



Synthesis, Crystal Structure and Hirshfeld Surface Analysis of Copper(II) Complex with Pentacoordinated N5 ligands [Cu(AEPN)(2PN)](ClO₄)₂

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The reaction of N-(2-aminoethyl)-1,3-propanediamine (AEPN) and 1,2-diaminopropane (2PN) with copper(II) acetate in the presence of sodium perchlorate in methanolic solution led to the formation of a copper(II) complex, [Cu(AEPN)(2PN)](ClO₄)₂ (**1**). The copper(II) center occupies a distorted square pyramidal environment defined by three N donors from N-(2-aminoethyl)-1,3-propanediamine ligand and two N donors from 1,2-diaminopropane. The Cu-N distances span the range of 2.023 (10)-2.238 (10) Å. There are hydrogen bonding interaction between primary and secondary nitrogen of the cation and the oxygen atom of the perchlorate anions. An investigation of the crystal packing and intermolecular interactions has been examined using the Hirshfeld surface analysis.

Keywords: Copper(II), X-ray crystal structure, Square pyramidal, Hydrogen bonding, Hirshfeld surface analysis.

INTRODUCTION

Simple diamines and triamines were extensively used as important precursors for the preparation of chelating complexes owing to their powerful coordination and H-bonding ability¹. Over the past few decades, these amines were also used as starting material for the synthesis of saturated polyaza macrocyclic complexes *via* metal template Mannich reaction². N-(2-aminoethyl)-1,3-propanediamine (AEPN) is a tridentate amine ligand which usually forms three coordination bonds with the central metal ion and it rarely acts as a bridging ligand in which the non-chelated arms of the triamine ligands forming a chain linked system of a hyper branched polymeric molecule^{3,4}. Copper is an essential micronutrient for various biological systems and shows diverse and interesting coordination chemistry⁵. Copper(II) complexes have attracted much attention because of their applications as chemical nuclease, catalyst and so forth^{6,7}. Several reports are available for the transition metal complexes with AEPN as a ligand which usually prefers hexa coordination geometry⁷⁻¹⁰. Here, we got a pentacoordinated copper(II) complex [Cu(AEPN)(2PN)](ClO₄)₂ (**1**), in which the two perchlorate anions are not coordinated with metal ion.

In order to explore the better understanding of intermolecular interactions in molecular crystal packing, it is crucial to get quantitative measurements of these interactions. Hirshfeld surface analysis¹¹⁻¹⁴ is a valuable tool for elucidating molecular crystal structures quantitatively and such quantitative measures of weak interactions in coordination complexes are poorly

documented in the literature¹⁵. In this context, we hereby report the quantitative crystal structure analysis of mixed ligand copper(II) complex (**1**).

EXPERIMENTAL

All chemicals were of analytical grade and used without further purification. Methanol used for the synthesis was purified using the available literature method¹⁶.

Synthetic procedure: To a stirred methanolic solution (30 mL) of Cu(OAc)₂.H₂O (4.41 mmol, 0.87 g) were added N-(2-aminoethyl)-1,3-propanediamine (AEPN) (4.41 mmol, 0.56 mL) and 1,2-propanediamine (PN) (4.41 mmol, 0.37 mL). The mixture was stirred for 0.5 h and the solution was filtered to remove insoluble material. An excess sodium perchlorate dissolved in methanol was added to the filtrate and the mixture was kept in the refrigerator until blue crystals formed. The crystals were filtered, washed with methanol, diethyl ether and air dried in vacuo. Blue crystals of suitable size were obtained by slow evaporation of the aqueous solution at room temperature. Yield: 85-90 %. UV-Visible (H₂O): λ_{max} (ε, M⁻¹ cm⁻¹) 586 nm (53). Λ_M (ohm⁻¹ cm² M⁻¹): 210.

X-ray crystallography: Single crystal X-ray structure data collection is performed on a Bruker AXS Kappa Apex II CCD diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) by the selection of appropriate suitable single crystal of size 0.3 mm × 0.2 mm × 0.2 mm. The crystal was coated with inert oil, mounted on a glass capillary

and crystal data were collected at 293 K. The reflections with $I > 2\sigma(I)$ were employed for structure solution and refinement. The SIR92¹⁷ (WINGX32) program was used for solving the structure by direct methods. Successive Fourier synthesis was employed to complete the structures after full-matrix least squares refinement on $|F|^2$ using the SHELXL97¹⁸ software.

Fourier syntheses led to the location of all of the non-hydrogen atoms. For the structure refinement, all data were used including negative intensities. Crystallographic data of the complex were shown in Table-1. Selected bond distances and bond angles are listed in Table-2 and the hydrogen bonds geometry is presented in Table-3. Hirshfeld surfaces and 2D finger plots were generated using Crystal Explorer 3.1¹⁹ based on results of single crystal X-ray diffraction studies. The function d_{norm} is a ratio encompassing the distances of any surface point to the nearest interior (d_i) and exterior (d_e) atom and the van der Waals radii of the atoms²⁰. A plot of d_i versus d_e is a 2D fingerprint plot which summarizes the existence of different types of intermolecular interactions through interactive computer graphics.

TABLE-1
CRYSTAL STRUCTURE DATA AND REFINEMENT

Data	[Cu(AEPN)(2PN)](ClO ₄) ₂
Empirical formula	CuC ₈ H ₅ N ₅ Cl ₂ O ₈
Formula weight	453.77
CCDC no.	691719
Colour	Blue
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	16.0341(13)
b (Å)	15.9750(12)
c (Å)	14.0597(10)
α (°)	90.0
β (°)	90.0
γ (°)	90.0
Volume (Å ³)	3601.3(5)
Z	8
D _{calcd} (mg/m ³)	1.674
λ (Å)	0.71073
T (K)	293(2)
Number of reflections collected	17156
Unique reflections	3161
No. of parameters refined	274
GOF on F ²	1.102
Final R indices [I ≥ 2σ(I)]	R ₁ ^a = 0.0855, wR ₂ ^b = 0.2805
R indices (all data)	R ₁ ^a = 0.1093, wR ₂ ^b = 0.2986
[a] R ₁ = Σ F _o - F _c /Σ F _o ; I _o > 2σ(I _o). [b] wR ₂ = [Σw(F _o ² - F _c ²) ² /Σw(F _o ²)] ^{1/2} .	

RESULTS AND DISCUSSION

Complex **1** crystallizes in orthorhombic crystal system with Pbc_a space group. Fig. 1 depicts the ORTEP representation of [Cu(AEPN)(2PN)](ClO₄)₂ (**1**) with atoms represented as 50 % anisotropic ellipsoids.

The chelate compound **1** have been synthesized in high yield (85-90 %) by the reaction of copper(II) ion with AEPN and 2PN in the presence of perchlorate anion under ambient conditions. The complex is soluble in water, acetone, MeCN and Me₂SO but insoluble in alcohol. The copper atom is coordinated by a tridentate chelating ligand AEPN and bidentate

TABLE-2
SELECTED GEOMETRICAL PARAMETERS (Å, °) FOR **1**

N1-Cu1	2.046(10)	N2-Cu1	2.238(10)
N3-Cu1	2.026(9)	N4-Cu1	2.023(10)
N5-Cu1	2.063(11)	C1-N1	1.530(3)
N1-Cu1-N5	174.4(5)	N4-Cu1-N3	151.5(5)
N4-Cu1-N1	91.8(5)	N3-Cu1-N1	91.6(4)
N4-Cu1-N5	93.9(5)	N3-Cu1-N5	83.6(5)
N4-Cu1-N2	104.8(5)	N3-Cu1-N2	103.7(5)
N1-Cu1-N2	81.8(4)	N5-Cu1-N2	96.3(4)

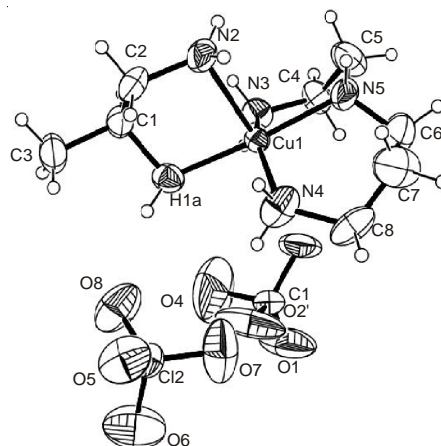


Fig. 1. ORTEP diagram of compound **1** with thermal ellipsoids at 50 % probability

chelating ligand 2PN that define a N₅ donor set and a distorted square-pyramidal geometry. All the three nitrogens from AEPN (N3, N4, N5) and a nitrogen from the bidentate 2PN (N1) form the square base at distances varying from 2.023(10) to 2.063(11) Å. The remaining nitrogen, N(2), belonging to the 2PN moiety, is situated more-or-less perpendicular to the square plane, but deviates slightly from the ideal value of 90°. The apical Cu-N(2) bond length is 2.238 (10) Å which is considerably greater than the equatorial Cu-N bond length due to the Jahn-Teller effect and is comparable with the reported pentacoordinated CuN₅ square pyramidal complex [Cu(dien)(en)](ClO₄)₂²¹. Thus, the crystal structure reveals that the tridentate AEPN occupies three equatorial positions and the bidentate 2PN occupies one equatorial and one axial position.

The quantification of degree of distortion from regular trigonal bipyramidal and square pyramidal geometry can be achieved on the basis of the changes in bond angle (Addison method)²² and bond distances (Hathaway method)²³. In Addison method, the angles between the donor atoms which forms the basal plane is used to calculate the parameter τ which is defined as $\tau = [(\theta - \phi)/60] \times 100$, where ϕ and θ are the two observed basal angles, represents the percentage distortion from square pyramidal geometry. The value τ is 0 % for ideal square pyramidal and 100 % for ideal trigonal bipyramidal geometry. For the complex **1**, $\tau = 38$ % indicates its geometry best described as trigonal-bipyramidally distorted square pyramidal geometry. The degree of distortion based on the M-N bond length can be evaluated using Hathaway method using the parameter tetragonality (T^5), defined as the ratio of the mean distance of the four in-plane coordination bonds to the distance of single out-of-plane bond. The value T^5 for complex **1** is calculated to be 0.911 which indicates there is a considerable

TABLE-3
 HYDROGEN BONDING GEOMETRY (Å, °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(D-H...A)
N(3)-H(3E)...O(1)#1	0.90	2.45	3.23(2)	146
N(1)-H(1A)...O(5)#2	0.90(10)	2.44(6)	3.267(14)	152(12)
N(1)-H(1B)...O(8)	0.90(10)	2.48(4)	3.349(16)	162(11)
N(2)-H(2C)...O(1)#3	0.90(10)	2.33(4)	3.19(2)	160(8)
N(2)-H(2D)...O(4')#1	0.90(10)	2.46(7)	3.22(4)	142(7)
N(4)-H(4D)...O(7)	0.90(10)	2.47(5)	3.14(2)	132(5)
N(5)-H(5)...O(6)#1	0.98(10)	2.12(11)	3.046(17)	157(8)

Symmetry code: #1 -x+3/2, y+1/2, z #2 x,-y+1/2, z+1/2 #3 x,-y+1/2,z-1/2.

deviation in bond distances from the regular geometry. Note that T^5 is unity for ideal trigonal bipyramidal and square pyramidal geometry.

In the chelate rings of AEPN, the bite angle of five membered Cu1-N3-C4-C5-N5 ring is 83.6° and those of six membered Cu1-C6-C7-C8-N4 ring is 93.9°. The C-C bond distance of five membered Cu1-N1-C1-C2-N2 ring containing the methyl group is 1.457 Å (C1-C2) which is slightly longer due to the significant strain than those of the corresponding unsubstituted five membered chelate ring (C4-C5). The average equatorial Cu-N (primary) distance of 2.031 Å is significantly shorter than the average Cu-N (secondary) distance of 2.063 Å, indicating comparatively strong coordination in the former. The perchlorate anions are not coordinated to metal ion and the Cu-O bond distance is in the range of 3.150-6.425 Å which is well beyond the coordination. The crystal network of the title compound is stabilized mainly through N-H...O hydrogen bonding which involves the primary and secondary amino hydrogens and the oxygen atom of perchlorate anion as shown in Fig. 2. In addition to this, the hydrogen atoms belonging to C4, C5 and C7 carbons are also involving in hydrogen bonding with anions which further stabilizes the crystal packing. Each cation is surrounded by seven perchlorate ions and each perchlorate ion by four cations in this structure. The perchlorate anions possess tetrahedral geometry, although some degree of disorder is apparent.

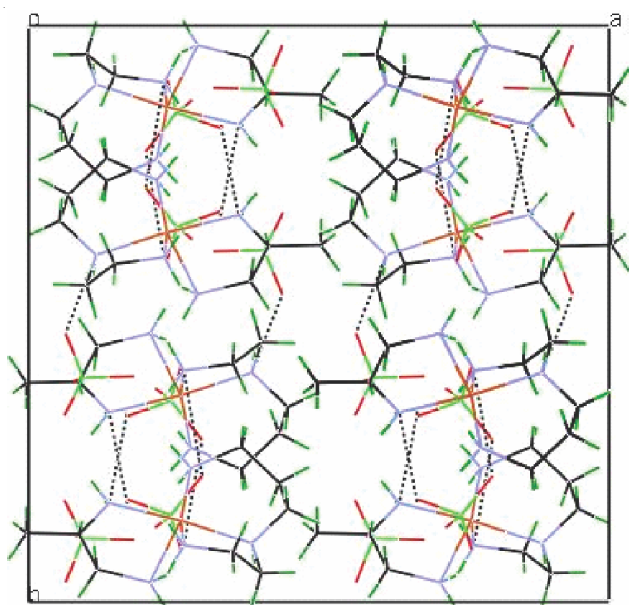


Fig. 2. Molecular packing diagram for the complex **1** down a-axis with hydrogen bonded interactions

In order to quantify the intermolecular interactions, Hirshfeld Surfaces and their associated finger print plots were generated using Crystal Explorer 3.1. Interestingly, there are no close contacts involving chlorine atom of perchlorate anion. The O...H-C/N contacts are seen as intense red spots in the Hirshfeld surface of **1**. From the FP plots (Fig. 3), it can be concluded that the back bone of the net supramolecular arrangements are dictated by the close contacts involving O...H-C/N (65 %) and the cooperativity of weak H...H contacts (34 %).

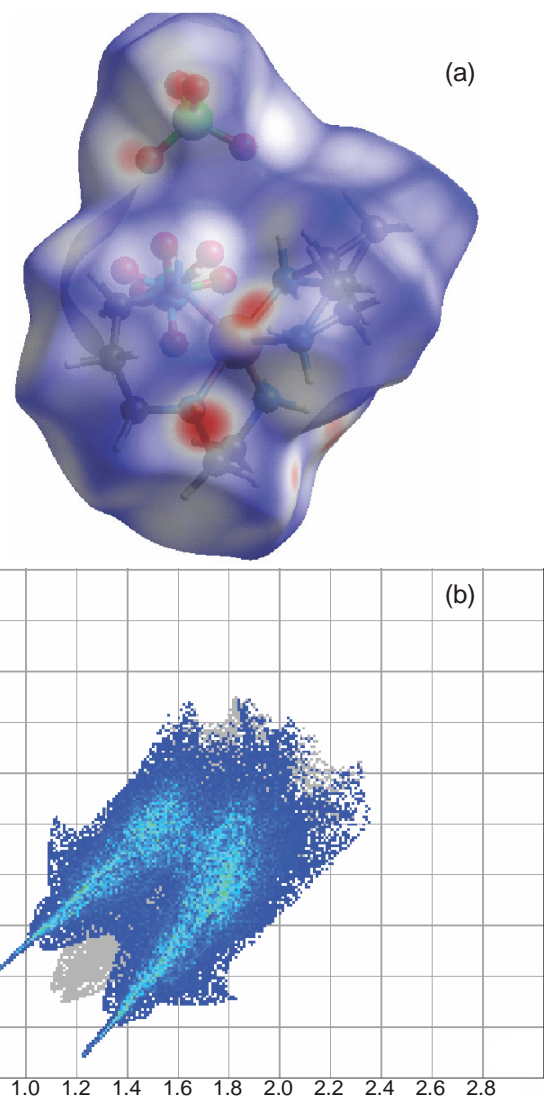


Fig. 3. (a) Hirshfeld surface of **1** with normalized contact distance ranging from -0.4 Å (red) to 2.0 Å (blue); (b) 2D fingerprint plot of O...H contact with d , and d_c ranging from 0.6 to 2.4 Å for **1**

Supplementary material: The cif file of complex **1** was deposited with the Cambridge Crystallographic Data Center (CCDC 691719). The data can be obtained free of charge from authors or the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

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