

A Novel Dinuclear Copper (II) Complex with a 22-Member TetraazaTetraimine Schiff Base Macrocyclic Ligand Having Anti-Ferromagnetic Interaction

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Abstract: Trituration of three solids namely 2,6-diformylpyridine, 1,4-diaminobenzene and cupric acetate in agate mortar with a pestle for more than half an hour vigorously produced a green crystalline solid by metal ion catalyzed template method. Characterization has been done on the basis of elemental analysis, conductivity measurement, magnetic moment data and spectral studies. Formula of the complex was found to be $[Cu_2(Abpene)(CH_3COO)_4]$ where Abpene stands for 22-member macrocyclic Schiff base ligand 1,7,12,18-tetraaza-8,9,10,11:19,20,21,22-dibenzo-3,4,5:14,15,16-dipyrido-cyclodocosa-1,6,12,17-tetraene. Strong antiferromagnetic coupling has been observed. Pi-electron delocalization over the entire macrocyclic cavity and compatibility between cavity size and acetate bridged copper ions seems to be the cause of stability of the complex.

Keywords: Schiff-Base, Copper Complex, Anti-Ferromagnetic Coupling, Macrocyclic Ligand

1. Introduction

Schiff base was originated by Hugo Schiff in 1864 [1] and propagated in his three classic papers [2-4]. But it took nearly 100 years when self condensation of ortho amino benzaldehyde took place in presence of metal ion resulting in the formation of two ligands TRI & TAAB. TRI stands for bzo_3 [12] hexaene N_3 and TAAB for bzo_4 [16] octaene N_4 . The size and stereochemistry of the controlling metal ion are obviously important factors in the self condensation reactions. Interest in the Schiff base complexes has been rejuvenated in recent years [6-10]. Consequently a binuclear copper (II) complex is being reported in the present communication in continuation of our earlier work [11].

The study of systems containing two or more metal atoms simultaneously complexed by one ligand is of great importance to such fields as: homogeneous catalysis, process of magnetic exchange between paramagnetic centers, electrical conductivity and bioinorganic chemistry [12-16]. In order to assemble binucleating ligands, dialdehydes that contain carbonyl groups separated by donor atom(s) suitably disposed for chelation such as in 2,6-diformylpyridine are most frequently used. Compounds containing terminal amino groups separated by not less than two CH_2 links are the partners such as in 1,4-diaminobenzene in the present case. Macrocyclic ring cavities having even numbers (22 in the present case) of atoms in the ring are stabler than those having odd numbers. π -electron conjugation is yet another factor for stability. Success and failure reports of literature have also been taken care of [17-20].

2. Experimental

All the three chemicals namely, 2,6-diformylpyridine (dfp), 1,4-diaminobenzene (dab), and cupric acetate ($CuAc_2$) were purchased from Sigma-Aldrich and used as such. dfp, dab and $CuAc_2$ were triturated in agate mortar with a pestle in equimolar ratio for half an hour to get the green crystalline product.

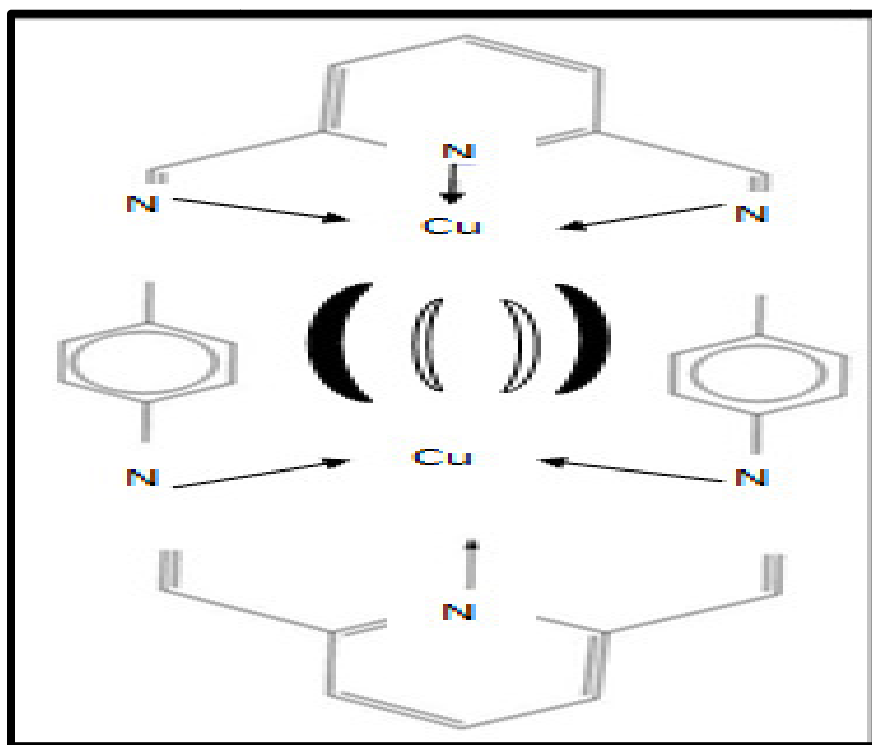
It was recrystallized from ethanol and analyzed as $[Cu_2 C_{34} H_{30} N_6 O_8]$. Found % Cu 16.32; C 52.06; H 3.85; N 10.78. Calculated % Cu 16.18; C 52.51; H 3.86; N 10.81.

The complex has also been prepared by refluxing the three components in equimolar ratio together in dilute ethanolic medium for two hours followed by slow evaporation under low pressure when green crystals appear. The crystals were filtered, washed, dried and analyzed to give similar analytical results as the compound obtained by trituration method but with lower yields.

3. Results & Discussions

The macrocyclic structure of the ligand has been verified by the absence of bands assignable to stretching vibrations of carbonyls and amino groups and by the presence of $\nu C=N(1595\text{cm}^{-1})$ in the I. r. spectra of the complex as well as by the mass spectra of template synthesis products. Presence of new bands in the far I. r. region assignable to $\nu Cu-N(620\text{cm}^{-1})$ and $\nu Cu-O(520\text{cm}^{-1})$ also supports the structure. ν mol value of 10 S/M indicate non electrolytic nature of the complex. Low effective magnetic moment (0.8 B.M.) is indicative of strong ligand field present in the complex and presence of antiferromagnetic interaction taking place through bridged acetate groups. Each Cu (II) ion is heptacoordinated by pyridyl nitrogen. Pair of azomethinic nitrogen and four oxygen from the four bridged acetate groups. The antiprismatic structure as shown below has been proposed on the basis of x-ray crystallographic study [21] on a similar complex.

The crescent symbols represent bridged acetate groups. Dark indicate above the plane and hollow, below the plane. All the nitrogen atoms along with pyridine nuclei from the molecular plane. Benzene nuclei lie perpendicular to the molecular plane.



Structure of $[Cu_2(Abpene)(CH_3COO)_4]$

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