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Synthesis and Crystal Structure of Diaquodiformatodi(4-methyl pyridine)copper(II)

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Ternary complex *i.e.*, diaquodiformatodi(4-methyl pyridine)copper(II) has been prepared and the solid state structure was determined using X-Ray structure analysis. The molecule crystallizes in monoclinic space group $P2_1/c$ with a = 9.6070 (5) Å, b = 11.5441 (5) Å, c = 7.7163 (5) Å, α = 90, β = 98.045 (4), γ = 90, V = 847.348 A^3. The structural data are consistent with the presence of Jahn-Teller distortion in the overall hexacoordinate octahedral geometry of the molecule. The crystal packing is through an extensive hydrogen bonding and ring-ring π-π interactions resulting in a supra molecular frame work.

Keywords: Synthesis, Crystal structure.

INTRODUCTION

The coordination compounds of amines consider of the most widespread compounds in inorganic chemistry[1]. Amines complexes have been considerable important in biological system, enzymes, synthetic molecules[2] and application for catalytic process[3]. The structural features of amine complexes play an important role in their physical properties of these complexes[4]. Copper(II) complexes with wide selection of coordination geometries with common ligands such as pyridine and water have been investigated and trends within this group of compounds have been studied[5].

Wide range of copper(II) structures containing pyridine, acetic acid[6,7], phthalic acid[8], benzoic acid[9] have been reported. On the other hand, compounds of 4-methylpyridine with formic acid are less well known.

In the present work, the synthesis and crystal structure for Diaquodiformatodi(4-methyl pyridine)copper(II) are reported.

EXPERIMENTAL

A blue coloured polycrystalline solid was obtained from reaction of $Cu(HCOO)_2 \cdot 2H_2O$ (20 mmol) with 4-methylpyridine (3 mL) in 20 mL ethanol at room temperature. Its recrystallization in ethanol produced light blue cubic crystals suitable for X-Ray crystallography. Overall yield = 75 %. Anal. Calc. for $C_{12}H_{16}N_2O_6Cu$ (m.w. 347.81) C 41.44, H 4.64, N 8.05 %; Found: 41.46, H 4.62, N 8.06 %.

On a glass fibre a light blue cubic crystal was mounted and all measurements were performed on BRUKER SMART APEX CCD diffractometer with graphite mono-chromator using MoK_α radiation (λ = 0.71069 Å). Cell constants and an orientation matrix for data collection were obtained from a least-square refinement using the setting angles of 21 carefully centered reflections in the range of 2.51\2h\25.99°. The structure was solved by the direct method and refined by full-matrix least-square techniques on F^2 using[12] SHELXL-97. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located from difference fourier maps or placed geometrically and positional parameters were refined with restrained OA---H distances but an unrestrained HA---OA---H angle except for non-coordinated H_2O.

RESULTS AND DISCUSSION

Treatment of copper formate and excess 4-methylpyridine in ethanol at room temperature produced blue colour microcrystalline solid in good yield (75 %). The recrystallization in ethanol at room temperature afforded a good crop of light blue colored cubic crystals whose analytical data are consistent with the formula $C_{12}H_{16}CuN_2O_6$ or $[Cu(4\text{-}MePy)(HCO_2)H_2O]_2H_2O$. The crystal data with structure refinements are given in Table-1 while selected bond lengths with bond angles and atomic parameters with equivalent isotropic thermal parameters are summarized in Tables 2 and 3, respectively. The molecular structure and packing diagrams are present in Figs. 1 and 2, respectively.

The molecular structure of the title compound Fig. 1 has a mononuclear structure. The Cu(II) atom lies on a center of symmetry and it is bonded to the formate group in a mono-

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT

Empirical formula	$C_{14}H_{20}N_2O_6Cu$
Formula weight	375.86
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.6070(5)
b (Å)	11.5441(5)
c (Å)	7.7163(3)
α (°)	90.00
β (°)	98.045(4)
γ (°)	90.00
Volume (Å^3)	847.35(7)
Z	2
ρ_{calc} (mg/mm^3)	1.473
m/mm^{-1}	1.319
F(000)	390.0
Crystal size (mm^3)	0.3 × 0.2 × 0.1
Radiation	MoK$_\alpha$ (λ = 0.71073)
2θ range for data collection	6.4 to 50°
Index ranges	-11≤ h ≤ 7, -13 ≤ k ≤ 8, -8 ≤ l ≤ 9
Reflections collected	2980
Independent reflections	1491 [R_{int} = 0.0252, R_{sigma} = 0.0407]
Data/restraints/parameters	1491/2/115
Goodness-of-fit on F^2	1.038
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0362, wR_2 = 0.0859
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.0939
Largest diff. peak/hole (e Å^{-3})	0.27/-0.40

TABLE-2
FRACTIONAL ATOMIC COORDINATES (× 10^4)
AND EQUIVALENT ISOTROPIC DISPLACEMENT
PARAMETERS (Å^2 × 10^3)

Atom	x	y	z	U(eq)
Cu1	0	5000	0	35.8(2)
O3	767(2)	3998.9(15)	1943(2)	40.3(5)
O2	1529(2)	3702.6(18)	4724(2)	47.0(5)
N1	1669(2)	6082.2(18)	464(3)	33.6(5)
O1	-1542(3)	6287(2)	1635(3)	53.9(6)
C7	1048(3)	4314(2)	3486(4)	37.2(7)
C3	3972(3)	7562(3)	1179(4)	46.9(8)
C4	4129(3)	6382(3)	1113(4)	49.6(8)
C1	1518(3)	7230(2)	501(4)	44.9(7)
C5	2979(3)	5677(3)	763(4)	42.8(8)
C2	2622(3)	7976(3)	873(4)	51.3(8)
C6	5217(4)	8357(3)	1549(6)	81.5(12)

TABLE-3
ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2 × 10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	37.4(3)	34.1(3)	32.7(3)	9.5(2)	-6.3(2)	-7.3(2)
O3	54.8(13)	30.8(10)	32(1)	2.2(9)	-5.2(9)	-2.6(10)
O2	55.0(13)	56.2(13)	28.2(10)	8.9(10)	-0.1(9)	3.2(11)
N1	34.7(13)	27.2(12)	37.7(12)	3.6(10)	1(1)	-1.8(10)
O1	84.3(18)	41.4(14)	37.2(12)	-2.8(11)	12.9(12)	-2.2(13)
C7	41.9(18)	34.6(17)	35.8(16)	-0.4(13)	8.3(14)	-1.4(13)
C3	41.2(18)	47.3(19)	52.3(18)	-5.2(15)	7.1(15)	-13.3(15)
C4	28.9(16)	50.0(19)	69(2)	-5.5(17)	3.8(15)	-0.2(15)
C1	36.9(16)	34.7(16)	60.8(19)	1.5(15)	-2.0(15)	4.9(14)
C5	39.2(18)	33.4(17)	54.7(19)	2.0(14)	2.7(15)	6.8(14)
C2	54(2)	26.6(15)	71(2)	-0.9(15)	3.1(17)	-5.6(15)
C6	55(2)	71(3)	116(3)	-14(3)	5(2)	-25(2)

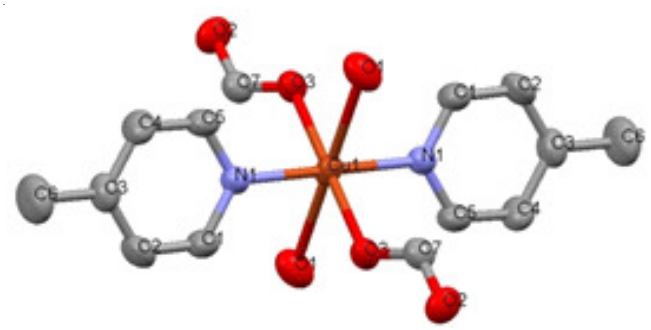

Fig. 1. ORTEP diagram of the complex with 50 % probability (H-atoms are omitted for clarity). Cu ion is located on an inversion center. Symmetry related atoms give the same name

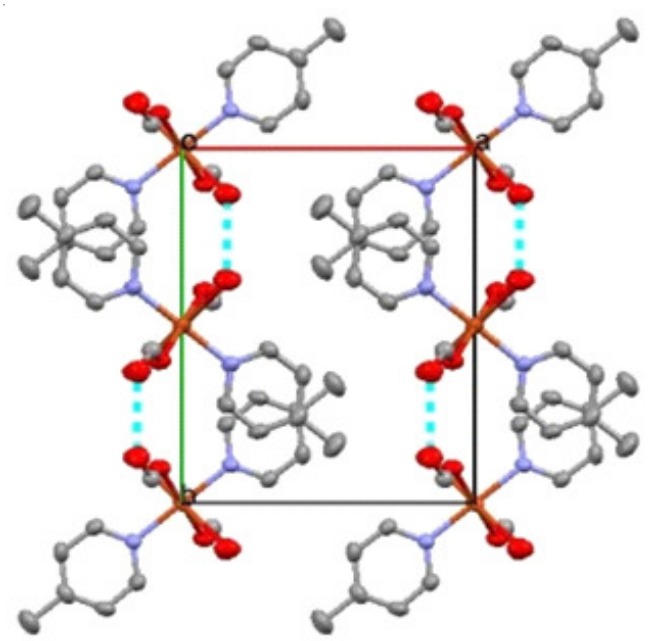

Fig. 2. Packing diagram of the complex. O-H···O Hydrogen bonding are shown as dotted blue lines

dentate fashion. The Cu(II) atom exists in an octahedral coordination geometry, defined by two pyridine N atoms [Cu-N = 2.025 (2) Å], two O atoms of different formate ligands [Cu-O = 1.954 (2) Å] and two water molecules [Cu-O = 2.553 (2) Å]. The *cis*-angles around the Cu atom range from 88.57 (7) to 91.43 (7). The O2-C7-O3 angle is 126.04 (2)o and the C7-O3 distance [1.238 (3) Å] is slightly longer than C7-O2 [1.225 (3) Å].

A supramolecular network (Fig. 3) were constitute through joined discrete unit through a wide spread H-bonds and π-π interactions. Two-dimensional layer framework structure (Table-2) formed due to intermolecular hydrogen bonds between the uncoordinated carboxy O atoms and water molecules. A supramolecular three-dimensional network structure is constructed by intermolecular hydrogen bonds and π-π stacking interactions between adjacent pyridine rings of 3.861 (4) Å (Fig. 2).

A stable polymeric structure is formed by the water molecules which act as bridges through H-bonds between each monomeric unit (Fig. 3). The reported H-bond distance, d(O-H-O) value is [c.f. d(O-H-O) = 2.728 Å][10] which is longer compared to the observed value d(O-H-O) is 2.142 Å.

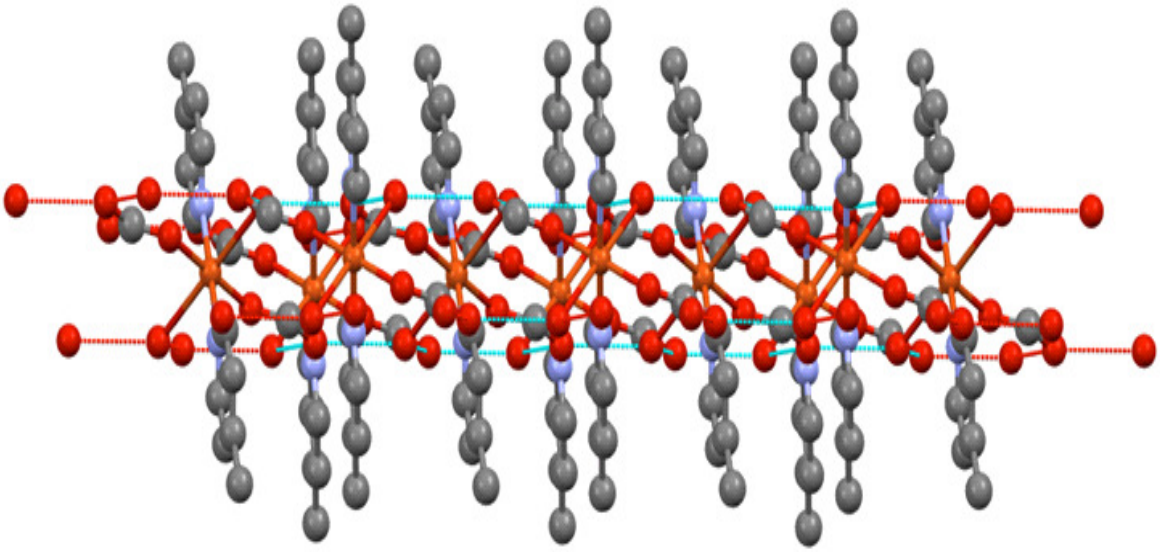

Fig. 3. H-bonded network of the compounds and two layers of the complex showing-interactions between 4-methylpyridine rings

The observed centroid(p)-centroid(p) distance *i.e.*, d(p-p) = 3.678 Å, for the present complex indicates an effective participation of the side-on ring-ring π-π interactions between the pyridine rings of the neighboring layers (Fig. 3) in the stacking or molecular recognition process[11].

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