

Synthesis and Structural Characterization of [Cu(NH₂CH₂C₆H₄N=CHC₅H₅N)Cl₂]

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The compound [Cu(NH₂CH₂C₆H₄N=CHC₅H₅N)Cl₂] (**1**) containing the tridentate Schiff base ligand, which is the 1:1 condensation product of pyridine-2-carboxaldehyde and 2-amino benzyl amine, was synthesised and its crystal structure has been determined. It is monomeric, space group P $\bar{1}$, $a = 7.704(1)$, $b = 9.308(2)$, $c = 11.228(2)$ Å, $\alpha = 68.97(2)$, $\beta = 82.23(1)$, $\gamma = 67.70(1)^\circ$ and $Z = 2$. The crystal structure of **1** is based on a five coordinate copper centre with trigonal bipyramidal geometry. The six membered chelate ring possesses a half-chair conformation with C7 most out of the plane made by Cu1, N2, N3, C8 and C9. There is a hydrogen bond between Cl2 and an amine hydrogen H2A of a neighbouring molecule related by a centre of inversion.

Introduction

In recent years, an increasing effort has been focused on the preparation of mono- or di-nuclear mixed ligand transition metal complexes containing neutral, chelating nitrogen ligands. Early and late transition metal complexes of this type have extensively been used as catalysts for a wide variety of reactions, including olefin polymerization [1 - 3] and oxygen activation [4 - 7].

In this context, Schiff base complexes are topical in connection with a diverse range of applications such as in organic synthesis [8 - 11], as liquid crystals [12], and as heterogeneous catalysts [13]. Copper complexes have extensively been studied in recent years. Their flexibility, facility of preparation and capacity of stabilising unusual oxidation states can explain their successful performance in mimicking peculiar geometries around the metal, leading to very interesting spectroscopic properties and varied reactivities [14 - 16]. The complexity of the stereochemistry of Cu(II) complexes is well known [17 - 19]. Owing to the plasticity of the coordination sphere, which is well-known as a feature of copper, copper(II) ion forms a variety of complexes with coordination number 4 - 6 [20]. The geometries around the central copper(II) atom are controlled primarily by the combinations of various ligands and the

steric constraints in the ligand itself. For example, five-coordinate copper(II) complexes, in most cases take on many different geometries ranging between square pyramidal (SP) and trigonal bipyramidal (TBP) [21]. The stereochemistry of five-coordinated copper(II) complexes has been reviewed and discussed comprehensively by Hathaway [22]. Harmjanz and co-workers prepared the complexes, [CuI(btmgp)] and [CuCl₂(btmgp)], using the novel chelate ligand [1,3-bis(N,N,N',N'-tetramethylguanidino)propane], (btmgp) [23]. Constable, Lewis and co-workers prepared the copper complex, [Cu(L¹)Cl]Cl (where L¹ = 8,8'-bis(aminomethyl)-2,2'-biquinoline) [24]. Here the copper atom is in a distorted five-coordinate square-based pyramidal environment with the co-ordinated chloride occupying the axial site. Chapman, Stephens and Vagg synthesised the copper(II) complex of N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene [25].

We have already reported some copper(II) complexes with tridentate [26] or tetradentate [27] Schiff base ligands. In both cases, the copper atom achieves a distorted square pyramidal geometry. In this paper, we report a new copper(II) complex, [Cu(NH₂CH₂C₆H₄N=CHC₅H₅N)Cl₂] with a tridentate Schiff base ligand [2-(2-aminobenzyl)pyridilideneimine]. The complex has been characterised by elemental analysis, IR and UV-vis spec-

tra. The structure of the complex was determined by X-ray diffraction using a single crystal. Here, the copper atom is five coordinated, having a trigonal bipyramidal geometry.

Experimental Section

Materials

All chemicals and solvents used for synthesis were of reagent grade. Pyridine-2-carboxaldehyde (Fluka), 2-amino benzyl amine (Aldrich) and copper(II) chloride (Loba Chemie, India) were obtained commercially and used as received.

Physical techniques

C,H,N analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. The infrared spectrum was recorded on a Perkin-Elmer 883-infrared spectrophotometer in the range of 4000 - 200 cm⁻¹ as KBr pellets. The electronic spectrum was measured on a Hitachi U-3400 (U.V.-vis.-N.I.R.) spectrophotometer in methanol. The room temperature magnetic susceptibility was measured with a model 155 PAR vibrating sample magnetometer fitted with a Waker Scientific 175FBAL magnet.

X-ray crystallography

A green crystal of the compound **1** was obtained by slow evaporation of a methanol solution of the compound and mounted on a glass fibre on a Bruker AXS P4 diffractometer. No significant crystal decay was found. Data were corrected for absorption by ψ scans. The structure was solved by direct and difference Fourier methods, and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were constrained to idealised positions and treated as riding atoms where the displacement parameter was 1.2 (NH₂, CH₂) or 1.5 (CH₃) times that of the bound atom, see Table 1. Crystallographic computing was performed using SHELXTL [28] programs.

Preparation of the ligand L

The ligand L was synthesised by refluxing a methanolic solution of pyridine-2-carboxaldehyde (0.192 ml, 2 mmol) and 2-amino benzyl amine (0.246 g, 2 mmol) for half an hour. The resulting mixture gave a yellow solution containing the liquid ligand.

Synthesis of [Cu(NH₂CH₂C₆H₄N=CHC₅H₄N)Cl₂] (**1**)

To the methanolic solution of the ligand L (2 mmol), CuCl₂·2H₂O (0.347 g, 2 mmol) in a minimum amount

Table 1. Crystallographic data for **1**.

Empirical formula	C ₁₃ H ₁₃ Cl ₂ CuN ₃
Formula Weight	345.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.704(1)$ Å $b = 9.308(2)$ Å $c = 11.228(2)$ Å $\alpha = 68.97(2)^\circ$ $\beta = 82.23(1)^\circ$ $\gamma = 67.70(1)^\circ$
Z	2
Density(calculated)	1.728 g/cm ³
Absorption coefficient	1.952 mm ⁻¹
$F(000)$	366
Crystal size	0.04 × 0.34 × 0.22 mm ³
θ Range for data collection	1.94 to 24.99°
Reflections collected	2972
Independent reflections	2391 [$R_{\text{int}} = 0.0529$]
Max. and min. transmission	0.9892 and 0.7836
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0355$, $wR2 = 0.0848$
R indices (all data)	$R1 = 0.0480$, $wR2 = 0.0905$
Largest diff. Peak and hole	0.420 and -0.437 e·Å ⁻³

of water was added and the resulting mixture was kept at room temperature. After a few days green crystals formed on slow evaporation of the solvent. Yield: 70%. Analysis for C₁₃H₁₃Cl₂CuN₃: calcd. Cu 18.36, C 45.12, H 3.76, N 12.14; found Cu 18.32, C 45.28, H 3.91, N 12.32.

Results and Discussion

IR spectrum

The IR spectrum of the complex **1** is consistent with the structural data presented in this paper. The broad absorption band at 1604 cm⁻¹ may be due to the coordination of the copper(II) ion by the azomethine nitrogen atom [29]. The pyridine ring breathing mode observed at 971 cm⁻¹ is affected by copper-nitrogen bond formation. The characteristic IR active band for $\nu(\text{N-H})$ of the NH₂ group appeared at 3186 cm⁻¹. The bands at 321 and 300 cm⁻¹ are assigned to the Cu-Cl bonds.

Electronic spectrum

Electronic spectra of copper Schiff base complexes can be an indicator of geometry [30]. The electronic spectra of **1** in methanolic solution show an absorption band in the region of 800 - 850 nm. It

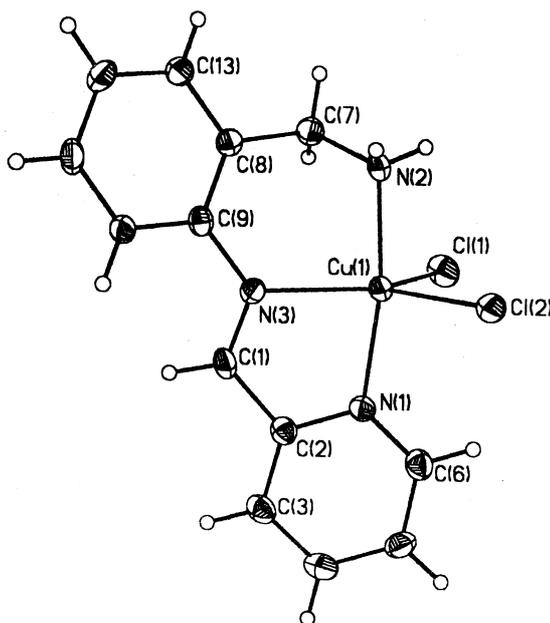


Fig. 1. Molecular structure of [Cu(NH₂CH₂C₆H₄N=CHC₅H₅N)Cl₂] showing the atom numbering scheme. The hydrogen atoms are not labelled for clarity.

is assigned to a Cu(II) d-d transition and indicates a five coordinated trigonal bipyramidal geometry [31, 32]. The bands at 203 and 265 nm may be assigned to intraligand transitions.

Magnetic susceptibility

The room temperature magnetic moment (1.74 μ_B) of the complex **1** fits well with the spin only value for a copper(II) system (1.73 μ_B).

Crystal structure

Figure 1 shows a perspective drawing of the molecule together with the selective atomic labelling. The crystal structure features of a five coordinate copper centre with trigonal bipyramidal geometry. The six-membered chelate ring possesses a half-chair conformation with C7 most out of the plane made by Cu1, N2, N3, C8 and C9. Cu1, N2, N3 are co-planar and make an angle of 26.2(1)° with the pyridine ring. The metal has the N3 atom occupying one equatorial site and the chloride ions the other two. The Cl(1)-Cu(1)-Cl(2) angle is 106.59(4)°. The N1 and N2 atoms are occupying the axial positions with the N(2)-Cu(1)-N(1) angle, 170.3(1)°. The copper is displaced towards the amino nitrogen donor atom [Cu(1)-

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Cu(1)-N(2)	1.969(3)	Cu(1)-N(1)	1.994(3)
Cu(1)-Cl(1)	2.388(1)		
Cu(1)-Cl(2)	2.352(9)	N(1)-C(2)	1.357(4)
N(3)-C(1)	1.28(4)	N(2)-C(7)	1.4(4)
C(1)-C(2)	1.469(5)	N(3)-C(9)	1.418(4)
C(7)-C(8)	1.509(4)	C(8)-C(9)	1.4(5)
N(2)-H(2A)	0.9	N(2)-H(2B)	0.9
N(2)-Cu(1)-N(1)	170.37(1)	N(2)-Cu(1)-N(3)	90.19(1)
N(1)-Cu(1)-N(3)	80.22(1)	N(2)-Cu(1)-Cl(2)	93.03(9)
N(1)-Cu(1)-Cl(2)	93.81(8)	N(3)-Cu(1)-Cl(2)	129.86(7)
N(2)-Cu(1)-Cl(1)	88.25(9)	N(1)-Cu(1)-Cl(1)	96.27(8)
Cl(2)-Cu(1)-Cl(1)	106.59(4)		
C(7)-N(2)-H(2A)	109.1	Cu(1)-N(2)-H(2A)	109.1

Table 3. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
N(2)-H(2A)...Cl(2) ^{#1}	0.900	2.410	3.295(3)	166.3

Symmetry transformations used to generate equivalent atoms:
^{#1} $-x, -y + 2, -z$.

N(2), 1.969(3) Å] away from the pyridine nitrogen [Cu(1)-N(1), 1.994(3) Å] (Table 2).

There is a hydrogen bond (2.41 Å) between Cl2 and an amine hydrogen H2A of a neighbouring molecule related by a centre of inversion (Table 3).

A more highly substituted version of this N₃-donor ligand has been used in Mn and Cu complexes, where a fourth N binds to Cu via a pendant arm attached to an aromatic ring [24].

A less substituted version of L has been used with copper to form a cyanide linked polymeric Fe(II)-CN-Cu(II) species [33], which has two types of copper centres, one with the same tetradentate ligand and a second type which is bound by a smaller tridentate ligand (2-pyridylmethylene-1,3-propanediamine). This second type of copper centre is bound to two bridging cyanides, thereby propagating the M-CN-M chain.

The copper complex [25], aqua-[N,N'-bis(2'-pyridinecarboxamido)-1,2-benzene]-copper(II) is the most closely related, where an ortho-substituted benzene is included to form a macrocycle. The unit cells are coincidentally rather similar. [$a = 7.443(3)$, $b = 9.560(2)$, $c = 11.197(4)$ Å; $\alpha = 92.63(2)$, $\beta = 100.02(2)$, $\gamma = 84.50(2)^\circ$].

Supplementary data

Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre with deposition number 181766. Copies of the infor-

mation may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax:+44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>)

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