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Synthesis and Crystal Structure of [*cis*-Dichloro(2-Pyridin-2-yl-1*H*-Benzoimidazole) (1*H*-Imidazole) Copper(II)] Complex

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ABSTRACT: A mixed ligand complex [*cis*-Dichloro(2-(2-Pyridyl)benzimidazole) (1*H*-Imidazole)Copper(II)] (**1**) has been prepared by the reaction of 2-(2-pyridyl)benzimidazole, 1*H*-imidazole with copper(II)chloride in ethanol medium. The structure of **1** was determined by single crystal X-ray diffraction. The results gives that the complex **1** belongs to monoclinic, space group P21/C with a = 9.3566(19) Å, b = 12.504(3) Å, c = 14.018(3) Å, α = 90°, β = 105.30(3)°, γ = 90°, V = 1582.0(6) Å^3, Z = 4 and final R_1 = 0.0529, ωR_2 = 0.07. The complex molecules form 1D chain structure by the H-Cl-H intermolecular hydrogen bond interaction. The complex exhibits trigonal bipyramidal distorted square based pyramidal (TBDSBP) coordination geometry.

Keywords: benzimidazole, imidazole, copper(II) chloride, complex, X-ray

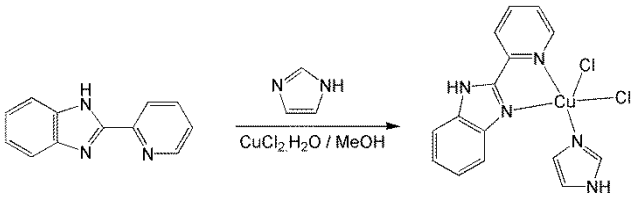
1. Introduction

The coordination chemistry of copper (II) attracts much attention because of its biological relevance and its own interesting coordination geometry, variable redox properties and different oxidation states [1]. Several copper complexes have been now proposed as potential anticancer substances, demonstrating remarkable anticancer activity and showing general toxicity lower than platinum compounds [2]. As synthetic analogues of the active sites of various metalloproteinase have been useful in elucidating the relation between their structure, electronic properties and functions, copper complexes of imidazole ligands are of interest as models for copper proteins. On the other hand, substituted benzimidazole possesses pharmacological activities. Benzimidazole derivatives too contributed in various methods for of biological activities including anticancer, antiviral, antibacterial, antifungal and antioxidant [3, 4]. Further, there is considerable interest in the study of mixed ligand coordinated complexes in view of their unusual magnetic, catalytic and biochemical behaviours. Further, metal complexes with mixed ligands are an area of current interest due to their structural diversity. Coordination chemistry is about tuning properties of metal ions using different ligands. This includes stabilization of different oxidation states, modulation of the solubility and its photophysical properties. In the present work we prepared copper (II) complex with mixed ligands 2-pyridyl) benzimidazole and 1H-Imidazole in methanol solution and their structure was determined using X-ray single crystal diffraction analysis method.

2. Experimental procedure

2.1. Synthesis of [*cis*-dichloro (2-(2-pyridyl)Benz imidazole) (1*H*-imidazole) copper(II)] (1)

A methanolic solution (15 mL) of copper(II)chloride (0.17 g, 1.0 mmol) was added to a solution of 2-(2-pyridyl)benzimidazole (0.195 g, 1 mmol), 1*H*-imidazole (0.068 g, 1 mmol) in methanol with vigorous stirring. The blue coloured precipitate obtained was washed with cold methanol and diethyl ether and dried under vacuum. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of acetonitrile solution of the complex (Scheme 1). Yield: 0.298 g, (75 %). Anal. Calcd for $CuC_{15}H_{13}N_5Cl_2$. C45.29, H 3.29, N 17.61; Found: C 45.31, H 3.27, N 17.65.



Scheme 1. Synthesis of Complex **1**

2.2. Single crystal X-ray studies

A single crystal for X-ray diffraction studies was grown by slow evaporation of acetonitrile solution of **1** at room temperature. A suitable crystal was mounted on glass fibers for data collection. Data was collected on an Oxford Diffraction Xcalibur Eos Gemini diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). The data was solved using direct methods with SHELXS and

refined using SHELXL-2014 [5]. The graphics interface package used was PLATON, and the Figs were generated using the ORTEP 3.07 generation package [6]. The positions on all the atoms were obtained by direct methods. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to the carbon were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 Ueq of their parent atoms. The crystal was found to be monoclinic with a = 9.3566(19), b = 12.504(3), c = 14.018(3) Å and β = 105.30(3)°. The structure was solved in the space group P21/c space group. The crystallographic data and details of the data collection for 1 are given in Table 1. The selected bond lengths and angles are presented in Table 2.

3. Result and Discussion

3.1. Description of the crystal structure of 1

An ORTEP view of complex **1** including the atom numbering scheme is depicted in Fig 1. The crystallographic structural parameters are provided in Table 1 and the selected bond lengths and bond angles are given in Table 2. The asymmetric unit cell of the compound consists of one complex molecule. The Cu(II) of complex **1** is coordinated to three nitrogen atoms and two chloride ions. The geometry of a five-coordinate system may be confirmed by the Addison parameter (τ) where τ is one for perfect trigonal bipyramidal geometry and is zero for a perfect square pyramidal geometry [7]. The value of the Addison parameter τ = 0.55; [$\tau = (\beta - \alpha)/60$] where, α = 169.84° and β = 136.95° which confirms that the structure of complex **1** adopts a distorted trigonal bipyramidal distorted square based pyramidal (TBDSBP) geometry. The corners of the square plane of the geometry are occupied by N1, N2 and N4 nitrogen atoms of the bidentate and monodentate ligands and one chloride (Cl2) atom and the axial position by the other chloride atom (Cl1).

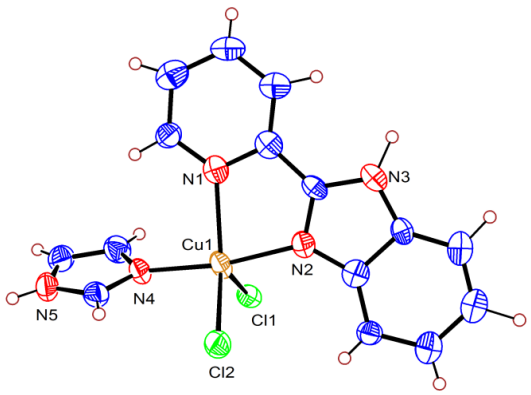


Fig 1. ORTEP representation of the crystal structures of complex 1.

Table 1. Crystallographic data and structure refinement parameters for **1**.

Formula	$C_{16}H_{14}Cl_2CuN_4$
crystal system	Monoclinic
space group	P21/c
a (Å)	9.3566(19)
b (Å)	12.504(3)
c (Å)	14.018(3)
α (deg)	90
β (deg)	105.30(3)
105.30(3)	90
V (Å^3)	1582.0(6)
Z	4
ρ_{calc} mg/mm^3	1.666
final R indices	R_1 = 0.0569 wR_2 = 0.0739
R_1[a]	0.1356
wR_2[b]	0.1279
[a] $R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$. [b] $_wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}_{1/2}$.	

Table 2. Selected inter atomic distances [Å] and bond angles [°] for complex **1**

Inter atomic Distance	Bond angels[°]
Cu1-N4	1.962(4)
Cu1-N2	1.962(4)
Cu1-N1	2.190(5)
Cu1-Cl2	2.2988(17)
Cu1-Cl1	2.6488(17)
N4 -Cu -N2	169.84(18)
N4- Cu1-N1	92.15(17)
N2- Cu1-N1	78.86(17)
N4- Cu1-Cl2	94.17(13)
N2 -Cu1-Cl2	95.64(13)
N4 -Cu1-Cl1	89.40(13)
N2 -Cu1-Cl1	89.29(13)
N1- Cu1-Cl1	N1- Cu1-Cl1
N1 -Cu1-Cl2	N1 -Cu1-Cl2
Cl2 -Cu1-Cl1	112.37(6)

As observed, the Cu1-$N1_{py}$ bond length (2.190(5)Å) is sligh The Cu-N_{py}, Cu-N_{bim} and Cu-N_{im} bonds formed by the bidentate and monodentate ligands are comparable to those for other Cu(II) complexes containing the same ligands [8]. tly shorter than the Cu1-$N2_{bim}$ (1.964(4) Å) and Cu-$N4_{im}$ (1.944(4) Å) bond distances. Furthermore, the Cu-Cl1 (2.6488(16)Å) bond is significantly longer than the Cu1-Cl2 (2.2988(16)Å) bond distance. This increase in Cu-Cl_{axial} is resulted from a reduction of electron density on the axial chloride ions due to a formation of the intermolecular hydrogen bonds between the axial chloride ions and the amine hydrogens [9].

Summary

A new compound of [*cis*-dichloro (2-(2-pyridyl) benzimidazole) (1*H*-imidazole) copper(II)] was synthesized and analyzed by elemental analysis. X-ray structural analysis reveals that the compound crystallizes in the monoclinic space group P21/c with unit cell parameters: a = 9.3566(19), b = 12.504(3), c = 14.018(3) Å and β = 105.30(3)° and Z=4. The complex exhibits trigonal bipyramidal distorted square based pyramidal (TBDSBP) coordination geometry.

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