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SYNTHESIS AND STRUCTURE OF ONE-DIMENSIONAL LINEAR COPPER(II) COORDINATION POLYMER BRIDGED BY DICYCLOPENTANOPYRAZINE[‡]

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Abstract – Crystalline Copper(II) coordination polymers bridged by dicyclopentanopyrazine (**1**), CuCl₂–**1**, were synthesized. The coordination geometries of the metal centers were tuned to square planar, orthogonal to the plane of the pyrazine ring, by steric hindrance from the methylene chains of pyrazine derivatives.

INTRODUCTION

Continuous interactions between metal centers and ligands give rise to crystalline coordination polymers as supramolecular entities. Crystal engineering of coordination polymers is of great interest because of the potential for manipulation of physical and chemical properties such as electric conductivity, magnetism, photochemical behavior, inclusion of small molecular, and catalysis.^{1,2} During this past decade, much effort has been devoted to constructing supramolecular architecture. The systematic combination of metal centers and ligands has been investigated to control the topology and dimensionality of the supramolecular framework. Among the many structural patterns of coordination polymers, one-dimensional chains have for a long time attracted much attention because of not only their structural simplicity but also their potential technological impact.

Pyrazine (Pz) is the simplest neutral bridging ligand which may act as a linear linker.² Supramolecular structures of pyrazine-bridged coordination polymers are determined by the geometry of the metal center and anionic ligand. Among a variety of pyrazine-bridged coordination polymers, copper(II) complexes are widely investigated. Most of these pyrazine-bridged Cu(II) complexes form a linear chain motif by

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the continuous interaction with the octahedral copper(II) center.³ Bridging anion ligands, such as halogen, interact with two copper centers of adjacent chains to form 2-D networks.^{3a} Systematic analysis of the geometry of Cu(II) complexes by CSD (Cambridge Structural Database⁴) shows the coordination axis of the copper center, defined by the shorter Cu–X bond axis and Cu–N bond axis, is tilted from the pyrazine plane with a θ value of ca. 50° (Figure 1a). This structural feature suggests that orbital overlap between copper and pyrazine is not to be expected. In order to make higher order electronic interactions through π^* – d_{xy} orbitals, the Cu–X bond axis must be perpendicular to the pyrazine plane (Figure 1b). Since the energy level of the d_{xy} orbital is raised by the elongation of the Cu–X' bond, the higher-level d_{xy} orbital of a square planar metal center is ideal for interaction with the π^* orbital. The coordination site of the copper center would be blocked by introduction of a substituent, R, on the 2, 3, 5, and 6 positions of pyrazine. Due to the steric hindrance of the R groups, the Cu–X bond would be raised up so as to be orthogonal to the pyrazine plane, and another coordination atom X' would not be able to approach the copper center, sterically protecting the out-of-plane sites of the pyrazine-containing coordination plain. Based on these strategies we report the synthesis and structure of 1-D coordination polymer of CuCl₂ with dicyclopentanopyrazine.

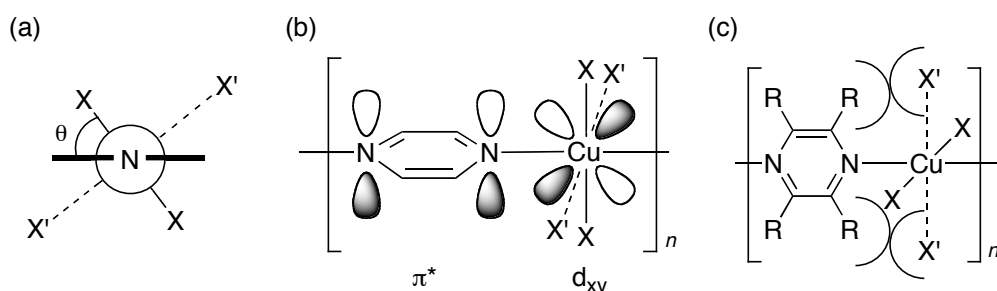
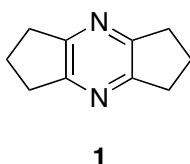


Figure 1. Schematic drawing of geometric aspect of typical pyrazine-bridged Cu(II) coordination polymer. (a) The view along long-chain axis (y axis) with the definition of dihedral angle θ . θ is defined as a tilt angle of the Cu–X axis from the pyrazine plane.; (b) The view from the side of the pyrazine ring with supposed orbital interaction between pyrazine π^* and copper d_{xy} ; (c) The view from above the pyrazine plane with substituent, R.

RESULTS AND DISCUSSION

Dicyclopentanopyrazine (**1**)⁵ was chosen for the bridging ligand, because of its conformational rigidity and the potential for steric hindrance from its methylene groups. Rapid complexation was observed by mixing a 1 M water solution of CuCl₂ and 1 M ethanol solution of **1**, forming a green precipitate. Since this solid was insoluble in most organic solvents and in water, recrystallization was not possible. Thus, in order to obtain single crystals suitable for X-ray structural analysis, a diffusion method with a double-tube system was employed. The crystallization process was as follows: A 10- ϕ test tube was set in a 20- ϕ test tube. A 1 M water solution of CuCl₂ (0.5 mL, 0.5 mmol) was charged to the inner tube and a 1 M ethanol solution of **1** (0.5 mL, 0.5 mmol) to the outer tube. Ethanol was carefully overlaid on these

solutions until the surface of ethanol was gone over the top of inner tube. The outer tube was capped with a rubber septum and allowed stand at room temperature for over 40 h. Two kinds of prismatic crystals, green and dichroic (green–red), were obtained of an appropriate size for analysis. Crystallographic data of these two crystals are listed in Table 1.



Coordination polymers of CuCl_2 –**1** crystallized as two different polymorphs, monoclinic $P2_1$ space group for the green crystal and triclinic $P1$ space group for the dichroic (green–red) crystal. Unit structures and packing orientation with characteristic structural parameters are shown in Figure 2. The major difference between the two polymorphs is the

Table 1. Crystallographic Data for Crystalline Coordination Polymer of CuCl_2 –**1**

crystal color, habit	green, prismatic	dichroic (green red), prismatic
crystal size/ mm^3	0.20 x 0.10 x 0.20	0.20 x 0.20 x 0.20
crystal system	monoclinic	triclinic
space group	$P2_1$	$P1$
a/ $\text{\AA}$	6.787(3)	6.836(2)
b/ $\text{\AA}$	6.481(2)	7.824(2)
c/ $\text{\AA}$	12.796(3)	5.959(5)
α/deg	90	94.13(2)
β/deg	90.21(1)	89.84(2)
γ/deg	90	115.79(1)
vol/ $\text{\AA}^3$	562.8300	286.0900
Z	2	1
R	0.0421	0.0448
R _w	0.1124	0.1187

packing pattern of the polymers. The $P2_1$ crystal packed as a herringbone while the $P1$ crystal packed as a brick wall type motif. The dichroism of the $P1$ crystal was attributed to the highly anisotropic brick wall type orientation. Both unit structures of the 1-D polymer clearly show a nearly orthogonal geometry between the pyrazine plane and the coordination plane of the square planar copper center. Since the interchain $\text{Cu}\cdots\text{Cl}$ distances (from 5.046 to 5.260 $\text{\AA}$) are more than twice the Cu–Cl bond lengths (2.242 and 2.212 $\text{\AA}$), the chloride bridge, X' in Figure 1, can be regarded as negligible and the copper center has

a completely square-planar geometry. The tilt angle (θ) as defined in Figure 1 is 88.7° and 75.59° for $P2_1$ and $P1$ crystal, respectively.

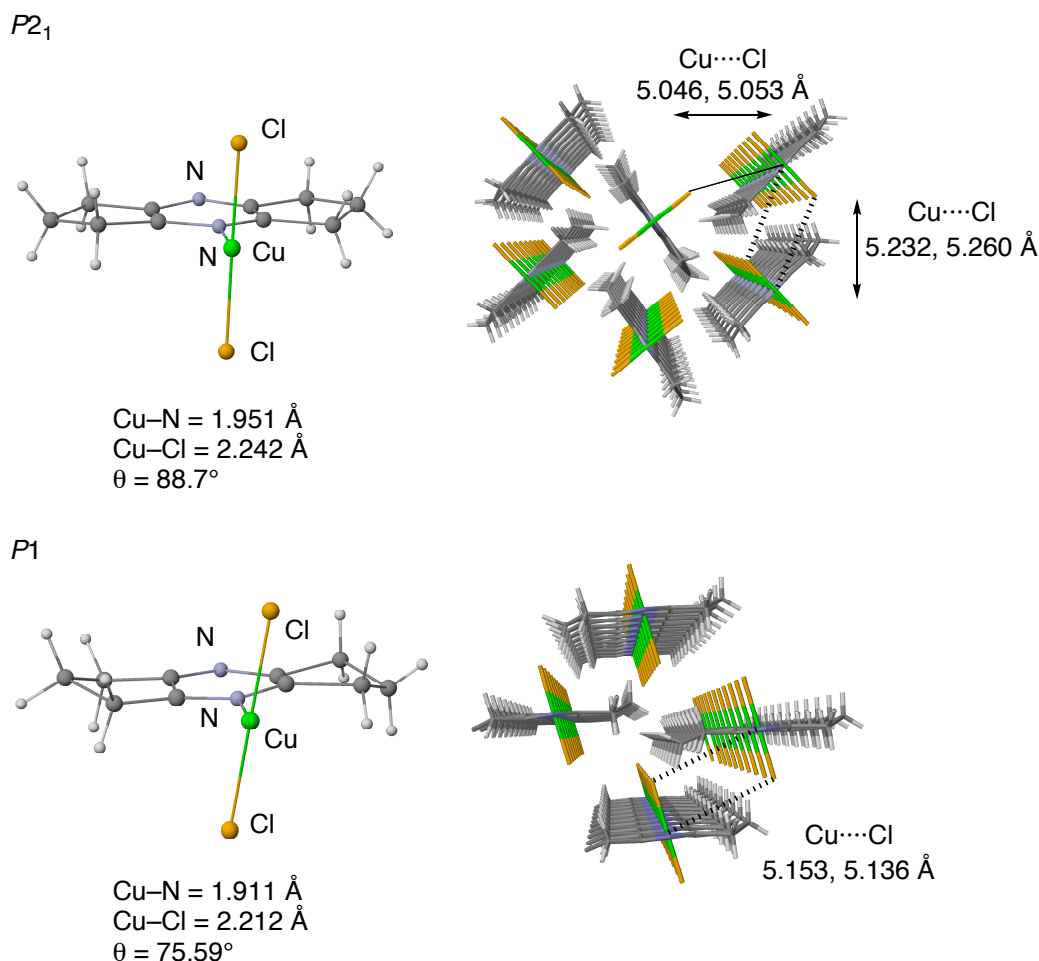


Figure 2. Crystal structure of coordination polymers $\text{CuCl}_2\text{-1}$. For definition of θ see Figure 1a.

In summary, crystalline coordination polymers of dicyclopentanopyrazine **1** with CuCl_2 were synthesized. One-dimensional linear polymers with square planar metal centers were successfully constructed. Since the methylene groups of pyrazine derivative **1** cover the metal coordination sites, the Cu-Cl bond axis is forced to adopt a position perpendicular to the pyrazine plane. These geometrical features make it possible for the relatively high d_{xy} orbital of the square planar metal center to interact with the π^* orbital of the pyrazine derivative. This is a novel approach to generate one-dimensional coordination polymer, and increases the possibility of developing functional materials.

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