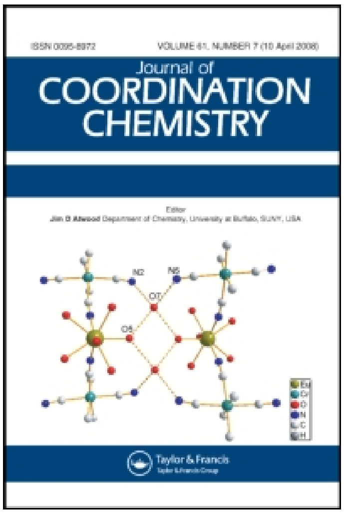

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Synthesis and structure of a novel three-dimensional compound formed by copper(II) and picolinic acid

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A novel compound formed by copper(II) and picolinic acid of formula $[Cu(PCA)_2(H_2O)_2]$ (PCA = picolinate) has been synthesized. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.4479(11)$, $b = 10.910(2)$, $c = 10.396(2)$ Å, $\beta = 98.22(3)^\circ$ and $Z = 2$. X-Ray analysis reveals that the Cu(II) ion lies in the usual distorted octahedral environment; two nitrogen atoms and two oxygen atoms from the PCA form the basal plane and two oxygen atoms from coordinated water molecules occupy the axial position. $[Cu(PCA)_2(H_2O)_2]$ units are connected in a three-dimensional structure by intermolecular hydrogen bonds.

Keywords: Picolinic acid; Copper(II) complex; Molecular structure

1. Introduction

Supramolecular chemistry and crystal engineering of coordination compounds have attracted considerable interest due to a fascinating structural diversity and potential applications as functional materials [1,2]. Generally, higher architectures are formed through hydrogen bonds, π–π stacking interactions or other weak interactions between the molecules [3,4]. Pyridine carboxylic acids are attracting considerable attention for their ability to link metals to form various 0D, 1D, 2D or 3D structures [5,6].

In the present case, we have obtained a novel three-dimensional complex $[Cu(PCA)_2(H_2O)_2]$ (PCA = picolinate). We report herein the synthesis, characterization and crystal structure of the complex.

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2. Experimental

2.1. *General*

All reagents were of analytical grade and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Perkin-Elmer 240 instrument. The infrared spectrum was measured on a Shimadzu 408 spectrophotometer in the 4000–600 cm^{-1} region, using KBr pellets. The electronic spectrum was recorded on a Shimadzu UV-12101 PC spectrophotometer and the X-band ESR spectrum was obtained using a Bruker ER200 D-SRC ESR spectrometer.

2.2. *Synthesis*

A mixture of picolinic acid (0.2 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) and water (15 cm^3) was sealed in a 25 cm^3 Teflon-lined stainless-steel reactor. The mixture was heated to 150° for 72 h and then cooled to room temperature to give crystals suitable for X-ray diffraction analysis. Yield 38%. Anal. Calcd. For $C_{12}H_{12}CuN_2O_6$ (%): C, 41.86; H, 3.49; N, 8.14. Found: C, 41.54; H, 3.56; N, 8.32.

2.3. *X-Ray data collection and structure determination of [Cu(PCA)$_2$(H$_2$O)$_2$]*

A blue crystal of dimensions 0.20 × 0.20 × 0.17 mm was mounted on a glass fiber in a random orientation. The determination of the unit cell and data collection were performed on a computer-controlled Bruker Smart 1000 diffractometer. 1246 Independent reflections ($R_{int} = 0.0264$) in the range $2.72 \leq \theta \leq 27.52°$ with index ranges $0 \leq h \leq 6$, $-13 \leq k \leq 14$, $-13 \leq l \leq 13$ were collected at 291(2) K using Mo Kα radiation with a graphite monochromator ($\lambda = 0.71073$ Å). Analysis revealed that the compound belongs to the monoclinic system, space group $P2_1/c$. The structure of the complex was solved by direct methods using the SHELX-97 program [7]. Copper was located from an E-map and other non-hydrogen atoms were determined by successive difference Fourier syntheses. Final refinement involved full-matrix least-squares methods using SHELX-97. The refinement converged to $R = 0.0404$, $R_w = 0.1181$. Crystallographic data and refinement parameters are listed in table 1.

3. Results and discussion

3.1. *Crystal structure*

An ORTEP drawing of $[Cu(PCA)_2(H_2O)_2]$ is shown in figure 1. Copper is six-coordinate in a distorted octahedral CuN_2O_4 environment. The equatorial plane is formed by O(1) and N(1) atoms from two PCA ions (*trans*). The Cu–O bond length in the basal plane is 1.985(2) Å and Cu–N is 1.990(3) Å. Axial positions are occupied by oxygen atoms of two coordinated water molecules, Cu–O 2.397(3) Å.

A sketch of the intermolecular hydrogen bonds in the solid is shown in figure 2. Intermolecular hydrogen bonds occur between two oxygen atoms of a carboxyl group and a coordinated water molecular (O(3B)–H(3FC)···O(1A), 2.896 Å, 166.6°). Thus $[Cu(PCA)_2(H_2O)_2]$ units are connected as a three-dimensional net (see figure 2).

Table 1. Crystal data, data collection and refinement details.

Compound	$[Cu(PCA)_2(H_2O)_2]$
Color/shape	blue/prismatic
Chemical formula	$C_{12}H_{12}CuN_2O_6$
Formula weight	343.78
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unite cell dimension/Å,°	$a = 5.4479(11)$ $b = 10.910(2)$ $c = 10.396(2)$ $\beta = 98.22(3)$
Z	2
Volume/$Å^3$	611.5(2)
Dc/$Mg\,m^{-3}$	1.867
Absorption coefficient/mm^{-1}	1.818
F(000)	350
λ/Å	0.71073
Scan mode	ω/ϕ
θ Range (°)	2.72–27.52
Number of reflections collected	2146
Number of independent reflections	1246
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1246/2/106
Goodness-of-fit on F^2	1.116
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0404$, $wR2 = 0.1181$
R indices (all data)	$R1 = 0.0527$, $wR2 = 0.1221$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.695 and −0.953

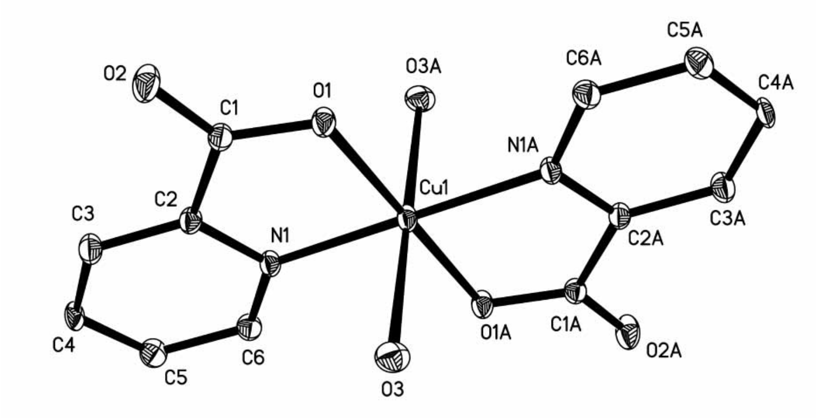

Figure 1. Structure of the complex with relevant atoms labeled; 30% probability ellipsoids are shown.

Final atom positional parameters, selected bond distances and angles are listed in tables 2 and 3, respectively.

3.2. *Spectroscopic measurements*

The infrared spectrum of the complex shows characteristic absorptions of a coordinated carboxylic acid. Strong bonds at 1640 and 1685 cm^{-1} are assigned to $\nu(C{=}O)$ and another strong absorption at 1360 cm^{-1} is due to $\nu(C{-}O)$. The difference between

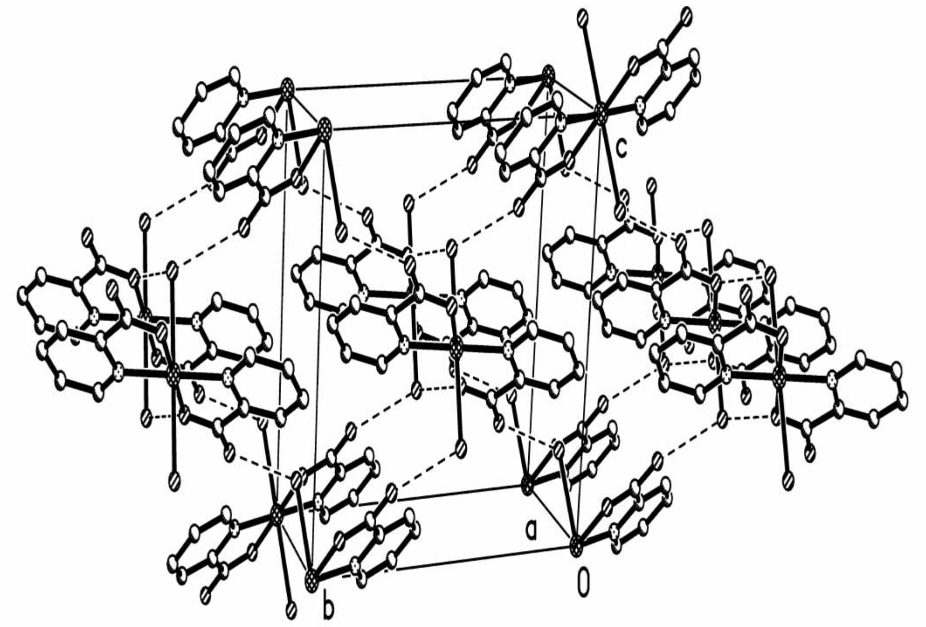

Figure 2. The packing of the complex in the unit cell.

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

	x/*a*	*y*/*b*	*z*/*c*	$U_{(eq)}$
Cu(1)	0	0	0	26(1)
O(1)	−2198(4)	−634(2)	1215(2)	30(1)
O(2)	−2986(5)	−2319(3)	2292(3)	42(1)
N(1)	1125(5)	−1736(2)	23(3)	24(1)
C(2)	54(6)	−2422(3)	869(3)	24(1)
C(4)	2458(6)	−4164(3)	471(4)	28(1)
O(3)	3106(5)	231(2)	1865(3)	36(1)
C(1)	−1856(6)	−1764(3)	1529(3)	26(1)
C(3)	745(7)	−3632(3)	1074(4)	33(1)
C(5)	3491(7)	−3485(3)	−363(4)	34(1)
C(6)	2803(6)	−2262(3)	−604(3)	30(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances (Å) and angles (°) for the complex.

Cu(1)–O(1)	1.985(2)	O(1)#1–Cu(1)–O(1)	180.00(17)
Cu(1)–N(1)	1.990(3)	O(1)–Cu(1)–N(1)	82.73(10)
Cu(1)–O(3)	2.397(3)	O(1)–Cu(1)–N(1)#1	97.27(10)
O(1)–C(1)	1.282(4)	N(1)#1–Cu(1)–N(1)	180.00(15)
O(2)–C(1)	1.230(4)	O(1)#1–Cu(1)–O(3)	93.32(10)
N(1)–C(6)	1.327(4)	O(1)–Cu(1)–O(3)	86.68(10)
N(1)–C(2)	1.349(4)	N(1)–Cu(1)–O(3)	84.82(10)

Symmetry code #1: $-x+2$, $-y+2$, $-z+2$.

ν(C=O) and ν(C–O) is nearly 300 cm^{-1}, indicating that the carboxyl groups are monodentate, in accordance with the structure determination. Ring wagging vibrations of the pyridine were observed at 680, 735 and 775 cm^{-1}. The electronic spectrum of [Cu(PCA)$_2$(H$_2$O)$_2$] in methanol solution shows strong absorptions at 226 and 268 nm, assigned to a ligand transition or charge transfer. The band in the visible region is very broad, centred at 760 nm with a shoulder at 891 nm. The X-band powder ESR spectrum of complex [Cu(PCA)$_2$(H$_2$O)$_2$] at room temperature displays a broad asymmetric absorption with $g = 2.14$.

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