Crystal Structure of Dinicotinato-tetraaqua-copper(II)

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Solid state structures of metal carboxylate form interesting crystal networks. Molecules are bonded to each other either linearly or bulky by hydrogen bonds, coordination bonds and carboxylate bridges.[1-3] In this study, copper(II) nicotinate was crystallized and its molecular structure was identified.

A quantity of 0.01 mol (1.23 g) nicotinic acid and 0.005 mol (0.850 g) of $CuCl_2 \cdot 2H_2O$ were dissolved in 50 ml of water by warming. A solution of 0.01 mol (1.06 g) Na_2CO_3 in 20 ml of hot water was added to this mixture with stirring and then the mixture was left at room temperature for 6 – 7 d in ambient air. The light blue prismatic crystals which formed were collected by filtration, washed with ethanol and then dried in ambient air.

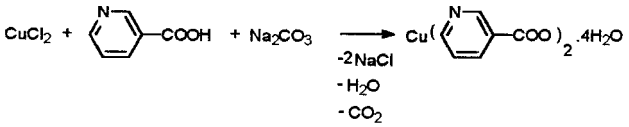

Table 1 Crystal and experimental data

Formula: $C_{12}H_{16}CuN_2O_8$	
Formula weight=379.81	
Crystal system: triclinic	
Space group: $P\bar{1}$	Z=1
a=7.0300(11)Å	
b=7.1743(12)Å	
c=8.6829(12)Å	
α=68.157(2)°	
β=68.576(2)°	
γ=62.586(2)°	
V=350.70(9)Å^3	
D_x=1.798 g/cm^3	
μ(Mo K$_\alpha$)=1.604 mm^{-1}	
T=295 K	
Light blue	
F(0 0 0)=195	
Crystal size: 0.4×0.3×0.2 mm	
Radiation=Mo K$_\alpha$	
R=0.018	
Rw=0.027	
Δ/σ=0.00015	
$(\Delta\rho)_{max}$=0.172 eÅ^{-3}	
$(\Delta\rho)_{min}$=0.236 eÅ^{-3}	
No. of reflection used=1158	
No. of parameters=111	
Goodness-of-fit=1.04	
Measurements: Enraf Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: MolEN	
Treatment of hydrogen atoms: The water H atoms were found from a difference map. H atoms bonded to C atoms were placed geometrically 0.95 Å from their parent atoms and a riding model was used for all H atoms.	
Refinement: full matrix least-squares (MolEN)	

Table 1 shows the crystal and experimental data, while final atomic parameters are given in Table 2. The bond distances and angles are shown in Table 3. The intramolecular hydrogen bond geometry is given in Table 4. The molecules in the unit cell and possible hydrogen bondings are shown in Fig. 2.

As shown in Fig. 1, the coordination of copper atom has an octahedral structure and the coordination sphere is made up with four oxygen and two nitrogen atoms originating from water and nicotinic acid (O_4N_2) respectively. Carboxylate groups do not participate in coordination and are fixed by forming 8 hydrogen bonds with water molecules in the neighboring complexes, as shown in Table 4 and Fig. 2. Similar structures of related nicotinamides and benzoates have been reported elsewhere.[4,5]

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	x	y	z	B_{eq}/Å^2
Cu1	0.000	0.000	0.000	1.643(4)
O1	-0.2621(2)	0.2523(2)	0.0718(2)	2.83(3)
O2	0.2016(2)	0.2375(2)	-0.0874(1)	2.50(2)
O3	0.1749(2)	0.4001(2)	-0.8293(1)	2.35(2)
O4	0.4116(2)	0.2478(2)	-0.6629(1)	2.94(3)
N1	-0.0601(2)	0.1211(2)	-0.2337(1)	1.75(2)
C1	-0.2603(2)	0.1636(2)	-0.2502(2)	1.99(3)
C2	-0.3126(2)	0.2469(2)	-0.4064(2)	2.18(3)
C3	-0.1564(2)	0.2941(2)	-0.5511(2)	1.94(3)
C4	0.0496(2)	0.2547(2)	-0.5353(2)	1.65(2)
C5	0.0918(2)	0.1637(2)	-0.3740(2)	1.67(2)
C6	0.2270(2)	0.3040(2)	-0.6876(2)	1.79(3)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

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Table 3 Bond distances (Å) and angles (˚)

Cu1-O1	1.9977(9)	O1-Cu1-N1	88.56(4)
Cu1-N1	2.006(1)	O1-Cu1-O2	84.67(5)
Cu1-O2	2.442(2)	O2-Cu1-N1	87.76(5)
O3-C6	1.260(2)	Cu1-N1-C1	119.17(8)
O4-C6	1.245(2)	Cu1-N1-C5	122.1(1)
N1-C1	1.348(2)	C1-N1-C5	118.7(1)
N1-C5	1.339(1)	N1-C1-C2	122.1(1)
C1-C2	1.375(2)	C1-C2-C3	119.0(1)
C2-C3	1.385(2)	C2-C3-C4	119.4(1)
C3-C4	1.391(2)	C3-C4-C5	118.1(1)
C4-C5	1.386(2)	C3-C4-C6	122.1(1)
C4-C6	1.511(2)	C5-C4-C6	119.8(1)
		N1-C5-C4	122.6(1)
		O3-C6-O4	125.4(1)
		O3-C6-C4	117.1(1)
		O4-C6-C4	117.5(1)

Table 4 Hydrogen bonding geometry (Å,˚)

D-H…A	D-H	H…A	D-A	D-H…A
O1-H1'-O3	0.7800(11)	2.0183(12)	2.7542(17)	157.24(11)
O1-H2'-O4	0.8081(12)	1.7907(11)	2.5928(16)	171.56(10)
O2-H22-O3	0.8418(13)	2.0056(15)	2.820(2)	162.40(9)
O2-H23-O3	0.8883(11)	1.9223(12)	2.8035(17)	171.21(9)

As shown in Table 3, the bond distances between Cu and two of the water molecules are shorter 1.9977(9) Å than those formed with the other two 2.442(2)Å. Distances between Cu and N are 2.006(1)Å. Thus, the coordination sphere is in elongated octahedral structure. The bond lengths are in agreement with those in the cited literature.[3,4]

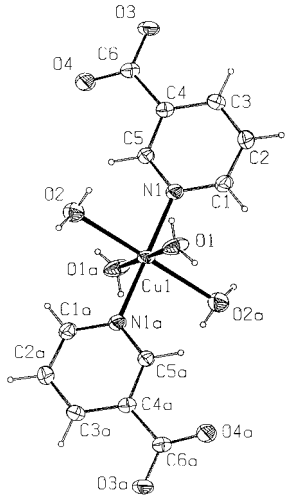

Fig. 1 The ORTEP drawing of the title compound with atom labeling.

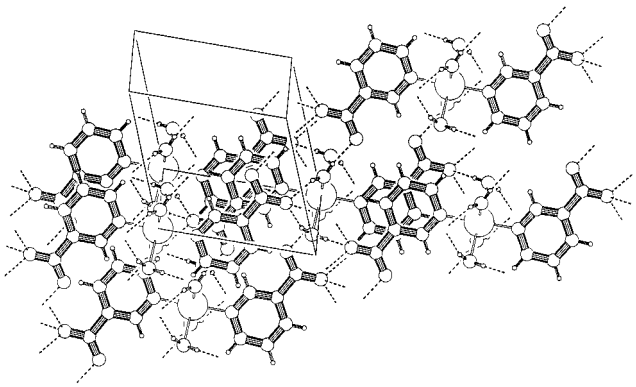

Fig. 2 The molecules in the unit cell and possible hydrogen bondings.

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