Synthesis, Spectral and Structural Characterisation of Chloro{*S*-benzyl-*β*-*N*-(5-methylpyrazole-3-yl)ethoxymethylenedithiocarbazato}copper(II) Derived from *S*-benzyl-*β*-*N*-(5-methylpyrazole-3-yl)methylenedithiocarbazide

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(Received March 4, 1998; CL-980158)

The reaction of $CuCl_2,2H_2O$ with S-benzyl-β-N-(5-methyl pyrazole - 3 - yl) methylene dithiocarbazide (H_2L) in dry ethanol affords a novel copper(II) complex [Cu(LOEt)Cl] (1) in which a unique transformation at the carbon site of the azomethine function of the parent ligand (H_2L) occurs and is ascertained by X-ray crystallographic data.

The parameter towards the relationship between structural and biological properties of copper(II) N-heterocyclic thiosemicarbazone(s) and S-alkyl dithiocarbazate(s) have been reviewed,[1,2] however, the mechanism of the biological activity of such copper(II) complexes is not yet quite transparent.[3] As part of our comprehensive effort[4] towards synthesis and structural characterisation of new complexes with pyrazole-derived thiosemicarbazone(s) and dithiocarbazate(s) in search of new materials with potential bioactivity, we report herein, in the process of analysing the X-ray crystal structure of the title copper(II) complex, an unique finding of an unusual transformation of -CH=N- to -C(OEt)=N- which appears to be an unprecedented conversion presumably favoured by copper(II) coordinated azomethine function.

The title ligand, H_2L (1mmol), synthesized and characterised for the first time,[5] dissolved in 40ml hot dry ethanol, was mixed with an ethanolic solution of copper(II) chloride dihydrate (1 mmol); an immediate precipitation of a green crystalline substance occured. On crystallisation of the product from 1:1 ethanol-acetonitrile, single crystals were obtained in 60% yield (based on metal).[6]

The title copper(II) complex is paramagnetic as expected (μ_{eff} = 1.81 BM at RT) and its solid state RT EPR spectrum is axial in nature ($g_{\|}$ = 2.16, $g_{\perp}$ = 2.03), consistent with a $d_{x^2-y^2}$ ground state and suggests a covalent environment with in-plane sigma- and pi-bonds provided by the ligand system. The characteristic IR bands are indicative of the above bonding of pyrazolyl nitrogen (tertiary), azomethine nitrogen and the thiolato sulphur atom to the central copper(II) ion; the bands at 420, 320 and 290 cm^{-1} assigned to ν_{Cu-N}(azom), ν_{Cu-S} and ν_{Cu-N}(Pz) respectively provide tacit support to the proposition. X-ray crystallographic study[7] of title copper(II) complex reveals its molecular structure as shown in Figure 1. It is transparent that copper(II) ion lies in a fairly square planar environment with the schiff base coordinated as uninegatively charged tridentate NNS donor via pyrazolyl nitrogen (N1), azomethine nitrogen (N3) and mercaptide sulphur (S1); the fourth coordination site is occupied by Cl-atom. Two five membered chelate rings formed by coordination of N(1), N(3) and N(3), S(1) donors of the tridentate ligand are fairly square planes (mean deviation 0.008Å and 0.003Å respectively). The dihedral angle between these two planes is 3.4^{0}. The donor atoms N(1), N(3), S(1) and the copper atom is deviated from the plane by 0.03Å. These values agree well with those found in similar four coordinated Cu(II) thiosemicarbazones.[8] The Cu-N(3), Cu-S(1) and Cu-Cl bond lengths are comparable with earlier results.[9] The C(4)-N(3) length (azomethine) is 1.298Å. This bond distance is in excellent agreement to those of similar copper(II) species[10] bonded to azomethine group pointing to the fact that the azomethine function (-C=N-) retains its identity even after nucleophilic substitution (of H) by OEt group. The O-C(4) length is 0.14Å shorter than O-C(4A) length due to different states of hybridisation at C (4) (sp^2) and C(4A)(sp^3). The fact that the ligand binds copper (II) as the iminothiolate form is substantiated by C(5)-S(1) bond length 1.74Å. All these parameters unambiguously show that an unique substitition occurs at C(4) by OEt group originating from the solvent (ethanol) in the deprotonated ligand system in presence of copper(II). It is significant that cobalt(III) does not bring about such substitution on azomethine function as evidenced from the crystal structure of $[Co(MPzSB)_2Cl]$.[5] Further work on copper(II) complexes with the title ligand system in other alcoholic solvents like methanol, propanol and butanol is in progress. We thank the Council of Scientific and Industrial Research, New Delhi, India for providing financial support.

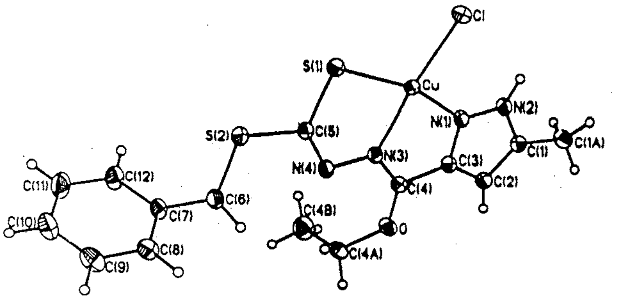

Figure 1. Molecular structure of $[Cu(C_{13}H_{12}N_4S_2.OC_2H_5)\ Cl]$ showing the atom numbering scheme. Slected bond distances (Å) and angles (^{o}) are follows; Cu-N(1)1.969(2), Cu-N(3) 1.997(2), Cu-S(1) 2.2223(9), Cu-Cl 2.2337(8), N(1)-N(2) 1.338(3), N(1)-C(3) 1.338(4), C(3)-C(4) 1.481(4), N(3)-C(4)1.298(4), N(3)-N(4) 1.396(3), N(4)-C(5) 1.288(4), S(1)-C(5) 1.745(3), O-C(4) 1.318(4), O-C(4A) 1.458(4), N(1)-Cu-Cl 96.55 (7), S(1)-Cu-Cl 99.76(3), N(1)-Cu-N(3) 79.97(9), N(3)-Cu-S(1) 84.23(7), N(1)-Cu-S(1) 162.36(8), N(3)-Cu-Cl 174.52(7), N(3)-N(4)-C(5) 110.8(2), C(3)-C(4)-N(3) 113.4(3), C(4)-N(3)-N(4) 121.3(2), O-C(4)-C(3)113.1(3).

References and Notes

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6 1; Anal. Found: C, 41.32; H, 3.65; N, 13.03%. Calcd for $C_{13}H_{12}N_4S_2.OC_2H_5.CuCl$: C, 41.62; H, 3.96; N, 12.94%. Selected spectral parameters: $\Delta\nu$(C=N) = 60, $\Delta\nu$ (C=S) = 50 and $\Delta\nu$(N=N) (pz) = 30cm^{-1}. UV-VIS λ_{max}(nm) (DMF): 640 (ϵ 273dm^{3}mol^{-1}cm^{-1}), 311 (ϵ 1358dm^{3}mol^{-1}cm^{-1}).

7 Crystal data of 1; $C_{13}H_{12}N_4S_2.OC_2H_5.CuCl$, M = 432.44, triclinic, space group $P\bar{1}$, Z = 2, a = 9.2061(4), b = 9.8276(6), c = 10.8050(5)Å, α = 76.805(4)^0, β = 86.822(3)^0, γ = 75.258(4)^0, V = 920.48(13)Å^3, T = 293(2)K, D_c = 1.560 g/cm^3, crystal dimension 0.57 × 0.43 × 0.08 mm. Source Mo–K_α, λ =0.7107Å. Data were collected in the range $2.20 < \theta < 27.49^o$ by the ω–scan method on a Siemens P4S diffractometer. Out of 4584 unique reflections, 4179 with $I > 2\sigma(I)$ (R_{int} = 0.0159) were used for structure solution. The structure was solved by direct methods (SHELXS) and refined by full matrix least–squares refinement of F^2. Data were corrected for absorption using SHELXA [T_{max} = 0.8903, T_{min} = 0.1181]. R1=0.0443 (wR2 =0.1095). All non hydrogen atoms were refined anisotropically while the hydrogen atoms were initially included in calculated positions and then refined isotropically.

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