

# Different classical hydrogen-bonding patterns in two Copper (II) Metal Complexes of Dinitrato bis(1,3-diaminopropane) copper(II) and (Tetraethylenepentamine) copper(II) Nitrate

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**ABSTRACT:** The asymmetric unit of the compound I,  $[\text{Cu}^{\text{II}}(\text{tetren})](\text{NO}_3)_2$ , contains one  $[\text{Cu}(\text{tetren})]^{2+}$  cation (tetren is Tetraethylenepentamine) and two nitrate. In the cation,  $\text{Cu}^{2+}$  ion is coordinated by four N atoms from Tetraethylenepentamine and two nitrate ligands in distorted octahedral geometry. In the crystal, the components are linked via N-H...O hydrogen bonds, forming sheets lying parallel to (001). The Metal complex  $[\text{Cu}^{\text{II}}(\text{tn})_2(\text{NO}_3)_2]$ , the  $\text{Cu}^{\text{II}}$  atom has a distorted octahedral coordination sphere and is coordinated by N atoms of two 1,3-diaminopropane and two nitrate ligands in the equatorial plane. The asymmetric unit is completed, which are involved in hydrogen bonding with N-H functionalities of the free nitrate groups. The crystal structure also features N-H...O hydrogen bonds formed by the  $\text{NH}_2$  groups, forming sheets and ribbon lying parallel to (001) for compound II. Anti-bacterial study reveals that complexes are better anti-microbial agents than three Schiff base due to bacterial cell penetration by chelation.

**KEYWORDS:** Copper (II), Tetraethylenepentamine, diaminopropane Crystal Structure, and hydrogen bonding.

<https://doi.org/10.29294/IJASE.6.1.2019.1239-1243>

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## 1. INTRODUCTION

There have been numerous reports of bis(propene-1,3-diamine) copper(II) complexes, essentially with the copper atom coordinated by the N atoms of the ligands in the equatorial plane of the copper octahedral coordination sphere and with two identical O-containing ligands in the axial positions, for example, trans-diaquabis(propene-1,3-diamine- $k^2\text{N,N'}$ ) copper(II) dithionate [1],  $[\text{N,N'}$ -Bis(6-methoxysalicylidene)-1,3-diaminopropane] copper(II) [2],  $[\text{N,N'}$ -Bis (5-bromosalicylidene) -1,3-di- aminopropane] copper(II) [3] and bis[aqua(1,3-diaminopropane- $k^2\text{N,N'}$ )] copper(II) difluoride [4]. Structures of the  $\text{Cu}(\text{II})$  complex which are comparable with the title compound have been reported several times [5]. The slight increase in metal-to-nitrogen bond distances in (I) and (II) may be attributed to the steric hindrance of the bulkier trimethylene group between the N atoms [6]. In order to further develop the coordination chemistry of such copper complexes, we report herein on the synthesis and crystal structure of the title complex, which has two different ligands in the axial positions of the octahedral coordination sphere of the copper atom. The Structure was solved by direct method and refined on  $F^2$  by least-squares procedure to be the final  $R_1$  of 0.0293 (Compound -I) and  $R_1$  of 0.0357 (Compound -II) using SHELXL programs.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. X-ray Structure Determination

Single crystal of the compound suitable for x-ray

diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker6 SMART APEX CCD Diffractometer using graphite monochromatized Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at Department of chemistry, IIT, Chennai, India. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares procedures using the SHELXL programs [7]. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3 [8]. The crystallographic data for the compound are listed in Table 1.

### 2.2. Synthesis

$[\text{Cu}^{\text{II}}(\text{tetren})](\text{NO}_3)_2$  complexes were prepared with modifications by following previously reported procedures [9]. Synthesis of mononuclear copper(II) complexes was achieved by copper(II) nitrate trihydrate ( $1 \times 10^{-3} \text{ M}$ ) was taken in 10 mL of distilled ethanol (about 99%) and warmed. To the warm solution 2.8 mL of tetraethylenepentamine ( $2 \times 10^{-3} \text{ M}$ ) were added very slowly, stirred well and the entire solution was kept for few hours in dark. Crystals of complexes separated out were filtered, washed and recrystallized from acetone to give the desired product and dried over vacuum for compound I. Synthesis of mononuclear  $[\text{Cu}^{\text{II}}(\text{tn})_2(\text{NO}_3)_2]$  complexes were prepared with modifications by

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Received: 12.06.2019

Accepted: 28.07.2019

Published on: 28.08.2019

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following previously reported procedures [10, 11, 12] Copper(II) complexes was achieved by copper(II) nitrate trihydrate ( $1 \times 10^{-3}$  M) was taken in 10 mL of distilled ethanol (about 99%) and warmed. To the warm solution 3.5 mL of 1,3 diaminopropane ( $2 \times 10^{-3}$  M) were added very slowly, stirred well and the entire solution was kept for few hours in dark. Crystals of complexes separated out were filtered, washed and recrystallized from acetone to give the desired product and dried over vacuum for compound II.

### 3. RESULTS AND DISCUSSION

#### 3.1 Structure description

The molecular structure of the title complex -I is illustrated in Fig.3. The  $\text{Cu}^{\text{II}}$  atom has a distorted octahedral coordination sphere, reflecting the characteristic Jahn-Teller distortion.  $\text{Cu}^{\text{II}}$  coordinated by amino atoms N1 and N2 with bond distance of 2.772 Å and other side amino atoms N3 and N4 bond distance of 2.809 Å. The angles N1-Cu-N2, N3-Cu-N4 and O-Cu-O are 86.11(6), 87.93(6) and 168.02(4)°, respectively. The three bond angles in the trigonal plane about  $\text{Cu}^{\text{II}}$  sum to 342.06(6)°.

The molecular structure of the title complex-II is illustrated in Fig.4. The  $\text{Cu}^{\text{II}}$  atom has a distorted

octahedral coordination sphere, reflecting the characteristic Jahn-Teller distortion. It is coordinated by the N atoms of two propane-1,3 diamine ligands in the equatorial plane with Cu-N bond lengths varying between 1.99(2) - 2.001(2) Å. The axial positions are occupied by the nitrate O3 and by atom O3a of a disordered, with Cu-O bond lengths of 2.564(2) and 2.564(2) Å, respectively.

#### 3.2 Packing details

In the crystal, N-H...O hydrogen bonds are formed between the  $\text{NH}_2$  groups of nitrate as hydrogen bond donors and O atoms of the O-N(H)-hydroxamate groups as hydrogen bond acceptors, forming ribbon shapes a three dimensional supramolecular network structure (Table 2 and Fig.5). In the crystal, the various components are linked via N-H...O and C-H...O hydrogen bonds forming sheets lying parallel to (001). The cations are arranged in sheets parallel to (001), with the centrosymmetric aminopropane cation located between two sheets. Each cation is acceptor of four N-H...O hydrogen bonds, forming a three dimensional network structure. : see table 2 and Fig.6. The intermolecular interactions of both compounds were analyzed using Hirshfeld surface analysis and two-dimensional fingerprint plots.

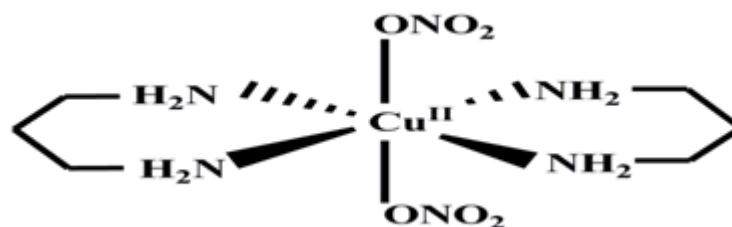


Figure 1 Scheme diagram compound I

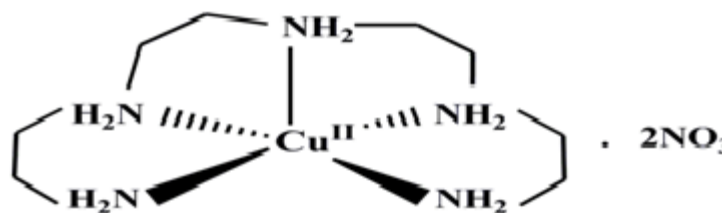


Figure 2 Scheme diagram compound II

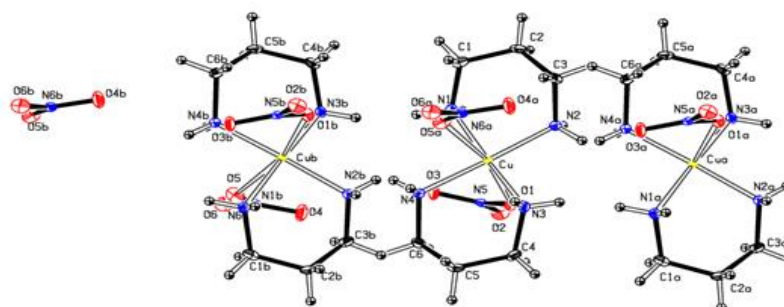


Figure 30 The molecular structure of compound I, with displacement ellipsoids drawn at the 30% probability level.

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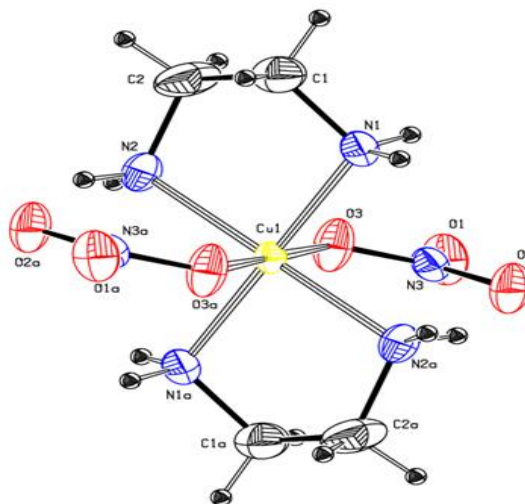


Figure 4. The molecular structure of compound (II), with the atom labeling. Displacement ellipsoids are drawn at the 50% Probability level. H atoms are shown as small spheres of arbitrary radius.

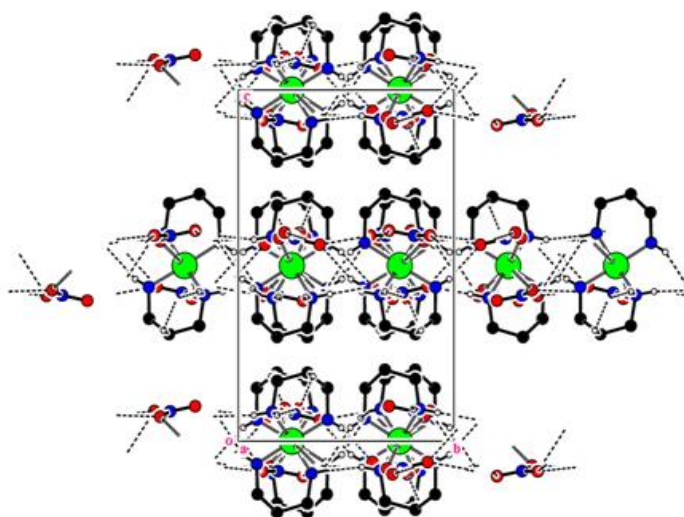


Figure 5. View along the a-axis of the crystal structure of the title compound, O-H...O and N-H...O hydrogen bonds are shown as dashed lines

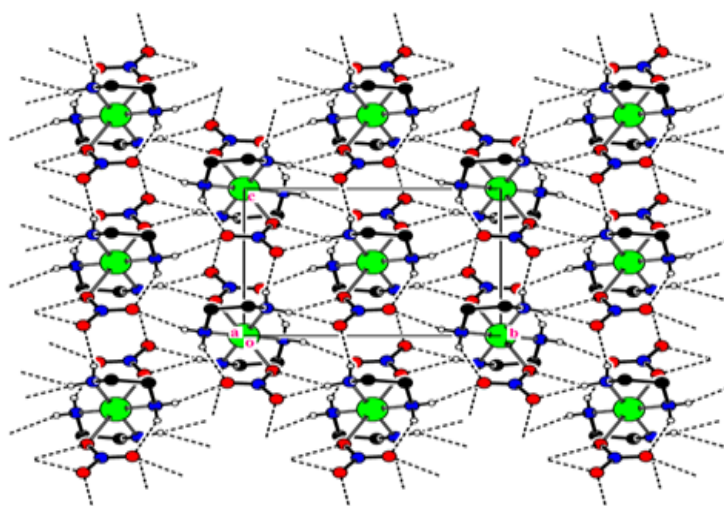


Figure 6 views along the a-axis of the crystal structure of the title compound, N-H...O hydrogen bonds are shown as dashed lines.

**Table 1** The crystallographic data for the compound

	<b>I</b>	<b>II</b>
Empirical formula	C <sub>6</sub> H <sub>20</sub> N <sub>6</sub> O <sub>6</sub> Cu	C <sub>4</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub> Cu
Formula weight	345.79	323.76
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
space group	Pbca	P2 <sub>1</sub> /c
Unit cell dimensions	a = 10.3915(4) Å	a = 8.2102(5) Å
	b = 15.7266(7) Å	b = 9.9609(4) Å
	c = 16.2350(8) Å	c = 7.9693(4) Å
	α = 90°	α = 90°
	β = 90°	β = 111.086(6)°
	γ = 90°	γ = 90°
Volume	2653.2(2) Å <sup>3</sup>	608.10(5) Å <sup>3</sup>
Z, Calculated density	9, 1.948 Mg/m <sup>3</sup>	3, 2.652 Mg/m <sup>3</sup>
Absorption coefficient	1.886 mm <sup>-1</sup>	2.739 mm <sup>-1</sup>
F(000)	1593	495
Crystal size	0.250 x 0.220 x 0.100 mm	0.250 x 0.220 x 0.100 mm
θ range	2.66 to 29.25°	3.35 to 29.14°
Index ranges	-13 ≤ h ≤ 13 -15 ≤ k ≤ 20 -19 ≤ l ≤ 21	-9 ≤ h ≤ 11 -12 ≤ k ≤ 8 -10 ≤ l ≤ 6
Completeness to theta	100.0 %	99.90%
Reflections collected / unique	3112 [R(int) = 0.0230]	1387 [R(int) = 0.0163]
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3112/0/172	1387/0/79
Goodness-of-fit on F <sup>2</sup>	0.874	1.035
Final R indices [I > 2σ(I)]	<b>R<sub>1</sub> = 0.0293</b> wR <sub>2</sub> = 0.0693	<b>R<sub>1</sub> = 0.0357</b> wR <sub>2</sub> = 0.0996
R indices (all data)	R <sub>1</sub> = 0.0588 wR <sub>2</sub> = 0.0735	R <sub>1</sub> = 0.0488 wR <sub>2</sub> = 0.1030
Largest diff. peak and hole	0.817 and -0.908 e.Å <sup>-3</sup>	0.875 and -0.514 e.Å <sup>-3</sup>

**Tables 2.** Hydrogen bondings and non - bonded interactions

Compound	D-H...A	D-H	H...A	D...A	D-H...A
<b>I</b>	N1 H1A O4	0.90	2.47	3.341(2)	164
	N1 H1B O3	0.90	2.09	2.989(2)	176
	N2 H2A O6	0.90	2.46	3.197(2)	139
	N2 H2B O6	0.90	2.37	3.214(2)	157
	N3 H3A O5	0.90	2.33	3.166(2)	155
	N3 H3A O6	0.90	2.33	3.116(2)	146
	N3 H3B O2	0.90	2.11	2.959(2)	156
	N4 H4B O3	0.90	2.31	3.168(2)	159
	C5 H5B O2	0.97	2.45	2.43(2)	139
<b>II</b>	N1 H1A O1	0.90	2.13	3.028(3)	175
	N1 H1A O3	0.90	2.57	3.229(3)	131
	N1 H1B O1	0.90	2.14	3.009(3)	161
	N2 H2A O2	0.90	2.30	3.030(3)	138
	N2 H2B O2	0.90	2.21	3.005(3)	148

CCDC-794326 and 794325 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK..

#### 4 CONCLUSION

We succeeded to synthesize and isolate for the first time, stable spin-labeled copper (II) in neutral form Dinitrato bis(1,3-diaminopropane) copper(II) and (Tetraethylenepentamine) copper(II) Nitrate. In the crystal, the various components are linked via N-H...O and C-H...O hydrogen bonds forming sheets lying parallel to (001). The crystal structures are an important prerequisite for understanding crystallographic defects. Crystallography is the determining the arrangement of atoms in crystalline solids.

#### ACKNOWLEDGMENTS

KA records his sincere thanks to the Council of Scientific and Industrial Research- HRDG, New Delhi, Department of Science and Technology- SERC, Government of India, New Delhi for financial support through major research projects.

#### REFERENCES

- [1]. Kim, Y., Skelton, B.W., White, A. H. 2003. Catena-poly [trans-bis(ethane-1,2-diamine- $k^2N,N^1$ Copper (II)- $\mu$ -dithionato- $k^2O:O^1$ ]and trans-diaquabis(propene-1,3-diamine- $k^2N,N^1$ )copper(II)dithionate. Acta Crystallographica section C. 59, m546-m548.
- [2]. Habibi, M.H., Makhtari, R., Harrington, R.W., & Clegg, W. 2007. [N,N'-Bis (6-methoxysalicylidene)-1,3-diaminopropane]copper(II). Acta Crystallographica section E.63, m1998.
- [3]. Kabak, M., Elmali, E., Kavalakoglu, E., Elerman, Y., Durlu, T.N.1999. [N,N'-Bis(5-bromosalicylidene)-1,3-diaminopropane] copper(II). Acta Crystallographica section C.55,1650-1652.
- [4]. Emsley, J., Arif, M., Bates, P. A., Hursthouse, M.B., 1988. Diaquabis(1,3-diaminopropane) copper(II)difluoride: X-ray structure reveals short hydrogen bonds between ligand waters and lattice fluorides. Inorganica Chimica Acta, 154, 17-20.
- [5]. Nathan, L.C., Koehne, J. E., Gilmore, J. M., Hannibal, K. A., Dewhirst, W. E. & Mai, T.D. 2003. The X-ray structures of a series of copper(II) complexes with tetradentate Schiff base ligands derived from salicylaldehyde and polymethyleamines of varying chain length. Polyhedron. 22, 887-894.
- [6]. Elamai, A., Zeyrek, C.T., Elerman, Y. & Svoboda, I. 2000. [N, N'-Bis (5-bromosalicylidene) -1,3-diaminopropane] nickel (II) and [N,N'-bis (5-chlorosalicylidene)-1,3-diaminopropane] copper(II). Acta Crystallographica section C.56. 1302-1304.
- [7]. Sheldrick, G. M. 2015a. Crystal structure refinement with SHELXL. Acta Crystallographica section A. 71, 3-8.
- [8]. Spek, A. L. 2009. Structure validation in chemical crystallography Acta Crystallographica section D. 65, 148-155.
- [9]. Khan, I.U., Ejaz, Sahin, o., Buyukgungor, O. 2010. Diazidobis(propene-1,3-diamine )-copper(II). Acta Crystallographica section E.66, m434-m435.
- [10]. Basu, G Basu, S. 1959. Electron transfer spectra in copper ammines. Analytical Chimica. Acta., 21, 187-189.
- [11]. Procter, I. M., Hathaway, B. J., Nicholls, P. 1968. The electronic properties and stereochemistry of the copper(II) ion. Part I. Bis(ethylenediamine)copper(II) complexes. Journal of Chemical Society A, 1678.
- [12]. Hathaway, B. J., Billing, D. E. 1970. The electronic properties and stereochemistry of mono-nuclear complexes of the copper(h) ion. Coordination Chemistry Reviews. 5,143-207.