

A New Copper(II) Coordination Polymer from the Methyl Ester of 2,3-Pyrazinedicarboxylic Acid: Crystal Structure Determination from Laboratory X-ray Powder Diffraction Data

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Introduction

Metal-catalyzed hydrolysis of amino acid esters is a well established and documented fact.¹ We have recently shown² that the reaction of CuCl₂ with the methyl ester of 2,5-dimethylpyrazine-3,6-dicarboxylic acid, which can also be considered to be an amino acid, resulted in the formation of a centrosymmetric mononuclear complex with the copper atom octahedrally coordinated to two partially hydrolyzed ligands and two water molecules. We then turned our attention to another pyrazine derivative, pyrazine-2,3-dicarboxylic acid. It has been shown that the reaction of this ligand with CuCl₂ leads to the formation of a one-dimensional coordination polymer.³ The ligand coordinates in a bis-bidentate fashion, and symmetry-related ligands are perpendicular to one another along the chain. The 5-fold coordination of the copper atom is completed by a chlorine atom. Interestingly this complex was shown to be ferromagnetic. Here we report the results of the reaction of the methyl ester of pyrazine-2,3-dicarboxylic acid with CuCl₂, which has led to partial hydrolysis of the ligand and the formation of a two-dimensional coordination polymer.

Experimental Section

Materials and Methods. Pyrazine-2,3-dicarboxylic acid (Fluka) was used as received without further purification. Infrared spectra were carried out on a Perkin-Elmer FT 1720X spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were recorded with a Du Pont Model No. 951 unit under nitrogen atmosphere between room temperature and 800 °C at a rate 10 °C/min. C, H, and N microanalyses were carried out from the Galbraith Laboratories, Knoxville, TN.

Preparation of Methyl Pyrazine-2,3-dicarboxylate. 2,3-Pyrazinedicarboxylic acid (5.05 g, 0.03 mol) was added to 80 mL of dry MeOH containing 4 mL of concentrated H₂SO₄ and refluxed at 75 °C for 16 h. The mixture was allowed to cool to room temperature and then poured into a solution of sodium acetate (20 g in 550 mL of H₂O). CH₂Cl₂ (3 × 100 mL) was used to extract the above solution. The extract was dried over MgSO₄ and the solvent removed under reduced pressure to give a pale yellow liquid (yield 5.2 g, 88%). ¹H NMR (CDCl₃): 3.994 (6H), 8.746 ppm (2H). Selected IR data (cm⁻¹): 3006 w, 2958 w, 1744 s, 1732 s, 1732 s, 1641 m, 1567 s, 1416 s, 1315 m, 1302 m, 1222 s, 1151 m, 1088 m, 1069 m, 1010 s.

Table 1. Crystallographic Data for [Cu(C₇H₅N₂O₄)₂]_n

formula	C ₁₄ H ₁₀ CuN ₄ O ₈
fw	425.80
space group	P2 ₁ /c (No. 14)
a (Å)	12.5346(3)
b (Å)	6.9371(2)
c (Å)	9.3150(3)
β (deg)	109.877(2)
V (Å ³)	761.73(4)
Z	2
λ (Å)	1.5406, 1.5444
T (K)	296
ρ _{calcd} (g/cm ⁻³)	1.856
μ (cm ⁻¹)	25.3
pattern range (2θ) (deg)	13–80
step size (2θ) (deg)	0.01
step scan time (s)	10
radiation source	rotating anode
no. of contributing reflns (Kα ₁ + Kα ₂)	917
no. of structural params	45
no. of profile params	5
R _{wp} ^a	0.036
R _p ^b	0.027
R _F ^c	0.039

^a R_{wp} = [Σw(I_o - I_c)²/ΣwI_o²]^{1/2}. ^b R_p = Σ|I_o - I_c|/ΣI_o. ^c R_F = (|F_o| - |F_c|)/|F_o|.

Preparation of [Cu(C₇H₅N₂O₄)₂]_n. A 400 mg (2 mmol) amount of methyl pyrazine-2,3-dicarboxylate was added to a solution of CuCl₂·2H₂O (410 mg, 2.4 mmol) in 25 mL of water. The mixture was refluxed at 75 °C for 30 min. On cooling a blue precipitate was formed, which was filtered off, washed with water and ethanol, and dried in air (yield 300 mg, 70%). Selected IR data (cm⁻¹): 3007 w, 2957 w, 1746 s, 1646 ss, 1587 m, 1450 w, 1450 w, 1421 m, 1358 s, 1302 w, 1202 w, 1197 m, 1169 m, 1119 s, 1066 w. Anal. Found: C, 38.65; H, 2.40; N, 13.28. Calcd for C₁₄H₁₀N₄CuO₈: C, 39.48; H, 2.35; N, 13.16.

X-ray Data Collection for [Cu(C₇H₅N₂O₄)₂]_n. Step-scanned X-ray powder data were collected on the finely ground sample (side loaded in a flat sample holder) by means of a Rigaku computer automated diffractometer in the reflection mode. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data were collected between 5 and 80° in 2θ with a step size of 0.01° and a counting time of 10 s per step. The powder pattern was indexed by Ito methods⁴ on the basis of the first 20 observed reflections. The best solution (FOM = 29) corresponded to a monoclinic unit cell with a = 12.554, b = 6.947, and c = 9.336 Å and β = 109.89°. The indexed reflections showed systematic absences of the type h0l, l = 2n, 00l, l = 2n, and 0k0, k = 2n, which is consistent with the space group P2₁/c. Full crystallographic details are given in Table 1.

Structure Solution and Rietveld Refinement for [Cu(C₇H₅N₂O₄)₂]_n. Integrated intensities were extracted from the profile over the range 5° < 2θ < 80° by decomposition methods as described by Rudolf and Clearfield.⁵ This procedure produced 45 single indexed reflections up to a 2θ limit of 55°. A Patterson map was computed using this data set in the TEXSAN⁶ series of single-crystal programs. However, the positions of the copper atom was not located from the Patterson map. Taking into consideration the metal ligand ratio (1:2) known from the elemental analysis and the unit cell volume, the copper atom has to be in a special position. Accordingly, the copper atom was placed at the origin, hence, for space group P2₁/c the molecule must possess C_i symmetry, and an octahedral coordination was built around the metal atom. This starting model was used for Rietveld profile refinement in GSAS⁷ using the profile over the range 13° < 2θ < 80°. The reflection (100) at 7.3° in 2θ was a very strong and very asymmetric peak. This

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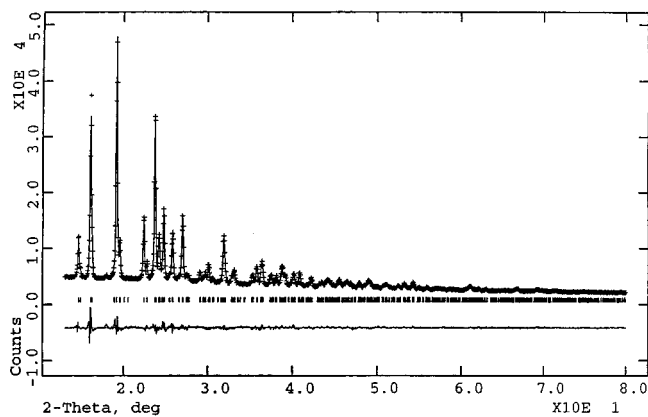


Figure 1. Observed (+) and calculated (-) profiles for the Rietveld refinement for $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n$. The bottom curve is the difference plot on the same intensity scale.

Table 2. Positional and Thermal Parameters for $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}},^a \text{ \AA}^2$
Cu1	0	0	0	0.030(1)
O1	0.0179(4)	0.2390(5)	-0.1078(6)	0.014(3)
O2	0.1150(4)	0.3675(7)	-0.2422(6)	0.018(3)
O3	0.3869(4)	0.2862(8)	-0.1550(6)	0.033(3)
O4	0.2838(5)	0.1718(8)	-0.3801(5)	0.029(2)
N1	0.1348(4)	-0.0735(7)	-0.0529(8)	0.010(4)
N2	0.3139(4)	-0.1595(8)	-0.1434(9)	0.020(4)
C1	0.1680(6)	0.0529(6)	-0.1403(10)	0.023(4)
C2	0.2705(4)	0.0210(7)	-0.1618(8)	0.015(4)
C3	0.2743(6)	-0.2925(7)	-0.0690(11)	0.030(4)
C4	0.1778(6)	-0.2536(7)	-0.0324(10)	0.027(4)
C5	0.1003(6)	0.2408(7)	-0.1558(11)	0.026(4)
C6	0.3236(5)	0.1481(9)	-0.2448(5)	0.021(5)
C7	0.4355(7)	0.4333(10)	-0.2300(8)	0.017(4)

$$^a U_{\text{iso}} = B_{\text{iso}}/8\pi^2.$$

Table 3. Bond Distances (Å) and Bond Angles (deg) for $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n^a$

Cu1-O1	1.990(3)	N1-C1	1.354(3)
Cu1-N1	1.982(2)	N1-C4	1.348(3)
Cu1-O2 ^a	2.517(4)	N2-C2	1.352(3)
O1-C5	1.257(3)	N2-C3	1.346(3)
O2-C5	1.247(3)	C1-C2	1.384(3)
O3-C6	1.340(3)	C1-C5	1.535(3)
O3-C7	1.480(5)	C2-C6	1.472(3)
O4-C6	1.199(3)	C3-C4	1.390(3)
O1-Cu1-O1 ^a	180.0	N1-C1-C5	109.5(3)
O1-Cu1-O2 ^b	87.1(2)	C2-C1-C5	129.3(4)
O1-Cu1-O2 ^c	92.9(2)	N2-C2-C1	118.8(2)
O1-Cu1-N1	80.6(1)	N2-C2-C6	112.8(4)
O1-Cu1-N1 ^a	99.4(1)	C1-C2-C6	126.0(4)
O2 ^b -Cu1-O2 ^c	180.0	N2-C3-C4	119.8(2)
O2-Cu1-N1 ^b	85.9(2)	N1-C4-C3	118.9(2)
O2-Cu1-N1 ^c	94.1(2)	O1-C5-O2	123.8(4)
N1-Cu1-N1 ^a	180.0	O1-C5-C1	116.9(3)
C6-O3-C7	116.8(4)	O2-C5-C1	117.4(3)
C1-N1-C4	119.7(3)	O3-C6-O4	120.3(4)
C2-N2-C3	119.8(2)	O3-C6-C2	112.2(3)
N1-C1-C2	118.3(3)	O4-C6-C2	122.3(4)

^a Symmetry codes: (a) $-x, -y, -z$; (b) $-x, y - 0.5, -z - 0.5$; (c) $x, 0.5 - y, z + 0.5$.

is characteristic for layered compounds, and the accepted procedure is to excluded it from further calculations.⁸ GSAS allows the use of only one set of peak profile coefficients to describe the entire pattern. Thus, the coefficients chosen for the remainder of the pattern did not describe this reflection very accurately. However, the integrated intensity of this reflection was checked against that calculated from the final model

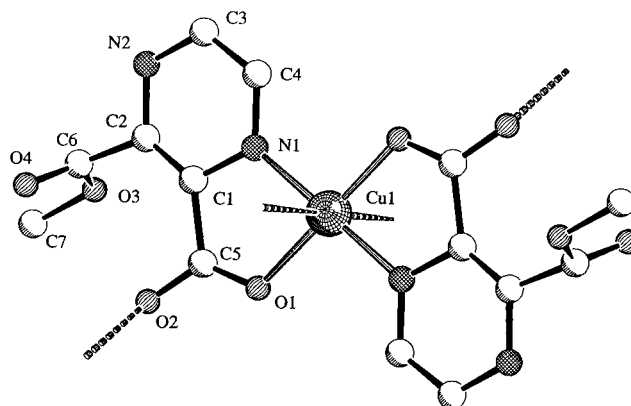


Figure 2. SCHAKAL^{10a} plot of the monomeric unit $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]$, showing the numbering scheme used.

and was found to be satisfactory. After the initial refinement of the scale, background, and unit cell constants, the atomic positions were refined using soft constraints which define the expected octahedral coordination sphere of the metal within some allowable errors. The Cu-O(N) distances were initially held at 2.00(1) Å. The copper octahedral geometry was obtained by constraining the N(O)-N(O) nonbonding distances to 2.83(1) Å. The atoms of the organic ligand were obtained from a series of difference Fourier maps and model building techniques and included in the refinement. The aromatic N-C and C-C bond lengths in the organic ligand were constrained to 1.34(1) and 1.38(1) Å and the C-C single bond at 1.50(1) Å, while the C-O bond length was held at 1.26(1) Å. During refinement it became evident that the Cu-O axial bond distances were longer than the Cu-N(O) distances in the basal plane so values as high as 2.50(2) Å were used. Final refinement was carried out with soft constraints for all the atoms. The weight for the soft constraints (F^7) was reduced, from an initial value of 200 to 50, as the refinement progressed, but the constraints could not be removed completely without reducing the stability of the refinement. This is normal when using limited laboratory data, that is, data measured with an X-ray rotating anode generator rather than synchrotron data. All atoms were refined isotropically, and in the final cycles of refinement the shifts in all parameters were less than their standard deviations which are of course underestimated. Neutral scattering factors were used for all atoms. A correction was made for the preferred orientation effect using the March-Dollase method⁹ in GSAS.⁷ The preferred orientation pole was found to lie along the a^* axis. The refined parameter for the ratio of the effect along this axis with respect to that along the perpendicular plane (bc) was found to be 0.835. No correction was made for absorption effects. A final Rietveld plot is given in Figure 1. Positional and thermal parameters are given in Table 2, and bond distances and angles in Table 3.

Results and Discussion

Thermal Analysis and Spectral Characterization of $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n$. Thermal analysis was performed for the title compound between room temperature and 800 °C under a nitrogen atmosphere. The copper polymer shows no weight loss up to 240 °C indicating that no solvent molecules are present in the structure. The decomposition including the decarboxylation of the ligand and the formation of copper oxide starts at 240 °C, and 75% of the organic moiety is lost at 600 °C. The calculated and observed weight losses (up to 800 °C) for the removal of the ligand molecules were 81.3% and 78.0%, respectively, taking into consideration the simultaneous formation of copper oxide.

The infrared spectra contain characteristic C-O vibration frequencies for the carboxylate groups and C-N and C-C

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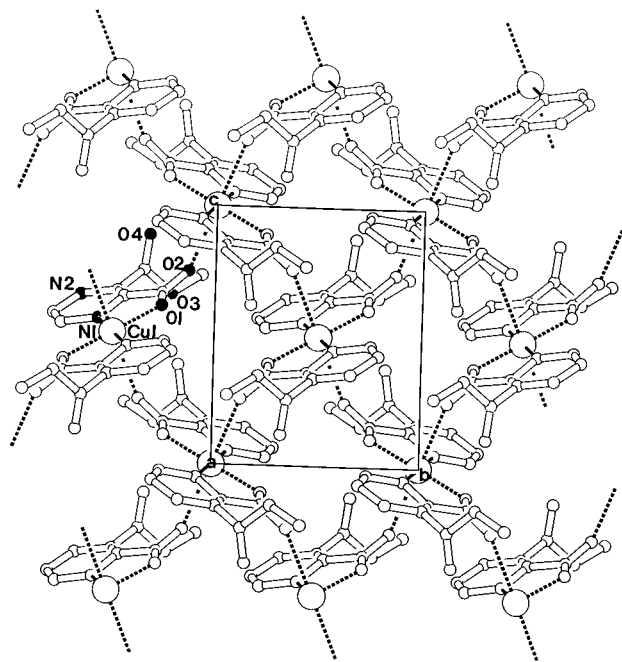


Figure 3. PLUTON^{10b} plot of the two-dimensional polymer $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n$, viewed down the a axis. The dashed lines indicate Cu–O(N) bonds.

vibration frequencies for the pyrazine ring of the pyrazine-2,3-dicarboxylic acid monomethyl ester. In contrast to the free ligand (ν_{CO} : 1744 and 1732 cm^{-1}) the complex shows two C–O absorption bands at 1746 and 1646 cm^{-1} indicating the presence of an uncoordinated $-\text{COOMe}$ group and a coordinated $-\text{COO}^-$ group, respectively. The C–N and C–C vibrational frequencies, due to the pyrazine ring, were found in the region between 1400 and 1600 cm^{-1} and are not significantly displaced compared with the free ligand. The absorption frequencies of C–H are located at 3007 cm^{-1} for the aromatic hydrogen atoms and at 2957 cm^{-1} for the methyl groups.

Structure of $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n$. The structure of this complex consists of $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]$ monomeric units (Figure 2). The Cu atoms in these units are linked by the carbonyl O atom of symmetry-related coordinated carboxylate groups to form a two-dimensional polymer with square rings of copper atoms (Figure 3). The adjacent uncoordinated $-\text{COOMe}$ group is rotated by almost 90° with respect to the plane of the pyrazine ring and is directed into the interlayer space. Such an arrangement of adjacent carboxylate groups has also been observed in a series of transition metal complexes formed with the ligand pyrazine tetracarboxylic acid.¹¹ The copper–copper intramolecular distances, bridged by the carboxylate group of the ligand, are 5.81 Å. In the basal plane the octahedrally coordinated copper is bonded to two nitrogens and two oxygens,

from two organic bidentate ligands, with Cu–N1 distances of 1.98 Å and Cu–O1 distances of 1.99 Å. These distances are similar to those observed in the linear chain polymer (2,3-pyrazinedicarboxylato)copper(II) hydrochloride.³ 2.00 and 1.99 Å, respectively. The two axial positions are occupied by the symmetry-related O2 atoms (Cu–O2^a 2.52 Å), completing the distorted octahedral coordination sphere. A similar coordination environment was observed in the single-crystal structure of the centrosymmetric mononuclear complex formed by the reaction of CuCl_2 with the methyl ester of pyrazine-2,5-methyl-3,6-dicarboxylic acid.² There the axial positions are occupied by two water molecules with a bond distance of 2.470(6) Å, while the Cu–N and Cu–O bond distances in the basal plane were 2.135(4) and 1.895(4) Å, respectively. This later coordination geometry is similar to that observed in the copper complexes formed with the ligand pyrazine tetracarboxylic acid.^{11b}

In the crystal the neutral layers of $[\text{Cu}(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2]_n$ lie in the bc plane and are held together by Van der Waals contacts between methyl groups from the methyl carboxylate substituent of the pyrazine ligand, which are located in the interlayer space. The shortest nonbonded distance between the methyl groups of different layers is 3.90 Å.

Conclusion

It can be seen that metal-catalyzed hydrolysis of amino acid esters can lead to the formation of new ligands, and hence, it is an extremely attractive manner to prepare new coordination compounds. In the case of the methyl ester of pyrazine-2,3-dicarboxylic acid it has led to the formation of an interesting two-dimensional polymer which is quite different from the linear chain polymer formed with the acid itself.³ The importance of single-crystal X-ray analysis to elucidate the structural characteristics of molecules in organic and inorganic chemistry has been recognized for many years. Structure analysis from powder diffraction data is a technique which will certainly be used more and more to solve relatively complicated problems in inorganic chemistry when no suitable single crystals are available, as shown here and elsewhere.¹²

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