RESEARCH ARTICLE

Different Classical Hydrogen–Bonding Patterns in Two Copper (II) Metal Complexes of Dinitrato bis(2-bromopyridine copper(II)) and Dinitrato bis(2-Chloropyridine) copper(II)

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ABSTRACT: In the title compounds, $[Cu^{II}(2\text{-brpy})_2(NO_3)_2]$ and $[Cu^{II}(2\text{-Clpy})_2(NO_3)_2]$, the Cu^{II} atoms are each in a distorted square-pyramidal environment, in which four O atoms from the four bridging copper ligand form the basel plane and the pyridine N atoms. The two bromopyridine and Chloropyridine are nearly coplanar, making a dihedral angle of 23.1(6)° for compound and for compound 4.4 (6)°. In the compund (I), molecules are linked by N-O...π interactions, leading to the formation of zigzag chains along [001]. In the crystal of (II), molecules are linked by C-H…O hydrogen bonds, forming chains along [010]. The chains are linked by C-H…O hydrogen bonds, forming layers parallel to (101). Within the layer there is C-H…π interactions present.

KEYWORDS: Copper (II), bromopyridine**,** Chloropyridine, Crystal Structure, and hydrogen bonding.

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1. INTRODUCTION

Copper (II) complexes play an important role in the active sites of a large number of metalloproteins in biological systems and potential application for numerous catalytic processes in living organisms that involve electron transfer reactions or activation of some antitumor substances [1]. In fact copper (II) chelates have been found to interact with biological systems and to exhibit antineoplastic activity [2] and antibacterial, antifungal [3], and anticancer activity [4]. Pyridines are common but vital heterocyclic compounds in organic synthesis, especially as agrochemicals and synthetic intermediates [5]. The titled Compound deals with Structure solvation and reduce the R-facting.

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 Bruker [6] SMART APEX CCD Diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) 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, 9]. The crystallographic data for the compound are listed in Table 1.

2.2 SYNTHESIS

Synthesis of mononuclear $[Cu^{II}(2\text{-brpy})_2(NO_3)_2]$ complexes were prepared by copper(II) nitrate trihydrate ($1*10^{-3}$ M) was taken in 10 mL of distilled ethanol (about 99%) and warmed. To the warm solution 4.2 mL of 2-bromopyridine 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 [10] for compound I. Synthesis of compound II, mononuclear $[Cu^{II}(2\text{-Clpy})_2(NO_3)_2]$ complexes were prepared by copper(II) nitrate trihydrate (1×10^{-3} M) was taken in 10 mL of distilled ethanol (about ~99%) and warmed. To the warm solution 4.7 mL of 2-Chloropyridine 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 acetonitrile to give the desired product and dried over vacuum. Colorless block-like crystals of the title compounds, suitable for X-ray diffraction analysis, were obtained by slow evaporation of solutions in ethanol.

3. RESULTS AND DISCUSSION

3.1 Structure description

The Cu^{II} atoms are six fold coordinated in a slightly

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distorted octahedral environment by two dinitrate in equatorial positions, and by two pyridine ligands an axial positions. The Cu-N and Cu-O bond lengths are comparable with related complexes [9]. The N2-Cu-N1, O1-Cu-O6 and O3-Cu-O4 angles are 176.1(3), 73.3(3) and 176.4(3)°, respectively. The two bromopyridine are nearly coplanar, making a dihedral angle of 23.1(6)°.

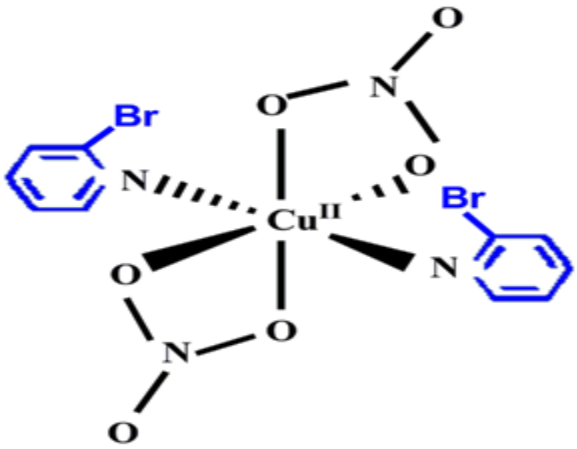

Figure 1 Scheme diagram compound I

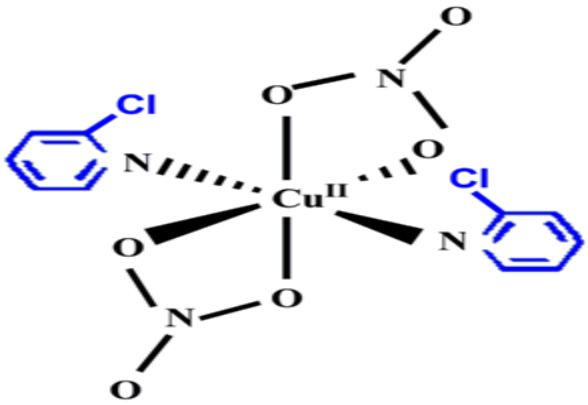

Figure 2 Scheme diagram compound II

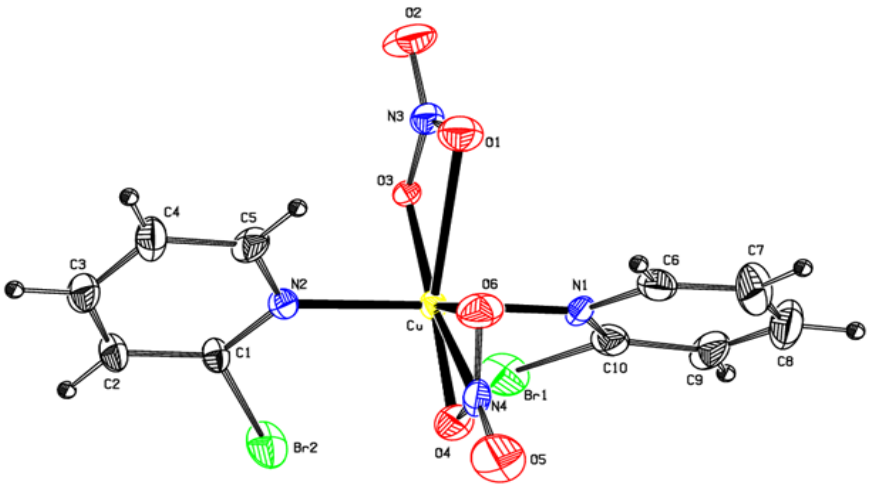

Figure 3 The molecular structure of compound I, with displacement ellipsoids drawn at the 30% probability level.

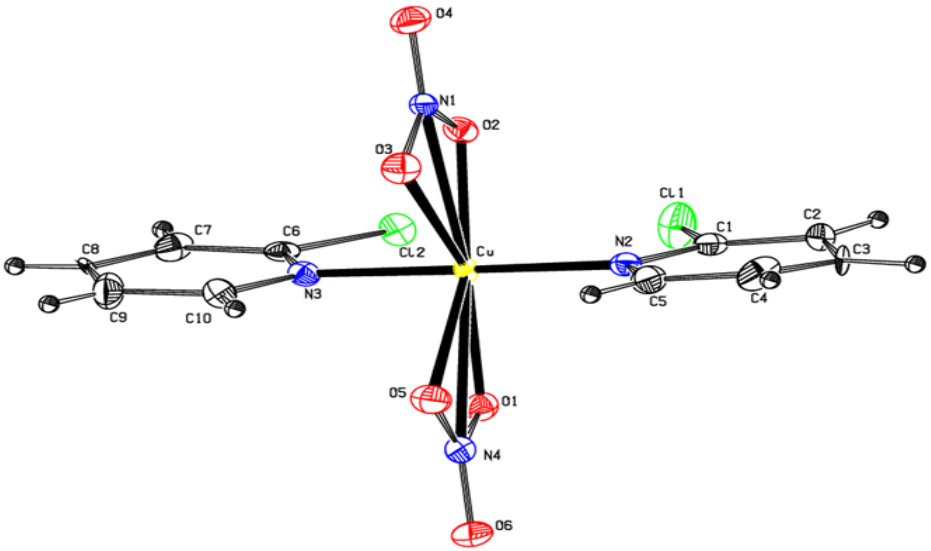

Figure 4 The molecular structure of compound (II), with the atom labeling. Displacement ellipsoids are drawn at the 30% Probability level. H atoms are shown as small spheres of arbitrary radius.

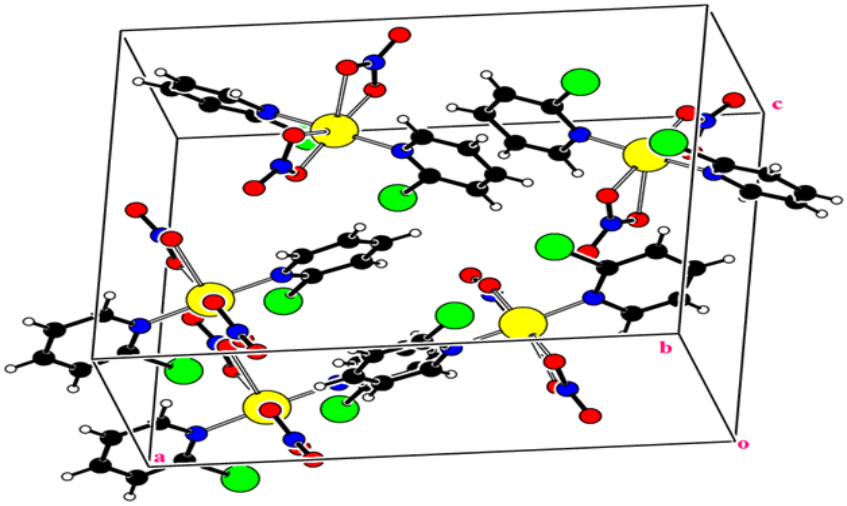

Figure 5 a partial packing diagram for compound I, viewed along the c-axis direction.

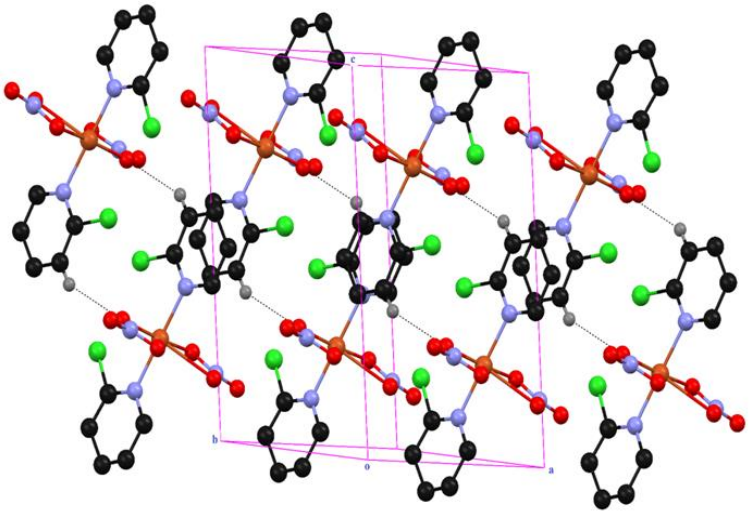

Figure 6 a partial packing diagram for compound II, viewed along the c-axis direction with the N-O...π stacking interactions shown by dashed lines.

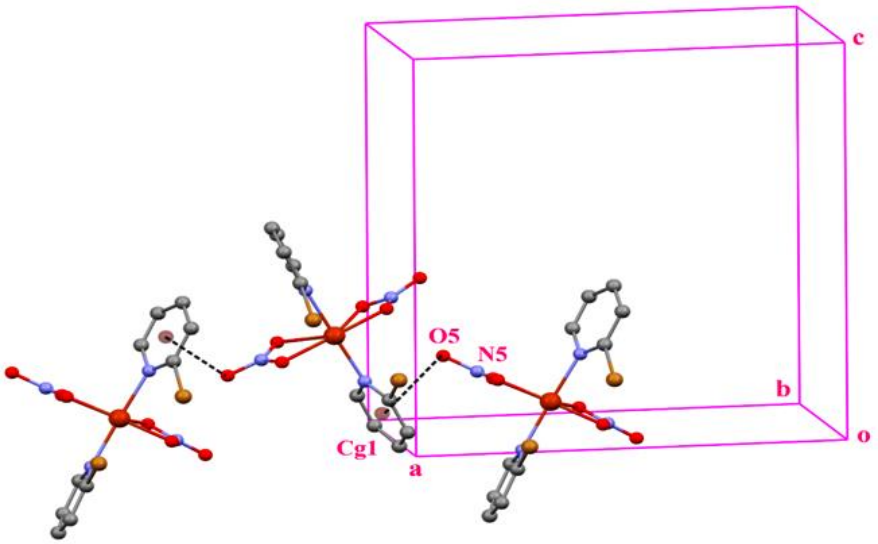

Figure 7 views along the c-axis of the crystal structure of compound II, C-H...O hydrogen bonds are shown as dashed lines.

Table 1 The crystallographic data for the compound are listed

`	I	II
Empirical formula	C_{10} H_8 Br_2 Cu N_4 O_6	$C_{10}H_8N_4O_6CuCl$
Formula weight	503.56	276.43
Wavelength	0.71073 Å	0.71073 Å
Crystal system space group	Orthorhombic P c a 21	Triclinic P -1
Unit cell dimensions	a = 15.1854(10) Å	a = 7.4962(8) Å
	b = 7.3495(4) Å	b = 7.9937(8) Å
	c = 14.0444(14) Å	c = 13.9761(12)Å
	α = 90°	α = 96.858(7)°
	β = 90°	β = 101.833(8)°
	γ = 90°	γ = 112.121(9)°
Volume	1567.4(2) $Å^3$	741.28(14)$Å^3$
Z, Calculated density	4, 2.134 Mg/m^3	3, 1.858 Mg/m^3
Absorption coefficient	6.526 mm^{-1}	1.870 mm^{-1}
F(000)	972	414
Crystal size	0.250 x 0.220 x 0.100 mm	0.250 x 0.220 x 0.100 mm
θ range	2.683 to 29.374°	2.818 to 24.999°
Index ranges	-19 ≤ h ≤ 19 -6 ≤ k ≤ 9 -13 ≤ l ≤ 17	-5 ≤ h ≤ 8 -9 ≤ k ≤ 8 -16 ≤ l ≤ 16
Completeness to theta	100.0 %	99.90%
Reflections collected / unique	4491 / 2749 [R(int) = 0.0258]	4424 / 2610 [R(int) = 0.0354]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2749 / 1 / 208	2610 / 0 / 208
Goodness-of-fit on F^2	0.953	1.140
Final R indices [I>2sigma(I)]	**R1 = 0.0500** wR2 = 0.1182	**R1 = 0.0974** wR2 = 0.2776
R indices (all data)	R1 = 0.0832 wR2 = 0.1257	R1 = 0.1058 wR2 = 0.2810
Largest diff. peak and hole	2.029 and -0.498 e.$Å^{-3}$	2.974 and -0.849 e.$Å^3$

Table 2 Hydrogen bondings and non – bonded interactions

D-H…A	D-H	H…A	D…A	D-H…A
C3 H3 O1	0.93	2.59	3.251(1)	128
C7 H7 O2	0.93	2.42	3.208(2)	143

Symmetry codes: i) 1-x,-y,1-z; ii) 1-x,-y,2-z;

Table 3 Selected Bond lengths (Å) and Selected Bond angles (º)

Bond	Length (Å)	Bond	Angle (°)
N(3)-O(1)	1.253(13)	C(1)-N(2)-C(5)	117.8(9)
N(3)-O(3)	1.277(11)	C(1)-N(2)-Cu	121.5(7)
N(4)-O(5)	1.233(16)	C(5)-N(2)-Cu	120.6(7)
N(4)-O(6)	1.255(14)	O(2)-N(3)-O(1)	123.5(12)
N(4)-O(4)	1.283(12)	O(2)-N(3)-O(3)	121.4(12)
O(3)-Cu	1.944(10)	O(1)-N(3)-O(3)	114.9(11)
O(4)-Cu	1.963(10)	O(5)-N(4)-O(6)	121.5(13)
C(1)-N(2)	1.333(15)	O(5)-N(4)-O(4)	120.3(12)
C(1)-C(2)	1.368(17)	O(6)-N(4)-O(4)	118.2(11)
C(1)-Cl(1)	1.706(12)	N(3)-O(3)-Cu	109.5(7)
C(2)-C(3)	1.530(17)	N(4)-O(4)-Cu	106.9(7)
C(3)-C(4)	1.252(18)	N(2)-C(1)-C(2)	124.2(11)
C(4)-C(5)	1.389(18)	C(2)-C(1)-Cl(1)	119.1(10)
C(5)-N(2)	1.351(15)	C(1)-C(2)-H(2)	122.5
C(6)-N(3)	1.336(14)	C(4)-C(3)-C(2)	117.6(9)
C(6)-C(7)	1.385(16)	C(4)-C(3)-H(3)	121.2
C(6)-Cl(2)	1.720(12)	C(2)-C(3)-H(3)	121.2
C(7)-C(8)	1.283(16)	C(3)-C(4)-C(5)	123.6(12)

CCDC- 785040 and 787442 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK..

3.2 Packing details

The molecular conformation is in part determined by a weak intramolecular C6-H6...O6 hydrogen bond that encloses an S(5) ring. In the crystal, molecules are linked by N5-O5...Cg1 (Cg1 are N1/C6-C10) interactions, leading to the formation of zigzag chains along [001] (see Tables 2). The crystal structure features π...π interactions for compound I (Fig .5). In the crystal of (II), molecules are linked by C3-H3…O1 hydrogen bonds, forming chains along [010] (Fig.6). The chains are linked by C7-H7…O2 hydrogen bonds, forming layers parallel to (101) (Fig.7). Within the layer there is C-H…π interactions present. The selected bond lengths and angles are listed in table 3.

4. CONCLUSION

We succeeded to synthesize and isolate, stable spin-labeled copper (II) in neutral form Dinitrato bis(2-bromopyridine) copper(II) and Dinitrato bis(2-Chloropyridine) copper(II) . In the crystal, the various components are linked via N-H...π and C-H...O hydrogen bonds forming of zigzag chains and sheets lying parallel to (001). In the compund (I), molecules are linked by N-O...π interactions, leading to the formation of zigzag chains along [001]. In the crystal of (II), molecules are linked by C-H…O hydrogen bonds, forming chains along [010]. The chains are linked by C-H…O hydrogen bonds, forming layers parallel to (101). Within the layer there is C-H…π interactions present.

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REFERENCES

[1]. Anbalagan, K., Tamilselvan, M., Nirmala, S. & Sudha, L. 2009. Chloridobis(ethylenediamine-k^{2}N,N^1)-(n-pentylamine-kN)cobalt(III) dichloridemonhydrate. Acta Cryst. E**65**, m836--m837.

[2]. Garcia-Tojal, J., Garcia-Orad, A., Diaz, A. A., Serra, J.L., Urtiaga, M.K., Arriortua, M.I. & Rojo,T. 2001. Biological activity of complexes derived from pyridine-2- carbaldehyde thiosemi carbazone Structure of $[Co(C_7H_7N_4S)_2]$[NCS]. Journal of Inorganic Biochemistry. Volume 84, Issues 3-4, pp271-278.

[3]. Chakraborty, A., Kumar, P., Ghosh, K and Roy, P. 2010. Evaluation of a Schiff base copper complex compound as potent anticancer moleculewith multiple targets of action. European Journal of Pharmacology, vol. 647, 1-3, 1-12.

[4]. Harinath,Y., Reddy, D. H. K., Kumar, B. N., Apparao, C and Seshaiah,K. 2013. Synthesis, spectral characterization and antioxidant activity studies of a bidentateSchiff base, 5-methyl thiophene-2-carboxaldehyde-carbohydrazone and its Cd(II),Cu(II), Ni(II) and Zn(II) complexes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 101, 264-272.

[5]. Liberta, A. E and West, D. X. 1992. Anifungal and antitumor activity of hetrocyclic thiosemicarbazones and their metal complexes: current status. Biometals, 5(2), 121-126.

[6]. Farrugia, L. J. 2012. WinGX and ORTEP for Windows: an update. Journal of Applied Crystal. 45, 849-54.

[7]. Oxford Diffraction (2009). CrysAlis CCD, CrysAlis RED and CrysAlis PRO. Oxford Diffraction Ltd, Yarnton, England.

[8]. Sheldrick, G. M. 2008. A short history of SHELXL. Acta Cryst. Section A. 64, 112--122.

[9]. Spek, A. L. 2009. Structure validation in chemical crystallography. Acta Crystal. Section D. 65, 148--155.

[10]. Marzano, C., Pellei, M., Tisato, F and Santini , C. 2009. Copper complexes as anticancer agents. Anti-Cancer Agents in Medicinal Chemistry, 9(2), 185-211.