

Solid-State Coordination Chemistry of Pyridinedicarboxylic Acid Isomers. II. Crystal and Molecular Structure of Sodium Bis(pyridine-2,4-dicarboxylato)cuprate(II) trihydrate

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The first crystal structure of a simple metal(II) derivative of pyridine-2,4-dicarboxylic acid (lutidinic acid) is reported. The title compound crystallises in the monoclinic space group $P2_1/a$, with $a=12.968(5)$, $b=8.3152(9)$, $c=16.004(2)$ Å, $\beta=103.36(2)^\circ$, $Z=4$. The structure was solved employing 2484 independent X-ray reflections with $I>2\sigma(I)$ by Patterson and Fourier methods and refined by full-matrix least-squares to $R_1=0.074$. The Cu^{II} ion is located in a pyramidal environment coordinating to two nitrogen atoms and two oxygen atoms from the lutidinate ligands; the apical position in the pyramid is occupied by a water group. The stereochemistry of the title compound is compared with that of other copper(II) pyridinedicarboxylates. Its thermal behaviour is also presented.

Pyridinedicarboxylic acids (H_2pydc) form stable complexes with d -metal(II) ions. The series includes the 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridinedicarboxylic acid isomers, all of which may form 1:1 and 2:1 metal derivatives that exhibit various coordination modes. In the solid state these compounds illustrate the influence of the ligand constraints and the electronic configuration of the metal center upon the crystal structure. All dicarboxylates in the series present five donor sites: the oxygen atoms of both carboxylate groups and the nitrogen atom in the pyridinic ring. Depending on their relative position, the coordinating atoms may adopt a planar structure that leads to molecular solids, as in some dipicolinic acid ($\text{H}_2\text{2,6-pydc}$) derivatives,^{1–6} or may present a withdrawal from planarity that leads to $2\text{D}^{7,8}$ or 3D^8 structures.

When the solid derives from a metal presenting a d^9 configuration, a conflict between stabilization from the Jahn–Teller effect and ligand geometrical requirements is found. Crystallographic studies on Cu^{II} pyridinedicarboxylates

show that distortions from regular geometry are always present. This fact is denoted in all the crystal and molecular structures so far obtained: $\text{Cu}(2,6\text{-pydc}) \cdot 2\text{H}_2\text{O}$ (monoclinic),⁹ $\text{Cu}(2,6\text{-pydc}) \cdot 2\text{H}_2\text{O}$ (triclinic),^{1,2} $\text{Cu}(2,6\text{-pydc}) \cdot 3\text{H}_2\text{O}$,^{2,3} $\text{Cu}(3,4\text{-pydc}) \cdot 3.5\text{H}_2\text{O}$,⁸ $\text{Cu}(\text{H}_2\text{2,6-pydc})(2,6\text{-pydc}) \cdot \text{H}_2\text{O}$,⁴ $\text{Cu}(\text{H}_2\text{2,6-pydc})(2,6\text{-pydc}) \cdot 3\text{H}_2\text{O}$,^{4–6} $\text{Cu}(2,3\text{-pydc})_2$ ⁷ and $\text{Na}_2\text{Cu}(2,3\text{-pydc})_2 \cdot 8\text{H}_2\text{O}$.⁸

As can be seen from above, structural data on copper derivatives of lutidinic acid ($\text{H}_2\text{2,4-pydc}$), where 2,4-substitution and the Jahn–Teller effect are illustrated, are not available, the structure of $\text{K}_3[\text{VO}(\text{O}_2)(2,4\text{-pydc})] \cdot 3\text{H}_2\text{O}$ being the only crystal and molecular structure thus far reported.¹⁰ Interest in lutidinic acid derivatives also centers on its biological activities: it is an immunosuppressant and fibrosuppressive compound,¹¹ it shows an effect on the growth and floral induction of certain species,^{12,13} it is an inhibitor for H^+ -ATPase,¹⁴ and it protects the enzyme glucose dehydrogenase from cells of *Bacillus subtilis* from heat inactivation.^{15,16}

In this paper we present the crystal and molecular structure of the first Cu^{II} lutidinate: $\text{Na}_2\text{Cu}[2,4\text{-pydc}]_2 \cdot 3\text{H}_2\text{O}$ and compare it with the known structures of other Cu^{II} pyridinedicarboxylates. The thermal behavior of the compound in a N_2 atmosphere is also presented.

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Experimental

Preparation, thermal analysis and characterization of the solid. The ligand lutidinic acid monohydrate (Aldrich Chemical Co.) was used as provided. $\text{Na}_2\text{Cu}(\text{2,4-pydc})_2 \cdot 3\text{H}_2\text{O}$ was prepared by adding 5 mL of a NaOH solution (1 M) and 15 mL of CuSO_4 solution (0.1 M) to a suspension of lutidinic acid (2.5×10^{-3} mol) in 100 mL of bidistilled water (final pH 4.13). The solid was obtained by slow evaporation of the solution at 298 K; the blue crystals formed were collected by filtration and washed with bidistilled water.

The metal content of the solid was measured in a Varian Techrom A-A5R atomic absorption spectrometer. Elemental analyses were performed in a Carlo Erba EA 1108 microanalyser. Found: Na, 8.90; Cu, 12.67; C, 34.82; H, 2.77; N, 5.77. Calc. for $\text{Na}_2\text{Cu}(\text{C}_{14}\text{H}_6\text{N}_2\text{O}_8) \cdot 3\text{H}_2\text{O}$: Na, 9.27; Cu, 12.87; C, 34.04; H, 2.43; N, 5.67.

Powder data were collected in a Siemens D5000 diffractometer using a graphite monochromated $\text{Cu K}\alpha$ radiation. DSC measurements were performed in a Shimadzu DSC-50 differential scanning calorimeter employing powdered samples of about 7 mg in weight under an N_2 atmosphere (temperature range 293–673 K) at a heating rate of 6 K min^{-1} .

Single-crystal diffraction data. A thin crystal of the compound was mounted in a CAD-4 diffractometer; the scanning mode was $\omega - 2\theta$, using graphite-monochromated $\text{Mo K}\alpha$ radiation, $\lambda = 0.71069$ Å. Details of the data, data collection procedure, structure determination methods and refinement results are summarized in Table 1. The crystal plates (obtained after several attempts at crystallization) turned out to diffract poorly. Only about 45% of the reflection intensities collected up to 0.71 Å resolution were above two standard deviations of the measurement errors. Most hydrogen atoms of the lutidinic ligands were located using a difference Fourier map. However, they were positioned on a stereochemical basis and were included in the refinement riding on the atom to which they were bonded with a common isotropic thermal parameter, which in the final run converged to $U = 0.018(9)$ Å².

Results and discussion

Structural results. The compound is monoclinic, space group $P2_1/a$. Final atomic coordinates and equivalent isotropic temperature parameters are given in Table 2. Selected bond distances and angles are shown in Table 3.* The structure was solved and refined to a final R -value of 7.4%; Fig. 1 shows an ORTEP²² drawing of the

* Supplementary material is available from the authors on request, comprising lists of atomic anisotropic thermal parameters (Table 4), hydrogen atom positions (Table 5), and calculated and observed structure factor amplitudes (Table 6).

Table 1. Crystal data and structure solution methods and refinement for $\text{Na}_2\text{Cu}(\text{C}_7\text{NO}_4\text{H}_3)_2 \cdot 3\text{H}_2\text{O}$.

Empirical formula	$\text{C}_{14}\text{H}_{12}\text{CuN}_2\text{Na}_2\text{O}_{11}$
Formula weight	493.78
Temperature	293(2) K
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions ^a	$a = 12.969(5)$ Å $b = 8.3153(9)$ Å $c = 16.004(2)$ Å $\beta = 103.36(2)^\circ$
Volume	1679.1(7) Å ³
Z	4
Density (calculated)	1.953 Mg m ⁻³
Absorption coefficient	1.424 mm ⁻¹
$F(000)$	996
Crystal size	0.04 × 0.32 × 0.46 mm
Crystal color/shape	Blue/plate
Scan width	0.8 + 0.35 tan θ
Standard reflections	(0, 4, -4); (-2, -3, 12)
Decay of standards	Less than 1%
θ range for data collection	1.31 to 29.97°
Index ranges	$-18 \leq h \leq 17$, $0 \leq k \leq 11$, $0 \leq l \leq 22$
Reflections collected	6025
Observed reflections [$I > 2\sigma(I)$]	2696
Data reduction and correction ^b	SDP, ¹⁸ SHELX-76, ¹⁹
structure solution ^c and refinement ^d programs	SHELX-86, ²⁰ SHELX-93 ²¹
Refinement method	Full-matrix least-squares on F^2
Weights, w	$w = [\sigma^2(F_o^2) + (0.188P)^2 + 2.82P]^{-1}$ $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$
Independent reflections	4057 [$R_{\text{sym}} = 0.036$]
Data/restraints/parameters	4057/0/272
Goodness-of-fit ^e on F^2	1.078
Final R indices ^f [$I > 2\sigma(I)$]	$R_1 = 0.074$, $wR_2 = 0.222$
R indices (all data)	$R_1 = 0.131$, $wR_2 = 0.293$
Largest difference peak and hole	1.03 and -1.15 e Å ⁻³

^aLeast-squares refinement of $[\sin \theta/\lambda]^2$ values for 25 reflections in the $20.4 < 2\theta < 41.4^\circ$ range. ^bData were corrected for Lorentz, polarization and absorption effects¹⁷ (max. and min. transmission factors of 0.948 and 0.716). ^cStructure solved by Patterson and Fourier methods. ^dNeutral atomic scattering factors. ^eGoodness-of-fit defined as: $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n and p are the number of reflections and parameters, respectively. ^f R indices defined as: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

compound showing the labeling of the non-hydrogen atoms and their vibrational ellipsoids at 50%.

The solid is monomeric, and the copper(II) ion is pentacoordinated by two lutidinate groups and a water molecule (O1W) in a slightly distorted square pyramidal polyhedron. The basal plane is defined by the two nitrogen atoms N(1) and N(2) in a *trans*-position and two oxygen atoms from the carboxylates in the 2-position (one from each lutidinate). The separation of the two donor atoms in the bidentate ligand determines the following distortions: angle O(11)–Cu–N(1) = 90.7° and angle O(21)–Cu–N(2) = 82.8°. The metal ion lies closer

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $\text{Na}_2\text{Cu}(\text{C}_7\text{NO}_4\text{H}_3)_2 \cdot 3\text{H}_2\text{O}$.

Atom	x	y	z	$U(\text{eq})/\text{\AA}^2$ ^a
Cu	0.1262(1)	0.1140(1)	0.0029(1)	0.022(1)
O(11)	0.1036(4)	-0.0991(6)	-0.0513(3)	0.024(1)
O(12)	0.0938(5)	-0.2167(7)	-0.1776(3)	0.028(1)
O(13)	0.0532(6)	0.4182(7)	-0.4124(4)	0.039(2)
O(14)	0.0392(5)	0.1541(6)	-0.4350(3)	0.024(1)
N(1)	0.0813(5)	0.1886(7)	-0.1194(4)	0.019(1)
C(11)	0.0813(5)	0.0674(8)	-0.1725(4)	0.017(1)
C(12)	0.0705(6)	0.0920(9)	-0.2595(4)	0.022(1)
C(13)	0.0552(6)	0.2474(8)	-0.2912(4)	0.016(1)
C(14)	0.0486(6)	0.3709(9)	-0.2365(5)	0.023(1)
C(15)	0.0626(7)	0.3391(9)	-0.1483(5)	0.024(2)
C(16)	0.0963(6)	-0.0974(9)	-0.1339(5)	0.023(2)
C(17)	0.0480(6)	0.2765(9)	-0.3880(4)	0.021(1)
O(21)	0.1275(5)	0.3240(6)	0.0573(3)	0.027(1)
O(22)	0.1543(5)	0.4416(6)	0.1874(4)	0.032(1)
O(23)	0.2096(5)	-0.1970(7)	0.4191(4)	0.031(1)
O(24)	0.1862(6)	0.0653(8)	0.4350(4)	0.037(2)
N(2)	0.1540(5)	0.0363(7)	0.1243(4)	0.018(1)
C(21)	0.1617(6)	0.1566(8)	0.1776(4)	0.019(1)
C(22)	0.1765(6)	0.1293(9)	0.2651(4)	0.021(1)
C(23)	0.1889(6)	-0.0284(8)	0.2962(4)	0.017(1)
C(24)	0.1840(6)	-0.1505(8)	0.2394(5)	0.020(1)
C(25)	0.1689(6)	-0.1147(9)	0.1526(4)	0.022(1)
C(26)	0.1473(6)	0.3221(9)	0.1389(5)	0.023(2)
C(27)	0.1959(6)	-0.0545(9)	0.3913(4)	0.021(1)
Na(1)	0.1208(3)	-0.0945(4)	-0.4599(2)	0.027(1)
Na(2)	0.1195(3)	0.3153(4)	0.4639(2)	0.032(1)
OW1	0.2975(5)	0.1113(7)	-0.0057(4)	0.033(1)
OW2	0.2942(5)	-0.0179(7)	-0.3723(4)	0.030(1)
OW3	0.0618(5)	-0.2724(7)	-0.3625(4)	0.033(1)

^a $U(\text{eq})$ for the non-H atoms is defined as one third of the trace of the orthogonalized U_{ij} tensor.

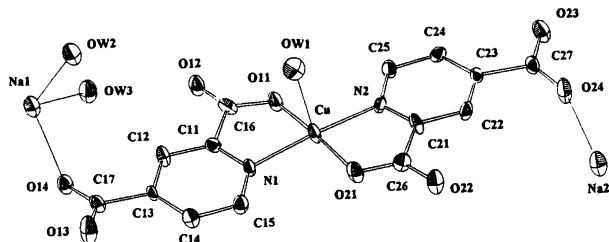


Fig. 1. ORTEP drawing of $\text{Na}_2\text{Cu}(\text{C}_7\text{NO}_4\text{H}_3)_2 \cdot 3\text{H}_2\text{O}$ showing the non-H atoms labeling and the vibrational ellipsoids at 50% probability.

to one of the aromatic rings [distances $\text{Cu}-\text{N}(1)=2.009(6)$, $\text{Cu}-\text{N}(2)=1.999(6)$, $\text{Cu}-\text{O}(11)=1.965(5)$ and $\text{Cu}-\text{O}(21)=1.949(6)$ Å]; the apical position in the distorted pyramid is occupied by a water ligand at a longer distance from the metal center [distance $\text{Cu}-\text{OW}(1)=2.259(6)$ Å and angles $\text{N}(1)-\text{Cu}-\text{OW}(1)=90.6(2)$ and $\text{N}(2)-\text{Cu}-\text{OW}(1)=95.6(2)^\circ$].

As can be seen in Fig. 2, all lutidinate groups are almost planar and lie approximately on bc -planes, the distance between the planes being 3.60 Å. Measured angles in the ligand are as follows: plane of ring 1 (PR1) with plane $\text{O}(11)\text{O}(21)\text{N}(2)\text{N}(1)$, 9.8° ; plane of ring 2 (PR2) with plane $\text{O}(11)\text{O}(21)\text{N}(2)\text{N}(1)$, 4.5° ; plane

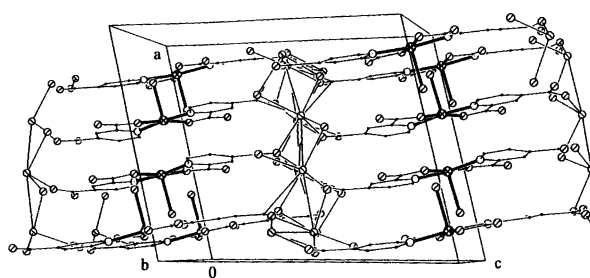
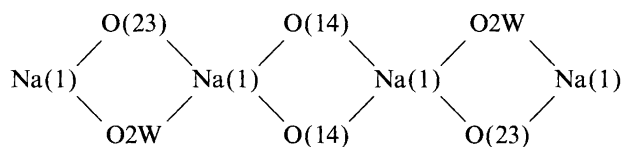


Fig. 2. Packing view of $\text{Na}_2\text{Cu}(\text{C}_7\text{NO}_4\text{H}_3)_2 \cdot 3\text{H}_2\text{O}$ showing the planar ligands.

of ring 1 (PR1) with plane $\text{C}(17)\text{O}(13)\text{O}(14)\text{C}(13)$, 11.6° ; and plane of ring 2 (PR2) with plane $\text{C}(27)\text{O}(23)\text{O}(24)\text{C}(23)$, 7.7° . All carboxylate groups differ in interatomic distances, presenting a shorter C–O length; this is attributable to the double bond character of the C–O bond; the carboxylate in the 2-position of ring 1 presents the more marked difference [distances $\text{O}(11)-\text{C}(16)=1.304(9)$ and $\text{O}(12)-\text{C}(16)=1.210(9)$ Å].

The two Na ions are not structurally equivalent and display an octahedral environment coordinating to water molecules OW(1) and OW(2) and to oxygen atoms from carboxylates in the 4-position; atom O(13) is coordinated only to Na(2). The six-coordination is achieved by sharing arista, and the Na polyhedra form chains that run along the a -axis (Fig. 3). All Na(1) form a double bridged chain:



Na(2) is also bridged to Na(2) and interconnects Na(1)

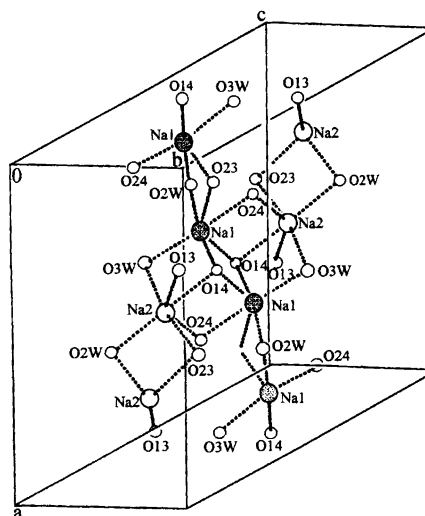


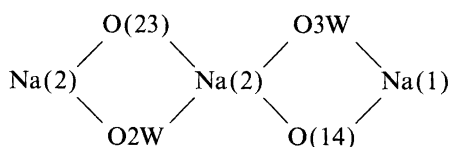
Fig. 3. Chain of Na coordination polyhedra running along the a -axis.

Table 3. Selected bond distances (in Å) and angles (in °) for Na₂Cu(C₇NO₄H₃)₂ · 3H₂O.

Bond distances			
Cu coordination			
Cu–O(21)	1.949(6)	Cu–O(11)	1.965(5)
Cu–N(2)	1.999(6)	Cu–N(1)	2.008(6)
Cu–OW1	2.259(6)		
Lutidinate (ring 1)		Lutidinate (ring 2)	
O(11)–C(16)	1.304(9)	O(21)–C(26)	1.271(9)
O(12)–C(16)	1.210(9)	O(22)–C(26)	1.251(9)
O(13)–C(17)	1.248(9)	O(23)–C(27)	1.264(9)
O(14)–C(17)	1.255(9)	O(24)–C(27)	1.241(10)
Na(1) coordination			
Na(1)–O(14)	2.397(6)	Na(1)–OW3	2.399(7)
Na(1)–O(14)#2	2.402(6)	Na(1)–OW2	2.443(7)
Na(1)–O(24)#1	2.444(7)	Na(1)–O(23)#1	2.615(7)
Na(2) coordination			
Na(2)–O(24)	2.339(7)	Na(2)–OW2#7	2.466(7)
Na(2)–O(13)#4	2.486(7)	Na(2)–O(14)#4	2.506(7)
Na(2)–O(23)#8	2.551(7)	Na(2)–OW3#6	2.554(7)
Bond angles			
Cu coordination			
O(21)–Cu–O(11)	171.9(3)	N(2)–Cu–N(1)	173.7(3)
O(21)–Cu–N(2)	82.8(2)	O(11)–Cu–OW1	90.7(2)
O(11)–Cu–N(2)	96.5(2)	N(2)–Cu–OW1	95.6(2)
O(21)–Cu–N(1)	97.4(2)	N(1)–Cu–OW1	90.6(2)
O(11)–Cu–N(1)	82.4(2)	O(21)–Cu–OW1	97.4(2)
Lutidinate (ring 1)			
N(1)–C(11)–C(16)	117.0(6)	C(12)–C(11)–C(16)	121.6(7)
C(14)–C(13)–C(17)	121.7(6)	C(12)–C(13)–C(17)	118.8(6)
O(12)–C(16)–O(11)	124.2(7)	O(12)–C(16)–C(11)	121.9(7)
O(11)–C(16)–C(11)	113.6(6)	O(13)–C(17)–O(14)	125.6(7)
O(13)–C(17)–C(13)	117.7(6)	O(14)–C(17)–C(13)	116.6(6)
Lutidinate (ring 2)			
N(2)–C(21)–C(26)	116.7(6)	C(22)–C(21)–C(26)	122.8(7)
C(24)–C(23)–C(27)	123.2(6)	C(22)–C(23)–C(27)	117.8(6)
O(22)–C(26)–O(21)	126.5(7)	O(22)–C(26)–C(21)	119.2(7)
O(21)–C(26)–C(21)	114.3(6)	O(24)–C(27)–O(23)	125.3(6)
O(24)–C(27)–C(23)	117.4(6)	O(23)–C(27)–C(23)	117.3(6)
Na(1) coordination			
O(14)–Na(1)–OW3	101.8(2)	(14)–Na(1)–O(14)#2	87.2(2)
OW3–Na(1)–O(14)#2	88.5(2)	O(14)–Na(1)–OW2	93.6(2)
OW3–Na(1)–OW2	100.3(2)	O(14)#2–Na(1)–OW2	170.8(2)
O(14)–Na(1)–O(24)#1	83.2(2)	OW3–Na(1)–O(24)#1	174.8(3)
O(14)#2–Na(1)–O(24)#1	90.6(2)	OW2–Na(1)–O(24)#1	80.4(2)
O(14)–Na(1)–O(23)#1	133.7(2)	OW3–Na(1)–O(23)#1	122.8(2)
O(14)#2–Na(1)–O(23)#1	82.6(2)	OW2–Na(1)–O(23)#1	90.3(2)
O(24)#1–Na(1)–O(23)#1	52.0(2)		
Na(2) coordination			
O(24)–Na(2)–OW2#7	982(2)	O(24)–Na(2)–O(13)#4	132.5(2)
OW2#7–Na(2)–O(13)#4	124.6(2)	O(24)–Na(2)–O(14)#4	83.1(2)
OW2#7–Na(2)–O(14)#4	176.4(2)	O(13)#4–Na(2)–O(14)#4	53.0(2)
O(24)–Na(2)–O(23)#8	79.1(2)	OW2#7–Na(2)–O(23)#8	91.3(2)
O(13)#4–Na(2)–O(23)#8	80.3(2)	O(14)#4–Na(2)–O(23)#8	85.7(2)
O(24)–Na(2)–OW3#6	94.5(2)	OW2#7–Na(2)–OW3#6	100.3(2)
O(13)#4–Na(2)–OW3#6	96.7(3)	O(14)#4–Na(2)–OW3#6	82.9(2)
O(23)#8–Na(2)–OW3#6	167.5(2)		

Symmetry transformations used to generate equivalent atoms: (#1) $x, y, z-1$; (#2) $-x, -y, -z-1$; (#3) $-x+1/2, y-1/2, -z+1$; (#4) $x, y, z+1$; (#5) $-x+1/2, y-1/2, -z$; (#6) $-x, -y, -z$; (#7) $-x+1/2, y+1/2, -z$; (#8) $-x+1/2, y+1/2, -z+1$.

chains;



Distances in the Na polyhedra reveal a stronger bond between Na(2) and O(24) [length Na(2)–O(24) = 2.339(7) Å] and weaker interactions with other oxygen atoms. Distances between Na–O are in the range 2.339–2.615 Å.

Again, the structure resolved may be explained in terms of the metal electronic configuration and ligand constraints. Copper(II) is a versatile ion that may present several coordination environments (typical coordination numbers are 4, 5 and 4+2) and a marked Jahn–Teller effect. For the 2:1 compound Na₂Cu[2,4-pydc]₂·3H₂O the metal coordination polyhedron is square pyramidal. The Cu^{II} is chelated by two lutidines through a carboxylate in a 2-position and the nitrogen atom. The relative position of both carboxylates in the ring determines that the ligand is almost flat and imposes only a slight distortion from regular geometry to the metal polyhedron. The –COO[–] in 4 is not coordinated to Cu^{II}. Because of metal and ligand characteristics the structure may be described as monomeric, and the square pyramidal coordination polyhedra are linked by Na chains.

If we compare the structure described with those exhibited by the copper dipicolinates, having the carboxylates located in the 2- and 6-positions, the crystal data reveal that 2,6-pydc^{2–} behaves as a tridentate planar ligand that forms a chelate with Cu^{II} in three coplanar positions. The remaining positions in the coordination polyhedron are completed in several ways:

(a) In the molecular compound Cu(2,6-pydc)·2H₂O (triclinic)^{1,2} (1) the Cu^{II} polyhedron is a square pyramid (Fig. 4); the basal plane in the pyramid is formed by a

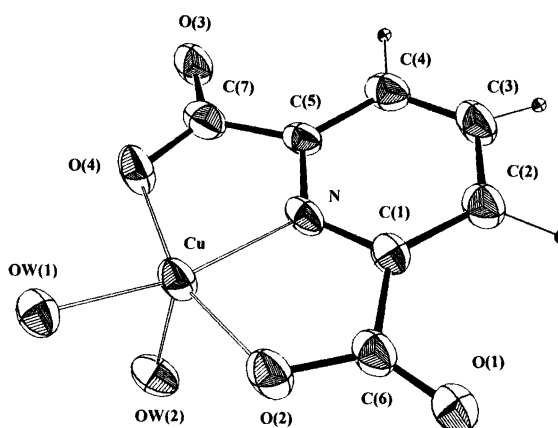


Fig. 4. ORTEP view of Cu(2,6-pydc)·2H₂O, triclinic (from Ref. 2).

planar tridentate dipicolinate anion and one water molecule. The constraints derived from the carboxylates in the 2- and 6-positions determine a large angular distortion from the ideal square-base geometry [bite angles are: N–Cu–O(2) = 80.5(4)° and N–Cu–O(4) = 80.3(4)°]. Two water molecules complete the pentacoordination; H₂O in the apical position is found at a longer distance [2.154(Å)] from the metal ion.

(b) In the octahedral complexes, Cu(2,6-pydc)·2H₂O (monoclinic)⁹ (2) and Cu(2,6-pydc)·3H₂O^{2,3} (3), as seen in Fig. 5, the copper ion is also hexacoordinated by an almost planar tridentate dipic^{2–} ion and one water molecule that define a distorted square planar arrangement around Cu^{II} [bite angles in the range 80.2(1)–80.6(1)°]. For compound 2, longer axial positions, as expected for a *d*⁹ ion, involve a water molecule [Cu–OW distance = 2.396(3) Å] and one bridging carboxylate oxygen atom from an adjacent molecule [Cu–O distance = 2.423(3) Å]; coordination polyhedra are thus linked in chains parallel to [001] plane. For compound 3, the distorted octahedron is completed by two water

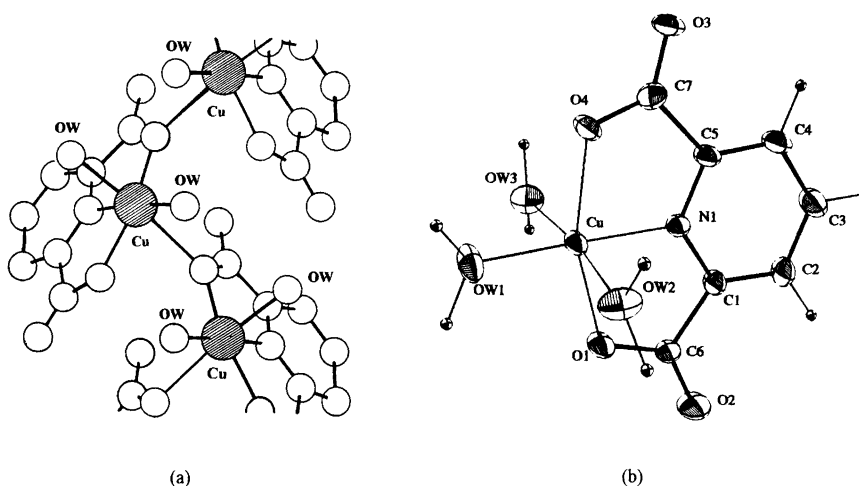


Fig. 5. Copper coordination polyhedra in compounds (a) Cu(2,6-pydc)·2H₂O, monoclinic (from Ref. 9) and (b) Cu(2,6-pydc)·3H₂O (from Ref. 2).

molecules at longer distances: 2.378(3) and 2.503(3)°. In both compounds, the dihedral angles between the planes formed by the aromatic ring and each carboxylate group are in the range 4.0(1)–9.0(6)°.

(c) For the 2:1 compounds $\text{Cu}(\text{H}_2\text{2,6-pydc})(\text{2,6-pydc}) \cdot \text{H}_2\text{O}^4$ (**4**) and $\text{Cu}(\text{H}_2\text{2,6-pydc})(\text{2,6-pydc}) \cdot 3\text{H}_2\text{O}^{4-6}$ (**5**) the copper ion is chelated by a dianion (2,6-pydc²⁻) and a neutral ligand ($\text{H}_2\text{2,6-pydc}$). Both solids present a similar, very distorted octahedral geometry (Fig. 6), the equatorial plane being defined by a trichelating dianion (2,6-pydc²⁻) and a nitrogen atom from the $\text{H}_2\text{2,6-pydc}$ [distances in the distorted square in the range 1.901(7)–2.063(8) Å and bite angles 79.9(3) and 80.4(3)°]; the dipic²⁻ lies closer to the metal atom. Longer apical positions are determined by oxygen atoms of the protonated ligand that is nearly perpendicular to dipic²⁻. The main factor in the existence of one dipic²⁻ and one H_2dipic species in each molecule may be the Jahn–Teller effect, which imposes a higher basicity on the axial ligand, thus leading to longer Cu–O distances. Thus the Jahn–Teller effect and the ligand constraints determine monomeric structures in which the ligand is planar and the copper coordination polyhedron is a very distorted octahedron.

When the copper(II) derivative is derived from a pyridinedicarboxylato ligand that presents the $-\text{COO}^-$ groups located on vicinal positions in the aromatic ring, as in $\text{Cu}(\text{2,3-pydc})_2$ (**6**),⁷ $\text{Na}_2\text{Cu}(\text{2,3-pydc})_2 \cdot 8\text{H}_2\text{O}$ (**7**)⁸ and $\text{Cu}(\text{3,4-pydc}) \cdot 3.5\text{H}_2\text{O}$ (**8**),⁸ electronic repulsion and/or steric hindrance between carboxylate groups determine a withdrawing from planarity that provokes the formation of two- or three-dimensional structures. For compounds **6** and **7**, derived from quinolinic acid ($\text{H}_2\text{2,3-pydc}$), the carboxylate in the 2-position is coplanar with the organic ring, whilst the 3-carboxylate is twisted by 83.6(6)°. Thus trichelation is precluded by the relative position of the carboxylate groups, and the quinolinate behaves as bidentate, forming a strong planar bond in an equatorial plane [bite angle 83.28(14)°] while the 3-carboxylate coordinates to another copper ion, forming a two-dimensional structure that can be described as chains composed by double links. These

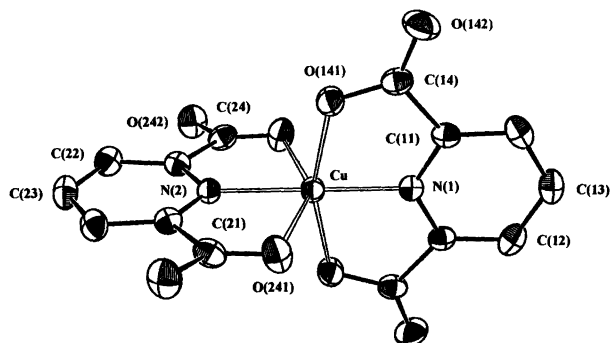


Fig. 6. ORTEP projection of $\text{Cu}(\text{2,6-pydc})(\text{H}_2\text{dipic}) \cdot \text{H}_2\text{O}$ showing the two perpendicular trichelate ligands (from Ref. 4).

double links are formed by two 2,3-pydc²⁻ and two octahedral metal(II) ions ($-\text{Cu}_{0.5}\text{L}_2\text{Cu}_{0.5}-$) (see Fig. 7 for compound **7**); Cu^{II} is situated on an inversion center and is bonded to two N atoms and two carboxylate O atoms in the pyridine 2-positions [for **7**, the Cu–N distance is 1.950(3) Å and Cu–O is 1.948(3) Å; distances in compound **6** are slightly shorter]. Again, axial bonds are longer than equatorial ones [Cu–O distance 2.660(4) Å], where the upper site is occupied by a carboxylate O atom from the former link in the chain and the lower site with a similar atom from the following link. The chains are transversally connected via hydrogen bonds for compound **6** and through double bridges $\text{Na}-(\text{H}_2\text{O})_2-\text{Na}$ for compound **7**. All Na ions display an octahedral coordination in which the polyhedra share common edges.

In compound **8**, derived from cinchomeronic acid ($\text{H}_2\text{3,4-pydc}$), carboxylates in both the 3- and 4-positions are displaced from the pyridinic ring [angles in the range 16(1)–85(1)°], and the ligand behaves as tridentate but coordinating to three different Cu^{II} ions; thus a highly interconnected structure is formed and the final three-dimensional structure may be attributed to the two constrained twisted carboxylates. The copper ion is found in two elongated octahedra, where the angular geometry is slightly distorted, and one pyramidal environment [equatorial distances in the range 1.907(8)–2.032(6) Å, axial distances in the range 2.498(7)–2.588(8) Å]. Coordination is always accomplished to H_2O and to N and O atoms from different 3,4-pydc²⁻ groups.

Thermal behavior. The DSC data of the compound show one endothermic minimum (at 182 °C) corresponding to dehydration. Ligand decomposition together with redox phenomena take place in two steps at 307 °C (endo) and at 325 °C (exo). Final products at 400 °C are C, Cu^0 and Na_2CO_3 , the last two being characterised by XRD.

The thermal behavior is typical of Cu^{II} carboxylates^{23,24} where the copper(II) carboxylate decom-

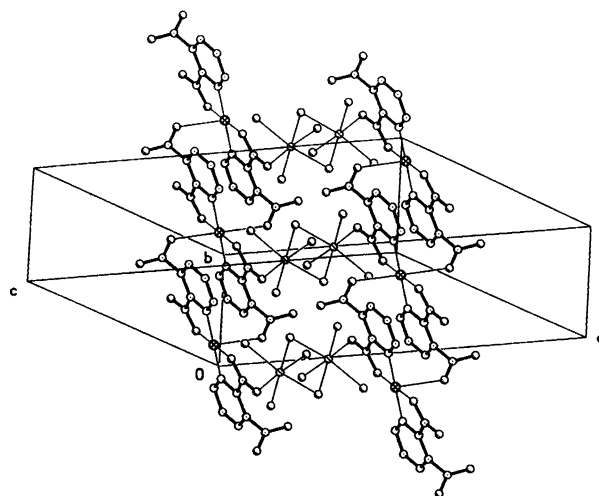


Fig. 7. Interlinked chains in $\text{Na}_2\text{Cu}(\text{2,3-pydc})_2 \cdot 8\text{H}_2\text{O}$.

poses through a redox process triggered by internal electron transfer (O–Cu homolytic bond breakage) that yields Cu⁰. The process is followed by CO₂ release and subsequent decomposition of the organic moiety. For Na⁺ homolytic bond breakage is accomplished in C–O and/or C–C bonds, rather than in Na–O bonds and the final product is Na₂CO₃.

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