

Crystal Structure of [Aqua (2, 2'-bipyridine) (6-carboxypyridine-2-carboxylato) copper (II) Nitrate Monohydrate Complex at 150 K

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Abstract: The reaction of copper (II) nitrate with pyridine-2,6-dicarboxylic acid, (pydcH₂) and 2,2'-bipyridine (2,2'-bipy) led to the formation of the title compound, [Cu(C₇H₄NO₄)(C₁₀H₈N₂)(H₂O)]NO₃.H₂O, or [Cu(pydcH)(2,2'-bipy)(H₂O)]NO₃.H₂O. The crystal system of the complex is triclinic with space group $P\bar{1}$ and two molecules per unit cell. The unit cell parameters are: $a = 7.0438(6) \text{ \AA}$, $b = 11.3215(10) \text{ \AA}$, $c = 12.9148(9) \text{ \AA}$, $\alpha = 107.498(4)^\circ$, $\beta = 94.557(5)^\circ$ and $\gamma = 104.325(5)^\circ$. The final R value was 0.03 for 3601 observed reflections. The cationic complex features six-coordinate Cu^{II} with a distorted octahedral geometry with a significantly longer Cu1—O4 bond [2.5491(16) Å]. Considerable C=O \cdots π stacking interactions between the C=O groups with distance of 3.498(2) Å are observed. In addition, distinct intermolecular O—H \cdots O and N—H \cdots O hydrogen bonds lead to the formation of R₂²(12) and C₂²(12) graph sets motifs. In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (O—H \cdots O, O—H \cdots N and C—H \cdots O), π — π [centroid—centroid distances of 3.5193(13) Å and 3.6876(13) Å] and C=O \cdots π stacking interactions connect the various components into a supramolecular structure.

Keywords: Cu (II) complex; Crystal structure; pyridine-2,6-dicarboxylic acid; 2,2'-bipyridine; Hydrogen bonding; π — π and C=O \cdots π stacking interactions.

Introduction

In recent years, the crystal engineering of supramolecular architectures based on metal and organic building blocks has rapidly emerged as an exciting area of supramolecular chemistry because of their novel and diverse topologies and potential applications in host-guest chemistry, catalysis,

electrical conductivity and magnetism [1]. Pyridinedicarboxylic acids are of great interest in medicinal chemists, because of the wide variety of their physiological properties displaced by natural as well as synthetic acids. These acids are present in many natural products, such as alkaloids, vitamins and coenzymes. Pyridinedicarboxylic

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acid metal complexes are therefore, especially interesting model systems. In order to study the hydrogen bonding patterns in proton-transfer compounds, our research group has selected pyridine-2,6-dicarboxylic acid (pydcH₂) and 1,10-phenanthroline-2,9-dicarboxylic acid (phendcH₂) as proton donors, and piperazine (pipz), creatinine (creat) and 1,10-phenanthroline (phen) as proton acceptors. This has resulted in the formation of new proton-transfer systems, such as (pipzH₂)(pydcH)₂·3H₂O and (creatH)(pydcH)·H₂O, in which the (pydcH) fragment is present as mono-anionic section [2,3]. Also, some crystal structures have been reported in which 2,2'-bipyridine is present as proton-acceptor reagent serving as counter-ion [4-7]. Syntheses and characterizations of other proton transfer compounds and their metal complexes are discussed in our recently published review article [8].

Preparation and experiments

A solution of Cu(NO₃)₂·6H₂O (147 mg, 0.5 mmol) in water (5 ml) was added to an aqueous solution of pyridine-2,6-dicarboxylic acid (167 mg, 1 mmol) and 2,2'-bipyridine (312 mg, 2 mmol) in water (10 ml) in a 1:2:4 molar ratio and refluxed for an hour. Blue crystals of the title compound were obtained after allowing the mixture to stand for two weeks at room temperature.

The X-ray data was collected on a Bruker SMART diffractometer (MoK_α radiation) at 150 K. The crystal data and experimental parameters are given in Table 1. The crystal was solved by direct methods (SHELXS-97) and a refinement was carried out with full-matrix least-squares methods based on F² with SHELXL-97 [9].

Results and discussion

The molecular structure of the title compound is given in Fig. 1. The final atomic coordinates of non-hydrogen atoms are listed in Table 2 and selected bond lengths and angles are presented in Table 3. Also hydrogen bond geometries are given separately in Table 4. This compound crystallized in the triclinic system, space group $P\bar{1}$ with two formula in the unit cell. The final R value was 0.033 for 3601 measured reflections.

According to the crystal structure of the title compound, the Cu^{II} atom is six-coordinated by (pydcH)[−] fragment which acts as a tridentate ligand through one N and two O atoms, one (2,2'-bipy) group and one coordinated water molecule. In this structure, N1 atom from (pydcH)[−] and N3 atom from (2,2'-bipy) occupy the axial positions, while remaining O1, O4, O5 and N2 atoms form the equatorial plane. The N1—Cu1—N3 angle [174.48(7)°] deviates from linearity. The Cu1—O4 bond [2.5491(16) Å] is significantly longer than other Cu—O bonds probably due to Jahn-Teller distortion. Therefore, the geometry of the resulting CuN₃O₃ coordination can be described as distorted octahedral. There is also one uncoordinated water molecule and nitrate ion as counter-ion.

The O5—Cu1—N1 and O5—Cu1—N3 bond angles are 90.38 (7)° and 91.27 (7)° respectively, indicating that the axis of coordinated water molecule is almost perpendicular to the both (pydcH)[−] and (2,2'-bipy) aromatic rings.

A noticeable feature of the title compound is the presence of C=O... π stacking interactions between C=O group of carboxylate groups with aromatic rings of (pydcH)[−] units. The C=O... π distance (measured to the center of phenyl ring) is 3.498(2) Å for C1—O2...Cg1 (−x, −y, 1−z) with the angles of 98.25(13)°, [Cg1 is the centroid of N1,C2-C6] (Fig. 2). Also a considerable π - π stacking interactions between aromatic rings of 2,2'-bipy fragments with distances of 3.5193(13) Å for Cg2...Cg2 (−x, −y, 2−z) and 3.6876(13) Å for Cg2...Cg3 (1−x, −y, 2−z) are observed in the prepared compound [Cg2 and Cg3 are the centroids for N2/C8-C12 and N3/C13-C17 rings, respectively] (Fig. 3).

In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (of the type O—H...O, O—H...N and C—H...O with D...A ranging from 2.554(2) Å to 3.390(3) Å, ion-pairing, π - π and C=O... π stacking connect the various components into a supramolecular structure (Fig. 4). Also, distinct intermolecular O—H...O and N—H...O hydrogen bonds lead to the formation of R₂² (12) and C₂² (12) graph sets motifs (Fig. 5).

Table 1. Crystal and experimental data of the title compound

Formula = $C_{17}H_{16}CuN_4O_9$	
Formula weight = 483.88	
Crystal system = Triclinic	T = 150 (2) K
Space group = $P\bar{1}$	Z = 2
a = 7.0438 (6) Å	$\alpha = 107.498 (4)^\circ$
b = 11.3215 (10) Å	$\beta = 94.557 (5)^\circ$
c = 12.9148 (9) Å	$\gamma = 104.325 (5)^\circ$
V = 938.43 (13) Å ³	
Absorption coefficient = 1.23 mm ⁻¹	
F(000) = 494	
Crystal dimensions (mm) = 0.32 × 0.14 × 0.14	
R[F ² > 2σ(F ²)] = 0.033	
R _{int} = 0.034	
R _w (F ²) = 0.115	-9 ≤ h ≤ 9
θ range for data collection = 2.98 to 27.47 °	-14 ≤ k ≤ 14
Goodness to fit = 0.89	-16 ≤ l ≤ 15
Δρ _{max} = 0.36 e Å ⁻³	
Δρ _{min} = -0.52 e Å ⁻³	
Data collection = Bruker SMART diffractometer	
Absorption correction: SADABS	
No. of independent reflections = 4158	
No. of reflections collected with I > 2σ(I) = 3601, multi scan	
No. of parameters = 280	
Structural determination = SHELXL-97	
Refinement = full-matrix least-squares methods based on F ²	
CCDC Number: 763336 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif .	

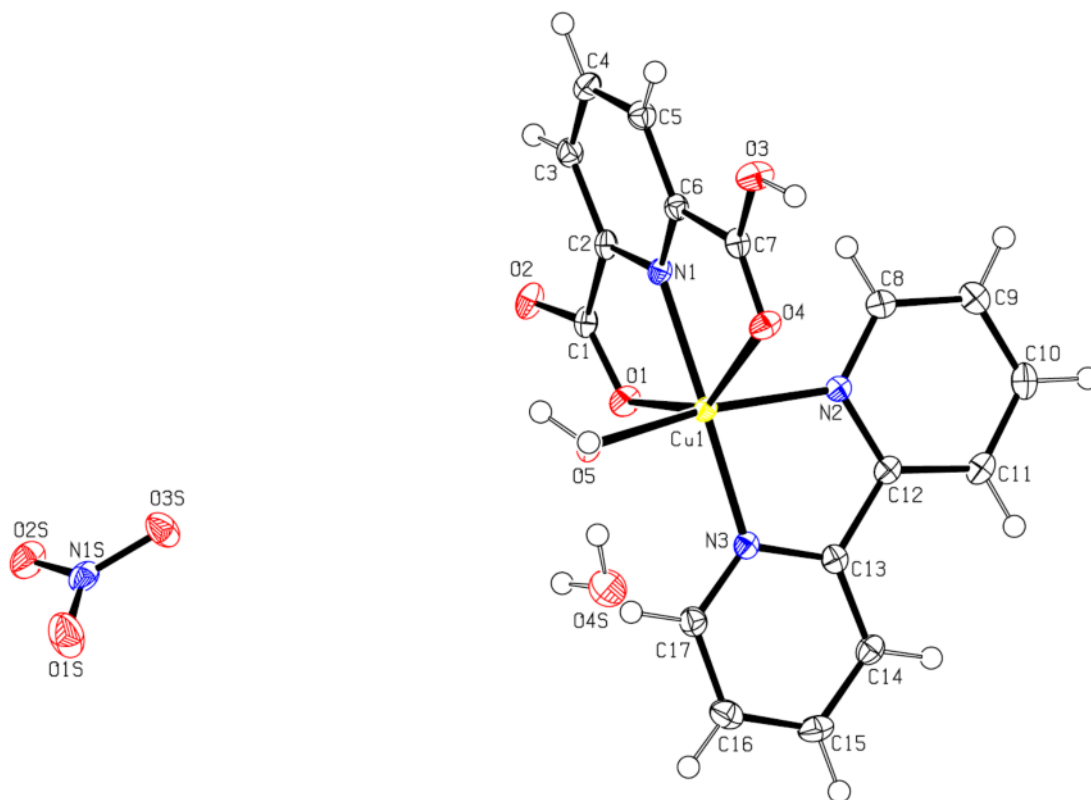
**Fig. 1** The molecular structure of the title compound, [Cu(pydcH)(2,2'-bipy)(H₂O)]NO₃·H₂O. Displacement ellipsoids are drawn at 50% probability level.

Table 2. Atomic coordinate ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for non hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _(eq)
Cu1	0.29659(3)	0.00835(2)	0.741869(18)	0.01153(11)
N1	0.1292(3)	-0.14802(18)	0.61379(14)	0.0123(4)
N2	0.2144(3)	-0.05567(17)	0.86566(14)	0.0121(4)
N3	0.4372(3)	0.16739(18)	0.86841(14)	0.0130(4)
O1	0.0229(2)	0.06760(15)	0.70028(12)	0.0172(3)
O2	-0.2469(2)	-0.00100(16)	0.57007(12)	0.0179(3)
O3	0.4249(2)	-0.36379(16)	0.58378(13)	0.0215(4)
O4	0.4832(2)	-0.16246(15)	0.70362(12)	0.0172(3)
O5	0.4436(2)	0.07922(15)	0.63709(11)	0.0146(3)
C1	-0.0938(3)	-0.0144(2)	0.61733(17)	0.0136(4)
C2	-0.0431(3)	-0.1403(2)	0.56744(17)	0.0129(4)
C3	-0.1650(3)	-0.2408(2)	0.47780(17)	0.0162(4)
C4	-0.1049(3)	-0.3510(2)	0.43283(18)	0.0176(5)
C5	0.0755(3)	-0.3571(2)	0.48025(18)	0.0163(4)
C6	0.1865(3)	-0.2544(2)	0.56990(16)	0.0129(4)
C7	0.3820(3)	-0.2547(2)	0.62722(17)	0.0142(4)
C8	0.1057(3)	-0.1753(2)	0.85574(18)	0.0159(4)
C9	0.0603(3)	-0.2102(2)	0.94730(18)	0.0178(5)
C10	0.1271(3)	-0.1189(2)	1.05102(18)	0.0176(5)
C11	0.2402(3)	0.0043(2)	1.06170(17)	0.0161(4)
C12	0.2814(3)	0.0333(2)	0.96751(17)	0.0132(4)
C13	0.4032(3)	0.1609(2)	0.96889(17)	0.0138(4)
C14	0.4789(3)	0.2670(2)	1.06388(18)	0.0166(4)
C15	0.5969(3)	0.3813(2)	1.05654(19)	0.0199(5)
C16	0.6333(4)	0.3865(2)	0.95391(19)	0.0208(5)
C17	0.5486(3)	0.2785(2)	0.86116(18)	0.0173(4)
N1S	0.2819(3)	0.47059(19)	0.28171(15)	0.0191(4)
O1S	0.4520(3)	0.5348(2)	0.28576(17)	0.0360(5)
O2S	0.1331(3)	0.48976(18)	0.23747(14)	0.0274(4)
O3S	0.2523(2)	0.38034(17)	0.32453(15)	0.0246(4)
O4S	0.0671(3)	0.33510(18)	0.82590(15)	0.0307(4)

Table 3. Selected bond distances (\AA), and bond angles ($^\circ$).

Cu1—N3	1.9961 (19)	Cu1—N1	2.0389 (18)
Cu1—O5	2.0029 (15)	Cu1—O1	2.2689 (15)
Cu1—N2	2.0130 (18)	Cu1—O4	2.5491(16)
O5—Cu1—N2	166.34 (7)	N3—Cu1—N1	174.48 (7)
O1—Cu1—O4	148.65 (5)	O5—Cu1—N1	90.38 (7)
N1—Cu1—O4	72.02 (5)	N3—Cu1—O5	91.27 (7)
N1—Cu1—O1	76.63 (6)		

Table 4. Hydrogen bond geometry (Å, °)

D—H···A	d(D—H)	d(H···A)	d(D···A)	<(D—H···A)
O3—H3A···O3S ⁱ	0.85	1.71	2.554 (2)	169
O3—H3A···N1S ⁱ	0.85	2.49	3.267 (2)	153
O3—H3A···O1S ⁱ	0.85	2.57	3.147 (3)	126
O5—H5B···O2 ⁱⁱ	0.85	1.85	2.691 (2)	172
O5—H5A···O2 ⁱⁱⁱ	0.85	1.82	2.671 (2)	175
O4S—H6B···O1	0.85	2.09	2.898 (2)	160
O4S—H6A···O2S ^{iv}	0.85	2.20	2.961 (2)	150
C4—H4···O1S ^v	0.95	2.57	3.257 (3)	130
C8—H8···O3S ⁱⁱ	0.95	2.40	3.176 (3)	138
C9—H9···O2S ⁱⁱ	0.95	2.55	3.221 (3)	128
C10—H10···O1 ^{vi}	0.95	2.56	3.390 (3)	145
C10—H10···O4S ^{vi}	0.95	2.58	3.379 (3)	142
C11—H11···O4 ^{vii}	0.95	2.34	3.203 (3)	151
C15—H15···O4S ^{viii}	0.95	2.55	3.310 (3)	137
C17—H17···O5	0.95	2.45	2.987 (3)	115
C17—H17···O1S ^{ix}	0.95	2.57	3.238 (3)	128

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y, -z+1$; (iii) $x+1, y, z$; (iv) $-x, -y+1, -z+1$; (v) $x-1, y-1, z$; (vi) $-x, -y, -z+2$; (vii) $-x+1, -y, -z+2$; (viii) $-x+1, -y+1, -z+2$; (ix) $-x+1, -y+1, -z+1$.

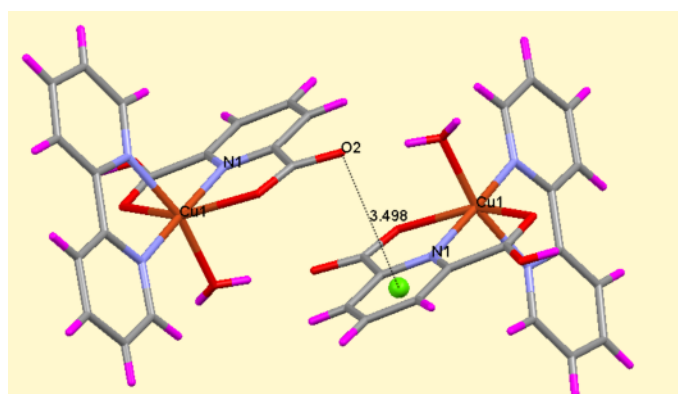


Fig. 2 C=O··· π Stacking interactions between C=O group of carboxylate groups with aromatic rings of (pydcH)[−] units. The C=O··· π distance (measured to the center of phenyl ring) is 3.498(2) Å for C1=O2···Cg1 ($-x, -y, 1-z$), [Cg1 is the centroid of N1,C2-C6]

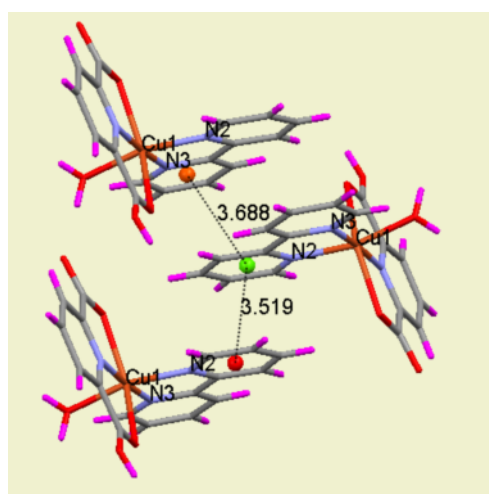


Fig. 3 π - π Stacking interactions between aromatic rings of 2,2'-bipy fragments with distances of 3.5193(13) Å for Cg2···Cg2 and 3.6876(13) Å for Cg2···Cg3 [Cg2=N2/C8-C12 and Cg3= N3/C13-C17 rings, respectively].

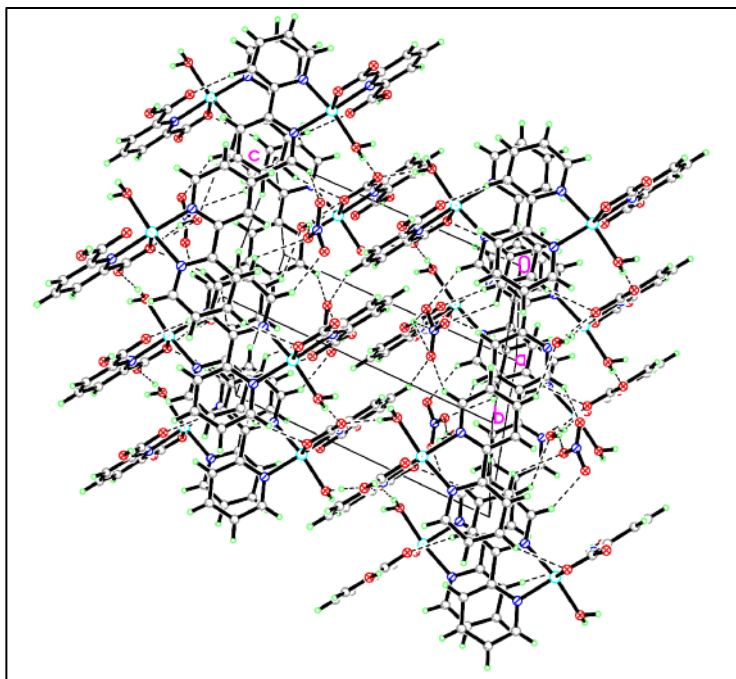


Fig. 4 Unit cell packing of the title compound viewed down *a* axis. Hydrogen bonds are shown as dashed lines.

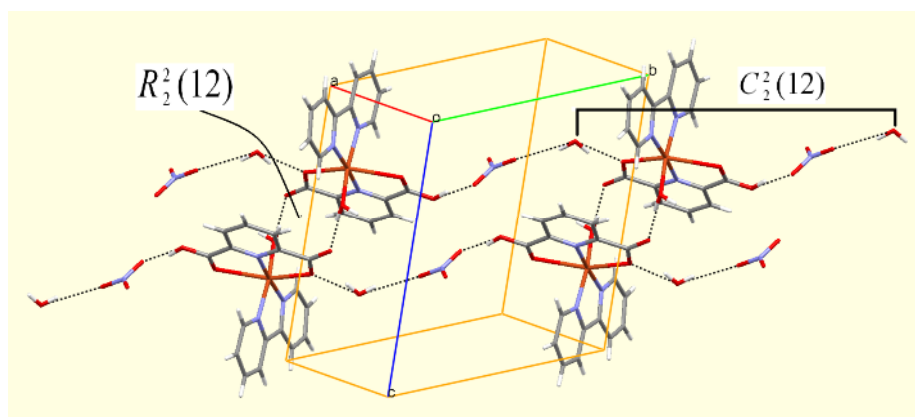


Fig. 5 The $R_2^2(12)$ and $C_2^2(12)$ graph sets motifs formed along *b* axis by distinct intermolecular O—H···O and N—H···O hydrogen bonds.

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