A Novel Macrocyclic Tetranuclear Copper(II)-Copper(I) Mixed-Valence Complex

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A novel macrocyclic tetranuclear copper(II)-copper(I) mixed -valence complex was prepared and charaterized by spectroscropic and crystallography structure analysis. Each tetranuclear unit connected to the neighbor one by one using the Cu...S bond with the type of apical Cu(1)...S(3B) bond forming an infinite step chain.

Recently, macrocyclic polynuclear metal cations and molecules have attracted much attention within the fields of supramolecular chemistry and coordination chemistry.[1-4] The presence of metal ions in such arrangement may possess many varied physicochemical properties such as electrochemical, spectroscopical, electronical, magnetic, mechanical and catalytic activity for example.[5,6] However, most of these metal ions used are unique, few of them are mixed with different types of metals or one type of metals with different valences. In the present work, We report on the novel structure of a macrocyclic tetranucelar copper(II)-copper(I) mixed-valence complex.

According to the literature methods[7] by replacement of di(2-pyridine) ketone with 2-benzoyl pyridine, when 2-benzoyl pyridine was treated with thiosemicarbazide in methanol at reflux by adding acetic acid as catalysis, a white solid (HL, 2-benzoyl pyridine thiosemicarbazone) was readily formed. Interaction of $CuCl_2$ with HL in methanol at boiling temperature gave black-green solids. A brown darked solid product[8] was obtained *via* self-assembly by mixing the green solids with KSCN in acetonitrile solution at refluxing for 3 h.

The KSCN as expected can serve both as a ligand and as a reducing reagent[9] and the solvent acetonitrile molecule served as one of ligands. The complex[10] has tetra-nuclear unit forming by two Cu(II) atoms [Cu(1) and Cu(1A)] and two Cu(I) atoms [Cu(2) and Cu(2A)] [1-x, -y,1-z] moieties with crystallographic center of inversion as shown in Figure 1. The geometry of the Cu(1) moiety is distorted square planar. The pyridine nitrogen N(4), the imino nitrogen N(3) and the thiosemicarbazato sulphur S(1) together with the thiocyanato nitrogen N(5) comprise coordinated plane. The mean deviation of the plane Cu(1), S(1), N(3), N(4) and N(5) is 0.056 Å. The Cu(2) atom is coordinated by the sulphur S(1) from the thiosemicabazato, one thiocyanato nitrogen atom N(6), one acetonitrile nitrogen N(7) and one thiocyanato sulphur atom S(2A) from the symmetry related half of the unit forming a tetrahedron. In each of the tetranuclear unit, there are two ways bridged the Cu(1) and Cu(2) as a square. One is the monoatomic sulphur bridge of the thiosemicarbazato, another is the thiocyanate bridge. The Cu(I)...Cu(II) separation in the two bridging ways is *ca* 3.58 Å and 5.74 Å, respectively. The Cu(1)...Cu(1A), Cu(2)...Cu(2A) separation is *ca* 7.23 Å and 6.25 Å, respectively. Each tetranuclear unit connected to the neighbor one by one through the unbridged thiocyanato group with the type of apical Cu(1)...S(3B)[2.878(2) Å] (symmetry code B: 1+x, y, z) bond forming an infinite step chain. The hydrogen atom attached to the nitrogen atom N(1) forms a hydrogen-bond with the imino nitrogen atom N(2C)(symmetry code C: 2-x, 1-y, 1-z) in the corresponding molecule. The N... N separation is 3.034 Å, the angel around the hydrogen atom is 148.3(5)^0.

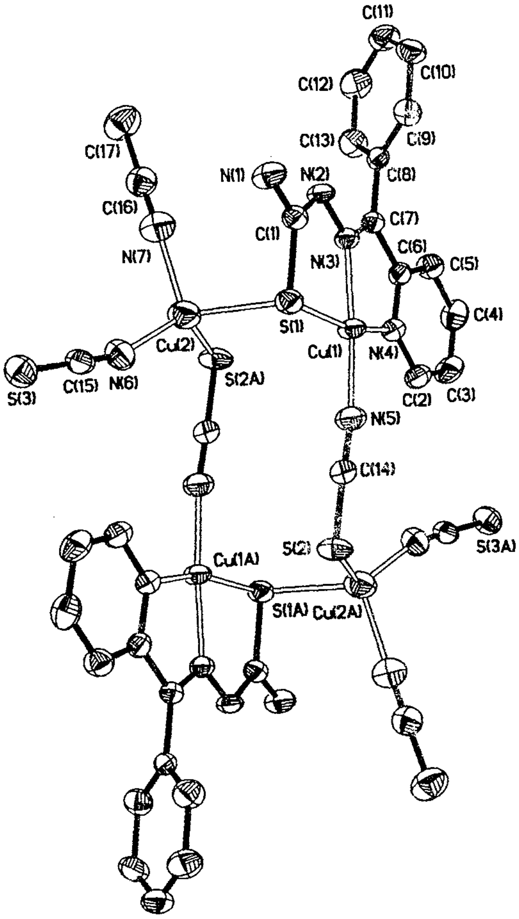

Figure 1. ORTEP of tetranuclear title complex with atomic-numbering scheme, showing the non-hydrogen atoms as 30% probability thermal ellipsoids. Symmetry code A: 1-x, -y, 1-z. Representative bond distances (Å) and angles (°): Cu(1)-N(3) 1.970(3), Cu(1)-S(1) 2.274(1), Cu(2)-S(1) 2.485(1), N(1)-C(1) 1.335(5), N(3)-C(7) 1.298(4), Cu(1)-N(4) 2.014(3), Cu(2)-N(7) 2.030(4), Cu(1)-N(5) 1.937(3), Cu(2)-N(6) 1.958(4), Cu(2)-S(2A) 2.363(1), S(1)-C(1) 1.747(4), S(2)-C(14) 1.635(4), S(3)-C(15) 1.645(4), N(2)-C(1) 1.323(5), N(2)-N(3) 1.358(4), N(3)-Cu(1)-N(4) 80.8(1), N(3)-Cu(1)-N(5) 174.9(1), N(4)-Cu(1)-N(5) 98.0(1), N(3)-Cu(1)-S(1) 84.3(1), N(4)-Cu(1)-S(1) 163.7(1), N(5)-Cu(1)-S(1) 96.3(1), N(6)-Cu(2)-N(7) 112.9(2), N(6)-Cu(2)-S(1) 123.6(1), N(7)-Cu(2)-S(1) 100.2(1), N(6)-Cu(2)-S(2A) 107.3(1), N(7)-Cu(2)-S(2A) 107.7(1), S(1)-Cu(2)-S(2A) 103.4(1), Cu(1)-S(1)-Cu(2) 97.4(1)

The ESR spectrum of the complex in DMF at 110K is exhibites an intense signal with clear resolution of the four copper hyperfine ligand g_{II}=2.13. A_{II} = 176G, and $g_{\perp}$=1.98, $A_{\perp}$= 78G.. The fact that $g_{//} > g_{\perp}$ suggests that there is square plane with d_{x2-y2} ground state.

The room temperature magnetic moment of the complex (2.73μB) exhibits that there are two single electrons in the tetranuclear complex, that means, for the four copper atom only two of them are Cu(II), the other two is Cu(I), this result is in agreement with that of ESR and support idea that the square coordinated Cu(1) is Cu(II), the tetrahedral coordinated Cu(2) is Cu(I), and the macrocyclic complex is a mix-valence Cu(II)/Cu(I) complex. The plot of the reciprocal of the molar susceptibility corrected for both diamagnetism and temperature-independent paramagnetic as temperature afforded the value of θ = -25K. The value of g = 2.21 is a little larger than[11] that measured by ESR.

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8 Methanol(20ml) solution of HL (0.52 g, 2 mmol) and $CuCl_2 \cdot 2H_2O$ (0.34 g, 2 mmol) were mixed. After the solution were refluxed for 4 h, the green solids formed was isolated and mixed with KSCN (0.10 g, 1 mmol) in acetonitrile solution. Dark green solid of the title complex was obtained by refluxing the mixture for 4h(Yield 31%). Crystals of good quality were obtained by slowly evaporating a acetonitrile solution in air. (Found: C, 38.2; H, 2.8; N, 18.3. Calcd. for $C_{17}H_{14}Cu_2N_7S_3$: C, 37.8; H, 2.5; N, 18.1%). IR (cm^{-1}): ν(C≡N), 2128, 2083; ν(C=N, C=C) 1623, 1593, 1497, 1440; ν(C-S), 1053.

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10 Crystal data for $C_{17}H_{14}Cu_2N_7S_3$: triclinic, space group, *P-1*; a = 9.536(1), b =10.332(1), c = 12.187(2) Å, α = 86.15(3), β = 68.22(2), γ = 67.83(1)°, V= 1028.9(2) $Å^3$, Z = 2, *F(000)* = 554 μ = 2.391 mm^{-1}, $D\,c$= 1.745 Mgm^{-3}, T= 293K. A total of 3868 unique data for $2\theta_{max}$ =50.0° was collected of which 3626 were independent. The intensities were collected on a Simens P4 four-circle diffractometer with monochromated MoKα(λ = 0.071073 Å) radiation using ω/2θ scan mode with variable scan speed 5.0-60^0 min^{-1} in ω. The crystal structure was solved by direct method (SHEXTLE 1995). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms of the metal complex were placed in their calculated positions with C-H 0.93 Å, assigned fixed thermal parameters (1.2 times of the atoms they attached). All computations were carried out on a Pc-586 using the SHEXTL program package. The *R and Rw* factors after refinement of 262 parameters using 3124 observed reflections [$I > 2\sigma$ (I)] were 0.0472 and 0.1228, respectively. The max. and min. Residual electron densities were 0.726 and -1.702 $eÅ^3$, respectively.

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