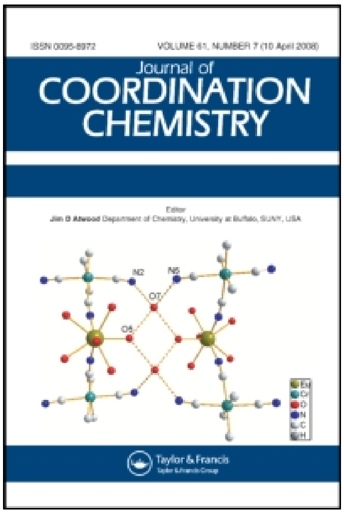

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Synthesis and crystal structure of polymeric aqua (2,2'-bipyridine)(μ-isonicotinato)copper(II) nitrate dihydrate

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Synthesis and crystal structure of polymeric aqua (2,2′-bipyridine)(μ-isonicotinato)copper(II) nitrate dihydrate

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The title complex has been prepared and its crystal structure determined by X-ray diffraction methods. The complex crystallizes in the monoclinic space group $P2_1/c$. Cu(II) assumes a square pyramidal coordination geometry, formed by two isonicotinate anions, a bipyridine ligand and a coordinated water molecule. Each isonicotinate bridges two Cu atoms through pyridine-*N* and carboxyl-*O* atoms, respectively, to form zigzag polymeric chains. Between the polymeric chains, aromatic stacking and hydrogen bonding are observed.

Keywords: Copper(II) complex; Polymeric complex; Crystal structure; Aromatic stacking; Isonicotinate

1. Introduction

As nicotinic acid and isonicotinic acid play important roles in the metabolism of all living cells, metal complexes with nicotinate or isonicotinate ligands have attracted much interest in the past decade. Some X-ray structures have revealed that nicotinate and isonicotinate anions play the role of a bridging ligand to link metal complexes into infinite polymeric chains [1–3]. We present here the structure of a polymeric Cu(II) complex bridged by the isonicotinate anion, in which the molecular chains form a supramolecular structure by non-covalent interactions such as aromatic stacking and hydrogen bonding.

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2. Experimental

2.1. *Synthesis*

$CuNO_3 \cdot 2H_2O$ (0.60 g, 2.5 m mol) and 2,2′-bipyridine (0.39 g, 2.5 m mol) were dissolved in ethanol (40 cm^3). Isonicotinic acid (0.31 g, 2.5 m mol) and NaOH (0.1 g, 2.5 m mol) were dissolved in water (60 cm^3). The aqueous solution was added dropwise to the ethanol solution with stirring at 75°C. The mixture was refluxed for 1 h and filtered after cooling to room temperature. Blue crystals were obtained from the filtrate after 2 w. C, N and H contents were analyzed on a Carlo-Erba 1160 instrument. Anal. Calc. for $[Cu(C_{10}H_8N_2)(C_6H_4NO_2)(H_2O)]NO_3 \cdot 2H_2O$ (%): C, 41.93; N, 12.23; H, 3.96; Found (%): C, 41.43; N, 12.49; H, 3.84. The IR spectrum was measured in KBr pellets in the range 4000–400 cm^{-1} using a Nicolet 5DX FT-IR spectrophotometer.

2.2. *X-Ray structure determination*

X-Ray diffraction intensities were collected on a Rigaku RAXIS-RAPID diffractometer up to $2\theta_{max}$ of 55.0° with Mo Kα radiation at 295 K. A total of 17500 reflections were collected including 4365 independent ones ($R_{int} = 0.036$), Of these, the number of observed reflections $[I > 2\sigma(I)]$ was 3664.

The crystal structure was solved by direct methods followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures using SHELX-97 on F^2 [4]. H atoms on carbon atoms were placed in calculated positions with C–H = 0.93 Å, and included in the final cycles of refinement in the riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms. H atoms of water were located in a difference Fourier map and were included in structure-factor calculations with the fixed positional parameters and U_{iso} equal to 0.05 $Å^2$.

2.2.1. Crystal data. $[Cu(C_{10}H_8N_2)(C_6H_4NO_2)(H_2O)]NO_3 \cdot 2H_2O$, $FW = 457.88$, monoclinic, space group $P2_1/c$, $a = 12.1290(10)$, $b = 11.5414(11)$, $c = 14.5056(12)$ Å, $\beta = 109.808(4)°$, $V = 1910.4(3)$ $Å^3$, $Z = 4$, $D_x = 1.592$ g cm^{-3}, μ(Mo-Kα) = 1.196 mm^{-1}, $F(000) = 940$, $S = 1.042$, $(\Delta/\sigma)_{max} = 0.001$, $(\Delta\rho)_{max} = 0.37$, $(\Delta\rho)_{min} = -0.34$ e.$Å^{-3}$. $R_1 = 0.033$ and $wR_2 = 0.080$ for 3664 observed reflections ($I > 2\sigma(I)$), $R = 0.044$ and $wR_2 = 0.084$ for 4365 independent reflections, $w = 1/[\sigma^2(F_o^2) + (0.0472P)^{2+}0.5679P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 1.

3. Results and discussion

The molecular structure of the title compound is shown in figure 1. Selected bond distances and angles are presented in table 2. The Cu(II) assumes square pyramidal coordination geometry. A 2,2-bipyridine ligand chelates to Cu(II) in the basal plane and two isonicotinates related by a screw axis coordinate via the pyridine-*N* and carboxyl-*O* atoms, respectively. A water molecule (O3) occupies the apical position. The Cu atom lies out of the basal plane by 0.1962(8) Å, a common situation in

Table 1. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for the complex salt.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Cu	2930(1)	4536(1)	5253(1)	28(1)
O(1)	4053(1)	5638(1)	6137(1)	34(1)
O(2)	3011(1)	5399(1)	7123(1)	41(1)
O(3)	3760(1)	4722(2)	4138(1)	49(1)
N(1)	1750(1)	5779(1)	4658(1)	32(1)
N(2)	1579(1)	3538(1)	4484(1)	31(1)
N(3)	6107(1)	8231(1)	8959(1)	32(1)
C(1)	3833(2)	5841(2)	6927(1)	31(1)
C(2)	4641(2)	6678(2)	7639(1)	29(1)
C(3)	4414(2)	7026(2)	8469(2)	38(1)
C(4)	5156(2)	7797(2)	9104(2)	38(1)
C(5)	6335(2)	7876(2)	8162(2)	39(1)
C(6)	5628(2)	7121(2)	7488(2)	37(1)
C(10)	1579(2)	2379(2)	4415(2)	41(1)
C(11)	594(2)	1769(2)	3868(2)	51(1)
C(12)	−402(2)	2356(2)	3377(2)	51(1)
C(13)	−415(2)	3550(2)	3436(2)	43(1)
C(14)	593(2)	4120(2)	3997(1)	30(1)
C(15)	685(2)	5392(2)	4109(1)	31(1)
C(16)	−233(2)	6150(2)	3694(2)	45(1)
C(17)	−49(2)	7323(2)	3836(2)	52(1)
C(18)	1047(2)	7713(2)	4386(2)	53(1)
C(19)	1929(2)	6918(2)	4785(2)	43(1)
O(4)	1785(2)	4611(2)	2361(2)	83(1)
O(5)	1753(2)	4728(2)	886(2)	89(1)
O(6)	3072(2)	5594(2)	2034(2)	84(1)
N(4)	2193(2)	4965(2)	1752(2)	51(1)
O(1W)	3569(2)	4245(2)	9005(2)	77(1)
O(2W)	3982(2)	5971(2)	469(2)	77(1)

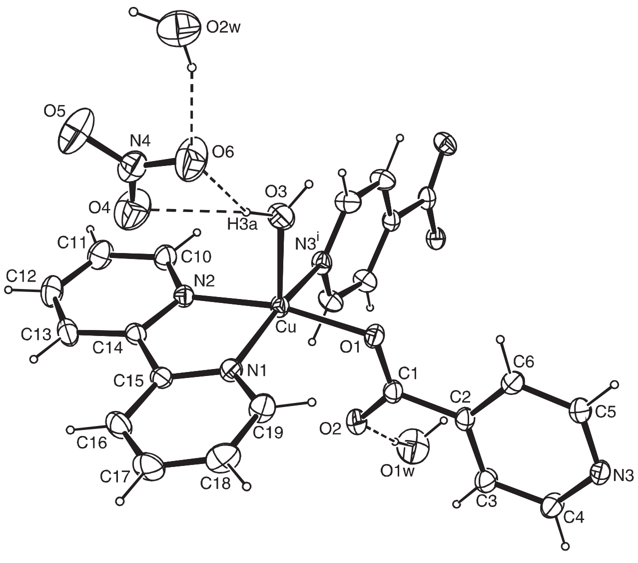

Figure 1. The molecular structure of the complex salt with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding. Symmetry code: (i) $1-x$, $-1/2+y$, $3/2-z$.

Table 2. Selected bond lengths [Å] and angles [°] for the complex salt.

Cu–O(1)	1.9831(13)	Cu–O(3)	2.1868(15)
Cu–N(1)	2.0034(16)	Cu–N(2)	2.0050(16)
Cu–N(3)^i	2.0086(15)	O(1)–C(1)	1.284(2)
O(2)–C(1)	1.236(2)	N(3)–C(4)	1.338(3)
N(3)–C(5)	1.341(3)	C(1)–C(2)	1.508(2)
C(2)–C(3)	1.381(3)	C(2)–C(6)	1.386(3)
C(3)–C(4)	1.375(3)	C(5)–C(6)	1.372(3)
O(1)–Cu–O(3)	91.58(6)	O(1)–Cu–N(1)	93.04(6)
O(1)–Cu–N(2)	168.88(6)	O(1)–Cu–N(3)^i	88.51(6)
O(3)–Cu–N(1)	92.95(6)	O(3)–Cu–N(2)	98.01(6)
O(3)–Cu–N(3)^i	99.77(6)	N(1)–Cu–N(2)	80.91(7)
N(1)–Cu–N(3)^i	167.14(7)	N(2)–Cu–N(3)^i	95.36(6)
C(1)–O(1)–Cu	112.89(12)		

Symmetry code: (i) $-x + 1$, $y -$, $-z + 3/2$.

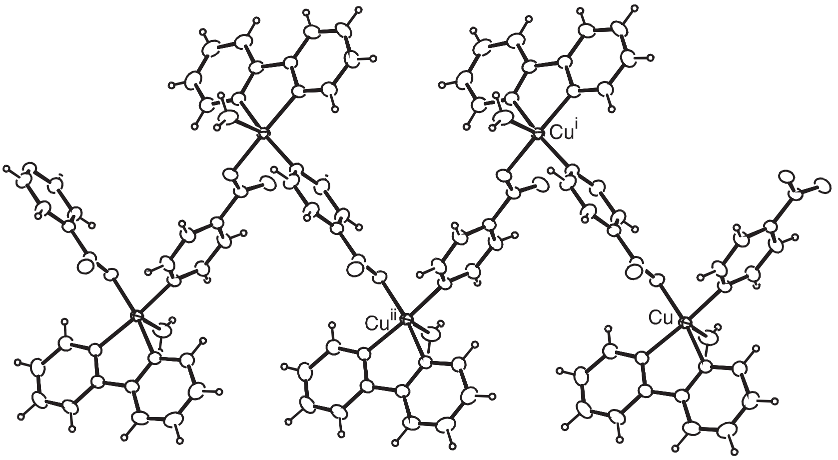

Figure 2. Polymeric molecular chains of the title complex. Symmetry codes: (i) $-x+1$, $y-1/2$, $-z+3/2$. (ii) x, $-1+y$, z.

square pyramidal complexes [5]. The Cu–O3 bond [2.1868(15) Å] in the axial direction is about 0.2 Å longer than the Cu–O1 bond [1.9831(13) Å] in the basal plane; this shows a typical Jahn-Teller distortion [6] for the Cu(II) complex.

The isonicotinate displays a planar configuration with the maximum atomic deviation being 0.080(1) Å (O1) and is nearly perpendicular to the coordination basal plane with a dihedral angle of 86.46(4)°. Each isonicotinate anion bridges two neighboring Cu atoms through terminal carboxyl-*O* and pyridine-*N* atoms to form a zigzag polymeric chain (figure 2) along the crystallographic *b* axis. Overlapped arrangements of parallel pyridine rings of adjacent polymeric chains are observed in the crystal as shown in figure 3. The distance of 3.529(3) Å between neighboring, parallel pyridine rings is significantly shorter than the van der Waals contact of 3.7 Å and suggests π–π stacking between pyridine rings.

An extensive hydrogen bond network occurs in the structure. The nitrate does not coordinate to the Cu atom but links with the complex via bifurcated hydrogen bonds O3–H3a $\cdots$ O4 and O3–H3a $\cdots$ O6 (figure 1 and table 3), the sum of the three

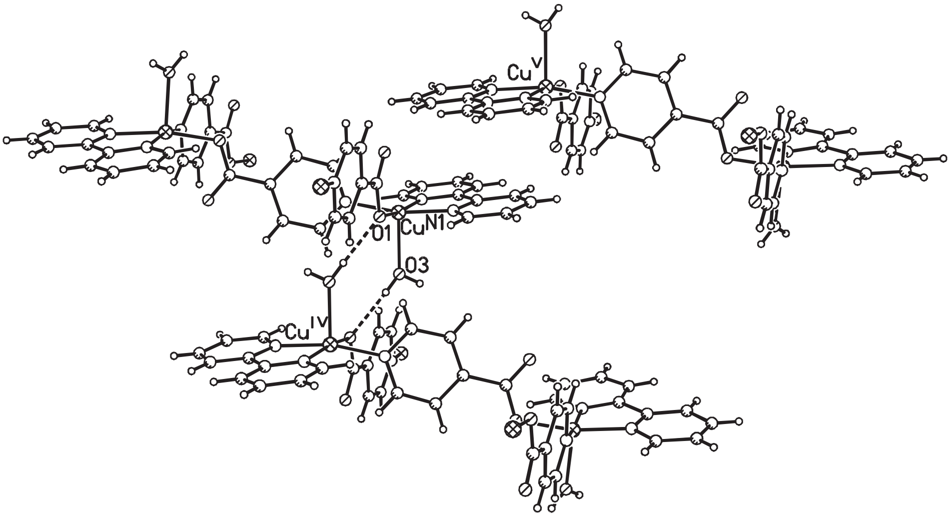

Figure 3. Supramolecular interactions between neighboring molecules. Symmetry codes: (iii) x, y, $-1+z$; (iv) $1-x$, $1-y$, $1-z$.

Table 3. Hydrogen bonding parameters [Å, °] for the complex salt.

D–H···A	D–H	H···A	D···A	D–H–A
O(1W)–H(1A)–O(2)	0.89	2.02	2.904(3)	175
O(1W)–H(1B)–O(2W)$^{\text{iv}}$	0.84	1.98	2.816(4)	177
O(2W)–H(2A)–O(6)	0.82	2.08	2.874(3)	164
O(2W)–H(2B)–O(1W)$^{\text{iii}}$	0.88	2.09	2.829(3)	140
O(3)–H(3A)–O(4)	0.84	2.11	2.866(3)	149
O(3)–H(3A)–O(6)	0.84	2.29	3.049(3)	151
O(3)–H(3B)–O(1)$^{\text{iv}}$	0.83	2.04	2.843(2)	165

Symmetry codes: (iii) x, y, $-1+z$; (iv) $1-x$, $1-y$, $1-z$.

angles about H3a being 357.2°. Isonicotinate is a monodentate ligand in the crystal; the uncoordinated carboxyl O2 atom is hydrogen bonded to a lattice water molecule. Coordinated water (O3) forms a hydrogen bond with the carboxyl group a neighboring complex molecule as shown in figure 3, resulting in a supramolecular structure involving adjacent polymeric chains.

The IR spectrum of the complex was assigned based on the crystal structure. The stretching vibration of the carboxyl group was observed at $1605\,\text{cm}^{-1}$ [ν_{as}(coo)] and $1387\,\text{cm}^{-1}$ [ν_{s}(coo)]. The $\Delta\nu$ value of $218\,\text{cm}^{-1}$ agrees with the monodentate coordination mode of the carboxyl group [7].

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