

Synthesis and Spectral and Structural Characterization of a Bridging Chloropicolinatocopper(II) Complex, $\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})\text{Cl}$

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Summary. The title complex of copper(II) chloride with picolinic acid was prepared and characterized by spectroscopic and X-ray crystallographic methods. The complex, $\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})\text{Cl}$, crystallizes tetragonal, space group $P4_2/n$ (No. 86), $a = 976.4(1)$, $c = 1499.6(4)$ pm, $N = 8$; $R_w = 0.048$ for 543 observed $\text{MoK}\alpha$ diffractometer data. In the structure of the complex two μ -chloro bridges form only slightly bent Cu_2Cl_2 rings [$\text{Cu}-\text{Cl} = 224.2(4)$ and $275.6(4)$ pm] with $\text{Cu} \dots \text{Cu}$ separation of $359.4(2)$ pm and $\text{Cl} \dots \text{Cl}$ separation of $348.7(5)$ pm. These edge-sharing copper coordination polyhedra are further linked via the N and O donor atoms of the picolinate anions at $\text{Cu}-\text{N}$ distances of $199.6(12)$ pm and $\text{Cu}-\text{O}$ bond lengths of $195.7(8)$ and $200.6(10)$ pm, to form a two-dimensional layer structure in which these layers are arranged along the ab plane. Each picolinate anion functions as a tetra-dentate ligand: N(1) and O(2) are coordinated to the same Cu(II) center whereas O(1) is bonded to a neighbouring Cu(II) center. O(2) is further bonded to the latter Cu(II) center at a long $\text{Cu}-\text{O}$ distance of $256.5(8)$ pm. The electronic, infrared and Raman spectra of the solid complex are reported and discussed.

Keywords. Chloro complex; Copper(II) complex; Crystal structure analysis; Picolinic acid; Vibrational spectroscopy.

Synthese und spektroskopische und strukturelle Charakterisierung eines verbrückten Chloropicolinatokupfer(II) Komplexes, $\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})\text{Cl}$

Zusammenfassung. Der Titelkomplex aus Kupfer(II)chlorid und Picolinsäure wurde dargestellt und mit spektroskopischen und Röntgen-Einkristall-Methoden charakterisiert. $\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})\text{Cl}$ kristallisiert tetragonal, Raumgruppe $P4_2/n$ (No. 86), $a = 976.4(1)$, $c = 1499.6(4)$ pm, $N = 8$; $R_w = 0.048$ für 543 beobachtete $\text{MoK}\alpha$ -Diffraktometerdaten. In der Kristallstruktur bilden zwei μ -chloro-Brücken nur wenig gewinkelte Cu_2Cl_2 -Ringe aus [$\text{Cu}-\text{Cl} = 224.2(4)$ und $275.6(4)$ pm], mit $\text{Cu} \dots \text{Cu}$ Abständen von $359.4(2)$ pm und $\text{Cl} \dots \text{Cl}$ Abständen von $348.7(5)$ pm. Die kantenverknüpften Koordinationspolyeder der Kupferatome sind in Richtung der ab -Ebene über die N- und O-Donoratome der

Picolinat-Anionen [mit Cu–N Abständen von 199.6(12) pm und Cu–O Abständen von 195.7(8) und 200.6(10) pm] zu einer zweidimensionalen Schichtstruktur verknüpft. Jedes Picolinat-Anion fungiert als vierzähliger Ligand: N(1) und O(2) sind zum selben Cu(II)-Zentrum gebunden; O(1) ist zum benachbarten Cu(II)-Zentrum koordiniert, zu dem O(2) einen langen Cu–O-Abstand von 256.5(8) pm ausbildet. Die elektronischen, Infrarot- und Raman-Spektren des Festkörper-Komplexes werden berichtet und diskutiert.

Introduction

The broad spectrum of the physiological effects of picolinic acid, otherwise called 2-pyridinecarboxylic acid, and its derivatives on the activity functions of both animal and plant organisms has been attributed to their ability to form complexes with transition metals [1]. This acid is known to form complexes of the type $M(pic)_2 \cdot nH_2O$ with $n = 0, 2,$ or 4 and $M = Mn, Fe, Co, Ni, Cu, Zn, Cd, Mg,$ and Pb [2–7]. Some of these complexes have been studied by means of X-ray single crystal analysis [5–9]. Further studies have previously led to the isolation of complexes of the types $M(pic)(pic-H)X$ with $X = Cl, Br,$ or SCN and $M = Co, Ni,$ and Cu with or without solvent molecules [10, 11] and $[M_2(pic)_3(pic-H)_3]X \cdot nH_2O$ where $M = Fe, Co, Ni,$ and $X = Cl, HSO_4, PF_6,$ and NO_3 [12]. Definite crystallographic data, however, are lacking for these latter materials.

Recently, we described the preparation and characterization of gold(II) halide complexes of picolinic acid together with the crystal structure of $[AuBr_4][K(pic-H)_2(H_2O)_2] \cdot (pic-H)_2$ [13] as well as the structure of $Mn(pic)(N_3)(H_2O)$ [14]. A further work led to the isolation of a new complex of the formula $Cu(picolinato)Cl$. As this is the first of this formula to have been isolated we determined its structure by spectroscopic and X-ray crystallographic methods in order to appraise its molecular and coordination geometry.

Results and Discussion

The reaction between picolinic acid and copper(II) chloride in EtOH afforded a complex of the formula $Cu(pic)Cl$, which differs from the well known $M(pic)_2 \cdot nH_2O$ complexes [2–9] as well as from those of the types $[M(pic)(pic-H)]X$ [10, 11] and $[M_2(pic)_3(pic-H)_3]X \cdot nH_2O$ [12].

Crystals of the title blue copper complex crystallize in the primitive tetragonal space group $P4_2/n$ (No. 86) with 8 molecules per unit cell. The principle structural features of the complex are given in Fig. 1. Each Cu(II) atom is coordinated to two picolinate anionic molecules and two chloride anions. The coordination environment of the metal center may be described as a very distorted tetragonal bipyramid with N(1) and O(2) of the picolinate molecule 1 [Cu–N(1) = 199.6(12), and Cu–O(2) = 195.7(8) pm], O(1) of picolinate molecule 2 at Cu–O distance of 200.6(10) pm, and Cl(a) in the basal sites [Cu–Cl(a) = 224.2(4) pm]. The axial sites are occupied by Cl at a long Cu–Cl distance of 275.6(4) pm and oxygen atom O(2b) of picolinate molecule 2 with a Cu–O(2b) distance of 256.5(8) pm. Cu–O bond lengths greater than 250 pm have been found for several copper-picolinato and picolinic acid derivative complexes, e.g. bis-(picolinato)copper(II) dihydrate [9]. In this latter complex, two picolinato ligands are bound centrosymmetrically to the Cu(II) by N and O atoms, and coordination number six is completed by two carbonyl oxygen

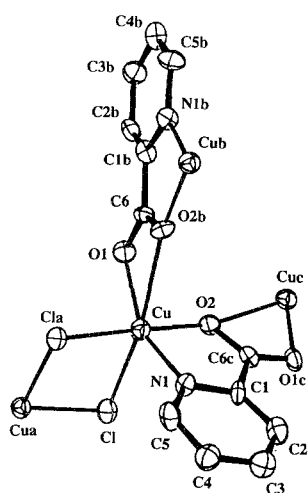


Fig. 1. Coordination figure and atom numbering scheme of $\text{Cu}(\text{pic})\text{Cl}$; symmetry code according to Table 3

atoms from neighbouring complexes at the apical positions at Cu–O distances of 275 pm [9]. In the structure of *bis*-(3,6-dichloropicolinato)copper(II), coordination number six is completed through oxygen atoms from adjacent complex molecules at Cu–O bond lengths of 194 and 270 pm [22].

In the structure of the title complex, two polyhedra have a common edge (two μ -chloro bridges form only slightly bent Cu_2Cl_2 rings with Cu...Cu separation of 359.4(2) pm and Cl...Cl separation of 348.7(5) pm). These edge-sharing dimeric copper coordination polyhedra are further linked via the N and O donor atoms of their picolinate anions to form a two-dimensional layer structure. The layers are arranged along the *ab* planes at $z = 1/4$ and $3/4$ (Fig. 2). The Cu...Cu separation is shorter than the corresponding value of 364.9(1) pm found in the structure of dichloro((diphenylethanedione)dioxime)copper(II) [23]. The Cu–Cl distances (Table 3) are comparable with those found in this latter complex (224.7(2) and 290.4(2) pm(axial)), as well as the Cu–Cl–Cu angle of 89.3° [23]. Each picolinate anionic molecule serves as a tetra-dentate ligand: N(1) and O(2) are coordinated to the same Cu(II) center whereas O(1c) is bonded to a neighbouring Cu(c) center.

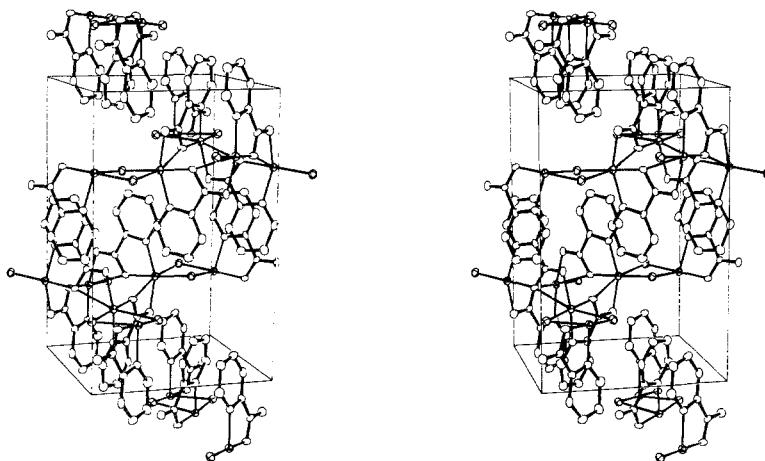


Fig. 2. Stereographic picture of the structure of polymeric $\text{Cu}(\text{pic})\text{Cl}$ viewed down the *a* axis

Each O(2) atom is further bonded to the latter Cu(c) atom giving rise to distorted tetragonal bipyramidal environments around the copper atoms.

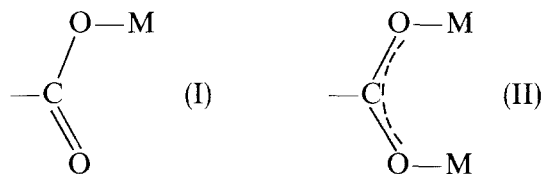
The room temperature infrared and Raman spectra of the crystalline picolinic acid, the sodium salt of the picolinic acid, and the chloropicolinatocopper(II) complex are given together with a tentative assignments of the bands in Table 4.

The (N–Cu–N) bending, (Cu–*pic*) torsion and (Cu–*pic*) rocking vibrational modes are expected to be of lower energy and are probably responsible for the complex group of bands between 40 and 150 cm^{-1} . Coupling of these modes with lattice vibrations may also produce spectral features in this region.

The vibrations related to the pyridine moiety, spreaded over all the spectra, are broad similar to those of pyridine itself and slightly shifted in the solid complex to higher wave numbers, *e.g.* the very strong band of the ring breathing mode at *ca.* 1010 cm^{-1} (IR and Raman) are shifted in the solid complex to 1030 (m; IR) and 1028 (vs; Raman) cm^{-1} .

The infrared and Raman spectra of free picolinic acid exhibit the following bands: 1719 s, br, 1655 ms (IR), 1691 ms, 1655 vw (Raman) as ($\nu_{\text{as}}(\text{COO})$), 1307 vs (IR), 1302 w (Raman) as ($\nu_{\text{s}}(\text{COO})$), 1410 wm (IR), 1410 vw (Raman) as ($\delta(\text{OH})$ in plane), 966 s (IR) as ($\delta(\text{OH})$ out of plane), 680, 688 vs (IR), 676 w (Raman) as ($\delta(\text{COO})$) in accordance with previous studies [24, 25].

The infrared spectrum of the sodium picolinate, on the other hand shows bands at 1655 s, 1625 s, as ($\nu_{\text{as}}(\text{COO})$), 1392 vs, as ($\nu_{\text{s}}(\text{COO})$), and all the deformation bands of (OH) and (COO) are vanished. Compared to the sodium salt and the free picolinic acid, the title complex shows a slight decrease of the ($\nu_{\text{as}}(\text{COO})$) to 1620 vs (IR) and 1615 w, 1596 m (Raman), and a consequent increase of the ($\nu_{\text{s}}(\text{COO})$) to 1392 s (IR) and 1390 w (Raman), which is characteristic of bonding type (II) rather than (I) [26].



In the far-infrared region, we tentatively assigned the bands at 355 s, 320 vs (IR) and 375 w, 322 m (Raman) to ($\nu(\text{Cu}-\text{O}(\text{pic}))$), 253 s (IR) and 251 vs (Raman) as ($\nu(\text{Cu}-\text{N}(\text{pic}))$). According to the bridging nature of the chloride ion, forming a four membered ring (Cu_2Cl_2), the ($\nu(\text{Cu}-\text{Cl})$) are shifted to lower frequencies at 184 s, sh, 170 vs (IR) and 210 m, 186 s (Raman). The assignments of both ($\nu(\text{Cu}-\text{N})$) and ($\nu(\text{Cu}-\text{Cl})$) are given in accordance with those reported earlier [27, 28] for complexes of the type CuL_2Cl_2 (L = substituted pyridine ligand) possessing octahedral geometry through bridging chlorides.

The room temperature magnetic moment of 1.916 BM found for the title compound is higher than the spin only value of Cu(II). A preliminary investigation of the susceptibility in the range 296–77 K shows an increase in the magnetic moment (1.985 BM at 77 K) with a θ value of 10.9 K suggesting ferromagnetic coupling through the chloride bridges.

The electronic spectrum of the solid complex exhibits a broad band centered around 14300 cm^{-1} characteristic for d–d transitions in tetra- and hexa-coordinated copper(II) complexes [29, 30].

The EPR spectrum of the polycrystalline powder of the complex is the same at 296 and 77 K, yielding an axial g factor with $g_{\parallel} = 2.186$ and $g_{\perp} = 2.093$ indicating an elongated tetragonal octahedral or square pyramidal stereochemistry of the copper atoms with a $d_{x^2-y^2}$ ground state [30, 31].

Experimental

Picolinic acid was obtained from Aldrich. The other chemicals were of analytical grade quality.

Preparation of the Complex. The chloropicolinatocopper(II) complex was prepared by mixing about 20 ml of an ethanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.9 g, 5.3 mMol) with the same volume (1.3 g, 10.5 mMol) of picolinic acid in ethanol dropwise with stirring. If there was any turbidity, the mixture was filtered off and the clear blue solution was allowed to stand for several days to obtain transparent blue, cubic shaped, crystals. The crystals were filtered, washed with a very little amount of ethanol, air dried and stored in a dessiccator. The complex is insoluble in many polar solvents, *e.g.* water, acetone, CHCl_3 , etc., as well as benzene and CCl_4 . Analysis (Calc. (Found)): C: 32.59% (32.42%), H: 1.82% (1.98%), N: 6.33% (6.34%), Cl: 16.03% (16.02%), Cu: 28.74% (28.98%).

Physical Measurements. The electronic spectra in the visible range of the solid complex have been recorded with a Brunis Instruments Omega-10 spectrophotometer. The magnetic susceptibilities of the powdered sample were measured in the temperature range 300–77 K using a modified Faraday balance (SUS-10, manufactured by A. Paar KG, Graz). The infrared spectra of the free acid, the sodium salt and the solid complex were measured in the regions 4000–400 and 600–50 cm^{-1} on Perkin-Elmer FTIR-1725 (as KBr pellets) and Nicolet 20F spectrometers (as pressed discs in polyethylene), respectively. Raman spectra were obtained using an equipment consisting of a Spex 1301 monochro-

Table 1. Crystallographic data of $\text{Cu}(\text{pic})\text{Cl}$

Chemical formula	$\text{C}_6\text{H}_4\text{ClCuNO}_2$
Formular mass	221.1
Crystal system	tetragonal
Lattice parameters.	$a = 976.4(1)$ pm $c = 1499.6(4)$ pm $V = 1.4297(4)$ nm^3
Space group	$\text{P4}_2/\text{n}$ (No. 86)
N	8
$F(\text{OOO})$	872
Calculated density	2.054 Mg/m^3
Temperature	$300(2)$ K
Approx. crystal dimensions	$0.13 \times 0.13 \times 0.12$ mm^3
Data collection limits	$2\theta < 55^\circ$; $hkl: 0, 0, 0/12, 12, 19,$
Scan mode	ω -scan, $\Delta\omega = 1.5^\circ$
$F_0 > 3\sigma(F_0)$	543
Least squares parameters	104
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 3.38$ mm^{-1}
R	0.054
R_w	0.048
Weighting function	$4.632/\sigma^2(F_0)$
Residual electron density	$0.59 \times 10^{-6}/-0.74 \times 10^{-6}$ e^-/pm^3

mator, C31034 photomultiplier tube, photon counting electronics and a Spectra-Physics Model 2016 argon ion laser ($\lambda_0 = 514.5$ nm). The power of the laser beam used was approx. 50 mW.

X-ray Analysis. Lattice parameters of the blue compound have been determined by least-squares refinement of X-ray powder patterns at 300(2) K (Philips APD 1700 powder diffractometer) with silicon (NIST 640b) as internal standard. Single crystal intensity data of the compound were collected on a modified STOE four circle diffractometer with graphite monochromated MoK α radiation ($\lambda = 71.069$ pm) and processed as usual (corrections: LP factor, absorption [15], no extinction). Crystallographic data are given in Table 1.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors ($\text{pm}^2 \times 10^{-1}$) of Cu(pic)Cl. U_{eq} was calculated as one third of the trace of the orthogonalized U_{ij} tensor [$T = \exp(-2\pi^2 U_{\text{eq}} \sin^2 \theta / \lambda^2)$]

Atom	x/a	y/b	z/c	U_{eq}
Cu	7352(2)	666(2)	2165(1)	37(1)
Cl	9272(3)	2725(3)	2029(2)	43(1)
O(1)	7004(8)	261(9)	3457(7)	40(6)
O(2)	8845(9)	-661(8)	2280(6)	37(5)
C(6)	6196(12)	-740(13)	3446(9)	31(8)
N(1)	7535(10)	154(10)	882(8)	36(7)
C(1)	8539(13)	-760(13)	728(10)	34(8)
C(2)	8806(13)	-1259(14)	-112(10)	43(9)
C(3)	8036(14)	-804(14)	-830(11)	49(10)
C(4)	6998(14)	126(14)	-699(11)	50(10)
C(5)	6781(14)	588(14)	179(11)	48(10)

Table 3. Selected bond distances (pm) and angles (deg) of Cu(pic)Cl

Cu...Cu(a)	359.4(2)	Cu...Cu(c)	449.0(2)
Cl...Cl(a)	348.7(5)	Cu-Cl(a)	224.2(4)
Cu-Cl	275.6(4)	Cu-O(1)	200.6(10)
Cu-O(2)	195.7(8)	Cu-N(1)	199.6(12)
Cu-O(2b)	256.5(8)	O(1)-C(6)	125.6(15)
O(2)-C(6c)	127.3(15)		
Cl-Cu-O(1)	109.3(3)	Cl-Cu-O(2)	89.0(3)
Cl-Cu-N(1)	92.9(3)	Cl-Cu-Cl(a)	87.9(1)
Cl-Cu-O(2b)	165.3(2)	O(1)-Cu-O(2)	84.9(3)
O(1)-Cu-N(1)	153.7(4)	O(1)-Cu-Cl(a)	96.1(3)
O(1)-Cu-O(2b)	56.0(3)	O(2)-Cu-N(1)	81.5(4)
O(2)-Cu-Cl(a)	176.9(1)	O(2)-Cu-O(2b)	89.5(3)
N(1)-Cu-Cl(a)	98.7(3)	N(1)-Cu-O(2b)	101.3(4)
Cu-Cl-Cu(a)	91.4(1)	Cu-O(1)-C(6)	104.3(8)
Cu-O(2)-Cu(c)	166.0(4)	Cu-O(2)-C(6c)	115.7(8)
O(1)-C(6)-O(2b)	121.2(12)	Cu-O(2b)-C(6)	78.0(7)

Symmetry code: a) $3/2 - x, 1/2 - y, z$; b) $1/2 - y, -1 + x, 1/2 - z$; c) $1 + y, 1/2 - x, 1/2 - z$

Table 4. Vibrational frequencies (cm^{-1}) in the infrared, far infrared and Raman spectra of Picolinic acid, Na-piccolinate and $\text{Cu}(\text{pic})\text{Cl}$

Picolinic acid		Na-pic	Cu(pic)Cl		Assignments
IR	Raman	IR	IR	Raman	
			170 vs	186 (80)	$\nu(\text{Cu}-\text{Cl})$
			184 s, sh	210 (20)	
			253 s	251 (95)	$\nu[\text{Cu}-\text{N}(\text{pic})]$
			320 vs	322 (35)	$\nu[\text{Cu}-\text{O}(\text{pic})]$
			355 s	375 (10)	
680 vs	676 (5)		670 vw	651 (10)	$\delta(\text{COO}^-)$
688 vs			696 vs	675 (5)	
966 s					$\delta(\text{OH})$ out of plane
1307 vs	1302 (10)	1392 vs	1392 s	1390 (10)	$\nu_s(\text{COO}^-)$
1410 wm	1410 (10)				$\delta(\text{OH})$ in plane
1655 ms	1655 (5)	1625 s	1620 vs	1596 (30)	$\nu_{as}(\text{COO}^-)$ and/or
		1655 s		1615 (10)	
1719 s	1691 (20)				$\nu_{as}(\text{COOH})$

ν very, m medium, s strong, w weak, sh shoulder; relative intensities of the Raman bands are given in brackets

The structure was solved by direct methods. Anisotropic displacement parameters were only applied to the non-hydrogen atoms in full-matrix least-squares refinements. The hydrogen atoms were included in the final refinement cycles on calculated positions. The programs DIFABS [15], SHELX-76 [16], SHELXS-86 [17], PLATON [18] and THE XRAY SYSTEM [19] were used for computations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [20]. The final positional parameters are listed in Table 2, selected bond distances and bond angles are given in Table 3. For deposition materia, see Ref. [21].

Acknowledgments

Thanks are given to Austrian Exchange Service for the award of a studentship to Mr. *Abu-Youssef*. Mr. *Mautner* thanks Univ. Doz. *Ch. Kratky* for the use of experimental equipment.

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Received April 16, 1993. Accepted April 24, 1993