



**Synthesis and characterization of monomeric copper (II) complex,
“Di aqua-(Pyridine-2, 6-dicarboxylato)-Copper (II)” with pyridine
2, 6-Dicarboxylic acid**

**Manob Jyoti Borah,^{*1} R.K. Bhubon Singh,² Upasana Bora Sinha,¹ Toshienla Gurung³,
Pronob Jyoti Borah⁴**

1. Department of Chemistry, Nagaland University, Hqrs- Lumami, Nagaland, India
2. Department of Chemistry, Manipur University, Imphal, India
3. Department of Zoology, Nagaland University, Hqrs- Lumami, Nagaland, India
4. Department of Civil engineering, Indian Institute of Technology, Guwahati, Assam, India

ABSTRACT

A new monomeric complex of Copper with pyridine 2,6-dicarboxylic acid was synthesized, the structure of the complex was determined by single crystal X-ray crystallography and was characterized spectrally with the help of IR and UV spectrometers and the magnetic moments of the reported complex was recorded. The complex crystallizes in the triclinic space group P1. The complex has the molecular formula $C_7H_7 CuNO_6$; $a = 4.71930 (10) \text{ \AA}$; $\alpha = 81.1180^\circ$, $b = 8.9785(2) \text{ \AA}$; $\beta = 85.7300^\circ$, $c = 10.3400(2) \text{ \AA}$; $\gamma = 83.3380^\circ$. The reported monomeric copper complex was observed to be penta-coordinated with two different types of donor atoms (nitrogen and oxygen). Details of the structures and spectroscopic properties have been discussed.

Keywords: Cu (II) complex - Pyridine 2, 6-dicarboxylic acid - X-ray structure - Spectral characterization.

INTRODUCTION

The research on the metal carboxylates has always been intriguing in that they play important roles not only in synthetic chemistry with the essence of labile coordination modes of carboxylate group, such as architecture of open and porous framework [1, 2] but also in biologic activities [3,4] and physiological effects [5].

The carboxylate ligand can have different binding modes and each of them may play role in the formation of supra molecular assembly [6-8]. The compounds having multiple carboxylic acid groups are good synthons for supramolecular architectures and coordination polymers [9-12]

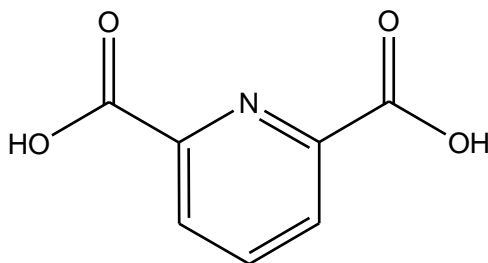
Pyridine-dicarboxylic acids and their derivatives belong to an interesting series of compounds with biological applications [13] Pyridine-2, 6-dicarboxylic acid (dipicolinic acid) is present in nature as an oxidative degradation product of vitamins, coenzymes and alkaloids and is a component of fulvic acids. It has frequently been cited in the literature as a plant sterilizing and water germicidal agent and an antioxidant for ascorbic acids in foods [14].

The d^9 configuration of Cu(II) in an octahedral field leads to a significant Jahn-Teller distortion that usually manifests itself as an axial elongation, consistent with the lability and geometric flexibility of Cu(II) complexes [15].

Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases have attracted much interest as they can display exceptionally high stability.[16-18] The use of transition metal complexes of iminodiacetic acid and nitrilotriacetic acid have been widely adopted in biology, and are gaining increasing use in biotechnology, particularly in the protein purification technique known as Immobilized Metal-ion Affinity Chromatography (IMAC)[19] Many drugs possess modified pharmacological and toxicological properties when administered in the form of metallic complexes. Probably the most widely studied cation in this respect is Cu^{2+} , since a host of low-molecular-weight copper complexes have been proven beneficial against several diseases such as tuberculosis, rheumatoid, gastric ulcers, and cancers [20-23].

The benefits of copper over other transition metals is that only very mild conditions are necessary for binding reactions to occur, facilitating *in vivo* studies of DNA structure [24].

In our present work, we have initiated a program to explore the coordination chemistry of a simple, easily synthesizable complex of Cu(II) with pyridine 2, 6-dicarboxylic acid (Scheme 1) and have described the synthesis, X-ray structure, spectral and magnetic properties of the complex.



Scheme 1: Pyridine 2, 6-dicarboxylic acid

MATERIALS AND METHODS

Reagent grade, pyridine 2, 6-dicarboxylic acid (Lancaster, U.K), and Ethanol (S.d. Fine chem. Limited), were used as received without any purification, aniline (S.d. Fine chem. Limited) was used after purification. Copper(II) perchlorate was synthesized as described in the literature [25]

Caution! Although no problems were encountered in this work, perchlorate salts in presence of organic materials are potentially explosive. Compounds should be prepared in small amounts and handled with care.

Synthesis of [Cu (2, 6-dipico)(H₂O)₂]

Pyridine 2, 6-dicarboxylic acid, 2mmol; (0.334) g is dissolved in 30ml of ethanol to it 1 m.mol of Cu(II) per chlorate (0.256 g), dissolved separately in 20 ml of ethanol; is added drop wise with constant stirring. The temperature of the solution is raised to 60°C and the stirring is continued for 1 hour. The blue colored solution obtained was then transferred to a reflux condenser and refluxed for two and half hours, cooled to room temperature filtered and kept for slow evaporation. After eighteen days, dark blue cubic shaped single crystals of [Cu (2, 6-dipico)(H₂O)₂] are formed, which are collected mechanically and dried in the air. The dark blue crystals of the complex was found to be stable in the air and was found to be suitable for single crystal X-ray diffraction.

Yield 62% for [Cu (2, 6-dipico)(H₂O)₂]

Calculated (%): C - 31.76; H - 2.67; Cu - 24.01; N - 5.29;

Found (%): C - 31.74; H - 2.66; Cu - 24.03; N - 5.28;

RESULTS AND DISCUSSION**Electronic spectroscopy**

The U.V visible spectra of [Cu(2, 6-dipico)(H₂O)₂] was recorded using a methanolic solutions of the complex and is shown in (figure 1.) It was reported that, square-pyramidal or tetragonally distorted octahedral complexes have an intense band between 600 and 750 nm with a shoulder at higher wavelength (*ca.* 850 nm), whereas trigonal-bipyramidal and trigonally distorted square pyramidal complexes have a *k*_{max} > 850 nm with a shoulder at higher energy. [28]

The U.V/ visible spectrum of the complex were recorded using a methanolic solution of the complex. Normally, two spin allowed transitions ${}^2A_1^I \rightarrow {}^2E''$ and ${}^3A_1^I \rightarrow {}^2E''_1$ are expected for trigonal bi-pyramidal complexes of Cu(II) d⁹ system. However in the reported complex, we have observed only one absorption band, near 745 nm which may be assigned due to ${}^2A_1^I \rightarrow {}^2E''$ transitions and indicates a five coordinated trigonal bi-pyramidal geometry.[29]

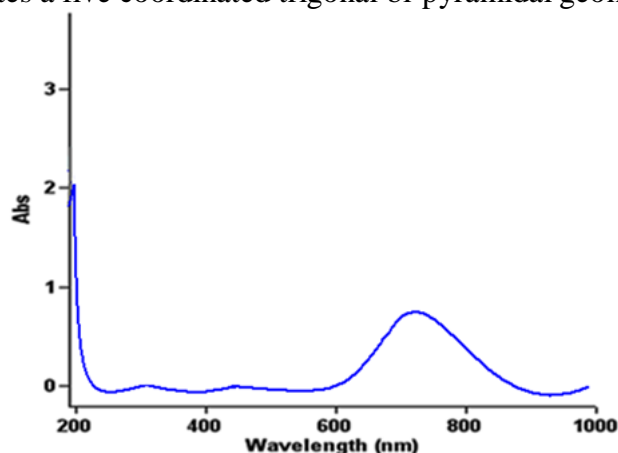


Figure 1: U.V/visible spectra of [Cu(2, 6-dipico)(H₂O)₂]

F.T.I.R spectroscopy

The FTIR spectra of the synthesized monomeric Copper complex [Cu (2, 6-dipico)(H₂O)₂], was recorded in the range of 4000 – 400.0 cm⁻¹ using KBr pellets. The presence of –COO⁻ group is reflected by IR spectrum in absorption bands of the $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ vibrations at 1620 and 1388 cm⁻¹, respectively. The difference between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$,

$\Delta\nu = 232 \text{ cm}^{-1}$, suggests a uni dentate binding mode of the carboxylate group to the Cu(II) ion. The absorption bands was observed at 588 and 516 cm^{-1} may be assigned due to ν (Cu-O) vibrations.[30] The sharp absorption band observed at 434 cm^{-1} is assigned due to Pyridine ν (Cu-N) vibrations. [31] The absorption bands observed at 3242 cm^{-1} may be assigned due to ν (O - H) vibrations and at 3109, 1681 and 852 cm^{-1} for δ_r (HOH) and ρ_w (HOH) vibrations, indicating the presence of coordinated water molecules in the crystal.

X- Ray data collection and structure refinement:

Good quality air stable light green crystals of [Cu (2, 6-dipico)₂] (C₆H₈N)₂ were selected and mounted on Bruker CCD area detector and Bruker SMART diffractometer. Data were collected at 296(2)K using graphite crystal monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 11,021 reflections (9,141, independent reflections, R(int) = 0.0482) were collected in the range of $2.79^\circ < \theta < 28.33^\circ$. The lattice components were determined by least – square refinements. The structures were solved by direct methods using SHELX – 97 programs [26] and refined by full matrix, least square methods using the SHELX – 97 programs [27]

The ORTEP structure of the synthesized monomeric copper complex, [Cu (2, 6-dipico) (H₂O)₂], with the molecular formula C₇H₇CuNO₆ is shown in *figure 2*. The structure shows that the Cu(1) chelates to one pyridine 2, 6-dicarboxylic acid ligand through three donor sites [N(1), O(1) and O(3)], acting as a tridentate ligand with NO₂ donor set, and the two oxygen atoms [O(5) and O(6)] from the two aqua ligands coordinating to the copper metal Cu(1), resulting a distorted trigonal bi-pyramidal structure. In the reported complex, the Cu(II) is penta - coordinated to the one nitrogen [N(1)] from the pyridine ring of pyridine 2, 6-dicarboxylic acid ligand and four oxygen atoms, two [O(1) and O(3)] from pyridine 2, 6-dicarboxylic acid ligand and the other two oxygen atoms [O(5) and O(6)] from two aqua ligands. The metal ion Cu(1) along with the three oxygen atoms, O(1), O(3) and O(6) lies in a trigonal equatorial plane while the other two donor atoms, N(1) and O(5) lies axially at the top and below the distorted horizontal square plane showing a distorted trigonal bi-pyramidal geometry. The bond angels N(1) - Cu(1) - O(1) = 81.0(2), O(5) - Cu(1) - O(1) = 96.3(2), O(5) - Cu(1) - O(6) = 93.1(2), N(1) - Cu(1) - O(3) = 80.4(3), O(5) - Cu(1) - O(3) = 99.2(2) [near 90°]and N(1) - Cu(1) - O(5) = 157.3(2) shows that N(1) and O(5) lies above and below the trigonal plane. The distorted nature of the complex was supported by the bond lengths Cu(1) - N(1) = 1.923 \AA and Cu(1) – O(5) = 1.961 \AA placed at the top and below the trigonal plane, was observed to be slightly shorter then Cu(1) – O(1) = 2.009 \AA , Cu(1) – O(3) = 2.008 \AA and Cu(1) – O(6)= 2.147 \AA , placed on the trigonal plane, showing Jahn Teller distortion in the synthesized monomeric Cu(II) complex. The two oxygen atoms of the carboxylate groups from pyridine 2, 6-dicarboxylic acid ligand after deprotonation, act as anions and contribute two negative charges. The other two oxygen atoms from the two neutral water molecules contributes no charges and the charge on the copper metal Cu(1) is assigned to be in the +2 state. Further details of the structural analysis for [Cu (2, 6-dipico) (H₂O)₂] are given in Table 1, Selected bond lengths are listed in table 2, Selected bond angles are listed in table 3, Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) are listed in table 4, Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) are listed in table 5, Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) are listed in table 6.

Table 1: Crystal data and structure refinement for [Cu (2, 6-dipico) (H₂O)₂]

CCDC Reference number	781734
Empirical formula	C ₇ H ₇ Cu N O ₆
Formula weight	231.74
Temperature	296(2) K
Wavelength	0.71073 Å
Space group	Triclinic
Space group H – M symbol	P1
a	4.71930(10) [Å]
b	8.9785(2) [Å]
c	10.3400(2) [Å]
α	81.1180(10) [°]
β	85.7300(10) [°]
γ	83.3380(10) [°]
Volume	429.238(16) Å ³
Z	2
Calculated density	1.793 Mg/m ³
Absorption coefficient	2.508 mm ⁻¹
F(000)	238
Crystal size	0.50 x 0.40 x 0.30 mm
Theta range for data collection	2.82 to 28.32 deg.
Limiting indices	-6<=h<=6, -11<=k<=11, -13<=l<=13
Reflections collected / unique	5749 / 3226 [R(int) = 0.0434]
Completeness to theta = 28.32	99.0 %
Max. and min. transmission	0.5199 and 0.3669
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3226 / 3 / 272
Goodness-of-fit on F ²	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1135
Absolute structure parameter	0.18(3)
Extinction coefficient	0.251(13)
Largest diff. peak and hole	1.046 and -1.070 e.Å ⁻³

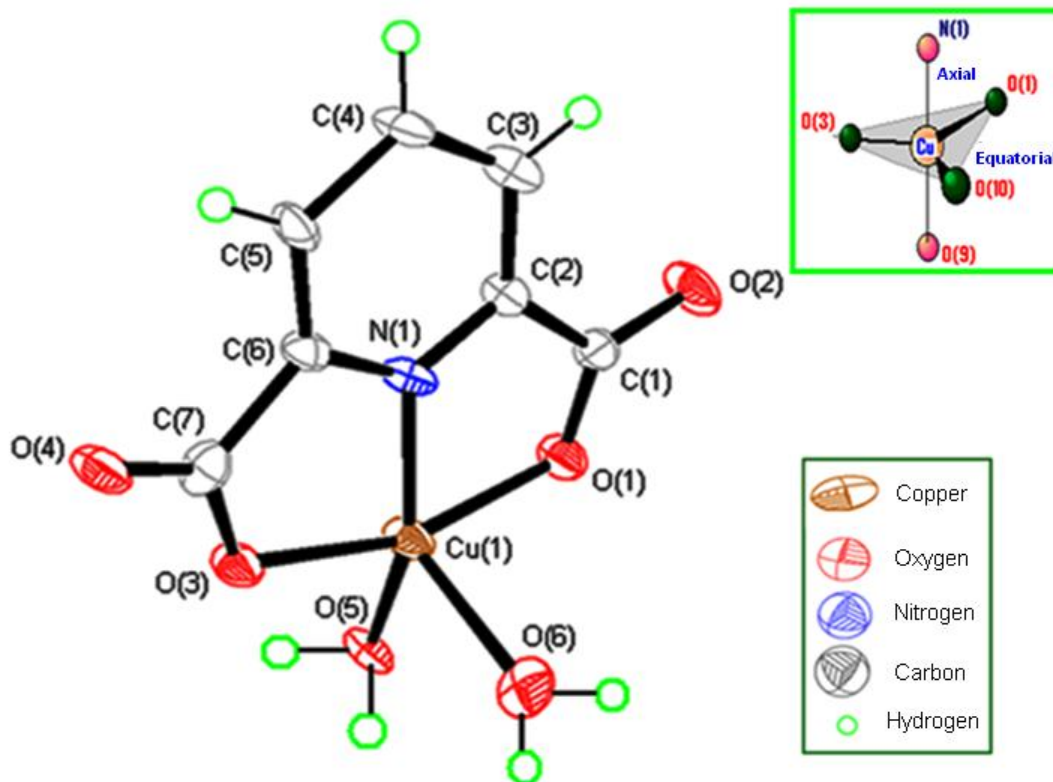


Figure 1 ORTEP structure of [Cu (2, 6-dipico) (H₂O)₂] with 50% ellipsoid probability Level.

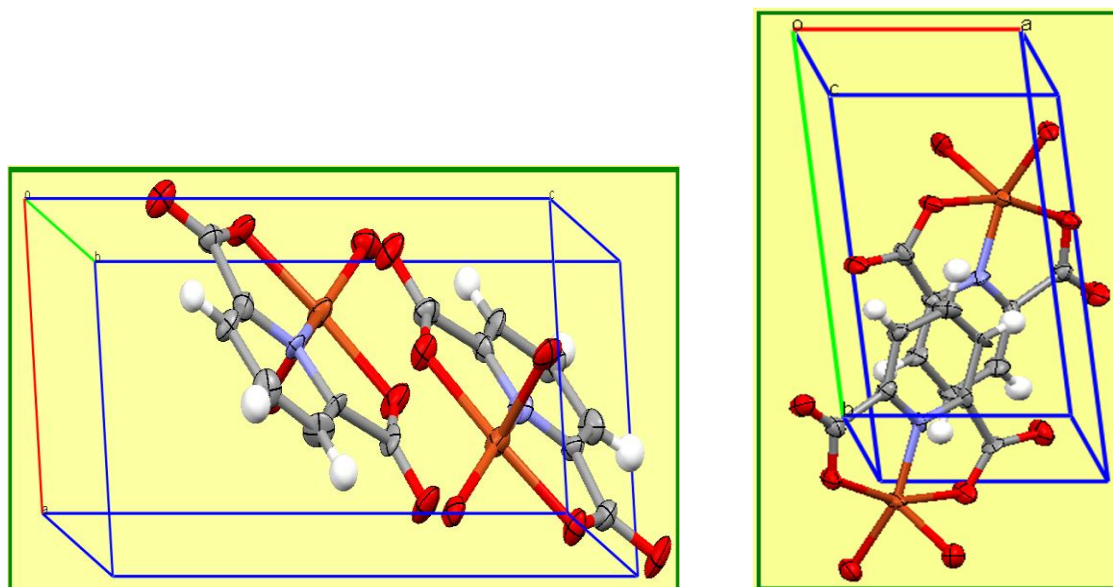


Figure 2: Packing plot of [Cu (2, 6-dipico) (H₂O)₂], in a unit cell along crystallographic axis b* and c*

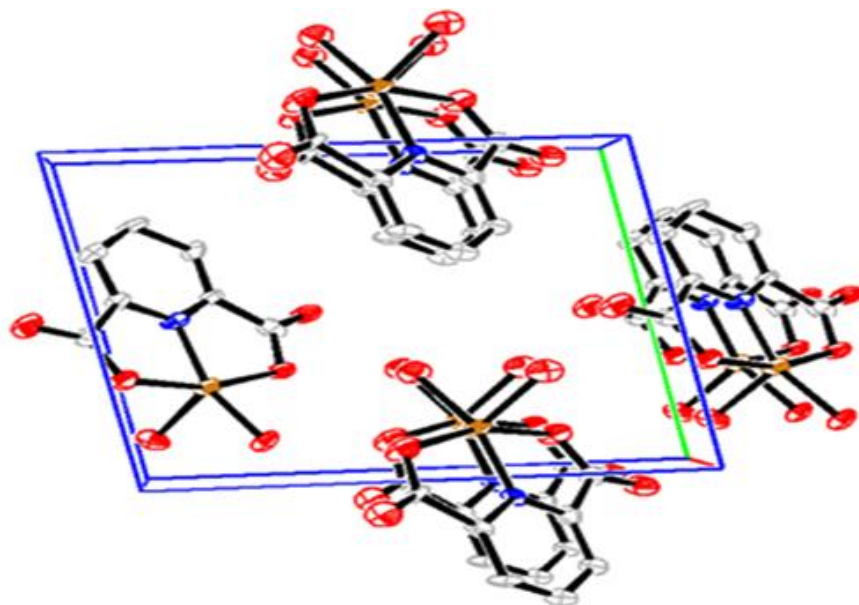


Figure 3: Fragment of crystal packing of [Cu (2, 6-dipico) (H₂O)₂]

Table 2: Selected Bond lengths [Å] for [Cu (2, 6-dipico) (H₂O)₂]

BOND	LENGTH [Å]
Cu(1) - N(1)	1.923(6)
Cu(1) - O(5)	1.961(5)
Cu(1) - O(3)	2.008(6)
Cu(1) - O(1)	2.009(5)
Cu(1) - O(6)	2.147(6)
O(2) - C(1)	1.253(8)
O(3) - C(7)	1.297(11)
O(1) - C(1)	1.289(10)
O(4) - C(7)	1.224(8)
N(1) - C(2)	1.317(8)
N(1) - C(6)	1.312(9)

Table 3: Selected Bond angles [$^{\circ}$] for [Cu (2, 6-dipico) (H₂O)₂]

BOND	ANGELS [$^{\circ}$]
N(1) - Cu(1) - O(5)	157.3(2)
N(1) - Cu(1) - O(3)	80.4(3)
O(5) - Cu(1) - O(3)	99.2(2)
N(1) - Cu(1) - O(1)	81.0(2)
O(5) - Cu(1) - O(1)	96.3(2)
O(3) - Cu(1) - O(1)	161.0(2)
N(1) - Cu(1) - O(6)	109.6(3)
O(5) - Cu(1) - O(6)	93.1(2)
O(3) - Cu(1) - O(6)	91.9(2)
O(1) - Cu(1) - O(6)	98.1(2)
C(7) - O(3) - Cu(1)	115.2(5)
C(1) - O(1) - Cu(1)	113.9(5)
C(2) - N(1) - C(6)	124.3(7)
C(2) - N(1) - Cu(1)	117.5(5)
C(6) - N(1) - Cu(1)	118.2(4)

Table 4: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{A}^2 \times 10^3$) for [Cu (2, 6-dipico) (H₂O)₂]

ATOM	X	Y	Z	U(eq)
Cu (1)	7145(1)	2941(1)	8372(1)	24(1)
O(2)	10398(13)	4978(8)	11037(6)	36(2)
O(3)	4214(13)	3334(8)	7014(6)	26(1)
O(1)	9778(12)	3291(7)	9709(5)	26(1)
O(4)	667(12)	5039(6)	6257(6)	30(1)
N(1)	5651(13)	4977(7)	8591(6)	23(1)
C(6)	3610(13)	5656(8)	7847(6)	20(1)
C(7)	2699(15)	4642(9)	6946(7)	26(1)
C(2)	6804(13)	5613(9)	9460(7)	19(1)
C(1)	9152(1)	4566(8)	10144(7)	22(1)
C(3)	5833(16)	7094(9)	9650(7)	30(2)
C(5)	2588(14)	7109(9)	7918(7)	24(1)
C(4)	3709(15)	7906(9)	8853(8)	27(2)
O(5)	9677(10)	1331(6)	7665(5)	24(1)
O(6)	4675(11)	1362(7)	9612(5)	30(1)

Table 5: Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [Cu (2, 6-dipico) (H_2O)₂]

ATOM	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Cu(1)	22(1)	21(1)	29(1)	-10(1)	-10(1)	3(1)
O(2)	42(3)	36(4)	35(3)	-16(3)	-25(3)	5(3)
O(3)	42(3)	36(4)	35(3)	-16(3)	-25(3)	5(3)
O(1)	30(2)	18(3)	30(3)	-9(2)	-12(2)	6(2)
O(4)	33(3)	23(3)	27(2)	-8(2)	-11(2)	5(2)
N(1)	25(3)	18(3)	29(3)	-11(2)	-2(2)	-5(2)
C(6)	22(3)	18(3)	21(3)	-8(2)	3(2)	-1(2)
C(7)	20(3)	27(4)	28(3)	2(3)	-6(2)	3(3)
C(1)	23(3)	22(4)	23(3)	-1(3)	-8(2)	-6(2)
C(2)	14(3)	21(3)	23(3)	-7(2)	-4(2)	2(2)
C(3)	30(3)	29(4)	33(4)	-17(3)	0(3)	-3(3)
C(5)	27(3)	28(3)	22(3)	-10(2)	-9(2)	-6(3)
C(4)	27(3)	19(3)	39(4)	-17(3)	-10(3)	4(3)
O(5)	22(2)	27(3)	27(2)	-16(2)	-7(2)	1(2)
O(6)	24(2)	31(3)	33(2)	5(2)	-15(2)	4(2)

Table 6: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [Cu (2, 6-dipico) (H_2O)₂]

ATOM	X	Y	Z	U(eq)
H(3)	6573	7537	10289	35
H(5)	1177	7596	7373	29
H(4)	3053	8909	8924	33
H(11)	5399	5659	3462	36
H(12)	1721	6881	2214	26
H(10)	7360	6749	4921	33

Magnetic moment measurements

The magnetic moment for [Cu (2, 6-dipico) (H_2O)₂] at room temperature was found to be 1.69 B.M. Which fits well with the spin only value for a copper(II) system ($1.73\mu\text{B}$).

APPLICATIONS

This Copper (II) complex can be applicable as a model in the synthesis of some bio-inorganic compounds like metalloproteins.

CONCLUSION

A monomeric complex of Cu(II) with pyridine 2, 6-dicarboxylic acid, [Cu(2, 6-dipico)(H_2O)₂], have been synthesized and fully characterized by analytical, spectroscopic, magnetic moment studies and single crystal x-ray crystallographic methods. The structure of the

complex exhibit a three dimensional network where the pyridine 2, 6-dicarboxylic acid ligand coordinates to Cu(II) through two different donor atoms O and N. The most interesting structural feature of the complex, is that, the bond lengths of Cu(1)- N(1)=1.923 Å and Cu(1) – O(5)=1.961 Å which were placed at the top and below the plane was observed to be slightly shorter than Cu(1) – O(1)= 2.009 Å, Cu(1) – O(3)=2.008 Å and Cu(1)– O(6)= 2.147 Å placed in the distorted trigonal plane, showing Jahn Teller distortion in the reported complex. This observations mean that Cu (II) ion undergoes t_{2g}^6 ; $d(x-y)^2, d(z)^1$ (e_g^3) configuration, resulting in more shielding of the Cu(II) nucleus along the X and Y axis as compared to the Z axis.

The extensions of this work to the synthesis with other metal ions, as well as the search for their applications, are under way in our laboratory.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 781734.

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