ground state is obtained.[23] The larger $A_{\parallel}$ value is consistent with stronger in-plane ligand strength in square planar copper(II) complex due to a better overlap between the magnetic orbital ($d_{x^2-y^2}$) and the ligand orbitals for a square planar geometry. From the parameters graphically evaluated, the value of the quotient $g_{\parallel}/A_{\parallel}$, which is a convenient empirical index[24] of four-coordination, is 117 cm. This is in full agreement with the X-ray structure of **4** and shows that the structural arrangement is maintained in solution.

In **4**, the presence of uncoordinated bidentate chelate ring (Fig.1) allowed consideration of this complex as a potential copper(II)-containing metallaligand capable of forming new homodinuclear species upon further complexation. Further metal coordination of **4** was explored by its reaction with [Cu(bpy)(MeOH)$_2$](ClO$_4$)$_2$ in a 1 : 1 molar ratio in MeOH at pH ~ 8.5 at room temperature. Room temperature UV-Vis spectroscopy was used to detect the dicopper complex formation. The characteristic d–d absorption band of the metallaligand at 550 nm is redshifted to 580 nm (ε = 82 l mol^{-1}cm^{-1}) for the neutral dicopper complex [Cu(LH$_{-4}$)Cu (bpy)] (**5**). The UV-Vis spectral change due to the formation of **5** is shown in Fig. 4.

Elemental analysis and solution molar conductivity data of the isolated compound are in agreement with the formation of a homodinuclear compound [Cu$_2$(LH$_{-4}$) (bpy)] through deprotonation of the second amide group and bridging by one amine-amide part of L.

Concluding remarks

It has been demonstrated that the hexadentate bis-amide ligand (L) reacts easily with copper(II) to show a unique type of coordination. The preference of the Cu^{2+} ion for a square planar ON$_3$ amide environment as against the available O$_2$N$_4$ one has been established. We have been able to synthesise the amide–phenol pendant copper(II) metallaligand which can further coordinate an other copper. The behaviour the present ligand is interesting for its different type of bridging ability. A more complete picture of the factors influencing the stereochemical properties of hitherto unknown hexadentate ligands, having thioether sulfur and/or ether oxygen donor atoms, could be obtained by studying the mode of chelation with copper(II) ion. Further investigations are underway to expand this approach.

Experimental

Triethylenetetramine (trien) was obtained from S.D. Fine Chem, India. Ethyl salicylate and $Cu_2(OAc)_4 \cdot 2H_2O$ were purchased from SRL, India. Dry DMF was prepared by the published method.[25] All other chemicals and solvents were reagent grade materials and were used as received without further purification. Microanalysis (C, H, N) were performed using a Perkin-Elmer 240 C elemental analyser. IR spectra were obtained on a Perkin-Elmer 883 spectrometer (200-4000 cm^{-1}) prepared as KBr pellets. ^1H and ^{13}C NMR spectra were obtained on a Bruker AC 200 NMR spectrometer using TMS as the internal standard. Solution electrical conductivity was measured using a Unitech type UI31C digital conductivity metre with a solute concentration of about 10^{-3} M. Electronic spectra were recorded on a Shimadzu UV/Vis/NIR 3100 (190–3200 nm) (1 cm quartz cell) spectrometer. Electrochemical measurements were made using a PAR model 173 potentiostat/galvanostat, 175 universal programmer, 178 electrometer, and 377-cell system. A planar Beckman 39273 platinum-disk working-electrode, a platinum-wire auxiliary-electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A digital series 2000 Omni Graphic recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. All chemical data were collected at 298 K and are uncorrected for junction potentials. Room temperature magnetic susceptibilities were measured using a home-built Gouy balance fitted with a polytronic DC power supply. Diamagnetic corrections for ligand susceptibilities were made using Pascal's constants.

Synthesis of the ligand L
The ligand was synthesised by the condensation of ethylsalicylate (3.00 g, 18 mmol) and triethylenetetramine (1.31 g, 9 mmol) by heating on water bath without any solvent for 7–8 hours. After cooling to room temperature the yellow gummy mass obtained, was dissolved in minimum amount of methanol and ice was poured to it. A white solid (L) thus obtained was separated by filtration through a G4 sintered bed and washed thoroughly with ethanol and water. Finally the isolated compound was dried *in vacuo* over P_4O_{10}. Yield 2.84 g (82%), m.p. 65–67°C. Anal. Calc. for $C_{20}H_{26}N_4O_4$: C, 62.2; H, 6.8; N, 14.5. Found: C, 62.4; H, 6.6; N, 14.5%. IR spectrum (cm^{-1}, KBr disk): ν(phenolic OH) 3321(s); ν(amide N–H) 2850(s); ν(carbonyl C=O) 1590(s); ν (phenolic C–O) 1348(s); ν(CH_2) 822(m); ν(aromatic CH) 760(m). ^1H NMR ($CDCl_3$, ppm): δ (H_8,amide NH) 8.17(b, 2H); (H_{1-4}) 6.60–7.57 (m, 8H); (H_5) 3.54 (t, 4H); (H_6) 2.72 (m, 4H); (H_7) 2.47 (m,4H); (H_9 amine NH) 2.68 (s,2H). ^{13}C NMR ($CDCl_3$, ppm): δ (C_7) 167.09; (C_1) 128.07; (C_2) 120.77; (C_3) 132.71; (C_4) 116.80; (C_5) 156.01; (C_6) 120.77; (C_8) 46.05; (C_9) 51.11; (C_{10}) 52.20.

Synthesis of the complexes
[Cu(LH$_{-2}$)] **(4):** The complex **4** was prepared by the reaction of L (0.50 g, 1.29 mmol) in methanol (15 ml) and an aqueous solution of $Cu_2(OAc)_4 \cdot 2H_2O$ (0.56 g, 1.41 mmol) with magnetic stirring at room temperature. Upon slow evaporation pink coloured crystals of [Cu(LH$_{-2}$)] suitable for X-ray diffraction were deposited during 7 days. Yield 0.521 g (90%). Anal. Calcd for $C_{20}H_{23}N_4O_4Cu$: C, 53.7; H, 5.2; N, 12.5; Cu, 14.2. Found: C, 53.5; H, 5.5; N, 12.4; Cu, 14.65%. IR (KBr, cm^{-1}): ν = 3231(s), 2857(s), 1632(s), 1597(vs), 1445(s), 1334(m), 1265(s), 1085(s), 877(b), 760(s), 656(s). Molar conductance, Λ_M: (DMF solution) 12 $\Omega^{-1}lit^2mol^{-1}$. UV-Vis spectra [λ_{max}, nm (ε, l $mol^{-1}cm^{-1}$)]: (DMF solution) 552 (111), 387 (242), 240 (1536). Magnetic moment (μ_{eff} at room temp.) 1.94 μ_B.

[Cu$_2$(LH$_{-4}$) (bpy)] (**5**): Complex **5** was prepared by the reaction of the metallaligand **4** (0.50 g, 1.11 mmol) in methanol (15 ml) and a methanolic solution of $[Cu(bpy)(MeOH)_2](ClO_4)_2$ (0.54 g, 1.11 mmol) with stirring at room temperature followed by the addition of Et_3N (0.31 ml, 2.24 mmol). The mixture was then stirred for 1.0 h after which complex **5** precipitated as a green solid. Yield 0.56 g (75%). The solid was isolated, washed with cold methanol, and dried *in vacuo* over P_4O_{10}. Anal. Calcd for $C_{30}H_{28}N_6O_4Cu_2$: C, 54.3; H, 4.25; N, 12.7; Cu, 19.14. Found: C, 54.5; H, 4.15; N, 12.3; Cu, 18.9. IR (KBr, cm^{-1}): ν = 2964 m, 1613(s), 1590(vs), 1438(m), 1278(s), 1235(s), 1085(s), 888(b), 759(s), 666(s). Molar conductance, Λ_M: (DMF solution) 17 $\Omega^{-1}lit^2mol^{-1}$. UV-Vis spectra [λ_{max}, nm (ε, l $mol^{-1}cm^{-1}$)]: (DMF solution) 580 (82), 387 (168), 238 (1252). Magnetic moment (μ_{eff} at room temp.) 1.68 μ_B/Cu.

X-ray crystallography:
Crystal data for complex **4** $C_{20}H_{23}N_4O_4Cu$. Molecular weight = 446.98, orthorhombic, P 212121, a = 11.481(2), b = 7.569(2), c = 22.918(4) Å, α = 89.99, β = 90.07, γ = 90.01°, U = 1991.6(8) $Å^3$, Z = 2, D_C = 1.491 g cm^{-3}, μ(Mo Kα) = 1.131 mm^{-1}, F(000) = 928, Crystal dimensions = 0.30 × 0.30 × 0.20 mm, final R_1 and wR_2 were 0.0977 and 0.1719 respectively. GOF = 0.957, largest difference peak and hole: 0.477 and –0.542 e$Å^{-3}$. Diffraction data for complex **4** were collected at 293(2) K on Bruker-Nonius Mach3 CAD4 X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Precise unit cell dimensions were determined from the least squares refinement of 25 well centred reflections having 2θ values 2.51–24.97°. The intensities of three reference reflections monitored every hour throughout the data collection shows no sign of crystal deterioration. The systematic absence are $0 \le h \le 13$, $0 \le k \le 8$, $-27 \le l \le 27$.The structure was solved by direct method, followed by successive Fourier synthesis and least-square refinement using SHELXS97 program.[26] Direct phase determination yielded Cu, and most of the C, N, O atoms. Anisotropic thermal parameters are used for the nonhydrogen atoms and isotropic parameters for the hydrogen atoms.

Supplementary material

Further details of the structure determination, including atomic coordinates, bond lengths and angles, thermal parameters of all non-hydrogen atoms for the structure are available on request as supplementary material from The Director, Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) (CCDC deposition number, 262369).

We thank DST, New Delhi, for the Single Crystal X-ray Diffractometer facility in the Department of Chemistry, IIT Kharagpur under its FIST program.

Received 1 February 2006; accepted 13 May 2006
Paper 6/3743

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